

Intermedia Priority Pollutant Guidance Documents

Prepared and Edited by,

Robert Kayser, Ph.D.
Doreen Sterling, Ph.D.
Donn Viviani, Ph.D.

Chemical Coordination Staff
Office of Toxic Substances
U.S. Environmental Protection Agency

July 1982
(Revised October 1984)

Introduction

The Intermedia Priority Pollutant (IPP) Guidance Documents are designed to provide an overview of current regulatory and technical information on a group of toxic chemicals of intermedia concern. Topics covered include: physical/chemical properties; health and environmental effects; production, use, release, and exposure; regulatory status; recommended criteria and standards; spill clean-up/disposal; and analytical methodologies. Key program office contacts are also provided.

The original IPP chemicals were selected in December 1980 by a work group composed of a representative from each regulatory program office and the regions using a composite candidate list of all chemicals that each program office considered a "priority". Each chemical was considered in terms of its intermedia transport properties, health effects, exposure patterns, and other factors that would indicate that the chemical was an intermedia and, therefore, inter-office problem.

These documents were prepared using published technical documents submitted by involved program offices, which CCS abstracted. All of the documents were reviewed in draft by both the program offices and the regions, and appropriate revisions have been made.

The IPP documents have been formatted so that they can be updated as needed and new chemicals suggested by the Regional Offices added.

We hope you find this document useful. Your comments or suggestions are welcome.

Steven D. Newburg-Rinn
Acting Director
Chemical Coordination Staff
Office of Toxic Substances

October, 1984

Intermedia Priority Pollutant (IPP) Chemicals

Acrylonitrile

Arsenic

* Asbestos

Benzene

* Cadmium

Chlorinated Organic Solvents

Trichloroethene (TCE)

Tetrachloroethene (PCE)

1,1,1-Trichloroethane (methylchloroform)

Carbontetrachloride

Methylene Chloride

Chloroform

Chlorophenols

Chromium

Dichlorobenzenes

1,2-Dichloroethane (Ethylene dichloride or EDC)

* Formaldehyde

* Lead

Mercury

PCBs

Phthalate Esters

2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD)

Toluene

* Selected sections have been updated.

Acrylonitrile

ACRYLONITRILE

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-3
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-1
Land Releases	3-1
<u>Exposure Routes</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
Other Exposure Routes	4-1
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-1
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2
Other Actions	6-2

<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
 <u>Spill or Other Incident Clean-Up/Disposal</u>	 8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-2
 <u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
Solid Waste	9-3
Other Samples	9-3
Quality Assurance	9-3
 <u>References and Office Contacts</u>	 R-1

ACRYLONITRILE

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Acrylonitrile is a chemical intermediate used in the production of synthetic fibers, plastics, and elastomers. Synthetic acrylic and modacrylic fibers are widely used in apparel and home furnishings, while high-impact acrylonitrile resins are used in appliances, automobiles and housewares. Acrylonitrile ranked forty-second in overall domestic production in 1980 with a production volume of 830,000 metric tons (1.8 billion lb).

Some of the important properties of acrylonitrile are listed in Table 1. Acrylonitrile is a toxic, volatile liquid which is moderately soluble in water. Acrylonitrile is highly flammable (flash point -4.4°C) and the vapors are explosive. The characteristic odor of this reactive chemical is unpleasant and irritating (ECAO, 1981).

1.2 Chemistry and Environmental Fate/Transport

All acrylonitrile is currently produced using propylene as the raw material. Most processes utilize a mixture of propylene, ammonia, and air in the presence of a catalyst; acetonitrile and hydrogen cyanide are by-products of this process. Commercial acrylonitrile is a highly pure product and is stabilized against self-polymerization with water and methylhydroquinone (35-50 ppm) (ECAO, 1981).

Polymerization, the most important commercial reaction of acrylonitrile, may be initiated by free radicals or light; oxygen is a powerful inhibitor of this process. Acrylonitrile is used commercially to produce acrylamide ($\text{CH}_2=\text{CHCONH}_2$) and adiponitrile, a raw material for nylon production. The double bond in acrylonitrile is also susceptible to attack at the terminal carbon atom in the double bond (i.e., $\text{CH}_2=\text{CH}-\text{CN} + \text{YH} \longrightarrow \text{CH}_2\text{Y}-\text{CH}_2-\text{CN}$); this addition reaction is called cyanoethylation (ECAO, 1981; OWRS, 1979).

Acrylonitrile is thought to be primarily an airborne hazard due to its volatility. Acrylonitrile contains a carbon-carbon double bond which should enhance its reactivity toward atmospheric photo-oxidation by hydroxyl radicals or other oxidants. Expected products include hydrogen cyanide (HCN), carbon monoxide (CO), formaldehyde (HCHO), and formic acid (HCOOH). Laboratory studies suggest that acrylonitrile vapor has an estimated atmospheric half-life of 9-10 hours (OAQPS, 1979).

There is limited information on the fate of acrylonitrile in the aquatic environment. However, the volatility of this pollutant indicates that transport to the atmosphere is likely. Hydrolysis and photolysis reactions of acrylonitrile are probably not relevant in natural surface waters. On the basis of the octanol/water partition coefficient, acrylonitrile is not expected to undergo significant

adsorption on organic sediment or bioaccumulation in aquatic organisms. However, the reaction of acrylonitrile with nucleophiles in proteins (amino and sulfhydryl groups) may lead to accumulation of the cyanoethylated form. Acrylonitrile is degraded by sewage sludge and is susceptible towards biodegradation in natural waters at low concentrations (<50 ppm) (OAQPS, 1979; OWRS, 1979).

The volatile products produced from combustion of acrylonitrile and acrylonitrile resins are toxic. Thermal degradation of acrylonitrile, polyacrylonitrile, acrylonitrile-styrene resins (AS), and acrylonitrile-butadiene-styrene plastics (ABS) result in the release of hydrogen cyanide as the predominant volatile product. Acrylonitrile contained in acrylic fibers and in non-food contact ABS/SAN will not migrate under normal use. However, acrylonitrile monomer is reported by FDA to migrate from nitrile resins used in beverage containers (OAQPS, 1979).

TABLE 1: PROPERTIES OF ACRYLONITRILE*

Synonyms: Cyanoethylene, 2-propenenitrile
vinyl cyanide, AN

CAS Number: 107-13-1

Molecular Formula: C_3H_3N

Structure:

$$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{C}\equiv\text{N} \end{array}$$

Physical Properties:

Melting point:	-83.5°C
Boiling point:	77.5 - 79°C
Vapor pressure (25°C):	110 - 115 torr
Flash point (closed cup):	-4.4°C
Density (20°C):	0.806 g/ml; vapor: 1.83 (air = 1)
Solubility in water (20°C):	73.5 g/l
Partition coefficient (octanol/water):	log P = -0.92 (calculated)
Conversion Factor:	1 ppm in air = 2.17 mg/m ³

*Source: (ECAO, 1981).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACT: Bob McGaughy, FTS 755-3968)

2.1.1 Acute Toxicity

The acute toxic effects of acrylonitrile are reported to be similar to those from cyanide poisoning. Worker exposure to 16-100 ppm for 20-45 min. was reported to lead to headache, vertigo, vomiting, tremors, and convulsions. Other symptoms may include mild jaundice, nasal and respiratory oppression, and diarrhea.

Acrylonitrile acute toxicity varies widely among animal species. Acute oral (LD₅₀) for laboratory animals ranges from 27 to 113 mg/kg; mice appear to be the most sensitive with LD₅₀ values of 25 to 48 mg/kg. With respect to inhalation exposure, fatalities in experimental animals occurred after four hours exposure to levels ranging from 100 ppm (dogs, 7 out of 7 died) to 576 ppm (guinea pigs, 10 out of 16 died) (ECAO, 1981; OTS, 1978).

2.1.2 Chronic Toxicity

Long-term occupational exposure to acrylonitrile may affect the central nervous system, the liver, and blood. Exposed workers have exhibited hematological effects, including low hemoglobin, leucocyte, and erythrocyte counts, at exposure levels of 1.2 to 2.3 ppm. Dermal exposure produces diffuse erythema, blistering, and swelling. In animals, long-term administration may affect growth, food and water intake, adrenal function, and the central nervous system. However, of more concern is recent evidence concerning the carcinogenic potential of acrylonitrile.

Carcinogenicity, Mutagenicity, and Teratogenicity - Based on evidence from animal experiments, epidemiologic investigations, and mutagenicity assays, both IARC (the International Agency for Research on Cancer) and EPA (Office of Health and Environmental Assessment) consider acrylonitrile an animal carcinogen and a potential human carcinogen. Animal studies have involved exposure by ingestion and inhalation.

All four animal studies in which rats received acrylonitrile in drinking water showed increased incidences of tumors in the brain (astrocytomas) and ear canal (zymbal gland); excess tumors in various other organs were noted in some of the studies. In three studies tumors were observed at doses as low as 10 to 100 ppm (equivalent to daily dosages of approximately 1.2 to 12 mg/kg body weight, respectively) over treatment schedules of 19 to 26 months. The other drinking water study was actually a three-generation reproductive study in which tumors were observed in the second generation. Exposure of rats by inhalation is also reported to increase tumor incidence. In one study, rats exposed to 5 to 40 ppm acrylonitrile in air (4 hrs/day, 5 days a week, for 12 months) showed marginal increases in tumors of the mammary region and stomach. A study by Dow

Chemical Company confirmed the increase in tumor incidence in rats exposed to acrylonitrile by inhalation (20 to 80 ppm in air for 6 hrs/day, 5 days/week, for 24 months) (ECAO, 1981; IARC, 1979).

An occupational epidemiology study that involved workers exposed to acrylonitrile at a DuPont textile fibers plant indicates an excess risk of cancer (most notably, lung and colon cancer). However, lack of monitoring data prevents the calculation of a reliable quantitative estimate of worker exposure or risk (ECAO, 1981).

Based on the brain tumor incidence (astrocytomas) in female rats induced by acrylonitrile in drinking water, EPA (Office of Health Research) has calculated a risk factor for cancer in humans. Based on the above data, ingestion of about 1.3 ug/day is estimated to result in an increase in cancer risk of 10^{-5} (1 in 100,000). Using this risk factor, OWRS has calculated the following human Water Quality Criteria for acrylonitrile: for ingestion of contaminated water and aquatic organisms, 0.58 ug/l corresponds to an increased cancer risk of 10^{-5} ; for consumption of aquatic organisms only, the level would be 6.5 ug/l (OWRS, 1980).

The mutagenicity of acrylonitrile has been examined in various bacterial and mammalian systems (ECAO, 1981). Mutagenic responses were observed in the Ames Salmonella test in the presence of a mammalian activation system. Base-pair substitution may result from a possible carcinogenic metabolite of acrylonitrile. One of the proposed metabolic pathways for acrylonitrile postulates an epoxide as a transient metabolite; epoxides as a group are regarded as being potential carcinogens. Also, acrylonitrile itself has been shown to react (cyanoethylation) with ring nitrogen atoms of certain tRNA nucleosides and this suggests that acrylonitrile may react with base residues in DNA. However, it is not known if these nucleotide reactions occur under physiological conditions.

Adverse maternal and fetal effects, including teratogenic effects, were reported after pregnant rats were given oral doses of acrylonitrile at 65 mg/kg/day during gestation. Lower doses (10 to 25 mg/kg/day) caused no significant adverse effects. Acrylonitrile has also been described as embryotoxic to pregnant mice by other workers. (ECAO, 1981; OWRS, 1980).

2.1.3 Absorption, Distribution, and Metabolism

Acrylonitrile is readily absorbed by inhalation or ingestion; dermal absorption is comparatively poor. Acrylonitrile or its metabolites are distributed to all tissues, with high levels found in red blood cells, skin, and stomach, regardless of route or dose. Acrylonitrile is metabolized in animals to cyanide ion (CN^-) which is then converted to thiocyanate (SCN^-). However, blood protein binding and other reactions with tissue nucleophiles via cyanoethylation compete with conversion to cyanide. The oxidative pathway which leads to

cyanide is thought to involve conversion by mixed function oxidases. For example, oxidation of acrylonitrile may lead to an epoxide which could be hydrated, rearrange, or react with nucleophiles; in any case, cyanide would be produced (ECAO, 1981).

There has been considerable disagreement about the mechanism of acrylonitrile toxicity. While the liberation of cyanide was originally thought to produce all toxic reactions, the prevalent opinion now is that toxicity results largely from direct effects of the acrylonitrile itself or other organic metabolites (such as an epoxide). The blocking of important sulfhydryl group containing enzymes by cyanoethylation has been suggested as a possible mechanism for acrylonitrile toxicity (ECAO, 1981).

2.2 Environmental Effects (CONTACT: Richard Carlson, FTS 783-9511)

2.2.1 Aquatic Effects

The data base for acrylonitrile is deficient in several important aspects. Acute toxicity data are lacking for planktonic or benthic crustaceans, benthic insects, detritivores, and salmonid fishes. Of the data available, only one of the 96-hour LC₅₀ values for the fathead minnow was generated in a flow-through test, the rest being static tests; all acute tests used unmeasured concentrations. The range of EC₅₀ and LC₅₀ values is from 7,550 to 33,500 ug/l. The chronic data are limited to one inconclusive test with Daphnia magna and a 30-day LC₅₀ value for the fathead minnow of 2,600 ug/l.

Despite these limitations, there is enough information available to indicate that acrylonitrile merits some consideration of its possible toxicological effects on freshwater aquatic life. In particular, these data suggest that acrylonitrile has a definite chronic or cumulative effect and that adverse effects can be expected to occur at concentrations below 2,600 ug/l in fish exposed to this compound for more than 30 days. The only datum on saltwater species is a 24-hour LC₅₀ value of 24,500 ug/l for the pinfish (OWRS, 1980).

3. ENVIRONMENTAL RELEASE

Acrylonitrile is manufactured for use as feedstock in the synthesis of a variety of materials and chemicals. During 1978 the industry produced 800,000 metric tons of acrylonitrile. The major use for acrylonitrile is in the production of acrylic and modacrylic fibers and acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins. Acrylonitrile is also used as a raw material in the manufacture of nitrile elastomers and barrier resins and as an intermediate in the production of adiponitrile and acrylamide. Approximately 17% of the domestic production was exported during 1978.

The total discharge of acrylonitrile to the environment is estimated to be about 2% of the total annual production. Acrylonitrile, a volatile compound, is released primarily through air emissions from production facilities and acrylic fiber and ABS/SAN resin manufacturing operations. Air releases account for about 87% of the total releases, while water releases account for nearly all of the other 13%. Releases in solid waste are considered to be relatively small. Current release estimates are based on limited data and are subject to a high degree of uncertainty.

A summary of acrylonitrile production, consumption, and environmental release for 1978 is presented in Table 2. The major sources of environmental release of acrylonitrile to air and water are listed below. Accidental spills are also considered a potential source of release because acrylonitrile is liquid, volatile, and highly soluble in water, and therefore readily released to the environment if spilled.

3.1 Air Releases (CONTACT: Nancy Pate, FTS 629-5502)

Significant Sources

- Acrylonitrile production plants (SIC 2869)
- Acrylic and modacrylic fiber manufacturing plants (SIC 2824)
- ABS/SAN resin manufacturing plants (SIC 2821)
- Adiponitrile production (SIC 2869)
- Acrylamide plants (SIC 2869)

3.2 Water Releases

Significant Sources

- Acrylic and modacrylic fiber manufacturing plants (SIC 2824)
- ABS/SAN resin manufacturing plants (SIC 2824)

3.3 Land Releases

No significant sources. Wastes from acrylonitrile production plants and facilities using acrylonitrile, and accidental spills are possible sources of minor releases.

TABLE 2: ACRYLONITRILE SUPPLY, CONSUMPTION, AND RELEASES (1978)*

	<u>Supply (kkg)</u>	<u>Consumption (kkg)</u>	<u>Airborne Emissions (kkg/yr)</u>	<u>Water Releases (kkg/yr)</u>
I. Production and Emissions				
Acrylonitrile production	800,000	---	5,300	40
II. Uses and Emissions				
Acrylic and modacrylic fiber		326,000	3,300	850
ABS/SAN resins		167,000		
Adiponitrile		87,500	800	90
Nitrile elastomers		24,000	40	20
Latex Production		7,760	10	NEG
Acrylamide		25,700	400	NEG
Nitrile barrier resins		10,200	100	20
Minor miscellaneous uses		11,800	NA	NA
Exports		135,000	140	40
<u>Totals</u>		<u>794,960</u>	<u>11,790</u>	<u>1,830</u>

*Source: (OTS, 1980).

NA = not available NEG = negligible

Total land/solid waste releases are considered negligible (less than 1 kkg/yr).

4. EXPOSURE ROUTES

The National Institute of Occupational Safety and Health (NIOSH) has estimated that 125,000 people are potentially exposed to acrylonitrile in the workplace. EPA has estimated that 2.6 million people are exposed to an annual average concentration of acrylonitrile ranging up to 20 ug/m³ (OAQPS, 1979).

Acrylonitrile is readily absorbed in humans by inhalation and oral routes. The principal route of exposure for acrylonitrile is ambient air. Exposure may also occur to a limited extent via drinking water, dermal absorption, and food.

4.1 Air Exposure

Exposure estimates for air were calculated by SRI for EPA using dispersion modeling. Annual average atmospheric concentrations of acrylonitrile ranged up to 20.0 ug/m³. Estimates are presented in Tables 3 and 4 of the number of people exposed to various increments of acrylonitrile concentrations (OAQPS, 1979).

4.2 Water Exposure

No exposure estimates for drinking water were available. However, since less than 2000 metric tons of acrylonitrile are released to the water (roughly 15% of the amount released to the air), it is probable that exposure via drinking water is not great. The volatility of acrylonitrile also aids in intermedia transfer to the air.

4.3 Other Exposure Routes

Dermal Absorption

Acrylonitrile is not readily absorbed through the skin. Studies of dermal absorption of acrylonitrile vapor found the penetration rate of the vapor through the skin to be about one percent relative to the quantity absorbed by the lungs (ECAO, 1981).

Food

The U.S. Food and Drug Administration banned the use of acrylonitrile resin in the production of soft drink bottles; however, this is currently under revision. The use of this resin is allowed in other food packaging. Although no exposure estimates are available, food contaminated with acrylonitrile resin is a potential, albeit minor, exposure route.

**TABLE 3: ESTIMATED HUMAN EXPOSURES TO ATMOSPHERIC
ACRYLONITRILE FROM PRODUCERS**

<u>Annual Average Atmospheric AN Concentration (ug/m³)</u>	<u>Number of People Exposed</u>
10.0-14.9	50
5.0-9.99	240
1.0-4.99	64,000
0.500-0.999	140,000
0.100-0.499	1,800,000
0.050-0.099	<u>600,000*</u>
Total People	2,600,000 (approx.)

Source: (OAQPS, 1979).

*Exposures in these ranges are underestimated because calculations were made only for exposures within 30 km of each plant.

**TABLE 4: ESTIMATED HUMAN EXPOSURE TO ATMOSPHERIC ACRYLONITRILE
FROM PLANTS THAT USE ACRYLONITRILE**

<u>Annual Average AN Concentration ug/m³</u>	<u>Chemical Product</u>			
	<u>ABS/SAN Resin</u>	<u>Acrylic and Modacrylic Fibers</u>	<u>Nitrile Elastomers</u>	<u>Adiponitrile</u>
15.0-19.9	2,700			
10.0-14.9				
5.00-9.99	850	4,700	1,800	
1.00-4.99	73,000	52,000	22,000	
0.500-0.999	79,000	70,000	81,000	
0.100-0.499	680,000	370,000	650,000	22,000
0.050-0.099	1,200,000	190,000	690,000	32,000
0.010-0.049	1,400,000+	260,000+	2,700,000	65,000+
0.005-0.009	510,000+	0+	5,100+	0+
0.001-0.004	<u>790,000+</u>	<u>0+</u>	<u>93,000+</u>	<u>0+</u>
Total People (approx.)	<u>4,700,000</u>	<u>950,000</u>	<u>4,200,000</u>	<u>120,000</u>

Source: (OAQPS, 1979).

+Exposures in these ranges may be underestimated because calculations were made only for exposures within 30 km of each plant.

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA, which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS numbers (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available on the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purpose of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. For further information contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information, contact Delores Evans at FTS 382-3546 or Irv Weiss at FTS 382-3524.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base that is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses source material only at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Delores Evans at FTS 382-3546 or Ingrid Meyer at FTS 382-3773.

5.5 Chemical Substances Information Network (CSIN)

The prototype CSIN, operational since November 1981, has been developed by merging the technologies of computer networking and distributed data base management. CSIN is not another data base, but a library of systems. Through the CSIN front-end intermediary management computer, the user may access and use independent and autonomous information resources that are geographically scattered, disparate for data and information content, and employ a variety of types of computer hardware, software, and protocols. Users may converse in and among multiple systems through a single connection point, without knowledge of or training on these independent systems.

Currently, six independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), CIS, EPA-CICIS, CAS-On-Line, SDC-orbit, and two files of Dialog: CRGS and TSCA Inventory. The CSIN management computer allows the user to create, retrieve, store, manipulate data and queries. This eliminates the need for re-entering long lists of chemical identifiers or other information elements that are part of the original query or that have been identified and acquired from one or more of the CSIN resources. For further information contact Dr. Sid Siegal at FTS 382-2256.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 475 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. For further information, contact Charlene Sayers at FTS 755-9112.

The following data bases contain information on acrylonitrile:

BAT Review Study for the Timber Products Processing, Gum and Wood, Chemicals, and the Printing and Publishing Industries
Best Management Practices, Timber Industry Effluent Guidelines -
Runoff
Best Management Practices, Timber Industry Effluent Guidelines -
Sludge
Chemicals in Commerce Information System
Compliance Sampling Toxicant Surveys
Consolidated Permits Program-Application Form 1,2b,2c
Data Collection Portfolio for Industrial Waste Discharges
Distribution Register Organic Pollutants in Water
Energy and Mining Point Source Category Data Base
Federal Facilities Information System
Fine Particle Emissions Information System
Food Industry Group
Fugitive Emissions Information System
Gaseous Emissions Data System
Hazardous Waste Site Tracking System
Hazardous Waste Data Management System
Hemlock, Michigan Environmental Samples

Humacao Ambient Data Base
 IFB Organics Data Base
 Indicatory Fate Study
 Industrial Process Evaluations
 Innovative Technology, Timber Industry Effluent Guidelines
 Inorganic Chemicals Industry Regulation Record
 LiParí Landfill
 Liquid Effluents Data System
 Listing of Organic Compounds Identified in Region IV
 Love Canal Data Handling System
 Method Validation Studies of Priority Pollutants
 National Electronic Injury Surveillance System
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Permit Compliance
 Nationwide Urban Runoff Program
 Needs Survey
 New York Bight Ocean Monitoring Program
 Organic Chemicals/Plastics Industry
 Paint and Ink Analytical Data
 Permit Compliance System
 Pesticide Incident Monitoring System
 Pesticide Product Information System
 Pharmaceutical Screening/Verification Data Base
 Precision and Accuracy for Screening Protocols
 Priority Pollutants-Region I
 Priority Pollutants-Region III
 Publicly Owned Treatment Works (POTW) Analytical Data
 Publicly Owned Treatment Works (POTW) Quality Control
 Puerto Rico Reservoirs
 Regional Toxics Monitoring Program
 Resource Conservation and Recovery Act (RCRA)-Hazardous Waste Site
 Inspections
 Screening Sampling Program
 Sources of Toxic Pollutants Found in Influent to Sewage Treatment
 Plants
 Spill Prevention Control and Countermeasure
 System for Consolidated Permitting and Enforcement Data Base
 Textile Industry BAT Study-Toxic Sampling Data
 Toxics Monitoring
 U.S. Virgin Islands-St. Thomas, St. Croix
 Verification Data Base
 Waste Characterization Data Base
 Water Quality Information System

6. REGULATORY STATUS (Current as of 4/16/82)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- Section 311 - Acrylonitrile is classified as a hazardous substance (40CFR116.4) and discharges are subject to reporting requirements (40CFR117.3).
- Sections 301, 304, 306, and 307 - Acrylonitrile is listed as a toxic pollutant (40CFR401.15) and is subject to effluent limitations. Effluent guidelines or standards have not yet been promulgated, however, NPDES permit applicants in specified industrial categories are required to report quantitative data for several organic pollutants including acrylonitrile; analytical methods are specified (40CFR122.53(d)(7)).

Resource Conservation and Recovery Act (RCRA)

- Section 3001 - Acrylonitrile is listed as hazardous waste number U009 (40CFR261.33). The following solid wastes are designated hazardous wastes due, in part, to the presence of acrylonitrile (40CFR261.32).

Organic Chemicals Industry:

- (K011) - bottom stream from stripper in acrylonitrile production
- (K013) - bottom stream from acetonitrile column in production of acrylonitrile
- (K014) - bottoms from acetonitrile purification during acrylonitrile production

- Sections 3002 to 3006 - Regulations for generators and transporters of hazardous waste and standards for treatment, storage and disposal are applicable (40CFR262 to 265).

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- Sections 3 and 25(a) - Pesticide products containing acrylonitrile in combination with carbon tetrachloride are classified for restricted use (40CFR162.31).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- Sections 6 and 8 - Permissible exposure level as an 8-hr. TWA concentration, is 2 ppm, with a ceiling of 10 ppm for any 15-minute period. Exemptions and other safeguards are described (29CFR1910.1045).

DOT - Hazardous Materials Transportation Act

- Acrylonitrile is classified as a flammable liquid and a poison. Complete regulation is required regardless of amounts shipped; it is forbidden on passenger-carrying aircraft or railcar (40CFR172.101); other regulations exist for transporting and packaging (40CFR171-177).

FDA - Food, Drug, and Cosmetic Act

- FDA regulates the use of acrylonitrile in a variety of polymer and copolymer products if the use involves contact with food; such materials may be used under certain conditions (21CFR173 to 181). Use in fabrication of beverage containers is prohibited (21CFR177).

6.2 Proposed Regulations

6.2.1 EPA Programs

CAA

- A New Source Performance Standard (NSPS) has been proposed to control fugitive emissions from the manufacture of volatile organic chemicals (VOCs) from new process units within the synthetic organic chemical manufacture industry (46FR1136).

CWA

- Self-monitoring for acrylonitrile is proposed for various processes used to produce ABS and SAN polymers and acrylic fibers (44FR47113).
- Proposal to add 40CFR125 establishing ocean discharge criteria including toxic pollutants listed in 40CFR401.15; includes acrylonitrile (45FR9549).

6.3 Other Actions

- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) - CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites. (42USC9601; PL96-510). EPA is developing regulations concerning the designation of hazardous

substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46FR54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47FR10972). Hazardous substances as defined by Section 101(14) of CERCLA include: hazardous wastes designated under Section 3001 of the RCRA; hazardous air pollutants regulated under Section 112 of the CAA; and water pollutants listed under Sections 307 and 311 of the CWA (and also any substances regulated in the future under Section 7 of TSCA and Section 102 of CERCLA). Therefore, acrylonitrile is a hazardous substance under CERCLA and will be subject to regulations developed under Superfund.

- Acrylonitrile is under consideration for listing under Section 112 of the CAA, which would authorize NESHAPS to control release from specific sources (46FR54025).
- Human health-based Water Quality Criteria for acrylonitrile have been calculated on the basis of carcinogenic potential (45FR79324).
- After a preregulatory assessment, the Office of Drinking Water has decided that national drinking water regulations under SDWA will not be developed at this time. In the event of drinking water contamination problems, the Office of Drinking Water, Criteria and Standards Division should be contacted for assistance (Contact: William Lappenbusch, FTS 472-6820).

7.1 Air

- ## 7.2 Water

- * See Appendix A for a discussion of the derivation, uses, and limitations of these Criteria and Standards.

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL
(CONTACT: National Response Center, 800-424-8802; 426-2675 in the Washington, D.C. area)

8.1 Hazards and Safety Precautions

Acrylonitrile readily volatilizes to a poisonous vapor. Symptoms include headache, vertigo, nausea, tremors, and nasal and respiratory oppression. The chemical has an irritating odor.

Acrylonitrile is extremely flammable and may be ignited by heat, sparks, or flames; vapor is explosive. Fire produces toxic combustion products (Hydrogen cyanide).

Pure acrylonitrile may polymerize violently with evolution of heat in the presence of light or at elevated temperature.

8.2 First Aid

Move victim to fresh air; give artificial respiration if not breathing and oxygen if breathing is difficult. In case of contact, flush with running water; remove and isolate contaminated clothing. Effects may be delayed.

8.3 Emergency Action

Spill or Leak - Stay upwind, isolate area, and wear breathing apparatus, eye protection, and protective clothing. Remove all ignition sources. Use water spray to reduce vapors.

Fire - For small fires use dry chemical, CO₂, water spray, or foam. For large fires use water spray or foam. Cool containers with water until well after fire is out.

Isolate for 1/2 mile in all directions if tank or tankcar is involved in a fire.

8.4 Notification and Technical Assistance

Section 103(a) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) requires notification of the National Response Center (NRC) 800-424-8802 (in Washington, D.C. area, 426-2675) if releases exceed reportable quantities (100 lb in the case of acrylonitrile).

For emergency assistance call:

CHEM TREC: 800-424-9300.

For information call EPA, Division of Oil and Special Materials (1-202-245-3045).

8.5 Disposal

Generators of more than 1,000 kg of hazardous waste (or residues from spill clean-up) per month are subject to RCRA regulations. Specific waste streams subject to Subpart D regulations are listed in Section 6.1.1 of this document.

Small quantities can be poured on sand and ignited. Protective apparatus should be worn due to toxic combustion products. Chlorine solutions will convert acrylonitrile to less toxic cyanates.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air (CONTACT: Robert H. Jungers, FTS 629-2331)

Acrylonitrile is not a regulated air pollutant*; therefore, no Agency approved or reference procedure is available. However, a sampling and analysis procedure using charcoal for sampling, gas chromatography for separation, and flame ionization detection for analysis has been used for monitoring around production and user facilities (NIOSH Method S-156, NIOSH Manual of Analytical Methods, No. 77-157-C; Recovery of Acrylonitrile from Charcoal Tubes at Low Levels; American Industrial Hygiene Association Journal (40) October 1979, p. 923-925).

The sampling method is currently being evaluated using 1000 mg charcoal tubes sampled for 24 hours at a rate of 500 cc/min and 150 mg charcoal tubes sampled for 24 hours at a rate of 150 cc/min. The desorbing solvent is carbon disulfide with 2% by volume acetone. A gas chromatographic column of 80/100 mesh Durapak OPN/Porosil C is utilized to achieve the best peak separation with the flame ionization detector.

9.2 Water (CONTACT: Thomas Bellar, FTS 684-7311
James Lichtenberg, FTS 684-7308)

Acrylonitrile (CAS No. 107-13-1) is a proposed parameter under Section 304(h) of the Clean Water Act. It is listed as one of the priority pollutants.

There are three proposed procedures for the analysis of acrylonitrile in natural, waste, and drinking waters. Two of the methods call for direct aqueous injection; the third uses the purge and trap procedure. For all proposed methods, detection and quantitative analysis are made using a gas chromatograph equipped with a flame ionization detector.

Direct Aqueous Injection:

EPA Method #626

ASTM # D3371-79

Major Equipment: Gas Chromatograph

Three to five ul of the sample is injected directly into the gas chromatograph. The detection limit is approximately 1 mg/l when a flame ionization detector is used.

Purge and Trap: EPA Method #603

Major Equipment: Gas chromatograph equipped with a purge and trap apparatus.

* Although acrylonitrile is indirectly regulated as a volatile organic compound (VOC), no specific analytical procedure is approved for acrylonitrile.

An inert gas is bubbled through a 5 ml water sample contained in a heated purging chamber. Acrylonitrile is transferred from the aqueous to the vapor phase. The vapor is swept through a sorbent trap where the acrylonitrile is retained. After the purge is completed, the trap is heated and backflushed with inert gas to desorb the compound onto a gas chromatographic column. Detection is made with a flame ionization detector, the method detection limit is 0.5 ug/l.

Sampling

The samples are collected in narrow-mouth bottles filled to overflowing in such a manner that no air bubbles pass through the liquid. The samples must be stored headspace free and iced or refrigerated at 4°C from the time of collection until analysis. If the sample contains free or combined chlorine, add sodium thiosulfate preservative to the sample bottles before filling (10 mg/40 ml is sufficient for up to 5 ppm Cl₂.) All samples must be analyzed within 14 days of collection.

List of Procedures for Acrylonitrile

Method ^a	Type ^b	MDL	% Recovery ^c	Standard Deviation %	Status (March 1981)
EPA 603	P&T	0.5 ug/l	107	5.6	Proposed
EPA 626	DAI	1 mg/l	-	-	Proposed
ASTM #D3771-79	DAI	1 mg/l	-	-	Proposed

(a) See references below.

(b) P&T = Purge and Trap; DAI = Direct Aqueous Injection.

(c) Single laboratory recovery from spiked reagent water or wastewater.

References for Water Analysis

"Acrolein and Acrylonitrile" Method #626, October 1980, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. Also see 44FR69532.

"Standard Test Method for Nitriles in Aqueous Solution by Gas-Liquid Chromatography," Annual Book of ASTM Standards, 1980, Part 31, Water, ASTM D 3371-79.

"Methods for Organic Chemical Analysis of Water and Wastes by GC, HPLC, and GC/MS," Method 603: Acrolein and Acrylonitrile, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. Also see 44FR69479.

9.3 Solid Waste (CONTACTS: M. Hiatt, FTS 545-2118;
W. Beckert, FTS 545-2137)

Method 8.03 (Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods; EPA/SW-846 (1980)) is approved for analyses of acrylonitrile in solid wastes.

Commonly used techniques include GC/MS for the determination of acrylonitrile in wastes. Sample preparation may be by extraction, purge-trap, or vacuum extraction. For extraction techniques see I. R. DeLeon, et al., Journal of Chromatographic Science, 18, 85-88 (1980).

Purge and trap methods are described by David Speis in "Determination of Purgeable Organics in Sediment Using a Modified Purge and Trap Technique." Protocol, USEPA, Region II, Edison, N.J., October 10, 1980. The Love Canal Study also required purge-trap methods (see CONTACTS).

Vacuum extraction of volatiles and collection in a liquid-nitrogen trap permits analysis at 100 ppb with a precision of 8% and 89% recovery. Total sample preparation takes about 36 minutes. See above CONTACT (M. Hiatt) for details.

9.4 Other Samples

No approved method for the analyses of acrylonitrile in soil or sediment has been published. However, a recent EPA document contains procedures for monitoring industrial sites for soil contamination (Environmental Monitoring Near Industrial Sites; EPA-560/6-79-003; OTS (1979)). The desorption methods used were ultrasonic agitation of water extracts and the purge-trap technique.

9.5 Quality Assurance

Water

Single laboratory test data on simple spiked matrices have been collected by EPA. Quality control and performance evaluation samples are available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, USEPA, Cincinnati, Ohio 45268 (See Water CONTACTS).

Solid Waste

Standards can be obtained from Radian Corporation or EMSL-Las Vegas. Supelco supplies diluted standards but the concentrations are not verified. Standard solutions may also be prepared in the laboratory from reagent-grade acrylonitrile to the appropriate dilution using methanol. (See Solid Waste CONTACTS).

REFERENCES

The major references used in preparation of this document are listed below. EPA documents are listed by the EPA office of origin and the year of publication. For further information refer to the contacts given throughout this document or contact the relevant EPA Program Offices given at the end of this section.

- (IARC, 1979) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 19, pp. 73-113; International Agency for Research on Cancer, World Health Organization (1979).
- (ECAO, 1981) Health Assessment Document for Acrylonitrile; EPA-Contract No. 68-02-3277, Environmental Criteria and Assessment Office, (1981).
- (OAQPS, 1979) Assessment of Human Exposure to Atmospheric Acrylonitrile; EPA-Contract No. 68-02-2835, Office of Air Quality Planning and Standards, (1979).
- (OTS, 1978) Investigation of Selected Environmental Contaminants: Acrylonitrile; EPA-560/2-78-003, Office of Toxic Substances, (1978).
- (OTS, 1980) Level I Materials Balance: Acrylonitrile; Draft Final Interim Report, EPA-Contract No. 68-01-5793, Office of Toxic Substances, (1980).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants; Vol II, Chapter 105; EPA-440/4-79-029b, Office of Water Regulations and Standards, (1979).
- (OWRS, 1980) Ambient Water Quality Criteria for Acrylonitrile; EPA-440/5-80-017, Office of Water Regulations and Standards, (1980).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWSR)

Criteria and Standards Division	755-0100
---------------------------------	----------

Effluent Guidelines Division	426-2571
------------------------------	----------

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergenices call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ, Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information and Analysis Program

382-2249

Arsenic

ARSENIC

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-3
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-1
<u>Exposure</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
Other Exposure Routes	4-3
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPA CASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-1
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2
Other Actions	6-3

<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Hazardous Waste	7-1
Other	7-2
 <u>Spill or Other Incident Clean-up/Disposal</u>	 8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-2
Disposal	8-2
 <u>Sampling, Acceptable Analytical Techniques and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
Solid Wastes	9-3
Other Samples	9-3
Quality Assurance	9-3
 <u>References and Office Contacts</u>	 R-1

ARSENIC

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Arsenic, which is a naturally occurring element, is produced commercially as a byproduct during the processing of nonferrous metal ores. Although most of the arsenic produced is in the form of arsenic trioxide, there are approximately 50 other arsenic compounds produced in the United States. Table 1 lists the physical/chemical properties of arsenic compounds with environmental significance (OTS, 1979).

1.2 Chemistry and Environmental Fate/Transport

The chemistry of arsenic is complex due to the stability of three oxidation states (+5, +3, -3) and also because of the propensity of arsenic compounds to undergo complexation, precipitation, adsorption, and biotransformation. Inorganic arsenic is generally in ionic form as trivalent arsenite (+3 state, AsO_3^{-3}) or pentavalent arsenate (+5 state, AsO_4^{-3}) salts. Cacodylic acid and methylarsonic acid and its salts are the only widely used organic derivatives (NRC, 1977; OWRS, 1979).

Arsenic compounds are generally nonvolatile, except for the gaseous arsines (e.g., AsH_3) which are rare, and arsenic trioxide (As_2O_3). Due to the relatively low sublimation temperature (193°C) of arsenic trioxide, nonferrous smelting results in significant release of this arsenic compound to the atmosphere. The use of arsenical pesticides and coal combustion are other major emission sources (NRC, 1977).

Arsenic is extremely mobile in the aquatic environment and may cycle through several components, i.e., the water column, the sediments, and the biota. Inorganic arsenate salts are very soluble in water and are usually the predominant forms of arsenic in natural waters. However, the reducing action of aquatic microorganisms metabolizes arsenate to form arsenite and a variety of methylated organoarsenicals (i.e., methylarsonic acid and dimethylarsinic acid). Inorganic arsenic is removed from waters primarily by adsorption onto clays, iron oxides, aluminum hydroxides, and organic material; coprecipitation with various metal ions is also effective in removing arsenic from water. In most cases the sediment is the major sink for arsenic, but the mobilization by underwater microorganisms returns much of this arsenic to the water column (OWRS, 1979).

The predominant fate of arsenic applied to soil is the formation of inorganic arsenate bound as insoluble salts. Soluble arsenical species are converted to insoluble forms by metal cations in the soil or by adsorption. The equilibrium between insoluble and soluble species can require from several days to months depending on amounts applied and soil variables. Soluble arsenicals may be leached deeper into the soil or be carried away as runoff into groundwater or streams.

TABLE 1: PROPERTIES OF ARSENIC COMPOUNDS^a

Chemical Name and Formula	CAS Number and Synonyms	Oxidation State	Transitions Points	Water Solubility (per liter)	Specific Properties
Arsenic pentoxide As_2O_5	1303-28-2 Arsenic oxide [As_2O_5]; arsenic acid; arsenic anhydride	+5	Decomposes at 315°C to As_2O_3 vapor	1.5 kg (16°C)	Forms arsenic acid, H_3AsO_4 , in water, the salts of which are known as arsenates.
Arsenic acid $\text{H}_3\text{AsO}_4 \cdot 1/2 \text{H}_2\text{O}$	7778-39-4 Orthoarsenic acid	+5	bp 160°C	170g (20°C)	Triprotic acid with pKa values of 2.2, 7.0, and 11.5. ^b
Calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$	7778-44-1 Arsenic acid, [H_3AsO_4], calcium salt (2:3)	+5	---	0.13g (25°C)	
Lead arsenate PbHAsO_4	7784-40-9 Arsenic acid, [H_3AsO_4], lead (+2) salt (1:1); schultenite	+5	Decomposes at 720°C	v.sl.soluble	Occurs in mineral form as schultenite.
Sodium arsenate Na_3AsO_4	7631-89-2 Arsenic acid, [H_3AsO_4], sodium salt	+5	---	389 (16°C)	Also available as the the potassium salt, KH_2AsO_4 . The name "sodium arsenate" is applied to both the disodium and tri- sodium salts.
Arsenic trioxide As_2O_3	1327-53-3 Arsenic [As_2O_3] oxide; arsenous acid; white arsenic	+3	Begins to sublime at 193°C.	21 (25°) ^b Rate of dis- solution is very slow ^b	Forms arsenous acid $\text{As}(\text{OH})_3$ in water, ^b the salts of which are known as arse- nites.

TABLE 1: PROPERTIES OF ARSENIC COMPOUNDS (cont.)

Chemical Name and Formula	CAS Number and Synonyms	Oxidation State	Transitions Points	Water Solubility (per liter)	Specific Properties
Sodium Arsenite NaAsO_2	7784-46-5 Arsenous acid, sodium salt	+3	---	v.sol.	Available as the potassium salt $\text{KH(AsO}_2)_2$.
Arsenic sulfide As_2S_3	1303-33-9 Arsenic sulfide [As_2S_3]; arsenic yellow; orpiment	+3	mp 320°C bp 707°C	0.5 mg (18°C)	Burns in air forming $\text{As}_2\text{O}_3 + \text{SO}_2$. Occurs naturally as orpiment ^b .
Arsenic As	7440-38-2 Arsenic black; metallic arsenic	0	Sublimes at 613°C	insoluble	When heated in air sublimes and is oxidized to As_2O_3 .
Arsine AsH_3	7784-42-1 Arsenic hydride; hydrogen arsenide	-3	bp -55°C	200 ml (20°C)	Faint garlic odor. Vapor density is 2.7 times that of air.
Monosodium methylarsonate $\text{CH}_3\text{AsO}_3\text{HNa}$	2163-80-6 Methane arsonic acid, monosodium salt; arsonic acid, methyl-, monosodium salt; MSMA	Organo- metallic	mp 115- 119°C	570g (25°C)	Also available as disodium salt, disodium methyl- arsonate (DSMA).
Cacodylic acid $(\text{CH}_3)_2\text{AsO}_2\text{H}$	75-60-5 Dimethyl- arsinic acid; Arsine oxide, hydroxydimethyl-.	Organo- metallic	mp 200°C	830g (22°C)	Available as the sodium salt (sodium cacodylate).
Arsanilic acid $\text{C}_6\text{H}_4\text{NH}_2\text{AsO}_3\text{H}_2$	98-50-0 Arsonic acid, (4-aminophenyl)-	Organo- metallic	mp 232°C	sol. (Hot)	Available as the sodium salt, sodium arsanilate.

^a Source: (IARC, 1980) unless otherwise noted.^b (NRC, 1977)

In soils, microbiological oxidation and reduction processes act chiefly on organic arsenicals (methylarsonic and cacodylic acids). Eventually the organic arsenicals and inorganic arsenites are oxidized, either chemically or biologically, to carbon dioxide and arsenate. Arsenic removal by volatilization is reported to occur by bacterial formation of arsines, e.g., dimethylarsine (NRC, 1977; OTS, 1976).

An important concept with respect to the distribution of arsenic in the environment is the dynamic nature of the ecological cycling of this element. Arsenic is ubiquitous in nature and is released from natural sources such as weathering of minerals, volcanic action, and decay of plant matter. Man may modify the arsenic cycle by causing localized high concentrations through inadvertent contamination from industrial activity, or through the widespread use of arsenic compounds such as arsenical pesticides. Arsenic exists in a variety of chemical forms which are subject to numerous chemical and biological transformations in the environment. Because the chemical speciation of arsenic is important in determining its adverse health and ecological effects, transformations may significantly alter the mobility and toxicity of arsenic (NAS, 1977).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACTS: Jerry Stara, FTS 684-7531; Les Grant, FTS 629-2266; Ed Ohanian, FTS 472-6820)

Chemical species of arsenical compounds differ greatly in their toxicity. For example, trivalent species (e.g., arsenites) of inorganic arsenic are generally considered more toxic than pentavalent species (e.g., arsenates). Organic arsenic species (e.g., cacodylic acid) are much less toxic than the inorganic species; organoarsenicals found in seafood are essentially nontoxic. Arsine and its methyl derivatives are the most acutely toxic of all the arsenical compounds.

2.1.1 Acute Toxicity

Acute arsenic toxicity can cause severe intestinal injury, accompanied by shock, pain, vomiting, diarrhea, muscle cramps, and cardiovascular disturbances. In some cases, these can progress to convulsions, paralysis, and death from circulatory failure. Delayed-onset injury to the motor and sensory nerves, congestive heart failure, and skin lesions are also seen, as well as severe red blood cell breakage and kidney failure. The acute lethal dose for humans appears to range from 70 to 180 mg for trivalent arsenic. Subacute doses in the range of 50 mg over a 2-week period may produce demonstrable clinical effects such as anorexia, fainting, nausea and some vomiting, dry throat, shooting pains, diarrhea, nervous weakness, tingling of the hands and feet, jaundice, erythema, and peripheral neuropathy. Longer exposure can result in dry, falling hair; brittle, loose nails; eczema; darker skin; exfoliation; and hyperkeratoses of the palms and soles (OWRS, 1980; ECAO, 1980).

Exposures to arsine concentrations of 25 ppm for 30 minutes can be fatal, and 3 to 10 ppm can cause symptoms within a few hours. Animal studies indicate that "blood changes" occur within a period of several weeks following exposures to concentrations between .5 and 2 ppm for 3 hours a day. Arsine exposure results in hemolytic anemia, and clinical signs characterized by nausea, headache, anemia, coppery skin coloration, and shock within 2-24 hours after exposure (OTS, 1976; IARC, 1980).

2.1.2 Chronic Toxicity

The effects of extended, lower-level exposure to inorganic arsenic can include heart and blood vessel injury, damage to the peripheral (motor and sensory) nervous system (accompanied by motor weakness, muscle soreness and in extreme cases, paralysis), liver damage (such as cirrhosis), and various skin lesions, such as patch scaling and hyperpigmentation (OWRS, 1980).

Carcinogenicity, Teratogenicity, and Mutagenicity

- Based on clinical, occupational, and epidemiological studies, inorganic arsenic is generally considered to be a human carcinogen. Both the EPA's Office of Health and Environmental Assessment and IARC have concluded that there is sufficient evidence that inorganic arsenic is

a lung carcinogen when inhaled and a skin carcinogen when ingested. In general, however, animal studies have not shown carcinogenicity for arsenic compounds even when administered near the maximum tolerated dosage for long periods (ECAO, 1980; IARC, 1980; Pershagen, 1981).

Occupational lung cancers have been associated with inorganic arsenic exposure for: miners of gold-bearing ores, workers exposed to arsenical insecticides or sheep dip, and copper smelter workers exposed to arsenic trioxide. It must be recognized however, that these occupational environments are usually complex and the interaction of arsenic with other pollutants (e.g., sulfur dioxide) as well as with tobacco smoking is not well understood (NAS, 1977).

Skin cancers have been reported in several groups exposed to arsenic via drugs or drinking water. The best documented case is in Taiwan where the arsenic levels in drinking water ranged from 0.01 to 1.8 mg/l with a median of about 0.5 mg/l. The prevalence of skin cancer, hyperpigmentation, and kerotosis correlated with the arsenic content of the water; for skin cancer, the rate was 10.6 per 1,000. EPA has used this study to estimate risk factors for consumption of arsenic in drinking water (OWRS, 1980).

However, several aspects of the Taiwan study noted above have resulted in some controversy concerning the carcinogenic potency of ingested arsenic. In general, these uncertainties arise from the presence of other bioactive organic chemicals in the water supply, and the nutritionally deficient diet of the exposed population (OWRS, 1980). Other difficulties in assessing the carcinogenic potency of arsenic include the lack of a satisfactory animal model for arsenic carcinogenicity and the observed nutritional necessity of arsenic in some nonhuman mammals (NAS, 1977; NAS, 1980).

Teratogenic effects of arsenic compounds have been demonstrated at relatively high single dose levels (15 to 45 mg/kg) in hamsters, rats, and mice. Effects included reduced fetal and birth weights, increased fetal resorption, skeletal defects, and other malformations. However, studies of chronic oral exposure to low levels of arsenic (e.g., 5 ppm in drinking water during pregnancy) have not shown significant effects on fetal development. Thus, extrapolation of the results in experimental animals to man is especially difficult in light of the failure to demonstrate effects at low exposure levels. Human epidemiology data is not sufficient to demonstrate specific associations between arsenic exposure and teratogenic or embryotoxic effects (ECAO, 1980).

Studies performed on the mutagenic activity of arsenic have yielded conflicting results. An increased frequency of chromosome aberrations has been found in lymphocytes of wine growers, in psoriatic patients treated with arsenic, and in arsenic-exposed copper smelter workers (OWRS, 1980). However, arsenite and arsenate were both inactive in the Ames assay (S. typhimurium). Evidence for arsenicals causing DNA damage in other bacterial systems (i.e., B. subtilis) is contradictory. Arsenic is reported to interfere with enzymatic DNA repair processes in E. Coli (Sirover, 1981).

2.2 Environmental Effects (CONTACTS: Charles E. Stephan, 783-9510 and John Gentile, FTS 838-4843)

2.2.1 Aquatic Effects (OWRS, 1980)

The chemistry of arsenic in water is complex and the form present in solution is dependent on such environmental conditions as Eh, pH, organic content, presence of suspended solids, and sediment characteristics. Based on freshwater data, trivalent inorganic arsenic (with the exception of arsenic trisulfide) and the pentavalent form appear to be similarly toxic to aquatic organisms. Organic arsenic compounds and arsenic trisulfide were much less toxic but additional data are needed to adequately determine their effect on aquatic life.

Acute data for 14 freshwater species show that differences in toxicity were not related to the type of exposure (i.e., static or flow-through tests). Acute values for trivalent inorganic arsenic ranged from 812 to 41,760 ug/l. A life cycle test was conducted with Daphnia magna which gave a chronic value of 912 ug/l. No chronic tests with freshwater fish species were reported.

The freshwater residue data indicate that arsenic is not bioconcentrated to a high degree and that lower forms of aquatic life may accumulate higher arsenic residues than fishes. Arsenic accumulation in freshwater aquatic organisms does not appear to be greatly affected by the form of arsenic present, although the highest residues were seen in exposures with the trivalent inorganic form. The highest arsenic bioconcentration factor was found in one test with a saltwater bivalve mollusc which indicates that these organisms may accumulate more arsenic than freshwater organisms.

The other toxicological data revealed a wide range of toxicity based on tests with 16 freshwater species and several endpoints of effect. Comparisons of these data with acute tests showed that arsenic toxicity was increased with increased exposure time. Higher temperatures also appeared to increase arsenic toxicity whereas water hardness had no significant effect. Effects of other parameters such as pH, suspended solids, and organic content in the water were not found in the literature.

Early life stages of freshwater aquatic organisms appear to be the most sensitive indicator of arsenic toxicity and should be used as the basis for formulating criteria for arsenic in water. The lowest effect concentration for arsenic and freshwater organisms is 40 ug/l.

Trivalent inorganic arsenic acute values for saltwater fish species were 16,000 ug/l for Atlantic silverside and 15,000 ug/l for the fourspine stickleback; and, among three invertebrate species, acute values ranged from 508 ug/l for a copepod and 7,500 ug/l for the American oyster. No chronic, plant, or equilibrium residue data are available for any saltwater species and arsenic.

2.2.2 Other Effects

Arsenic is a natural element which can be found in various forms in nearly all living organisms and soils. Arsenic accumulates in soils and can interact with several plant nutrients. Phosphate, for example, can increase or decrease absorption of arsenic by plants depending on conditions. If soils have a high fixation for arsenic, the addition of phosphate can increase the amount of soluble arsenate and quicken the leaching of the arsenic from top soil into deeper soil. The phytotoxicity of organic arsenical herbicides is characterized by a relatively slow kill; chlorosis, cessation of growth, and browning are followed by dehydration and death (NAS, 1977; OTS, 1976).

Poisoning of forage-eating livestock by inorganic and methylated arsenical compounds, especially those used as herbicides and defoliants, has been reported. Most cases result from accidental or careless contamination of forage. The use of phenylarsonic animal feed additives as recommended is beneficial and does not constitute a health hazard. The mechanism of action of these feed additives remains obscure; these additives are absorbed and excreted without significant metabolic change (NAS, 1977).

3. ENVIRONMENTAL RELEASE (CONTACT: Michael Slimak, FTS 426-2503)

Several EPA program offices have evaluated and ranked source categories of arsenic release. Even though the reported quantities emitted to the environment differ, there is general agreement as to the major sources of arsenic release. Table 2 lists both the uses of arsenic and its releases to the environment by media. The release data are only crude estimates and have not been verified in most cases by sampling and analysis.

Estimates of the relative importance of natural releases of arsenic into the environment vary widely, from a value of about 7,000 kkg per year (OWRS, 1981) to a range of 45,000 to 120,000 kkg per year (OTS, 1979). Natural releases occur primarily into water by weathering of minerals in soils and continental rock. The major anthropogenic sources of arsenic release are pesticide use/production, copper smelting, and fossil fuel combustion. About 81% of the total anthropogenic release of arsenic occurs to land, 16% is emitted to air, and only 3% is discharged to water.

3.1 Air Releases (CONTACT: Warren Peters, FTS 629-5645)

Significant sources

- Primary copper smelters (SIC 3331)

Other sources

- Lead smelters (SIC 3332)
- Primary zinc smelters (SIC 3333)
- Glass manufacturing, using arsenic in production processes (SIC 332)
- Pesticide manufacturing (SIC 2679)
- Cotton gins processing arsenic desiccated cotton (SIC 0724)

3.2 Water Releases (CONTACT: Michael Slimak, FTS 426-2503)

Significant sources

- Zinc smelters (SIC 3333)

Other sources

- Phosphate rock mining (SIC 1475)
- Copper smelters (SIC 3331)
- Iron and steel foundries (SIC 332)

TABLE 2: ANTHROPOGENIC SOURCES OF ARSENIC TO THE ENVIRONMENT (kkg/yr and %)a

I. <u>USES OF ARSENIC</u>		Estimated Rate (kkg/yr)	% of Total Uses	
A.	Pesticides	10,250	70.0	
B.	Wood preservatives	2,930	20.0	
C.	Glass manufacture	730	5.0	
D.	Nonferrous alloys	440	3.0	
E.	Small volume (feed additives, veterinary chemicals, electronics, catalysts)	290	2.0	
II. <u>RELEASES TO ENVIRONMENT</u>		Estimated Rate (kkg/yr)	% of Discharges to Land	% of Total Releases
A.	Land Discharges			
	1. Energy production ^b	14,000	32.5	26.3
	2. Pesticide prod./use ^c	8,680	20.2	16.3
	3. Copper production	8,100	18.8	15.2
	4. Iron & steel prod.	5,700	13.2	10.7
	5. Arsenic prod.	1,200	2.8	2.3
	6. Lead & zinc prod.	1,100	2.6	2.1
	7. Phosphorus prod.	640	1.5	1.2
	Land Total	43,000		80.9
B.	Airborne Emissions ^d	Estimated Rate (kkg/yr)	% of Emissions to Air	% of Total Emissions
	1. Pesticide prod./used	3,150	37.4	5.9
	2. Copper prod.	2,450	29.1	4.6
	3. Lead & zinc prod.	1,600	19.1	3.0
	4. Glass manufacture	580	6.9	1.1
	5. Energy production ^c	540	6.4	1.0
	6. Iron & steel prod.	88	1.0	0.2
	7. Arsenic production	3	<0.1	<0.1
	8. Phosphorus production	<1	<0.1	<0.1
	Air Total	8,410		15.9

TABLE 2: ANTHROPOGENIC SOURCES OF ARSENIC TO THE ENVIRONMENT
(kkg/yr and %) (cont.)

C. Aquatic Discharges	Estimated Rate (kkg/yr)	% of Discharges Direct	% of Total Emissions
1. Industrial discharges			
a. Pesticide use	720	42.3	1.3
b. Lead & zinc prod.	560	33.0	1.0
c. Phosphorus prod.	160	9.4	0.3
d. Energy prod. ^c	150	8.8	0.3
e. Copper prod.	38	2.2	<0.1
f. Iron & steel prod.	9	<0.1	<0.1
g. Nonferrous metals	7	<0.1	<0.1
2. POTW's	<57	<0.7	<0.1
Water Total	1,700		3.1
Total Releases	53,100		

^a Source, unless otherwise noted: (OWRS, 1981).

^b Energy production = combustion of fossil fuels.

^c Includes cotton ginning.

^d From (OAQPS, 1980).

4. EXPOSURE ROUTES

Human exposure to the various forms of arsenic occurs primarily through ingestion and inhalation. While ingestion is the most significant pathway for exposure in the general population, airborne arsenic poses more of a problem in occupational settings and to populations in the vicinity of smelters. Furthermore, much of the arsenic in food is probably in the form of less toxic organoarsinicals and average levels are not considered hazardous (ECAO, 1980).

Table 3 summarizes estimated average daily intake of arsenic from the major exposure routes. The procedures used in arriving at these estimates are discussed in detail below.

4.1 Air Exposure (CONTACT: Warren Peters, FTS 629-5645)

Air exposure to arsenic occurs primarily at locations with major arsenic emission sources (copper, lead, and zinc smelters; glass and pesticide manufacturing plants; secondary smelters; and cotton gins) and arises from stack and/or fugitive emissions.

Atmospheric arsenic concentration data for 1974 in 267 locations in the United States are available from the National Air Sampling Network conducted by EPA. The annual average concentrations for all sites ranged from below the detection limit ($.001 \text{ ug/m}^3$) to 0.083 ug/m^3 ; the mean arsenic level was 0.003 g . For eight locations near nonferrous smelters the average was 0.03 ug/m^3 , and the average for eight remote rural areas was 0.0004 ug/m^3 (assuming a concentration of zero for samples reported to be below the detection limit) (OAQPS, 1980).

The extent of respiratory absorption of arsenic in humans depends on a number of variables such as particle size and the chemical form of arsenic. Experiments with human subjects indicate an overall absorption efficiency of about 30% for inhaled arsenic. The average daily exposure to airborne arsenic may be estimated from the average arsenic levels by assuming a daily ventilation rate of $20 \text{ m}^3/\text{day}$. Therefore, the estimates for arsenic absorbed via inhalation shown in Table 3 are obtained from the daily exposures using an absorption efficiency of 30% (ECAO, 1980).

Limited data suggests that the predominate form of airborne arsenic is inorganic. Both trivalent and pentavalent arsenic have been detected in air samples of mixed origin; arsenic from smelters, however, is thought to be primarily in the trivalent form (As_2O_3). While the presence of inorganic arsenic in the air is of concern due to its association with lung cancer, ambient levels are normally far below the excessive arsenic levels observed in the occupational exposures associated with cancer (ECAO, 1980).

4.2 Water Exposure (CONTACT: Michael Slimak, FTS 426-2503)

In an EPA national study of residential tap water, two-thirds of the samples (from 3,834 residences) had arsenic levels above 0.1 ug/l .

TABLE 3: AVERAGE ARSENIC EXPOSURE LEVELS AND DAILY ABSORBANCE^a

Exposure Route	Average Arsenic Levels	Daily Exposure (ug)	Estimated Daily Absorbance (ug)	Major Chemical Species
<u>Air</u>				
All sites	0.003 ug/m ³	0.06	0.018	inorganic trioxide and pentoxide
Near smelters	0.03 ug/m ³	0.6	0.18	
Remote sites	0.0004 ug/m ³	0.008	0.002	
<u>Drinking Water</u>	2.4 ug/l ^b	4.8	4.8	probably arsenates
<u>Food</u>				
	13 ppb (fruits)	15	15	organo-arsenicals
	44 ppb (meat, fish)	from average diet	from average diet	
	<1 ppb (other foods)			
<u>Cigarettes</u>	1.5 ppm (1.5 ug/cigarette)	6 ug/pack	2 ug/pack	unknown

^a Estimates were calculated as described in the text; most of the data is summarized in (ECAO, 1980) except where otherwise noted.

^b (OWRS, 1981)

The average, minimum, and maximum arsenic levels detected were 2.37, 0.50 and 214 ug/l, respectively. There have been a number of reports of isolated instances of high concentrations of arsenic in well water sources associated with geochemical enrichment in arsenic. These wells are mainly found in the western U.S. and Alaska. Arsenic is widely distributed in low concentrations in U.S. surface waters. A survey of a large number of community water supplies revealed that only 0.4% exceeded 10 ug/l. Since arsenic in drinking water is predominately in soluble form (probably arsenates) virtually all of it is absorbed from the GI tract (OWRS, 1980; ECAO, 1980).

Using an average arsenic level in drinking water of about 2.4 ug/l, it can be estimated that approximately 4.8 ug of mostly inorganic arsenic is absorbed from an average daily consumption of 2 liters of drinking water.

Concentrations of arsenic for the entire U.S. in various media are reported in the STORET Water Quality data base. The median levels for total recoverable arsenic are: water, 3 ppb; fish, 100 ppb; sediment, 5,000 ppb. Sediment concentrations are generally 3 orders of magnitude greater than ambient waters (OWRS, 1981).

4.3 Other Exposure Routes

Food

There is a wide diversity in estimates of daily intake of arsenic in foods. While older estimates suggested that the average diet could provide arsenic intake near 1 mg/day (OWRS, 1980), more recent analysis by FDA indicates the level is probably much less in recent years. For 1974, FDA has calculated that the total daily dietary intake for a standard diet was about 15 ug; this represents a marked drop from the FDA estimate of about 75 ug/day for 1967-1969. This decrease was ascribed to decreasing use of arsenical pesticides and changes in analytical methods. Approximately 80% of the 15 ug/day intake is attributed to meats, poultry and seafood; levels in seafood can be exceedingly high (ECAO, 1980; OWRS, 1981).

Assuming arsenic in food is all absorbed, the estimated daily absorbance from food is 15 ug. However, the chemical forms of arsenic in various types of foodstuffs are crucial for assessment of risk since most of arsenic intake is from this source. Based on available data, arsenic in marine life is present in complex organoarsenical forms of limited toxicity. Also, part of the arsenic in terrestrial food animals is present as cacodylic acid, a form much less toxic than inorganic arsenic (ECAO, 1980).

Tobacco

Tobacco-borne arsenic will also contribute to the respiratory burden of cigarette smokers. Recent data indicates an average level of about 1.5 ppm of arsenic in tobacco. Assuming a cigarette has a mass of one gram, and that only 20% of the arsenic is released in mainstream smoke, the inhaled amount would be approximately 6 ug/pack of

20 cigarettes. Of the 6 ug inhaled, approximately 30% would be absorbed by the lungs; therefore 2 ug/pack of cigarettes is the estimate for daily absorbance from cigarette smoke (ECAO, 1980).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available on the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purpose of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. For further information contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information contact Delores Evans at FTS 382-3546 or Irv Weiss at FTS 382-3524.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base that is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Delores Evans at FTS 382-3546 or Ingrid Meyer at FTS 382-3773.

5.5 Chemical Substances Information Network (CSIN)

The prototype CSIN, operational since November 1981, has been developed by merging the technologies of computer networking and distributed data base management. CSIN is not another data base, but a library of systems. Through the CSIN front-end intermediary management computer, the user may access and use independent and autonomous information resources that are geographically scattered, disparate for data and information content, and employ a variety of types of computer hardware, software, and protocols. Users may converse in and among multiple systems through a single connection point, without knowledge of or training on these independent systems.

Currently, six independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), CIS, EPA-CICIS, CAS-On-Line, SDC-orbit, and two files of Dialog: CRGS and TSCA Inventory. The CSIN management computer allows the user to create, retrieve, store, manipulate data and queries. This eliminates the need for reentering long lists of chemical identifiers or other information elements that are part of the original query or which have been identified and acquired from one or more of the CSIN resources. For further information contact Dr. Sid Siegal at FTS 382-2256.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 475 individual data bases and models that contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained by offices within EPA. For further information, contact Charlene Sayers at FTS 755-9112.

The following data bases contain information on arsenic compounds.

Baseline Survey of Public Water Supplies on Indian Lands
BAT Review Study for the Timber Products Processing, Gum and Wood, Chemicals, and the Printing and Publishing Industries
Best Management Practices, Timber Industry Effluent Guidelines - Runoff
Best Management Practices, Timber Industry Effluent Guidelines - Sludge
Boone County Field Site
Chemicals in Commerce Information System
Compatibility Studies to Determine Effectiveness of Treatment Alternatives for Selected Industrial Wastewaters
Compliance Data System
Compliance Sampling Toxicant Surveys
Consolidated Permits Program-Application Form 1,2b,2c
Continuous Monitoring Subset
Contrary Creek Project-803801
Crete, Illinois Metals Environmental Samples
Data Collection Portfolio for Industrial Waste Discharges
Discharge Monitoring Report
Discharge Monitoring Report Files

Drinking Water
 Drinking Water Special Study
 Energy and Mining Point Source Category Data Base
 EPA, Region X, Point Source File
 Federal Facilities Information System
 Federal Reporting Data System
 Federal Reporting Data System-Regional
 Fine Particle Emissions Information System
 Fish Kills
 Food Industry Group
 Fugitive Emissions Information System
 Hazardous Waste Site Tracking System
 Heavy Metals, Minerals, and Nutrient Data Base
 Hemlock, Michigan Environmental Samples
 Hewlett-Packard
 Humacao Ambient Data Base
 IFB Organics Data Base
 Indicatory Fate Study
 Industrial Process Evaluations
 Inhalable Particulate Analysis Bank
 Inhalable Particulate Network
 Innovative Technology, Timber Industry Effluent Guidelines
 Inorganic Chemicals Industry Regulation Record
 Inventory (Regional National Pollutant Discharge Elimination System)
 LiPari Landfill
 Liquid Effluents Data System
 Love Canal Data Handling System
 Metals Data Base-New Mexico
 Method Validation Studies of Priority Pollutants
 Model State Information System
 Multimedia Assessment of the Inorganic Chemicals Industry
 National Electronic Injury Surveillance System
 National Pollutant Discharge Elimination System (NPDES) Permit
 Compliance-Region III
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Monitoring Reports-Region VII
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Monitoring Reports-Region I
 National Water Quality Surveillance System
 Nationwide Urban Runoff Program
 Needs Survey
 New York Bight Ocean Monitoring Program
 Organic Chemicals/Plastics Industry
 Paint and Ink Analytical Data
 Permit Compliance System
 Pesticide Incident Monitoring System
 Pesticide Product Information System
 Pharmaceutical Screening/Verification Data Base
 Priority Pollutants-Region I
 Priority Pollutants-Region III
 Priority Pollutants Data Base
 Publicly Owned Treatment Works (POTW) Analytical Data
 Publicly Owned Treatment Works (POTW) Quality Control
 Puerto Rico Reservoirs

Regional Air Pollution Study-Ambient
 Regional Air Pollution Study-Point and Area Source
 Regional Toxics Monitoring Program
 Resource Conservation and Recovery Act (RCRA)-Hazardous Waste Site
 Inspections
 Salsbury Laboratories
 Screening Sampling Program
 Sludge Distribution and Marketing Regulations-Community Impact Survey
 Soil, Water, Estuarine Monitoring System
 Solid Discharge Data System
 Sources of Toxic Pollutants Found in Influent to Sewage Treatment
 Plants
 Southeast Ohio Exposure-Assessment
 Spill Prevention Control and Countermeasure
 Storage and Retrieval of Aerometric Data
 System for Consolidated Permitting and Enforcement Data Base
 Textile Industry BAT Study-Toxic Sampling Data
 Toxic Metals
 Toxics Monitoring
 U.S. Virgin Islands-St. Thomas, St. Croix
 United Nuclear Corporation (UNC) Spill-Rio Puerco Monitoring
 UPGRADE
 Utility Simulation Model Data Base
 Verification Data Base
 Wasteload Allocation File
 Water Enforcement Regional System
 Water Quality Information System
 Wisconsin Power Plant Impact Study Data System

6. REGULATORY STATUS (Current as of 4/23/82)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Air Act (CAA)

- Section 112 - Inorganic arsenic is listed as a hazardous air pollutant based on the chemical's potential carcinogenicity and significant public exposure (45FR37886). However, emission standards (NESHAP) have not been promulgated. New Stationary Source Performance Standards (NSSPS) for primary copper smelters require monitoring of arsenic levels present in copper ore processed (40CFR60.165(a)).

Clean Water Act (CWA)

- Section 311 - The following arsenic compounds have been designated as hazardous materials and are subject to reportable quantities of 5,000 lbs: arsenic disulfide, arsenic pentoxide, arsenic trichloride, arsenic trioxide, and arsenic trisulfide (40CFR116.4 and 117.3).
- Sections 301, 304, 306 and 307 - Arsenic and its compounds are listed as priority pollutants (toxic pollutants, 40CFR401.15). Effluent limitations and/or pretreatment standards for arsenic have been issued for sections of the following industries:

Inorganic chemicals (40CFR415)
Nonferrous metals (40CFR421)
Timber products (40CFR429)
Ore mining and dressing (40CFR440)
Pesticides (40CFR455)

Safe Drinking Water Act (SDWA)

- Section 1412 - Establishes a maximum contaminant level (MCL) for arsenic in drinking water supplies (40CFR141.11).
- Sections 1421 to 1424 - Requirements are set forth for state programs to protect underground drinking water. The regulations cover operators of wells which inject hazardous wastes, such as arsenic, (40CFR146).

Resource Conservation and Recovery Act (RCRA)

- Section 3001 - A number of arsenic compounds are designated as acute hazardous or toxic wastes (40CFR261.33). These chemicals are hazardous/toxic wastes when they are discarded or intended to be discarded as commercial products, or off-specification species. Container residues and spill residues are also included. Total extractable arsenic may also characterize wastes as

hazardous (EP toxicity, 40CFR261.24). Specific sources of hazardous waste which contain arsenic and the hazardous waste numbers are: pesticides (K031), coking (K060), veterinary pharmaceuticals (K084, K101, K102) (40CFR261.32 and App. VII). Arsenic compounds are also listed as hazardous constituents (40CFR261, App. VIII).

- Sections 3002 to 3006 - Hazardous wastes containing arsenic are subject to further control under RCRA. Regulations cover generators (40CFR262), and transporters (40CFR263) of such waste; and treatment, storage, and disposal are subject to interim standards (40CFR264 and 265).

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- Labeling requirements for arsenical pesticides include a statement of ingredients and the percentage of water soluble arsenic (40CFR162.10(g)).
- Tolerance levels are established for arsenic residues on a variety of agricultural commodities (40CFR180.3(d)(4), and .192 to .196).
- Procedures are recommended for the disposal of arsenic-containing pesticides and containers of such pesticides (40CFR165.7 to .11).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- For inorganic arsenic the permissible exposure limit (PEL) is 10 ug/m³ (8-hour time-weighted average); workers in some occupations are excluded. Inorganic arsenic is regulated as a carcinogen (29CFR1910.1018). For organic arsenic compounds the PEL is 0.5 mg/m³ and for arsine the PEL is 0.2 mg/m³ (29CFR1910.1000).

DOT - Hazardous Material Transportation Act

- Regulations cover the packaging, labeling, and shipping of hazardous materials such as arsenic compounds (49CFR171 to 177, parts).

FDA - Food, Drug, and Cosmetic Act

There are numerous regulations which control the amount of arsenic which may be contained as an ingredient or as a "specification" in certain food, drugs, and cosmetics; a large number of these regulations involve food coloring additives. The regulations include the following:

- Tolerances are established for residues of arsenic in food-producing animals (21CFR556.60).

- The maximum contaminant level for arsenic in bottled water is 0.05 mg/l (21CFR103.35(d)).
- Warning labels are required for over-the-counter drugs which contain arsenic (21CFR369.20); more stringent labeling, container and testing requirements exist for trivalent organic arsenicals (21CFR680, Subpart B).

MSHA - Mine Safety and Health Act

- Reporting requirements (30CFR50.20-6(b)(7)) and respirator use are established for mines (30CFR11.130).

Atomic Energy Act

- Where discharges of licensed material containing arsenic exceed certain radioactive limits, waste disposal and reporting requirements take effect (10CFR20, App. B). Packaging and operating standards exist for transporting radioactive materials containing arsenic (10CFR71).

6.2 Proposed Regulations

6.2.1 EPA Programs

CWA

- Proposed ocean discharge criteria for issuing and reviewing NPDES permits for discharges into seas, contiguous zones, and oceans (45FR9549).

6.2.2 Other Programs

FDA

- Proposals have been issued to revise regulations concerning the use of arsenic drugs in food-producing animals (46FR2456).
- New or revised standards have been proposed for arsenic impurities in sugar, juices and other foods (43FR14679, 19866, 58576; 44FR10729, 10742, 10748; 46FR2456).

6.3 Other Actions

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) - CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the clean-up of hazardous waste disposal sites. (42USC9601; PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46FR54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA

have been issued in a proposed rule (47FR10972). Hazardous substances as defined by Section 101(14) of CERCLA include: hazardous wastes designated under Section 3001 of the RCRA; hazardous air pollutants regulated under Section 112 of the CAA; water pollutants listed under Sections 307 and 311 of the CWA (and also any substances regulated in the future under Section 7 of TSCA and Section 102 of CERCLA). Therefore, arsenic compounds are hazardous substances under CERCLA and will be subject to regulations issued under Superfund.

- CWA - Water quality criteria for arsenic have been issued for aquatic life and human health (45FR79318).
- OAQPS is evaluating the need for regulations under Section 112 of the CAA for several source categories of inorganic arsenic. The first priority for development is copper smelters processing high arsenic-containing ore.

7. STANDARDS AND RECOMMENDED CRITERIA^a

7.1 Air

- OSHA Standards (8-hr TWA)

Inorganic Arsenic (29CFR1910.1018)	10 ug/m ³
Organic Arsenic (29CFR1910.1000)	500 ug/m ³
Arsine (29CFR1910.1000)	200 ug/m ³
- NIOSH Recommended Limit (15 minute ceiling for inorganic arsenic) 2 ug/m³

7.2 Water

- Drinking Water Standard (MCL)^b
(40CFR141.11) 50 ug/l
- Water Quality Criteria (45FR79318)

Human Health (10 ⁻⁵ risk) ^b	0.022 ug/l
Freshwater Aquatic Life (trivalent arsenic)	440 ug/l
Saltwater Aquatic Life (trivalent arsenic)	508 ug/l
- The following arsenic compounds are designated as hazardous substances under Section 311 of the CWA and have reportable quantities for spills defined as over 5,000 lbs: arsenic disulfide, arsenic pentoxide, arsenic trioxide, and arsenic trisulfide (40CFR117.3).

7.3 Hazardous Waste

- Wastes which contain in excess of 5.0 mg/l of total extractable arsenic are classified as hazardous ("EP" toxicity, 40CFR261-.24).

^a See Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

^b EPA recognizes the widely differing values for arsenic for drinking water (50 ug/l) and WQC (0.02 ug/l at the 10⁻⁵ risk level). Health effects information and other available data pertinent to this issue (i.e., the carcinogenicity of ingested arsenic) are not sufficient or definitive enough to allow a clear decision. ORD has been directed to develop an epidemiologic study which might resolve the issue of the carcinogenic potential of arsenic in U.S. drinking water supplies. (Contact Charles Mitchell, FTS 426-2317 for information on how this is progressing).

7.4 Other

- Tolerance levels for arsenical pesticides in food are listed in 40CFR180.3(d)(4), and .192 to .196. Numerous other tolerances and standards exist for arsenic in a variety of foods, drugs and additives (see FDA citations in Section 6.1.2 of this document).

8. SPILL OR OTHER INCIDENT CLEAN-UP DISPOSAL (CONTACT: National Response Center, 800-424-8802 or 426-2675 in the Washington, D.C. area)

8.1 Hazards and Safety Precautions

Many inorganic arsenic compounds are poisonous materials which may be fatal if inhaled or ingested. Contact may cause burns to skin or eyes. Fire may produce irritating or poisonous gases. Runoff from fire control or dilution water may cause pollution.

Arsine is an extremely flammable gas and may be ignited by sparks and flame. Flammable vapor may spread from spill area. Container may explode in heat of fire. Vapor explosion and poison hazard exists indoors, outdoors, and in sewers.

Store arsenic compounds in tightly closed containers in well ventilated areas away from heat and water and from exposure to food. Arsenic trisulfide and arsenic should be kept away from exposure to oxidizing agents and acids. Avoid ingestion, contact with skin and eyes, and inhalation. Wear protective clothing including safety glasses, gloves, and a NIOSH-approved self-contained breathing apparatus. For workplace requirements see 29CFR1910.1018. In case of arsine spill, wear positive pressure breathing apparatus plus full protective clothing.

8.2 First Aid

Move victim to fresh air; call emergency medical care. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Remove and isolate contaminated clothing and shoes. In case of contact with material, immediately flush skin or eyes with running water for at least 15 minutes.

8.3 Emergency Action

Spill or Leak

Avoid contact and inhalation of the spilled cargo. Stay upwind; notify local fire, air, and water authorities of the accident. Evacuate all people to a distance of 200 feet upwind and 1,000 feet downwind of the spill. Wear full protective clothing including NIOSH-approved rubber gloves and boots, safety goggles or face mask, hooded suit, and either a respirator whose cannister is specifically approved for this material, or a self-contained breathing apparatus. Care must be exercised to decontaminate fully or dispose of all equipment after use.

The Department of Transportation's "Hazardous Materials 1980 Emergency Guidebook" recommends the following general procedures for containment and clean-up for arsenic spills (excluding arsine). Small spills, take up with sand, or other noncombustible absorbent material, then flush area with water. For small dry spills, shovel into

dry containers and cover; move containers; then flush area with water. Large spills, dike far ahead of spill for later disposal. Arsine concentration in air can be reduced by the use of water spray.

Fire

Fire can be extinguished with water in flooding quantities as fog, "alcohol" foam, dry chemical, or carbon dioxide. If water or foam is used, contain flow to prevent spread of pollution, keep from drains and sewers. Remove container from fire area if you can do it without risk.

In case of arsine fire, let burn unless leak can be stopped immediately. Otherwise, extinguish by method mentioned above; stay away from ends of tank. Cool containers that are exposed to flames with water from side until well after fire is out. For massive fire in cargo area, use unmanned hose holder or monitor nozzles. If this is impossible, withdraw from area and let fire burn. Withdraw immediately in case of rising sound from venting safety device or discoloration of tank.

8.4 Notification and Technical Assistance

Section 103(a) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) requires notification of the National Response Center if releases exceed reportable quantities (NRC: 800-424-8802; in Washington, D.C., 426-2675). Under Section 311 of the CWA, the reportable quantities for spills are 5,000 lbs. for arsenic disulfide, arsenic pentoxide, arsenic trichloride, arsenic trioxide, and arsenic trisulfide. Reportable quantities for hazardous arsenic compounds are being finalized under CERCLA (see Section 6.3 of this document).

For emergency assistance call:

CHEM TREC: 800-424-9300

For information, call EPA, Division of Oil and Special Materials (1-202-245-3045).

8.5 Disposal

The following arsenic compounds are designated as acutely hazardous wastes under Section 261.33(e) of RCRA: arsenic acid (P010), arsenic pentoxide (P011), arsenic trioxide (P012), and diethylarsine (P038). Generators of greater than 1 kg of any commercial or off-specification material, or greater than 100 kg of any spill residue resulting from clean-up, are subject to regulations under 40CFR262 to 265. Cacodylic acid is designated as a toxic waste (U136) under Section 261.33(f) of RCRA; in this case a small quantity generator which produces less than 1,000 kg per month of total hazardous waste is not subject to RCRA regulations. Finally, wastes that fail the EP toxicity test for arsenic under Section 261.24 are also subject to RCRA regulations.

The following wastestreams are subject to RCRA regulations and contain arsenic compounds. Hazardous wastes are listed by industry and hazardous waste number (see 40CFR261.32):

Pesticides (K031) - By-product salts generated in the production of MSMA and cacodylic acid.

Coking (K060) - Ammonia still lime sludge from coking operations.

Veterinary Pharamaceuticals - In the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds, the following are designated as hazardous wastes:

(K084) - Wastewater treatment sludge.

(K101) - Distillation tar residues from the distillation of aniline-based compounds.

(K102) - Residue from the use of activated carbon for decolorization.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

- 9.1 Air (CONTACTS: Larry Purdue, FTS 629-2665,
Robert Stevens, FTS 629-3156 or
Robert Shaw, FTS 629-3148)

Since arsenic is not yet a regulated air pollutant, EPA has not promulgated an analysis methodology; but arsenic measurements have been made for a number of years on selected samples from the National Air Monitoring Stations (NAMS) and its predecessor, the National Air Surveillance Network (NASN). Data from these networks are stored in the National Aerometric Data Bank under the jurisdiction of OAQPS.

The procedure used most recently is based on the collection of airborne particulate matter on glass fiber filters using the high volume sampling technique and the measurement of arsenic in the particulate matter using neutron activation analysis. The limit of detection is approximately 5 mg/m³, although this will vary with the composition of the glass fiber filters used for sampling. The relative standard deviation of the analytical measurement is approximately 20 percent. Both internal and external quality control procedures are available.

The Environmental Sciences Research Laboratory at Research Triangle Park has measured arsenic concentrations between 10 and 1,800 ng/m³ by X-ray fluorescence (X-RF). Despite possible complications due to the presence of lead, X-RF measurements are within ± 20 percent where arsenic concentrations exceed 0.5 ug/m³. A dichotomous sampler modified to collect volatile forms of arsenic has been developed for sampling near high temperature sources (e.g., smelters).

- 9.2 Water (CONTACTS: Gerald D. McKee, FTS 684-7372 or
Ted Marten, FTS 684-7312)

Arsenic is a Clean Water Act 304(h) parameter and is listed as an inorganic priority pollutant. It is also a drinking water parameter, with a maximum contaminant level of total arsenic set at 0.05 mg/l. The term "total arsenic" is defined as the sum of the concentrations of all forms of arsenic in both the dissolved and suspended fractions of the sample. When a sample containing suspended material is to be used for analysis of total arsenic, a sample digestion step is required. For the total analysis of dissolved arsenic by a colorimetric or gaseous hydride procedure, sample digestion is also required to ensure that the arsenic is in the proper chemical state and available for reaction.

There are a variety of approved methods for arsenic analysis ("Methods for Chemical Analysis of Water and Wastes, 1979", EPA-600/4-79-020). The spectrophotometric measurement at 535 nm of the complex formed by the reaction of silver diethyldithiocarbamate (SDDC) with arsine is a well-known procedure. This colorimetric method, however, is limited to the analysis of arsenic concentrations at or above 0.01 mg/l.

The gaseous hydride method is an atomic absorption procedure. After an acid digestion the arsenic is reduced to the trivalent form and converted to arsine using either zinc metal or sodium borohydride. Using an inert gas, the arsine is then swept into a hydrogen fueled flame or heated quartz tube for dissociation and atomic absorption measurement. The normal analytical working range for hydride methods is from 0.002 to 0.020 mg/l.

The graphite furnace method is also an atomic absorption method. For this analysis, the sample is digested with nitric acid and hydrogen peroxide and then stabilized with nickel nitrate. For every matrix analyzed, verification is necessary to determine that the method of standard addition (MSA) is not required. The optimum range for graphite furnace methods (for 20 ul injection) is 0.005 to 0.100 mg/l.

In response to the improved state-of-the-art of multi-element analysis, a water/wastewater related method which includes arsenic has been promulgated by EPA (Federal Register, 44, p. 69559, December 3, 1979). The revised method (200.7) uses inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The atomic-line emission spectra is processed by computer to subtract background and to correct for any spectral interference. While the estimated detection limit is 0.05 mg/l (at 193.7 nm), the optimum working range for arsenic by the ICP technique is considered to be from 0.25 mg/l to well above 100 mg/l.

The following table summarizes the approved methods with appropriate references:

LIST OF APPROVED TEST PROCEDURES FOR TOTAL ARSENIC

	<u>Reference Method No.</u>			
	<u>EPA</u> ¹	<u>Standard Methods</u> ²	<u>ASTM</u> ³	<u>USGS</u> ⁴
Sample Digestion ⁵	206.5	--	--	--
Spectrophotometric (SDDC)	206.3	303E	D2972-78(B)	I-3062-78
AA-Gaseous Hydride	206.4	307B	D2972-78(A)	I-3060-78
AA-Furnace	206.2	304	--	--
ICP-AES ⁶	200.7	--	--	--

1. "Methods for Chemical Analysis of Water and Wastes, 1979," EPA-600/4-79-020.
2. "Standard Methods for the Examination of Water and Wastewater," 15th Edition, American Public Health Association, Washington, D.C.

3. "Annual Book of ASTM Standards, Part 31, Water," American Society for Testing and Materials.
4. "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments" U.S. Department of the Interior, Geological Survey, Open-file Report 78-679.
5. Sample digestion for total arsenic may be omitted for AA graphite furnace and ICP analyses provided the sample has a low COD and the filtrate meets the following criteria: (a) visibly transparent, (b) no odor, (c) free of particulate matter following acidification.
6. Inductively Coupled Plasma Optical Emission Spectrometric Method (ICP) for Trace Element Analysis of Water and Wastes; Method 200.7 published by U.S. EPA, EMSL-Cincinnati.

9.3 Solid Wastes

Two approved methods for arsenic analysis in solid wastes are given in "Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods," (US EPA/SW-846/May 1980), Method No. 8.51. The graphite furnace method uses atomic absorption to analyze samples digested with $\text{HNO}_3/\text{H}_2\text{O}_2$. The gaseous hydride method also uses atomic absorption to measure arsenic levels in wastes which are digested with $\text{HNO}_3/\text{H}_2\text{SO}_4$. Both procedures are nearly identical to the atomic adsorption methods approved for arsenic determination in water.

9.4 Other Samples

Typical methods of analysis for arsenic levels in a wide variety of biological and other environmental matrices are listed in a monograph published by the International Agency for Research on Cancer, World Health Organization (IARC, 1980). In most cases, however, these methods are not "approved" procedures.

Recently, several procedures for species-specific analysis of arsenic have been published. Procedures have been developed for determination of nanogram amounts of methylarsonic acid and cacodylic acid, in addition to inorganic arsenic. (Andreae, M.O. (1977), Anal. Chem. 49, 820 and Braman, R.S., et al., (1977), Anal. Chem., 49, 621). NIOSH has developed an automated ion-exchange method for species-specific arsenic analyses which is capable of detecting as little as 3 ppb. A draft report has been published by the Health Effects Research Laboratory, Cincinnati ("Speciation of Arsenic Compounds in Water Supplies," HERL, Cinn. 1981) which summarizes the state-of-the-art for arsenic analyses.

A procedure is given for the determination of total arsenic in sediments and other solids in "Chemical Laboratory Manual for Bottom Sediments and Elutriate Testing," (EPA-905/4-79-014). The dried sediment is digested ($\text{HNO}_3/\text{H}_2\text{O}_2$) and heated in $\text{HNO}_3\text{-HCl}$ to solubilize the metal. Analysis is obtained by atomic absorption using the graphite

furnace method and standard addition techniques. A similar procedure for arsenic determination in sediment can be found in "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," (EPA/EMSL-Cinn./Aug., 1977, revised October 1980). This publication also contains a procedure for the analysis of fish for arsenic by a gaseous hydride-atomic absorption method.

9.5 Quality Assurance

ORD has a full range of Quality Assurance support available which includes the following items:

- unknown performance evaluation samples
- known quality control check samples
- recommended procedures for verification of results

These are available to the regions through the Quality Assurance Branch of EMSL-Cincinnati. (Quality Assurance Contact: John Winter, FTS 684-7325).

REFERENCES

The major references used in preparation of this document are listed below. EPA references are listed by EPA office of origin and the year of publication. For further information refer to contacts given throughout this document or contact the relevant EPA offices listed at the end of this section.

- (ECAO, 1980) Health Assessment Document for Arsenic, Environmental Criteria and Assessment Office, EPA - Draft, Research Triangle Park, N.C. (1980).
- (IARC, 1980) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals, Vol. 23, International Agency for Research on Cancer, World Health Organization (1980).
- (NAS, 1977) Drinking Water and Health, Vol. 1, pp. 316-344, National Academy of Sciences, Wash., D.C. (1977).
- (NAS, 1980) Drinking Water and Health, Vol. 3, pp. 337-345, National Academy of Sciences, Wash., D.C. (1980).
- (NRC, 1977) Arsenic, National Research Council, Wash., D.C. (1977).
- (OAQPS, 1980) Human Exposure to Atmospheric Arsenic, EPA contracts 68-01-4314 and 68-02-2835, Office of Air Quality Planning and Standards, Research Triangle Park, N.C. (1980).
- (OTS, 1976) Technical and Microeconomic Analysis. Task III - Arsenic and Its Compounds, EPA-560/6-76-016, Office of Toxic Substances (1976).
- (OTS, 1979) Status Assessment of Toxic Chemicals - Arsenic, EPA-660/2-79-210b, Office of Toxic Substances (1979).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, Vol. 1, Ch. 6, EPA-440/4-79-029a, Office of Water Regulations and Standards (1979).
- (OWRS, 1980) Ambient Water Quality Criteria for Arsenic, EPA 440/5-80-012, Office of Water Regulations and Standards (1980).
- (OWRS, 1981) Strategy for Controlling Environmental Exposure to Arsenic, EPA-Draft, Office of Water Regulations and Standards (1981).
- (Pershagen, 1981) "The Carcinogenicity of Arsenic," G. Pershagen, Environmental Health Perspectives, 40: 93-100 (1981).
- (Sirover, 1981) "Effects of Metals in in Vitro Bioassays," M.A. Sirover, Environmental Health Perspectives, 40: 163-172 (1981).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
---------------------------------	----------

Effluent Guidelines Division	426-2571
------------------------------	----------

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information and Analysis Program

382-2249

Asbestos

ASBESTOS

Table of Contents

	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-3
<u>Environmental Release</u>	3-1
Air Releases	3-1
<u>Exposure Routes</u>	4-1
Air Exposure	4-1
Water Exposure	4-2
Other Exposure Routes	4-2
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-3
Other Actions	6-3
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1

July, 1982

Spill or Other Incident Clean-Up/Disposal 8-1

Sampling, Acceptable Analytical Techniques, and Quality Assurance 9-1

Air 9-1

Water 9-1

Solid Wastes 9-2

Other Samples 9-2

Quality Assurance 9-4

References and Office Contacts R-1

ASBESTOS

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Fibrous asbestos minerals have found wide use because of a unique combination of resistance to heat and chemical attack, high tensile strength, and flexibility. Asbestos is found in thousands of commercial products including heat-resistant textiles, reinforced cement, filters, thermal insulation, and brake linings. As a consequence of the natural occurrence and wide use of this mineral, asbestos fibers are widely dispersed in the environment. Asbestos constitutes a health hazard for asbestos workers and is a potential threat unless it is completely sealed into a product (NIH, 1978; IARC, 1977).

Asbestos is a common name for a group of natural silicate minerals that separate into thin but strong fibers. Current usage of the term asbestos is usually reserved for the serpentine mineral chrysotile, and five fibrous minerals in the amphibole class (see Table 1). Identification of asbestos fibers is relatively simple with bulk samples due to the unique characteristics of these minerals; however, positive identification is difficult for submicroscopic samples. For regulatory purposes, asbestos has been defined as having a length to diameter (aspect) ratio of 3:1 or greater. Chrysotile is the major mineral form of asbestos and accounts for more than 95% of the fiber presently used in the United States (NIOSH, 1980).

1.2 Chemistry and Environmental Fate/Transport

Asbestos minerals are composed of silicon, oxygen, hydrogen, and various metal cations (sodium, magnesium, iron, calcium). Typical formulas for asbestos are given in Table 1 along with important properties and uses. Asbestos minerals are resistant to chemical attack; chrysotile, however, is susceptible to degradation by acids. All forms of asbestos will decompose to simpler components (i.e., pyroxenes and silica) when heated to temperatures in the range 600-1000°C (OWRS, 1979; Michaels, 1979).

Dry asbestos easily separates and forms dust which consists of fibers varying from several inches to microscopic in size. These microscopic fibers are hazardous and may remain in the atmosphere long enough to travel great distances. Because asbestos persists in the environment it can be widely redistributed by natural and human means. While not water soluble, asbestos may remain in suspension and travel great distances. The surface of asbestos fibers in water may carry either a net positive (chrysotile) or negative (amphiboles) charge. These charged surfaces permit the formation of stable suspensions in water. Some materials, notably trace metals and organic compounds, may be adsorbed onto or react with asbestos surfaces. Bioaccumulation and biotransformation processes are not significant in aquatic organisms. Suspended asbestos fibers eventually undergo physical

TABLE 1: PROPERTIES OF ASBESTOS FIBERS^a

Name	CAS Number and General Formula ^b	Decomposition ^c Temperature (°C)	Properties	Uses
Chrysotile	12001-29-5 $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	800-850	Usually white or pale in color; flexible, silky, and tough; high tensile strength.	Widely used in cement sheets & pipes, floor and ceiling materials, and friction products.
Crocidolite	12001-28-4 $\text{Na}_2(\text{Mg},\text{Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	800	Blue color, flexible, brittle and tough; high tensile strength.	Sparingly used for asbestos cement pipe.
Amosite	12172-73-5 $(\text{Mg},\text{Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	600-900	Usually pale brown and brittle.	Some use in asbestos cement sheet and as thermal insulation.
Anthophyllite (fibrous)	17068-78-9 $(\text{Fe},\text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	950	White in color and brittle; talc-like form.	Limited use in composite materials (plastic resins).
Actinolite (fibrous)	13768-00-8 $\text{Ca}_2(\text{Mg},\text{Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	1040	Pale to dark green in color.	Fibrous actinolite is of no commercial significance.
Tremolite (fibrous)	14567-73-8 $\text{Ca}_2(\text{Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	1040	White to grey; usually brittle.	Fibrous form has no significant uses, but is an impurity in talcs.

^a Source: (Michaels, 1979) unless otherwise noted.

^b (OWRS, 1979).

^c Typical temperature peak or range observed during differential thermal analysis (DTA) of the thermal breakdown to simpler products in an inert atmosphere.

degradation or chemical coagulation which allows them to settle into the sediment. Environmental release of asbestos occurs primarily through disposal of consumer wastes to land. Disposal to the land is also an important source of atmospheric asbestos (NIH, 1978; OWRS, 1979).

2. EFFECTS INFORMATION

- 2.1 Health Effects (CONTACT: Jerry Stara, FTS 684-7531; Les Grant, FTS 629-2266; Bob McGaughy, FTS 755-3968; Ed Ohanian, FTS 472-6820)

Disposition of Fibers in the Body

The disposition of inhaled asbestos fibers depends primarily on fiber size. Certainly some fibers are ultimately deposited in the airways and lung tissue. Some could also be expectorated or conveyed to the gastrointestinal tract by airway clearance mechanisms and possibly some to the pleural and peritoneal cavities via lymphatic drainage.

Of asbestos fibers found in human lungs, a majority are less than 5 um in length and seldom do they exceed lengths of 200 um or diameters of 3.3 um. One autopsy study of persons with occupational exposure demonstrated that all asbestos fibers examined in the lung were less than 0.5 um in diameter. This preponderance of small fibers in part reflects their ability to remain suspended in air for longer periods than larger fibers, but it is also a function of their deposition and clearance characteristics once they enter the respiratory tract. Studies with mammalian cells in culture indicate that these shorter fibers (usually less than 5 um) may be engulfed by alveolar macrophages and transported to lymphatic channels or the mucociliary blanket for excretion. Longer fibers may be only partially engulfed or may be engulfed by several macrophages at once (NIH, 1978).

Asbestos fibers may enter the gastrointestinal tract via the diet, or by ingestion of inhaled fibers cleared from the respiratory tract. While most of the swallowed asbestos is probably excreted in the feces, microscopic fibers can migrate through the gastrointestinal mucosa. Recent studies show significant asbestos levels in tissue samples (liver, jejunum, lung) of humans due to transmucosal uptake of fibers ingested by drinking asbestos contaminated water. Ingestion of asbestos by humans has been shown to lead to asbestos fibers in urine; this result also provides evidence for transmucosal passage of mineral fibers. Animal studies of gastrointestinal tract penetration by asbestos fibers have yielded conflicting results (OWRS, 1980).

2.1.1 Acute Toxicity

Acute effects are of little consequence in inhalation exposure to high asbestos concentrations. Temporary breathing difficulty due to air-flow abnormalities may result from short-term exposure to high levels.

2.1.2 Chronic Toxicity

Nearly all the positive evidence linking asbestos to human disease has come from occupational studies. Asbestosis requires the greatest degree of exposure, followed by bronchial carcinoma and mesothelioma, in that order. However, development of these diseases follows the opposite trend, so that heavy exposure to asbestos may lead to death by asbestosis or bronchial carcinoma long before mesothelioma arises (OWRS, 1980).

Asbestosis - Asbestosis is a long-term disease resulting from inhalation of asbestos fibers. Fibrous tissue is generated around the alveoli of the lungs and the thickened membranes impede the interchange of carbon dioxide and oxygen. Severely affected people develop shortness of breath and may eventually die of heart failure. All varieties of asbestos appear capable of producing asbestosis (NIH, 1978).

Carcinogenicity Mutagenicity and Teratogenicity - Exposure to airborne asbestos fibers has been conclusively shown to cause bronchial carcinoma (lung cancer), mesothelioma (a rare cancer of the membranes lining the chest and abdomen), and gastrointestinal tract cancers (IARC, 1977; NIH, 1978; OWRS, 1980).

Bronchial cancer is the major exposure-related cancer affecting asbestos workers. All commercially available asbestos forms are linked with increased incidences of lung cancer to varying degrees. Evidence indicates that combined exposure to both asbestos and cigarette smoke greatly increases the risk of lung cancer. Almost all reported cases of mesothelioma have been associated with exposure to asbestos. Epidemiological studies suggest that all commercial forms of asbestos (except possibly anthophyllite) may cause mesothelioma. There does not appear to be a synergistic effect between asbestos and cigarette smoking regarding mesothelioma (OWRS, 1980; IARC, 1977).

Epidemiological studies have shown that workers exposed to airborne asbestos also incur increased risks of developing cancers of the gastrointestinal tract (throat, stomach, colon, rectum). In the one study in which synergism has been investigated, esophagus cancers were increased in incidence only among smoking asbestos workers, not in their non-smoking co-workers. Stomach and colon-rectum cancer showed no smoking relationship. Cancers of the oropharynx and larynx were also concentrated among the smoking asbestos workers (OWRS, 1980; NIH, 1978).

For asbestos-related GI cancers discussed above, such exposure occurs principally via inhalation and by swallowing asbestos fibers cleared from the lung (in the sputum), and by ingestion of fibers trapped in the nose or mouth. However, no definitive study exists which establishes risk levels for ingested asbestos alone. To date, the studies which have examined the effects of asbestos in drinking water are not

conclusive. Also, two forms of asbestos (chrysotile and amosite) were recently found not to be carcinogenic in large-scale feeding experiments using hamsters (National Toxicology Program).

Chromosomal aberrations in hamster cells due to asbestos have been observed. However, mutagenicity in several bacterial systems was not observed in testing with various forms of asbestos. No data exist that link teratogenic effects with exposure to asbestos fibers, although transplacental transfer of asbestos has been reported (OWRS, 1980).

2.2 Environmental Effects

2.2.1 Aquatic Effects

No freshwater or saltwater organisms have been tested with asbestos minerals. The only available data result from field studies in which chrysotile and amphibole fibers were found in fish samples taken from freshwater with known concentrations of these fibers. While muscle tissue does not appear to accumulate asbestos, bioconcentration may occur in fish liver and kidney (OWRS, 1980).

3. ENVIRONMENTAL RELEASE (CONTACT: Phillip Cook, FTS 783-9523;
William Brungs, FTS 838-4843)

Chrysotile is the major type of asbestos used in the manufacture of asbestos products. These products include asbestos cement pipe, flooring products, brake linings and clutch facings, roofing products, and coating and patching compounds (see Table 2). Most of the asbestos used in the United States is imported; in 1980, for example, 80 kkg were produced in this country while 328 kkg were imported. Domestic use of asbestos has decreased significantly in recent years due, in part, to the well publicized undesirable health effects; e.g., 1980 consumption was less than one-half of 1972 consumption (SRI, 1982).

Total releases of asbestos to the U.S. environment have been estimated to be about 240,000 kkg (for 1980). Major sources include asbestos mining and milling; manufacturing and use of asbestos products; and disposal of asbestos wastes. Although these estimates are uncertain, several important conclusions are indicated (NIH, 1978).

- Land discharge accounts for nearly all releases; air emissions may total about 1% of asbestos released to the environment and water discharges are on the order of 0.2%.
- Solid waste disposal by consumers is by far the major discharge of asbestos.
- The potential for intermedia transfer of asbestos is significant due to its widespread use and persistence in the environment. For example, solid wastes produced from the manufacture and use of asbestos products, and from demolition can be emission sources of atmospheric asbestos. Water may become contaminated with asbestos due to: erosion from natural deposits; runoff from sites of asbestos disposal; and release of asbestos fibers from asbestos cement pipes used in water distribution systems.

3.1 Air Releases (CONTACT: Gilbert Wood or John Copeland
FTS 629-5595)

Significant Sources

- Asbestos mining operations; ore and tailings dumps (SIC 1499)
- Surfacing of roadways with asbestos tailings (SIC 1499 and 1611)
- Asbestos milling (SIC 1499)
- Manufacturing of
 - asbestos cloth, cord, or other textiles (SIC 2200 and 3292)
 - asbestos cement (SIC 3292)
 - asbestos fireproofing and insulation materials (SIC 3292)
 - asbestos friction products (SIC 3292)
 - asbestos paper, millboard and felt (SIC 2661)
 - asbestos floor tile (SIC 3292)
 - paints, coatings, and caulks which contain asbestos (SIC 2850)
 - plastics and rubbers which contain asbestos (SIC 2821 and 2822)

- Chlorine production (SIC 2812)
- Demolition operations (SIC 1795)
- Use of spray-on asbestos materials (SIC 174)
- Open storage of asbestos materials (SIC 4221)
- Fabrication of asbestos products (SIC 3292)

Other Sources

- Transportation (consumption of asbestos brake linings)
- Mining of minerals containing trace amounts of asbestos
- Disturbance of asbestos-bearing overburden by off-road vehicles during mining and road-building or for recreation.

TABLE 2: DOMESTIC CONSUMPTION OF ASBESTOS (1980)

(kkg/yr and %)		
<u>Uses of Asbestos</u>	<u>kkg/yr</u>	<u>% of Total Uses</u>
Asbestos cement pipe	144,000	40
Flooring products	90,000	25
Friction products	44,000	12
Roofing products	26,000	7
Packing and gaskets	13,000	4
Surface coats/sealants	11,000	3
Insulation	9,000	3
Asbestos cement sheet	8,000	2
Others	14,000	4
Total	<u>359,000</u>	

Source: (SRI, 1982)

4. EXPOSURE ROUTES

There is little data available in the published literature on non-occupational exposures to asbestos. Occupational exposures are commonly reported as optical-microscope-visible fibers/cm³ (or f/ml) greater than 5 μ m in length. However ambient levels are normally determined by transmission electron microscopy without a minimum length criterion. It is not known whether differences in fiber counts actually reflect differences in concentrations. In addition, techniques used to prepare samples for electron microscopic observation may cause alteration in fiber size.

4.1 Air Exposure (CONTACT: Gilbert Wood, FTS 629-5595)

Asbestos of the chrysotile variety is a ubiquitous contaminant of ambient urban air. Over 98 percent of the 24-hour samples monitored and analyzed had chrysotile asbestos concentrations of less than 20 ng/m³ and most samples were less than 2 ng/m³ (OWKS, 1980).

As one would expect, airborne asbestos can be found in the vicinity of asbestos mines, mills, manufacturing facilities, and waste dumps. But elevated levels of fibers also may be found near concentrations of braking vehicles, in buildings in which asbestos spray products have been used, and in cars and homes of asbestos workers who have contaminated them with dust brought from the work area on clothing, body, or equipment. Asbestos may be inhaled by persons who install their own asbestos roofing or flooring, or who repair such items as automobile brakes and clutches, home heating and plumbing systems, wires for toasters and waffle irons, or the walls of their homes (NIH, 1978).

Asbestos contamination has also been found in office buildings and schools where loose asbestos fireproofing material was applied to the structural steel surfaces. Current average exposure to asbestos in buildings containing accessible friable asbestos materials (i.e., materials not enclosed and easily crumbled or pulverized) has been estimated to be between 58 and 270 ng/m³ (OPTS, 1980).

Most asbestos is incorporated into finished products where the fibers are bound in a matrix (e.g., asbestos-cement pipe and sheet, flooring and roofing products, and friction products), and this reduces the possibilities for air contamination. Yet, by the application of sufficient energy, fibers may be dislodged from even tightly bound materials; automobile brake linings are an example.

Clearly, there are opportunities for human non-occupational atmospheric exposure during installation, use, and repair of asbestos products. However, since there are so many products that use asbestos or materials that may be contaminated with asbestos, it would be next to impossible to estimate human exposure for each product type.

4.2 Water Exposure (CONTACT: Phillip Cook, FTS 783-9523; William Brungs, FTS 838-4843; Ed Ohanian, FTS 472-6820)

Asbestos, usually chrysotile, is commonly found in domestic water supplies. Generally asbestos of all sizes in water is expressed as fiber concentrations using electron microscope techniques. Some estimates relate chrysotile fiber concentrations to mass concentrations. It has been concluded that the majority (about 95 percent) of water consumers in the United States are exposed to asbestos fiber concentrations of less than 10^6 f/l. This is equivalent to the range of 2×10^{-4} to 2×10^{-3} ug/l in water supplies. The mass concentration of chrysotile asbestos in city water with less than 10^6 f/l are likely to be less than 0.01 ug/l, which is equivalent to a daily intake of less than 0.02 ug. However, in areas with significant contamination from natural sources, man's activities, or erosion from asbestos cement water pipes by aggressive water, the intake of asbestos from water can exceed 2 ug/day (OWRS, 1980).

Although the fate of the asbestos in inspired air is only approximately known, it appears that eventually more than half the asbestos inhaled will be swallowed. Assuming that an individual breathes 10 m^3 in 24 hours, most ambient air levels of chrysotile (1 to 10 ng/m^3) result in exposures to the gastrointestinal tract of from 0.01 to 0.05 ug/day of asbestos, although, in some circumstances, inhalation could produce gastrointestinal exposures exceeding 0.1 ug/day. These exposures are to be compared with those from water ingestion which lead to daily intakes of less than 0.02 ug. It would appear that inhalation can give rise to exposures at least equal to that of direct ingestion for most of the population of the United States (OWRS, 1980).

4.3 Other Exposure Routes

Food - There is little information on the contribution of food products to human asbestos exposure. Beers and wines could contain quantities of asbestos fibers similar to those found in water systems (10^6 to 10^7 f/l). This contamination could be from natural water sources or from the erosion of asbestos fibers from purifying filters. Contamination of drinking water by fibrous glass and other synthetic fibers used in cartridge filters has been measured at concentrations in excess of 10^9 f/l (OWRS, 1980).

Erosion of chrysotile from asbestos filters, used to purify parenteral drugs, up to 1 mg/dose have been noted in about one-third of drugs tested. Therefore, the Food and Drug Administration has prohibited the use of asbestos filters for drug purification, without subsequent cleanup (41FR16933).

Occupational - Only after 1966 has occupational monitoring attempted to quantify asbestos exposures by fiber counting techniques. Since then, considerable data have accumulated on occupational exposure of workers to asbestos. A large compilation of such data is included in the 1972 Asbestos Criteria Document (NIOSH, 1972). Levels during the period from 1966 through 1971 were generally under 10f ($f > 5\mu m$)/cm³, although concentrations exceeding 100 f/cm³ were observed, particularly in two plants producing amosite insulation materials and in uncontrolled textile mills. Data on earlier exposures are lacking although some estimates have been made of insulation-workers' exposure and factory environments (OWRS, 1980).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available in the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568 or Robin Heisler at FTS 382-3557.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. (EPACASR is scheduled to be added to CIS in early 1984.) For further information, contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information, contact Dr. Steve Heller at FTS 382-2424.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Doug Sellers at FTS 382-2320.

5.5 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is a sophisticated switching network based on heterogeneous distributed data base management and networking concepts. CSIN offers efficient access to on-line information resources containing data and information relevant to chemical substances, as well as information covering other scientific disciplines and subject matters. The purposes of CSIN are two-fold: first to meet the growing chemical data and information requirements of industry, academe, government (Federal and State), public interest groups, and others; and secondly to reduce the burden on the private and public sector communities when responding to complex Federal legislation oriented to chemical substances.

CSIN is not another data base. CSIN links many independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems". Users may converse with any or all systems interfaced by CSIN without prior knowledge of or training on these independent systems, regardless of the hardware, software, data, formats, or protocols of these information resources.

Information accessible through CSIN provides data on chemical nomenclature, composition, structure, properties, toxicity, production uses, health and environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, seven independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), Chemical Information System (CIS), CAS-On-Line, SDC's ORBIT, Lockheeds's DIALOG, Bibliographic Retrieval Service (BRS), and the US Coast Guard's Hazard Assessment Chemical System (HACS). For further information contact Dr. Sid Siegel at 202-395-7285.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 500 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. The clearinghouse listed 71 citations for asbestos. For further information, contact Irvin Weiss at FTS 382-5918.

6. REGULATORY STATUS (Current as of 9/83)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Air Act (CAA)

- o Section 112 - Asbestos is listed as a hazardous air pollutant and EPA has issued National Emission Standards (NESHAP). The standards prohibit any visible emissions of asbestos from milling, manufacturing, demolition, renovation, and spraying operations. Use of specified air cleaning procedures may be used in lieu of the no visible emission standard. These emission standards apply to the following product manufacturing operations (40CFR61):

textile materials
cement products
fireproofing and insulation material
friction products
paper, millboard, and felt products
floor tile
paints, coatings, caulks, adhesives, sealants
plastics and rubber materials
chlorine
shotgun shells
asphalt concrete

For spray-on materials used for insulation or fireproofing, the standard limits asbestos content to no more than 1 percent. The use of friable asbestos in molded pipe insulation is prohibited. Also, waste management operations for manufacturing, demolition, renovation, and spraying processes are regulated.

Clean Water Act (CWA)

- o Sections 301, 304, 306 and 307 - Asbestos is listed as a Toxic Pollutant (40CFR401.15), also known as a priority pollutant, and is subject to effluent limitation guidelines. Guidelines have been promulgated for subcategories A through K of the asbestos manufacturing point source category. In addition, new point performance standards and pretreatment standards are also included in the regulations (40CFR427, Subparts A to K).

Toxic Substances Control Act (TSCA)

- o Section 8(a) - Naturally occurring chemical substances are included in the inventory reporting regulations. Asbestos is included under the definition of a naturally occurring chemical substance which is (1) unprocessed or (2) processed only by manual, mechanical or gravitational means; by dissolution in water; by flotation; or by heating solely to remove water (40CFR710).

- o Section 6 - School Program - This rule requires public and private elementary and secondary schools in the United States to identify friable asbestos-containing building materials, maintain records and notify employees, and notify the PTA of the inspection results (40CFR763, Subpart F)
- o Section 12 (b) - This regulation requires exporters of asbestos to notify the agency. This requirement applies to raw asbestos, although expansion to include asbestos-containing products is under consideration (40CFR707; 45FR82844).
- o Reporting and recordkeeping requirements have been issued for manufacturers, importers, and processors of asbestos (40CFR763 Subpart D).

Resource Conservation and Recovery Act (RCRA)

- o Although asbestos was originally listed as a hazardous waste (45FR33066), it has been deleted because disposal of asbestos wastes is already regulated under the Clean Air Act (NESHAP). Consideration is being given to regulating asbestos wastes under RCRA and deleting waste disposal regulations under CAA in order to concentrate all waste regulations in one program office.

6.1.2 Programs of Other Agencies

CPSC Consumer Product Safety Act

- o Section 8 and 9 - Consumer patching compounds and artificial emberizing materials (used in fireplaces to simulate live embers and ash) which contain asbestos are banned (16CFR1304 and 1305). General use garments containing asbestos are also banned (16CFR1500.17).

FDA - Federal Food, Drug, and Cosmetic Act

- o Sections 501, 502, and 701 - The content of asbestos particles in parenteral (injectable) drugs is restricted (21CFR133).
- o Sections 201 (s), 409, and 701 (a) - The use of the electrolytic diaphragm process in the production of salt for human consumption is prohibited due to asbestos impurities (21CFR121).
- o FDA also regulates asbestos as a component in packing material (21CFR175.105) and food contact surfaces (21CFR177).

MSHA - Federal Metal and Nonmetallic Mine Safety Act

- o Section 6 - Health and safety regulations exist for workers in mines concerning exposure to asbestos dust (30CFR55.5).

OSHA - Occupational Safety and Health Act

- o Sections 6 and 8 - These regulations list definitions of asbestos, set permissible exposure limits, and describe methods for compliance, measurement, monitoring and recordkeeping (29CFR1910.1001 and 1910.1002).

DOT - Hazardous Material Transport Act (HMTA)

- o These regulations cover the packaging and shipping of asbestos materials (49CFR172 to 177).

6.2 Proposed Regulations

6.2.1 EPA Programs

CAA

- o Amendments to the existing NESHAP have been proposed that would reinstate work practice and equipment provisions. These provisions had been disallowed by the Supreme Court in 1978 (48FR32126).

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund)

- o CERCLA provides for the liability, compensation, cleanup, and emergency response for the release of hazardous substances into the environment. The Act also deals with the cleanup of hazardous waste disposal sites (42USC9601; PL-96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities (RQ), claims procedures, and the confidentiality of business records (46FR54032).
- o Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47FR10972). Adjustments to the statutory reportable quantities have been proposed; however, until an Agency assessment of the carcinogenicity and other effects is complete, the statutory RQ of one pound is applicable for asbestos (48FR23552)

6.3 Other Actions

- o SDWA - The possible development of a drinking water standard for asbestos depends upon ongoing health hazard assessments for ingested asbestos by epidemiological and animal studies.
- o TSCA - EPA is evaluating the need for further regulation of remaining asbestos uses. Alternatives under consideration include labeling requirements and prohibition or otherwise restricting certain uses (44FR60056;CONTACT: Edward Klein, FTS 382-3938). EPA will coordinate its asbestos activities with those of the Federal Asbestos Task Force.

- o CPSC - The Commission has issued an ANPRM on asbestos in consumer products and convened a Chronic Hazards Advisory Panel (CHAP). Based on the findings of the Panel, CPSC will decide what regulatory actions, if any, are appropriate. The final report of the CHAP is available on request (301-492-6800; 48FR39486).
- o OSHA - An emergency temporary standard of 0.5 fibers/cm³ has been issued for asbestos. Emergency temporary standards are effective for six months or until superseded by a permanent standard or stayed judicially.

7. STANDARDS AND RECOMMENDED CRITERIA^a

7.1 Air

- OSHA permissible exposure limit (29CFR1910):

8 hr. TWA	2 f/cm ^{3b}
ceiling concentration	10f/cm ³

- NIOSH recommended limits:

8 hr. TWA	0.1 f/cm ^{3b}
ceiling concentration	0.5 f/cm ³

7.2 Water

- Water Quality Criteria for human health. This is a gastrointestinal cancer risk projected from occupational inhalation exposure and extrapolated to consumption of asbestos in drinking water (OWRS, 1980).

3 x 10³ f/l
for 10⁻⁵ risk

^a See Appendix A for a discussion of the derivation, use, and limitations of these criteria and standards.

^b Fibers (f) longer than 5 micrometers per cm³ of air using optical microscopy. Note that 1 f/cm³ = 10⁶ f/m³.

8. SPILL OR OTHER INCIDENT CLEANUP/DISPOSAL (CONTACT: National Response Center 800-424-8802; in Washington 426-2675)

General Information

Very little information was available on the cleanup and disposal of asbestos spills. It is recommended that asbestos-containing wastes be packaged in sealed bags or containers prior to transport or disposal in an approved landfill. Section 103(a) and (b) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 requires persons who release hazardous substances into the environment in reportable quantities determined pursuant to Section 102 of the Act to notify the National Response Center (NRC): 800-424-8802 (Washington, D.C., 426-2675). The CERCLA statutory reportable quantity of one pound applies until the Agency assesses asbestos for carcinogenicity and other toxic effects (48FR23552).

An example of ongoing remedial action concerning asbestos is the current Agency activity in Globe, Arizona. Asbestos contamination of the soil at a residential subdivision was discovered in Arizona in 1979. The development had been constructed at the site of a defunct asbestos mill. The site was given a six inch soil cap by the state of Arizona in 1980; however, the soil cap deteriorated due to natural erosion and human activity, once again exposing asbestos fibers. The site was eventually put on the Superfund list of hazardous waste dumps and the families relocated. The soil at the site will be sealed by fabric and fresh soil and re-vegetated. For further information concerning this incident and related Agency cleanup actions, contact the Office of Emergency and Remedial Response (Deborah Dalton, FTS 382-7788).

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES AND QUALITY ASSURANCE

9.1 Air (CONTACT: Michael E. Beard, FTS 629-2623)

EPA has not promulgated an analysis methodology for asbestos. A method for measurement of airborne asbestos by transmission electron microscopy (TEM) has been developed and is in provisional use as evaluation of the technique continues. Airborne asbestos is collected by drawing air through a polycarbonate or cellulose ester filter and the fibers are then examined by TEM at a magnification of 20,000X. Fibers with an aspect ratio of 3:1 (length to width) or greater are counted and identified as possible asbestos by morphology. The fiber identity is confirmed as amphibole or serpentine (chrysotile) asbestos by determining crystal structure with selected area electron diffraction (SAED) patterns and by determining chemical composition with x-ray fluorescence spectroscopy (XRF). Fiber concentration as fiber number and mass per cubic meter of air is reported. Detailed instructions for accomplishing the analysis are given in EPA-600/2-77-178 (Revised June, 1978), "Electron Microscope Measurement of Airborne Asbestos Concentrations, A Provisional Methodology Manual." Evaluation of this method is continuing (EPA Contract No. 68-02-3266) and further revision of the manual is anticipated.

A test of the provisional method by six laboratories gave a precision of 0.49 (ratio of spread between 95% confidence interval and mean value) for fiber number concentration and 1.57 for mass concentration on real samples containing chrysotile. A comparison of mass concentrations of laboratory prepared samples measured by the provisional method and by x-ray spectroscopy showed agreement within 10%. (EPA-600/2-78-038, June 1978).

9.2 Water (CONTACT: J. M. Long, FTS 250-3525)

More detailed information than that given below can be found in the "Interim Method for Determining Asbestos in Water" (EPA-600/4-80-005, January 1980). This method, although considered to be state-of-the-art, has not been designated as the approved procedure for determining asbestos in water.

Samples collected are treated with ultrasound for 15 minutes, and a known volume (generally 50-500 ml, depending on solids and asbestos concentration) of water sample is filtered through a 0.1 um Nuclepore filter to trap asbestos fibers. The filter is then carbon coated, a small portion of this filter with deposited fibers is placed on an electron microscope grid, and the filter material is removed by gentle solution in chloroform. The grids are then examined in a transmission electron microscope at a magnification of about 20,000X. The asbestos fibers are identified by their morphology and electron diffraction patterns and their lengths and widths are measured. The electron diffraction pattern obtained from the suspect fiber is compared with diffraction patterns from UICC standard material for confirmation as asbestos. The fiber must have an aspect ratio (length/width) greater than or equal to 3 to 1. The total area

The interim method has been developed primarily for the analysis of friable, sprayed-on insulation materials which may contain asbestos fibers. Core samples of the suspect material are taken with a clean container such as a 35mm film canister. Caution should be exercised during sampling to avoid generating dust; it is recommended that the material be lightly sprayed with water before sampling. At least three samples should be taken from each area homogeneous in appearance. Detailed instructions on sampling and survey program design are reported in EPA 560/13-80-017A, December 1980 (Asbestos-Containing Materials in School Buildings; Guidance for Asbestos Analytical Programs).

Samples are analyzed by polarized light microscopy (PLM). Samples may be treated to remove interferences such as binders and organic matrix material. Identification of asbestos requires the observation of diagnostic optical properties for each fiber type in the sample. The relative area occupied by asbestos fiber within microscope fields of view is determined by a point counting technique. The relationship between relative area and weight percent of asbestos in a sample is currently being investigated. Multiple laboratory analysis of replicate samples containing a known weight percent of asbestos in a predominately gypsum matrix has provided some information on the performance of the interim method. The bias of the method varies with asbestos type and weight percentage: for samples containing 10% chrysotile by weight, bias is 18.5%; for 50% chrysotile, bias is -24.2%; for 10% amosite, bias is 118.5%; for 50% amosite, bias is 12.1%. The coefficient of variation (CV) varies with the reported area percent value: at a mean reported value of 10% asbestos, CV = 79%; for 50% asbestos, CV = 41%. The rate of false negatives is such that the analysis of three samples of a suspect material, if each contained at least 5% asbestos by weight, would result in three false negatives with a probability less than 0.03 and possibly as low as 0.001.

The interim method includes procedures for x-ray powder diffraction (XRD) analysis should further information on a sample be required. It should be emphasized that XRD affords information only on crystal lattice structure and not on gross crystal morphology. Therefore, XRD cannot distinguish between the asbestos minerals and their non-asbestiform varieties. Particle morphologies must be determined by an optical technique such as PLM. It is therefore imperative that XRD be used only as a corroborative procedure with PLM and not as an independent analytical method. Although electron microscopy can be used for bulk samples, it is not recommended because only small quantities of sample can be analyzed at one time and multi-sample analysis becomes prohibitively expensive.

Procedures for Occupational Exposure

The "NIOSH Manual of Analytic Methods" contains several procedures for determining asbestos levels in air. A thermal analysis procedure

and a microscopic counting method (<450-x magnification) are described in Volume I (1977, Procedures 245 and 239, respectively). Volume V (1977, Procedure 309) contains an x-ray diffraction procedure for chrysotile.

Note that data currently relating concentrations of fibers (>5 um) counted by optical microscopy to concentrations measured by electron microscopy are limited (estimates of the ratio of >5 um fibers counted by electron to optical methods range from 15:1 to 1000:1).

9.5 Quality Assurance (CONTACT: M. E. Beard, FTS 629-2623)

Asbestos reference materials are currently being developed by the National Bureau of Standards (NBS) through an interagency agreement with EPA. The materials will consist of filters deposited with chrysotile and various species of amphibole asbestos in an urban air particulate matrix and will be available in 1982. Prototypes of these devices are available on a limited basis.

An external quality assurance program for PLM analysis of bulk samples is currently available through the EPA Asbestos-in-Schools Program. Presently there are no QC samples for asbestos in water.

REFERENCES

The major references used in preparation of this document are listed below. EPA references are listed by EPA office of origin and the year of publication. For further information refer to contacts given throughout this document or contact the relevant EPA offices listed at the end of this section.

- (IARC, 1977) IARC Monographs on the Evidence of the Carcinogenic Risk of Chemicals to Humans, Vol. 14, International Agency for Research on Cancer, WHO (1977).
- (Michaels, 1979) Asbestos - Properties, Applications, and Hazards, Vol. 1, L. Michaels and S. Chissick, Eds., Wiley (1979).
- (NIH, 1978) Asbestos - An Information Resource, National Institutes of Health, DHHS pub. no. (NIH) 79-1681 (1978).
- (NIOSH, 1972) Criteria For a Recommended Standard - Occupational Exposure to Asbestos, National Institute for Occupational Safety and Health, DHH pub. no. (NIOSH) 72-169 (1972).
- (NIOSH, 1980) Workplace Exposure to Asbestos, National Institute for Occupational Safety and Health, DHHS pub. no. (NIOSH) 81-103 (1980).
- (OPTS, 1980) Support Document: Asbestos-Containing Materials in Schools, EPA-560/12-80-003, Office of Pesticides and Toxic Substances (1980).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, Vol. 1, Ch. 7, EPA-440/4-79-029a, Office of Water Regulations and Standards (1979).
- (OWRS, 1980) Ambient Water Quality Criteria for Asbestos, EPA 440/5-80-022, Office of Water Regulations and Standards (1980).
- (SRI, 1982) Chemical Economics Handbook, "Asbestos-Salient Statistics", SRI International (1982).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
Effluent Guidelines Division	426-2571

Office of Solid Waste (OSW)

State Programs and Resource Recovery Division	755-9107
--	----------

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergenices call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information
and Analysis Program

382-2249

BENZENE

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-2
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-2
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-2
Land Releases	3-2
<u>Exposure</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
Other Exposure Routes	4-1
<u>Data Bases</u>	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical in Commerce Information System (CICIS)	5-2
Chemical Substances Information Network (CSIN)	5-2
Graphic Exposure Modeling System (GEMS)	5-3
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-3
Other Actions	6-5
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1

<u>Spill or Other Incident Clean-Up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-2
Disposal	8-2
 <u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
Solid Waste	9-2
Other Samples	9-3
Quality Assurance	9-3
 <u>References and Office Contacts</u>	 R-1

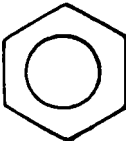
BENZENE

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Benzene is a volatile, flammable aromatic hydrocarbon which is produced domestically in large volume (14.8 billion lbs in 1980). A number of physical properties of benzene are listed in Table 1. The relatively high water solubility and volatility illustrate the high potential of benzene for intermedia transfer.

TABLE 1: PROPERTIES OF BENZENE^a

Synonyms:	Benzol, cyclohexatriene
CAS Number:	71-43-2
Molecular Formula:	C ₆ H ₆
Structure:	
Physical Properties:	
Melting point	5.55°C
Boiling point	80.1°C
Vapor pressure (25°C)	95.2 torr
Flashpoint (closed cup)	-11.1°C
Density (25°C, g/ml)	0.874
Water solubility (25°C)	1.8 g/l
Octanol/water partition coefficient (log P)	2.13

^a Source: Data as summarized in (OTS, 1975).

1.2 Chemistry and Environmental Fate/Transport

Benzene can undergo a wide variety of chemical transformations (substitution, oxidation, reduction) to yield many chemicals of commercial importance. In all cases these reactions are carried out with catalysts, strong acids, elevated temperatures, or high pressures and, therefore, are not likely environmental processes. Furthermore, the direct photolysis in the environment is unlikely because benzene does not absorb natural sunlight appreciably (OTS, 1975; OWRS, 1979).

Due to its high volatility, most of the benzene released to the environment is emitted to the atmosphere. The atmospheric photooxidation of benzene probably subordinates all other fate processes. The half-life ($t_{1/2}$) for benzene in the atmosphere has been estimated to be from 2.4 to 24 hours; benzene depletion is thought to arise primarily from attack of photochemically generated hydroxyl radicals. Because of its fairly high solubility in water, benzene is washed out of the atmosphere by precipitation (OTS, 1975; OWRS, 1979).

The predominate fate for benzene in water is volatilization to the atmosphere. However, due to the relatively high water solubility, persistence of some benzene in the water column is expected. Benzene which persists in the water is expected to biodegrade at a slow rate. The partition coefficient for benzene indicates a low bioaccumulation potential for benzene (OWRS, 1979).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACTS: Jerry Stara, FTS 684-7531; Bob McGaughy, FTS 755-3968; Penny Fenner-Crisp, FTS 472-4944)

2.1.1 Acute Toxicity

In humans acute benzene poisoning is characterized by nausea, vomiting, ataxia (a loss of the power of muscular coordination) and excitement followed by depression and coma. Death is usually the result of respiratory or cardiac failure. Benzene exposure causes acute toxic effects on the central nervous system (CNS). Single exposures of benzene in the air at a concentration of 20,000 ppm have proved to be fatal within 5 to 10 minutes. Effects include headache, nausea, staggering gait, paralysis, convulsions, and eventual unconsciousness and death, usually following cardiovascular collapse. Giddiness and euphoria have also been reported. Severe nonfatal cases have exhibited similar symptoms but recovered after a period of unconsciousness. Accidentally ingested benzene may result in ulceration of the gastrointestinal mucosa (OWRS, 1980).

2.1.2 Chronic Toxicity

Although CNS and gastrointestinal effects may result from chronic benzene exposure, the important toxic manifestations are related to injury of the blood-forming (hematopoietic) system. Benzene damages the bone marrow and may be unique among aromatic hydrocarbons solvents in this respect. Alkyl substitution of the benzene ring (e.g., toluene) markedly alters the metabolism and apparently largely removes the potential for bone marrow toxicity. Benzene is causally related to pancytopenia (reduced levels of red and white blood cells and platelets in the blood) which may be manifested by anemia, increased susceptibility to infections and/or a reduction in the blood's ability to clot. Aplastic anemia (reduced hematopoietic system cells in the bone marrow) is also linked closely to benzene exposure in occupational settings. Benzene exposure studies on numerous nonhuman animals have produced similar blood disorders (OWRS, 1980; Cheremisinoff, 1979).

Carcinogenicity, Mutagenicity and Teratogenicity - Studies linking benzene exposure to human leukemia are quite prevalent and have produced evidence that is considered conclusive (OWRS, 1980; NAS, 1976; IARC, 1980). The most common benzene-associated leukemia is myelogenous leukemia, also known as acute myeloblastic leukemia. These epidemiological studies have been performed on groups of workers which showed a rise in leukemia cases with the usage of benzene. However, the available literature is not considered adequate by EPA for calculation of accurate dose-response curves for the relationship of benzene exposure to the development of acute leukemia. In those studies of acute leukemia where benzene exposure levels have been reported, concentrations have generally been above 100 ppm, or 325 mg/m³ (OWRS, 1980).

Thus far, animal experiments have not yielded conclusive evidence that benzene is leukemogenic. However, recent studies have yielded some carcinogenic response. Rats have shown an increased incidence of Zymbal gland (inner ear) tumors, mammary gland carcinomas, and leukemia; in this study benzene was introduced by gavage (50 and 250 mg/kg, 4-5 times per week for 52 weeks). A recent inhalation study reported an increased incidence of thymic lymphoma in mice exposed to 300 ppm of benzene (OWRS, 1980).

While benzene has not shown mutagenic activity in the Salmonell-microsome in vitro assay, it has shown such activity in animals and man. Chromosomal abnormalities in bone marrow cells have been reported as a result of experimental benzene exposure in rats, rabbits, mice, and amphibians. Benzene is a mitotic poison, producing a decrease in DNA synthesis in animal bone marrow cells in vitro and in cultured human cells. Cytogenetic abnormalities in benzene-exposed humans have been observed and such abnormalities may persist for years after cessation of exposure. Studies on workers clearly indicate a causal relationship between benzene exposure and persistent chromosomal abnormalities. However, no direct evidence supports the linkage between chromosomal aberrations and the induction of leukemia in humans (OWRS, 1980).

From available data, it is unlikely that benzene administered by inhalation during the principal period of organogenesis constitutes a teratogenic hazard. However, the data is not sufficient for other stages of the reproductive cycle (OWRS, 1980).

2.2 Environmental Effects (CONTACTS: Bill Brungs - Freshwater; and John Gentile - Saltwater: FTS 838-4843)

2.2.1 Aquatic Effects (OWRS, 1980)

The acute toxicity of benzene to freshwater species has been measured with eight species and the species acute values range from 5,300 ug/l to 386,000 ug/l. No data are available for benthic crustaceans, benthic insects, or detritivores. However, the most important deficiency may be that only with the rainbow trout were the results obtained from a flow-through test and based on measured concentrations. Results based on unmeasured concentrations in static tests are likely to underestimate toxicity for compounds like benzene that are relatively volatile.

A life cycle test was conducted with one freshwater species, Daphnia magna, but no concentration up to 98,000 ug/l caused an adverse effect. On the other hand, concentrations which apparently did not adversely affect Daphnia magna in a life cycle test did affect other species in acute tests.

For saltwater species, species acute values are available for one fish species and five invertebrate species and range from 10,900 to 924,000 ug/l. These values suggest that saltwater species are about as sensitive as freshwater species. The one acute value from a flow-through test in which toxicant concentrations were measured was not

the lowest value, as was the case with the freshwater acute data. Saltwater plants seem to be about as sensitive as saltwater animals. Other data indicate that herring may have suffered stress and some mortality at 700 ug/l.

The available data for benzene indicate that acute toxicity to freshwater aquatic life occurs at concentrations as low as 5,300 ug/l and would occur at lower concentrations among species that are more sensitive than those tested. No data are available concerning the chronic toxicity of benzene to sensitive freshwater aquatic life.

The available data for benzene indicate that acute toxicity to saltwater aquatic life occurs at concentrations as low as 5,100 ug/l and would occur at lower concentrations among species that are more sensitive than those tested. No definitive data are available concerning the chronic toxicity of benzene to sensitive saltwater aquatic life but adverse effects occur at concentrations as low as 700 ug/l with a fish species exposed for 168 days.

3. ENVIRONMENTAL RELEASE

In recent years nearly all (96% in 1978) of the benzene produced domestically is obtained during the fractionation and enrichment of petroleum; the balance is produced from coke oven sources. Benzene is also a constituent of motor fuels. While present in low concentrations in crude oil, the benzene content of the crude increases during catalytic reformation. BTX (a mixture of benzene, toluene, and xylene) is separated from the refined oil and, if a higher content of aromatics is desired in the gasoline (to raise octane ratings), BTX may be blended back into the gasoline pool. Thus, benzene would not be counted in reports of total benzene production if it was not separated from the BTX mixture. Gasoline production and marketing contributes to the amount of benzene released to the environment even though this benzene is not included in reported production figures. Approximately one-half of the benzene in reformat is isolated for use, the remainder is left in the reformat and stays in gasoline at levels of 0.5% to 2% (OPTS, 1980).

The predominant use of benzene is as a feedstock for the synthesis of a wide variety of organic compounds. Most of these compounds are eventually incorporated into polymers (synthetic rubbers, plastics, resins, and fibers). Based on 1980 data, the largest use for benzene is in the production of ethylbenzene (51%), a precursor for styrene. Cumene (20%) and cyclohexane (14%) are other major products of benzene. Direct uses of benzene (e.g., as a solvent) are now negligible (SRI, 1982; OPTS, 1980).

Table 2 summarizes estimated annual releases (for 1978) from the production and use of isolated benzene; also included are releases arising from the presence of benzene in fuels. It is obvious from the data in the table that nearly all of the benzene released is emitted to the air.

3.1 Air Releases (CONTACT: Dave Patrick, FTS 629-5345)

Significant sources:

- Ethylbenzene/Styrene manufacturing (SIC 2869)
- Coke by-product plants (SIC 3312)
- Benzene storage vessels in refining and chemical plants (SIC 286, 2911)
- Chemical plant petroleum refinery fugitive emissions (SIC 286, 2911)
- Maleic anhydride plants (SIC 2869)

Although benzene release is heaviest from the marketing and use of fuels, the Agency has ranked this as low priority because: the relatively low individual risk to the exposed population; the projected decrease in benzene tailpipe emissions by 1985 to one-quarter of 1978 levels due to increased prevalence of catalytic converters and diesels; and the reduction of benzene evaporative emissions due to SIPs and other actions.

3.2 Water Releases (CONTACT: Charles Delos, FTS 426-2503)

- Solvent use
- Petroleum refinery
- Chemical plants

3.3 Land Releases

- Gasoline refinery
- Petroleum refinery

TABLE 2: ESTIMATED RELEASES OF BENZENE FOR 1978 ^a
(Metric tons/year)

Category	Production	Use	Destruction	Releases to			Unaccounted
				Air	Water	Land	
<u>Pure Sources of Production</u>							
From Petroleum	4,709,900		0	3,139	620	141	
From Coal Light Oil	65,400		0	?	?	?	
From Coal Coking	178,786		0	768	10	8	
Import	225,000		0	13	13	0	
Inventory Reduction	272,000		0	0	0	0	
<u>Pure Uses</u>							
Chemical Feedstock		5,251,000	5,107,300	10,681	235	?	10,865 ^b
Solvent		9,600	6,590	1,505	1,505	0	
Export		151,000	150,983	?	2	15	
Transport/Storage			0	7,200	72	?	
<u>Sources & Uses of Mixtures</u>							
Gasoline Refining	1,400,000		2,000	20,000	1	228	
- Imports	3,288,000		0	0	0	0	
- Transport/Storage			0	21,000	0	?	
- Consumption		4,440,000	4,254,000	165,000	0	0	
Other Fuel Prod.	959,410		0	?	?	?	
- Use		959,410	923,850	35,560	0	0	
Coal Coking ^b				30,000	?	?	
Impure Solvent Production	107,000		0	?	?	?	
- Use		107,000	?	?	?	?	107,000
Oil Spills		30	0	0	30	0	
Other Industry	148			?	148	?	
FOIW			0	90	30	5	
<u>Natural Sources</u>	<u>?</u>	<u></u>	<u></u>	<u>?</u>	<u>?</u>	<u>?</u>	<u></u>
TOTALS	11,205,644	10,918,040	10,444,723	294,956	2,666	397	117,865

^a Most of the data are from a Level II Materials Balance (OPTS, 1980); some release estimates were revised by OWS and OQPS based on more recent data.

^b Carry over into products.

^c Facilities not recovering benzene.

4. EXPOSURE

4.1 Air Exposure (CONTACT: Dave Patrick, FTS 629-5645)

The major route of human exposure to benzene is via inhalation. The annual average exposure for the general public to ambient benzene from all air sources is estimated to be about 1 ppb or 3.2 ug/m³ (OAQPS, 1978). The geographical distribution of benzene emission due to gasoline marketing and use probably approximates population density distribution. Concentrations of benzene around gas stations range from 0.3 to 3 ppm (OTS, 1975). The rural background levels for benzene are estimated to be 0.017 ppb (OWRS, 1980).

Specific sources likely to be exposure routes are:

- Continuous or semi-continuous emissions from benzene-containing process vents
- Fugitive leaks from valves, pumps, and compressors carrying benzene
- Evaporative emissions from improper disposal of benzene-containing storage tanks and handling systems
- Automobile tailpipe emissions; gasoline storage and marketing
- Accidental spills

4.2 Water Exposure (CONTACTS: Charles Delos, FTS 426-2503; Bill Coniglio, FTS 382-3035)

Four of ten water supplies surveyed by EPA contained benzene at concentrations of 0.1 to 0.3 ug/l; the highest level ever reported in finished drinking water was 10 ug/l. Based on the limited data, water intake is not a major route of exposure for benzene (OWRS, 1980).

Specific sources of aquatic benzene of most concern are:

- Accidental spills to water supplies
- Leaks of storage tanks to ground water
- Drinking water contamination from atmospheric wash out
- Waste water discharge downstream from chemical plant
- Food fish contamination

4.3 Other Exposure Routes

Although ingestion of benzene is not considered to be a problem for the general population, relatively high levels of benzene have been found in some foods such as eggs (500-1900 ppb) and rum (120 ppb). Certain occupational groups have the potential for exposure to benzene levels above ambient levels. The industrial activities of con-

cern include chemical manufacturing, coking operations, gasoline service stations, refineries, and solvent operations (OWRS, 1980). Benzene has also been reported in cigarette smoke. The presence of benzene is suspected to result from pyrolytic reformation of tobacco constituents during combustion.

5. DATA BASES

5.1 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. For further information, contact Jim Cottrell at FTS 382-3546.

CIS contains numeric, textual, and bibliographic information in the areas of toxicology, environment, regulations, and physical/chemical properties. Several of these data bases are described below.

5.1.1 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information.

EPACASR is now available on CIS for internal use by EPA personnel and is expected to be accessible from a public CIS account in the near future. The publication and computer tapes are also available through the National Technical Information Service (NTIS). For further information on EPACASR, contact Eleanor Merrick at FTS-382-3626.

5.1.2 Industry File Indexing System (IFIS)

IFIS is an on-line system which contains information relating to the regulation of chemicals by EPA through industry-specific legislation. IFIS enables the user to determine, for any particular industry, which chemicals are used and produced and how these chemicals are regulated. IFIS is currently available on CIS for internal use by some EPA personnel and is expected to be accessible from a public CIS account soon. For more information on IFIS, contact Daryl Kaufman at FTS 382-3626.

5.1.3 Scientific Parameters in Health and the Environment, Retrieval and Estimation (SPHERE)

SPHERE is being developed by the EPA Office of Toxic Substances as a system of integrated data bases, each representing a compilation of extracted scientific data. The system is being released to the public in stages as part of CIS, and the accessibility of component data bases should be confirmed with the contact given below. The

components currently available (either through public CIS accounts or the internal EPA system) include: DERMAL, which provides quantitative and qualitative health effects data on substances admitted to humans and test animals via the dermal route; AQUIRE, a component containing aquatic toxicity data for about 2,000 chemicals; GENETOX, a mutagenicity data base; ISHOW, and ENVIROFATE, both of which are compilations of physical/chemical parameters useful in assessing environmental fate and transport. For more information contact Paula Miles, FTS 382-3760.

5.1.4 Oil and Hazardous Materials Technical Assistance Data System (OHMTADS)

OHMTADS is a data base created by EPA to aid spill response teams in the retrieval of chemical-specific response information. The file currently contains data for approximately 1,200 chemicals including physical/chemical, biological, toxicological, and commercial information. The emphasis is on harmful effects to water quality. OHMTADS is available to the public through CIS.

5.1.5 Chemical Evaluation Search and Retrieval System (CESARS)

CESARS provides detailed information and evaluations on a group of chemicals of particular importance in the Great Lakes Basin. CESARS was developed by the State of Michigan with support from EPA's Region V. Presently, CESARS contains information on 180 chemicals including physical-chemical properties, toxicology, carcinogenicity, and some aspects of environmental fate. Information for most chemicals is extensive and consists of up to 185 data fields. CESARS is accessible through public CIS accounts.

5.2 Chemicals in Commerce Information System (CICIS)

CICIS is an on-line version of the inventory compiled under the authority of TSCA. This law required manufacturers of certain chemicals (excluding food products, drugs, pesticides, and several other categories) to report production and import data to EPA. CICIS contains production volume ranges and plant site locations (for 1977) for over 58,000 chemical substances. There is also a Confidential Inventory in which data for some chemicals are claimed confidential and are not available in the public inventory. A version of CICIS (TSCA Plant and Production, or TSCAPP) is now accessible through CIS. For more information contact Geri Nowak at FTS 382-3568.

5.3 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is not another data base, but rather a sophisticated switching network. CSIN links may independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems." Users may converse with any or all systems interfaced by CSIN without training on these independent systems, regardless of the hardware, software, data formats, or protocols of these information resources.

Information accessible through CSIN includes data on chemical nomenclature, composition, structure, properties, toxicity, production uses, environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, twelve independent information resources are accessible through CSIN, including: National Library of Medicine (NLM); Chemical Information System (CIS); CAS-On-Line; SDC's ORBIT; Lockheeds's DIALOG, and the Bibliographic Retrieval Service (BRS). For further information contact Dr. Sid Siegel at FTS 395-7285.

5.4 Graphical Exposure Modeling System (GEMS)

EPA has developed GEMS, an interactive computer system, to provide a simple interface to environmental modeling, physiochemical property estimation, statistical analysis, and graphical display capabilities. GEMS is being developed for use by the Office of Toxic Substances to support integrated exposure/risk analyses. The system provides environmental analysts who are unfamiliar with computer programming with a set of sophisticated tools to undertake exposure assessments. For information about the system and the current accessibility of GEMS, contact Bill Wood at FTS 382-3928.

6. REGULATORY STATUS (Current as of 6/84)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Air Act (CAA)

- o Section 112 - Benzene is designated as a hazardous air pollutant (42 FR 29332). National emission standards for hazardous air pollutants (NESHAP's) for benzene fugitive emission sources (equipment leaks), were promulgated on June 6, 1984, 49 FR 23498 (40 CFR 61, Subparts J and V).
- o Sections 202, 203, 205-208, 212 and 301(a) - Standards to control the release of air pollutants from motor vehicle exhaust emissions by limiting hydrocarbon emissions are established (40 CFR 85 and 40 CFR 86).
- o Section 111 - New source performance standards have been promulgated to control fugitive emissions from the manufacture of volatile organic chemicals (VOC's) from new process units within the synthetic organic chemicals manufacturing industry. Benzene is listed as a VOC (40 CFR 60.480-.482).

Clean Water Act (CWA)

- o Section 301, 304, 306, and 307 - Benzene is designated as a toxic pollutant (40 CFR 401.15). Accordingly, effluent limitations, pretreatment standards, new source performance standards, and standards of performance for new and existing sources have been issued for sections of the following industries:
 - Electroplating¹ (40 CFR 413, Subpart A, B, D-H),
 - Iron and steel manufacturing (40 CFR 420, Subpart A),
 - Steam electric power generating (40 CFR 423),
 - Metal finishing¹ (40 CFR 433), and
 - Copper forming¹ (40 CFR 468, Subpart A).
- o Section 311(b)(2)(A) - Benzene is designated a hazardous substance (40 CFR 116.4); discharges are subject to reporting requirements (40 CFR 117).
- o Section 318, 402, 405(a) - National Pollutant Discharge Elimination System (NPDES) permit testing requirements. Benzene is listed as an organic toxic pollutant based on gas chromatographic and mass spectroscopic analyses (40 CFR 122,

¹ Benzene is controlled by limiting the total toxic organics (TTO), which is the summation of all quantifiable values greater than 0.1 milligrams per liter.

Appendix D). Other permitting requirements are covered in the consolidated permit programs (40 CFR 123 and 124).

Safe Drinking Water Act (SDWA)

- o Sections 1421, 1423, 1424, 1431 and 1450 - Benzene is designated as a hazardous waste (40 CFR 144) on the basis of 40 CFR 261.3 and is subject to the requirements prescribed in the Underground Injection Control Program (UIC) (40 CFR 144) and to the criteria and standards developed under 40 CFR 146 to protect underground sources of water. State program requirements are covered by 40 CFR 145.

Resources Conservation and Recovery Act (RCRA)

- o Section 3001 - Commercial chemical products, off-specification products, residues, and intermediates containing benzene are classified as toxic hazardous wastes when discarded (40 CFR 261.33(f)).

Benzene is also identified as a toxic constituent of the following waste streams designated hazardous under 40 CFR 261.31-.32:

- Distillation or fractionation column bottoms from the production of chlorobenzenes (K085),
 - combined wastewater streams generated from nitrobenzene/aniline production (K104),
 - separated aqueous stream from the reactor product washing step in the production of chlorobenzenes (K105), and
 - wastes including but not limited to: distillation residues, heavy ends, tars, and reactor clean-out wastes from the production of chlorinated hydrocarbons having a carbon content from one to five, utilizing free radical catalyzed processes (FO24), Interim final rule, 49 FR 5312.
- o Sections 3002 to 3006 - Wastes identified as hazardous under Section 3001 are subject to a "cradle to grave" management system. Standards are established for generators of hazardous waste for hazardous waste determination (40 CFR 262.11); packaging, labeling, and marking (40 CFR 262.30-.34); recordkeeping and reporting (40 CFR 262.40-.43). Standards for transporters of hazardous waste are covered under 40 CFR 263. Additional control standards covering treatment, storage, and disposal facilities (40 CFR 264 and 265). Permit procedures are included in the consolidated permit regulations covered in 40 CFR 122 to 124.

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- o Section 6(a) - Benzene is designated as an air contaminant (29 CFR 1910.1000(b)(1-3)) in workplaces. Exposure of employees to

benzene is limited by 8-hour time weighted averages (29 CFR 1910.1000, Table Z-2).

- o Sections 4(b), 6(b), 8(a), and 8(c) - Benzene is designated as a potential occupational carcinogen, and procedures are prescribed for the identification, classification, and regulation of potential occupational carcinogens (20 CFR 1990).

CPSC - Federal Hazardous Substances Act

- o Section 30(a) - Under Section 3(b) of the FHSA, products containing 5 percent or more by weight of benzene require special labeling (16 CFR 1500.14). Poison prevention packaging requirements as prescribed by Section 30(a) of the Consumer Product Safety Act and Sections 1-9 of the Poison Prevention Packaging Act of 1970 are covered in 16 CFR 1700.1.

Department of Transportation (DOT) - Hazardous Materials Transportation Act

- o For purposes of transportation, DOT has designated benzene as a hazardous material, of the flammable liquid hazard class (I.D. No: UN 1114) (40 CFR 172.101). Additional parts of Title 49 applicable to benzene are reportable quantities (RQ's), and labeling requirements (49 CFR 172.101 and 172.102); packaging exceptions (49 CFR 173.118); specific requirements (49 CFR 173.119); carriage by rail (49 CFR 174, Subpart G); carriage by aircraft (49 CFR 175); carriage by vessel (49 CFR 176, Subpart I); and carriage by public highway (49 CFR 177, Subparts A-D).

Department of Transportation Act (DOTA)

Coast Guard, DOT (46 U.S.C. 391a)

- o Identification of incompatible hazardous materials and procedures for transporting those wastes (46 CFR 150).
- o Regulations for benzene and benzene-hydrocarbon mixtures prescribing transportation requirements (46 CFR 151.01-.10); permissible airborne concentrations (46 CFR 151.50-.60).
- o Requirements for self-propelled vessels transporting hazardous materials (46 CFR 153).

6.2 Proposed Regulations

6.2.1 EPA Programs

CAA

- o Section 112 - EPA has proposed to limit benzene emissions from new and existing coke oven byproduct recovery plants (49 FR 23522) through a combination of emission standards, equipment, work practices, and operational requirements. Standards that

were proposed for benzene emissions from maleic anhydride process vents (45 FR 26660); Ethylbenzene-styrene process vents (45 FR 83448); and benzene storage vessels (45 FR 83952) were withdrawn from proposal (49 FR 23558, June 6, 1984).

- o Section 111 - Standards of performance for new sources of VOC emissions from the synthetic organic chemical manufacturing industry distilling operations proposed on December 30, 1983. Benzene is listed as a VOC (48 FR 57538).

CWA

- o Sections 301, 304, 306, and 307 - Proposed effluent limitations, pretreatment standards, and new source performance standards have been proposed to limit benzene discharges from facilities engaged in the manufacture of organic chemicals and plastics (40 CFR 414), and synthetic fibers (40 CFR 416) (48 FR 11852, March 21, 1983).

EPA has proposed to regulate benzene by establishing effluent limitations, pretreatment standards, and new source performance standards for facilities engaged in the manufacture of pesticide chemicals (47 FR 54010, November 30, 1982).

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund).

- o Sections 102(b), 103(a)(b) - CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the clean-up of hazardous waste disposal sites (42 USC 9601; PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantity requirements (RQ's), claims procedures, and the confidentiality of business records (46 FR 54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued (47 FR 10972).

Benzene is a hazardous substance under CERCLA and will be subject to regulations developed under Superfund. EPA has proposed adjustments to the RQ's established under CERCLA and the CWA (48 FR 23552).

RCRA

- o Section 3001 - Regulations proposed to list as hazardous a group of wastes of generic category generated during the manufacture of chlorinated aliphatic hydrocarbons utilizing free radical catalyzed processes, having a carbon content ranging from one to five, and with varying amounts and positions of chlorine substitution; benzene is designated as a hazardous constituent (49 FR 5313).

6.3 Other Actions

Public Health Service (PHS) - National Toxicology Plan (NTP)

- o Benzene is cited as a substance known to be carcinogenic (Third Annual Report on Carcinogens, September 1983) (48 FR 17259).
- o Selected for mutagenicity testing FY 1984.
- o Carcinogenesis toxicity testing to be completed in FY 1984.

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

○ OSHA

8-hour time-weighted average (TWA) 10 ppm

Acceptable ceiling concentration 25 ppm

Acceptable maximum peak concentration 50 ppm
(Maximum Duration 10 minutes)

29 CFR 1910.1000, Table 2-2.

o American Conference of Government & Industrial Hygienists
(ACGIH)

8-hour TWA 10 ppm

Short Term Exposure Limit 30 ppm
(Maximum Duration 15 minutes)

7.2 Water

- o Water Quality Criteria for Human Health for ingestion of contaminated water and aquatic organisms; the criterion corresponding to an estimated lifetime cancer risk of 10^{-5} is 6.6 ug/l. For ingestion of contaminated aquatic organisms only the 10^{-5} risk level corresponds to a concentration of 400 ug/l.
- o Designated a hazardous substance under Section 311 of the CWA, notification is required if discharges of benzene are equal to or greater than 1,000 pounds (454 kg) (40 CFR 117.3). The reportable quantity proposed under CERCLA is the same (48 FR 23552).

*See Appendix A for a discussion of the derivation, use, and limitations of these Criteria and Standards.

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL (CONTACT: National Response Center, 800-424-8802; in the Washington area, 426-2675)

8.1 Hazards and Safety Precautions

Benzene is a flammable liquid which may be ignited by heat, sparks, and flames. Vapors may travel a considerable distance to a source of ignition and flash back. Vapors may cause dizziness or suffocation. Contact may irritate or burn skin and eyes. Liquid is harmful if swallowed. Fires may produce irritating or poisonous gases. Runoff from fire control or dilution water may cause pollution.

Outdoor or detached storage preferable. Indoor storage should be in standard flammable liquid storage rooms. Store in well-closed, non-glass containers in cool area. Spark resistant tools should be used. Wear chemical safety goggles, face shield, self-contained breathing apparatus and rubber protective clothing.

8.2 First Aid

Move victim to fresh air; call emergency and medical care. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. No adrenaline should be used as a respiratory stimulant. In case of contact with benzene, immediately flush skin or eyes with running water for at least 15 minutes. Remove and isolate contaminated clothing and shoes. If swallowed and victim is conscious, have victim drink water or milk.

8.3 Emergency Action

Spills or Leak

Avoid contact with liquid and vapor. Stay upwind; notify local fire, air, and water authorities of the accident. Evacuate unnecessary people immediately and isolate hazard area. Explosion hazard is great if ignition has not already occurred, hence civil defense authorities should be alerted. Water intakes are threatened and should be closed. Attempts should be made to contain slicks. Full protective clothing including self-contained breathing apparatus should be worn.

Small spills of benzene can be taken up by sorption on carbon or synthetic sorbent resins. The "Hazardous Materials 1980 Emergency Response Guidebook" recommends take-up with sand or other non-combustible material and then flushing the area with water. For large quantities, if response is rapid, benzene can be skimmed off the surface. Straw may be used to mop slicks. The following steps should be taken for spills occurring at manufacturing facilities: (1) inspect for malfunctioning control devices and leaks in major equipment, (2) if malfunction cannot be repaired within 72 hours, process shutdown should be considered, and (3) major leaks should be repaired within 15 days.

Fire

Use dry chemical, foam, or carbon dioxide. Water spray may be ineffective as an extinguishing agent, but water should be used to keep fire-exposed containers cool until well after the fire is out. Move containers from fire area if this can be done without risk. Stay away from ends of tanks. For massive fire in cargo area, use unmanned hose holder or monitor nozzles. If this is impossible, withdraw from area and let fire burn. Withdraw immediately in case of rising sound from venting safety device or discoloration of tank.

8.4 Notification and Technical Assistance

Section 103 (a) and (b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 requires persons who release hazardous substances into the environment in reportable quantities determined pursuant to Section 102 of the Act to notify the National Response Center (NRC): 800-424-8802 (in Washington, D.C. 426-2675).

Benzene is designated as a hazardous substance under CWA Section 311. Its reportable quantity is 1000 pounds.

For technical assistance, call CHEMTREC (Chemical Transportation Emergency Center): 800-424-9300. Other sources of technical information are (1) the EPA's Oil and Hazardous Materials - Technical Assistance Data System (OHM-TADS) contained in the NIH-EPA Chemical Information System (CIS) which provides information pertinent to emergency spill response efforts and (2) the CHRIS system which provides information on first aid, physical/chemical properties, hazard assessments, and response methods. Both systems can be accessed through NRC.

8.5 Disposal

Benzene is designated as a "toxic" waste under 40 CFR 261.33(f) of RCRA and generators of greater than 1,000 kg of waste are subject to the provisions of subpart D (Section 3004), Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities.

The following wastestreams are classified as hazardous wastes due, in part, to the presence of benzene (40 CFR 261.32):

- o Distillation or fractionation column bottoms from chlorobenzene production (K085).
- o Separated aqueous stream from the reactor product washing step in chlorobenzene production (K105).
- o Combined wastewater streams generated from nitrobenzene/aniline production (K104).

o Wastes including but not limited to, distillation residues, heavy ends, tars, and reactor clean-out wastes from the production of chlorinated hydrocarbons having a carbon content from one to five, utilizing free radical catalyzed processes (F024), interim final rule, 49 FR 5312.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES AND QUALITY ASSURANCE

9.1 Air (CONTACT: Larry Perdue, FTS 629-2665)

Since benzene is not yet a regulated criteria pollutant, ORD has not promulgated a criteria analysis methodology; but a monitoring approach has been developed. The methodology is reported in EPA-600/4-80-027 - May 1980 (Ambient Air Monitoring of Benzene). The method involves adsorption of benzene from ambient air onto a Tenax polymer resin. The benzene is then desorbed by heating the resin, cryogenically trapped on silanized glass beads in liquid nitrogen, and analyzed by gas chromatography using a flame ionization detector (FID).

The method described is applicable for measuring benzene in ambient air using a 24-hour sampling period.

The limit of detection is approximately $0.1 \mu\text{g}/\text{m}^3$. The relative standard deviation of replicate gas chromatographic analyses of standard gas mixtures is within 26%. The accuracy of the method is approximately 44%. Both internal and external quality control procedures are available.

It should be noted that monitoring data were collected before full development of satisfactory sampling and analytical techniques so that certain technical problems were in evidence. The major problems encountered were with the use of Tenax adsorbent. These problems included: (1) large residual benzene concentration in the Tenax compared to that of a field sample, (2) this concentration was highly variable, and (3) it could not be completely removed from the Tenax. Materials other than Tenax need to be considered. A solvent desorption technique would be preferable to thermal desorption.

9.2 Water (CONTACT: Jim Lichtenberg, FTS 684-7326)

Benzene is a contaminant regulated by the Clean Water Act 304(h) and therefore a water and wastewater related method has been promulgated by EPA (Federal Register, December 3, 1979, p. 69474). The revised analysis method is entitled "The Analysis of Aromatic Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method; Method 503.1" published by U.S. EPA, EMSL-Cincinnati, May 1980.

The method is applicable to the determination of various purgeable aromatics, including benzene, found in finished drinking water, raw source water, or drinking water in any stage of treatment.

The method incorporates an extraction/concentration technique which enhances the quantities of certain compounds by a factor of greater than 1,000 over direct gc injection. The method involves bubbling an inert gas through a 5 ml water sample contained in a specially designed purging chamber. The aromatics are transferred to the vapor phase which is then swept through a short solvent tube on which the aromatics are trapped. After the purge is completed, the trap is heated and backflushed with gas to desorb the aromatics into a gas chromatographic system. Temperature programming is used to separate aromatics before detection with a photoionization detector.

This method is recommended for use only by experienced residue analysts or under close supervision of such qualified persons.

The lower limit of detection is 0.02 µg/l. Analytical quality control procedures require organic quality control samples to be within 20% of the true value and the precision of replicate analyses should have an average relative standard deviation of 6%.

9.3 Solid Waste (CONTACT: D. Friedman, FTS 755-9187)

Benzene in waste solids may be determined as described by Method 8020 in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (Office of Solid Waste and Emergency Response, July 1982, SW-846, Second Edition). Method 8020 is used to determine the concentration of various aromatic volatile organic compounds in groundwater, liquid, and solid matrices.

Specifically, Method 8020 provides cleanup and GC conditions for the detection of aromatic volatile organic compounds including benzene. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID). The detection limit of this method for benzene using purge-and-trap procedure is 0.2 µg/l. The average recovery is 91 percent for benzene and the standard deviation is 10.0 percent.

9.4 Other Samples (CONTACT: Jim Lichtenberg, FTS 684-7308)

Sediments - "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue" (EPA; EMSL-Cin.; August 1977, revised October 1980) is a collection of draft methods for the analyses of fish and sediment samples for the priority pollutants. Prepared originally as guidance to the Regional Laboratories, two methods are applicable to benzene analysis:

- (1) determination of purgeable organics in sediments - the procedure applies a modified purge/trap technique in a direct analysis of an undiluted sediment sample. The method relies on the use of a mass spectrometer detection system, although other selective detectors may be used. Under ideal conditions, the minimum detectable limit has been determined to be 0.5 ppb.
- (2) analysis of fish for volatile organics by purge and trap analysis - a purge and trap analysis using GC/MS intended for both qualitative and semi-quantitative determinations.

9.5 Quality Assurance (CONTACT: John Winter, FTS 684-7325)

ORD has a full range of Quality Assurance support available which includes the following items:

- o Unknown performance evaluation samples
- o Known calibration check samples
- o A "d₆Benzene" surrogate compound

These are available to the Regions through the Quality Assurance Branch of EMSL-Cincinnati (see Contact).

REFERENCES

The major references used in the preparation of this document are listed below. EPA references are listed by the EPA office of origin and the year of publication. For further information refer to the contacts given throughout this document or contact the relevant EPA offices given at the end of this section.

- | | |
|-----------------------|--|
| (Cheremisinoff, 1979) | <u>Benzene</u> , P. Cheremisinoff and A. Morresi, Dekker, New York (1979). |
| (DOT, 1980) | <u>Hazardous Materials: 1980 Emergency Response Guidebook</u> , U.S. Department of Transportation (1980). |
| (IARC, 1980) | <u>Cancer Research</u> , 40: 1-12; report of IARC work group (1980). |
| (NAS, 1980) | <u>Health Effects of Benzene: A Review</u> , National Academy of Sciences, EPA-560/5-76-003 (1976). |
| (OAQPS, 1978) | <u>Assessment of Human Exposures to Atmospheric Benzene</u> , EPA-450/3-78-031, Office of Air Quality Planning and Standards (1978). |
| (OPTS, 1980) | <u>Level II Materials Balance for Benzene</u> , EPA-Draft, Contract No. 68-01-5793, Office of Pesticides and Toxic Substances (1980). |
| (OTS, 1975) | <u>Benzene: Environmental Sources of Contamination, Ambient Levels, and Fate</u> , EPA-560/5-75-005, Office of Toxic Substances (1975). |
| (OWRS, 1979) | <u>Water-Related Environmental Fate of 129 Priority Pollutants</u> , Vol. II, Ch. 71, EPA-440/4-79-029b, Office of Water Regulations and Standards (1979). |
| (OWRS, 1980) | <u>Ambient Water Quality Criteria for Benzene</u> , EPA-440/5-80-018, Office of Water Regulations and Standards (1980). |
| (SRI, 1982) | <u>Chemical Economics Handbook</u> , Manual of Current Indicators-Supplemental Data, SRI (1982). |

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-4173 (919-541-4173)

Carcinogen Assessment Group	382-7341
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	382-7571
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality and Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	382-7051
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
------------------------------	----------

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Information Management Division 382-3749

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division
Research Triangle Park, NC 629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division 382-7575

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division 755-0100

Effluent Guidelines Division 382-7120

Office of Solid Waste (OSW)

Permits and State Programs Division 382-4746

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division 382-2182
Hazardous Site Control 382-2443

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II 340-6635 (201-321-6635)

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis
Research Triangle Park, NC 629-2454 (919-541-2454)

Water Analysis
Cincinnati, OH 684-7311 (513-684-7311)

Waste Analysis
Las Vegas, NV

545-2137 (702-798-2137)

Office of Monitoring Systems
and Quality Assurance

382-5767

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Chemical Coordination Staff

Chemical Information
and Analysis

382-3375

CADMIUM

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-3
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-1
Land Releases	3-1
<u>Exposure</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
Other Exposure	4-3
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-1
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2

<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Hazardous Waste	7-1
Other	7-2
 <u>Spill or Other Incident Clean-up/Disposal</u>	 8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-2
Disposal	8-2
 <u>Sampling, Acceptable Analytical Techniques and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
Solid Wastes	9-3
Other Samples	9-3
Quality Assurance	9-3
 <u>References and Office Contacts</u>	 R-1

CADMIUM

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Cadmium is a relatively rare element which is produced commercially as a byproduct of primary metal industries, principally from the refining of zinc. Cadmium is a soft ductile metal with relatively low melting and boiling points. Due to the superior corrosion resistance of the metal, the largest use for cadmium is in electroplating. Other significant uses are in pigments, plastic stabilizers, alloys, and batteries. Properties and uses of various cadmium compounds are listed in Table 1. Although of limited commercial significance, cadmium is a toxic pollutant which is widely dispersed by the mining and production of metals and combustion of fossil fuels (Nriagu, 1980; IARC, 1976).

1.2 Chemistry and Environmental Fate/Transport

Cadmium is a member of Group IIb in the periodic table, below zinc and above mercury. In fact, cadmium is chemically similar to zinc and will be found wherever zinc occurs in nature. The only stable oxidized state of cadmium is the divalent cation, Cd^{+2} . Although organocadmium compounds are useful synthetic intermediates, they are unstable and rapidly decompose upon exposure to water or air. Divalent cadmium forms complexes with various inorganic ligands in solution, notably cyanide, ammonia, hydroxide, and chloride. Cadmium can also bind a variety of organic ligands, including sulfides (OWRS, 1979; ORNL, 1973).

The relatively low volatility of the metal permits the release of cadmium vapors during various thermal processes such as ore roasting and smelting, and incineration of wastes or combustion of fossil fuels. Cadmium vapors rapidly react with other gases to form finely divided and hazardous products. In the presence of carbon dioxide, oxygen, or water vapor, the products should be the carbonate, oxide, or hydroxide salt respectively. Cadmium-containing particles emitted settle out on the soil or water, the fallout rate being dependent on particle size, density and wind patterns (ORNL, 1973; OAQPS, 1979a).

Compared to other heavy metals, cadmium is relatively mobile in water and may be transported in solution as hydrated cations or as organic and inorganic complexes. The formation of complexes with organic matter (i.e., humic acids) facilitates sorption by sediments. In unpolluted waters sorption onto clay minerals, co-precipitation with hydrous metal oxides and substitution of Cd^{+2} for Ca^{+2} in carbonate minerals are also important factors. Although toxic, cadmium is strongly accumulated by aquatic organisms, especially in soft water. Biomethylation of cadmium has not been observed. Cadmium is less mobile in alkaline than in acidic waters (OWRS, 1979).

Because a major route of human cadmium exposure is through food, understanding the movement of cadmium through the food chains is important. Cadmium is distributed to soil through the addition of phosphate fertilizers or municipal sewage sludge containing cadmium to cropland and by deposition from air. Cadmium tends to concentrate in soil/sediment sinks due to the insolubility of carbonate, oxide, sulfide, and phosphate salts; the affinity of cadmium for organic matter also impedes transport. However, leaching and runoff of cadmium can occur, especially from sandy, acidic soil. In addition, cadmium concentrates in various food crops (potatoes, root crops, and leafy vegetables), especially when the soil is acidic. The availability of cadmium to plants is reduced in the presence of phosphates (OWRS, 1980; MERL, 1981).

TABLE 1: PROPERTIES OF CADMIUM COMPOUNDS^a

Chemical Name and Formula	CAS Number and Synonyms	Mp (°C)	Bp (°C)	Water Solubility (per liter)	Other Properties and Uses
Cadmium Cd	7440-43-9	321	765	insol.	d ²⁵ 8.65; oxidized slowly in air to CdO. Used in electroplating, alloys, solder, batteries.
Cadmium chloride CdCl ₂	10108-64-2 Cadmium dichloride	568	---	1.4 kg (20°C)	Hygroscopic; used in photography and phosphors.
Cadmium nitrate Cd(NO ₃) ₂	10325-94-7 Nitric acid, cadmium (2+) salt (1:2)	350	---	1.1 kg (0°C)	Tetrahydrate is major commercial form. Used in manufacture of nickel-cadmium batteries.
Cadmium oxide CdO	1306-19-0	900 (dec)	1560 (sublimes)	insol.	Used in electroplating and in electrodes for storage batteries.
Cadmium sulfide CdS	1306-23-6 Aurora yellow, Capsebon	--	980 (sublimes)	1.3 mg (18°C)	Used in heat stable pigments, and in phosphors. A major mineral form of cadmium (greenockite).

^a From (IARC, 1976).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACTS: Jerry Stara, FTS 684-7531; Les Grant, FTS 629-4173; Bob McGaughy, FTS 755-7315; Ed Ohanian, 382-7586)

2.1.1 Acute Toxicity

Symptoms of acute poisoning by ingesting as little as 15-30 mg of cadmium in food or drink appear within 15 to 30 minutes and include persistent vomiting, increased salivation, choking sensation, abdominal pain, and diarrhea. Acute poisoning symptoms by inhalation of cadmium oxide fumes appear within 4-6 hours after exposure and include cough, shortness of breath and tightness of the chest. Pulmonary edema may ensue within 24 hours, often to be followed by bronchopneumonia. Fifteen to 20 percent of cases result in fatality. Later effects from acute poisoning include pulmonary fibrosis, permanently impaired lung function and disturbed liver function. It is calculated that inhalation of $2,900 \text{ mg/m}^3$ for one minute is fatal. From this figure it may be estimated that inhalation of 5 mg/m^3 over an 8-hour period would result in death (OWRS, 1980; Friberg, 1974).

2.1.2 Chronic Toxicity

Two cardinal pathological lesions associated with chronic effects of cadmium are pulmonary emphysema and kidney damage. Cadmium-induced emphysema is apparently related only to the inhalation route of exposure. Regardless of exposure route, cadmium is a cumulative poison and is primarily stored in the liver and kidney. Pathological changes occur in the kidney (renal cortex) when cadmium concentrations reach 200-300 mg/kg net weight. Renal tubular damage is characterized by the urinary excretion of protein (B_2 microglobulin), glucose, phosphate, amino acids and calcium. The renal dysfunction rarely progresses to kidney failure. The most severe occurrence of such effects and their most extreme consequences can be found in itai-itai disease patients. On occasion, the renal lesion may be severe enough to produce osteomalacia and multiple fractures due to a negative calcium balance caused by excessive calcium excretion. Chronic cadmium toxic effects seem to be more prevalent in individuals suffering from multiple dietary deficiencies of protein, vitamin C or vitamin D. Since renal, bone, and body fluid cadmium levels are apparently higher in some hypertension patients, cadmium has been suggested as a factor in the etiology of essential hypertension. However, epidemiologic studies have failed to support this concept (OWRS, 1980; Friberg, 1974).

Carcinogenicity, Mutagenicity, and Teratogenicity - While cadmium has been associated with the etiology of prostate cancer and, to a lesser extent, kidney and respiratory tract cancer (IARC, 1976), the available epidemiological evidence is not conclusive. The human evidence for the carcinogenicity of cadmium is conjectural, based on small-scale studies, and confounded by exposure to other chemicals, e.g., arsenic (OWRS, 1980; OHEA, 1983).

Cadmium and various cadmium salts have produced injection site sarcomas in rats and interstitial cell testicular tumors in mice and rats after subcutaneous injection. Specifically, injection site sarcomas were produced by cadmium powder, cadmium sulfide, cadmium oxide, cadmium sulfate, and cadmium chloride, and interstitial cell tumors were produced by cadmium chloride, cadmium sulfate, and ferritin containing cadmium. However, three drinking water, two gavage, and two dietary studies using cadmium acetate, cadmium sulfate, or cadmium chloride have shown no excessive risk of cadmium carcinogenicity in rats and mice. A lifetime rat inhalation study has been completed which shows a dose-related induction of lung carcinomas by cadmium chloride aerosol. Estimates of carcinogenic risk from epidemiological studies of worker exposure via inhalation are about 100 times lower than the risk calculated from the animal study. No carcinogenic response has been observed in rats with ingested cadmium, thus the potency via the oral route is at least 200 times less than via inhalation in rats (OHEA, 1983).

There is no doubt that cadmium is a teratogen in several rodent species when given in large parenteral doses. Doses of this magnitude (4-12 mg/kg) would produce severe, if not fatal, toxic symptoms in humans. Furthermore, in humans only small amounts of cadmium cross the placental barrier. Experiments suggest that congenital abnormalities observed in exposed mice could be due to a cadmium-induced zinc deficiency (OWRS, 1980).

A definitive conclusion on the mutagenicity of cadmium is difficult to reach because of conflicting results and inadequate test protocols. Gene mutation studies in Salmonella, E.coli, yeast, and Drosophila are conflicting or inconclusive. However, gene mutation studies in mammalian cell cultures, rec-assays (DNA repair test) in bacteria, chromosomal nondisjunction studies in intact mammals, and other indirect evidence suggest that cadmium is weakly mutagenic (OHEA, 1983).

2.2 Environmental Effects (CONTACTS: John Eaton FTS 783-9557, John Gentile, FTS 838-4843)

2.2.1 Aquatic Effects (OWRS, 1980)

The forms of cadmium which are commonly found in bodies of water that are most toxic to aquatic life (or can be converted to the more toxic forms under natural conditions) are the free cadmium ion, the hydroxide, carbonate, and sulfate. Factors which affect cadmium toxicity to aquatic life include: the chemical form of cadmium, water hardness (toxicity decreases as hardness increases), water temperature, oxygen content, life stage of exposed species, salinity and water pH.

Freshwater - The results of acute toxicity tests on cadmium with 29 freshwater species range from 1 to 73,500 ug/l with both fish and invertebrates distributed throughout the range. The antagonistic effect of hardness on acute toxicity has been demonstrated with seven species. The seven available acute-chronic ratios are all between 66 and 431.

Freshwater aquatic plants are affected by cadmium at concentrations ranging from 2 to 7,400 ug/l. These values are in the same range as the acute toxicity values for fish and invertebrate species, and are considerably above the chronic values. Bioconcentration factors for cadmium reach 3,000 for some invertebrates and may be as high as 12,000 for some fish species.

Saltwater - The saltwater acute values for cadmium in five species of fishes ranged from 577 ug/l for larval Atlantic silversides to 114,000 ug/l for juvenile mummichog. Acute values for 26 species of invertebrates ranged from 15.5 ug/l for the mysid shrimp to 46,600 ug/l for the fiddler crab. The acute toxicity of cadmium seems to increase as salinity decreases and as temperature increases, although the magnitudes of the effects seem to vary with species. Two life cycle tests on Mysidopsis bahia under different test conditions resulted in similar chronic values of 5.5 and 8.0 ug/l, but the acute-chronic ratios were 2.8 and 14, respectively. These acute values appear to reflect the effects of salinity and temperature, whereas the chronic values apparently do not. Plant studies with microalgae report growth inhibition at 160 ug/l.

Tissue residues were reported for 1 species of algae, 10 species of invertebrates, and 1 species of fish. Bioconcentration factors for fish and crustaceans were generally less than 400, whereas those for bivalve mollusks were above 2,500 in long exposures, with no indication that steady-state was reached. Cadmium mortality is cumulative for exposure periods beyond four days. Chronic cadmium exposure resulted in significant effects on the growth of bay scallops at 78 ug/l and on reproduction of a copepod at 44 ug/l.

Water Quality Criteria - At water hardness of 50, 100 and 200 ug/l as CaCO_3 , the criteria to protect freshwater aquatic life are 0.012, 0.025 and 0.051 ug/l respectively, and the concentration of total recoverable cadmium should not exceed 1.5, 3.0 and 6.3 ug/l, respectively, at any time. For total recoverable cadmium, the criterion to protect saltwater aquatic life is 4.5 ug/l as a 24-hour average, and the concentration should not exceed 59 ug/l at any time.

2.2.2 Other Effects

Because food is one of the main sources of cadmium intake in non-occupationally exposed individuals, knowledge of its concentration levels in the soil is extremely important. The mobility and persistence of cadmium in the soil depends on the physical/chemical properties of the soil plus the cadmium speciation. However, the majority of applied cadmium is thought to remain in the soil at the zone of incorporation under normal conditions in agriculture systems. There is insufficient evidence documenting the half-life of cadmium in the soil. Cadmium uptake by plants depends upon the plant species. In particular, potatoes, root crops, leafy vegetables, rice and wheat tend to take up cadmium in considerable quantities in polluted areas. Soil pH is a critical factor determining cadmium uptake in plants: the lower the pH (more acidic), the higher the cadmium concentration (OWRS, 1980; Nriagu, 1980).

3. ENVIRONMENTAL RELEASE

Cadmium is a naturally occurring element in the earth's crust and ranks in abundance between silver and mercury. It is produced as a by-product in the recovery of primary zinc and from residuals of primary lead and copper production. In recent years, U.S. production has been decreasing so that imports now exceed domestic production. Cadmium is also present as an impurity in coal, petroleum, phosphate rock, and limestone. Cadmium enters the environment primarily from combustion of coal and fuel oil, mining and metals production, direct land application of POTW sludge, effluent from POTWs, incineration of POTW sludge, production and disposal of cadmium-containing products, phosphate production, and the use of phosphate fertilizers.

Its domestic uses were as follows for 1979:*

<u>Uses of Cadmium</u>	<u>kkg/yr</u>	<u>% of Total Uses</u>
Electroplating	2510	51
Batteries	1080	22
Paints and Pigments	640	13
Plastics	540	11
Other	155	3
TOTAL	4925	

Table 2 summarizes attempts to estimate cadmium releases to the environment. While numerous mass balances have been completed for cadmium, the estimates for various sources vary widely. The release data are only crude estimates and have not been verified by sampling or analysis.

3.1 Air Releases (CONTACT: Rayburn Morrison, FTS 629-5519)

Prioritization of industrial sources for cadmium emissions is currently being studied by EPA in order to determine whether or how cadmium will be regulated as an air pollutant. Cadmium releases are greatest from fossil fuel combustion in terms of total tonnages released; the impact of these sources, however, is generally small because fossil fuel cadmium emissions are distributed over thousands of widely scattered sources, the largest of these generally having taller stacks. (See Table 2 for itemized releases.)

Significant Sources

- Primary zinc smelting (SIC 3333)
- Primary cadmium smelting (SIC 3339)

* Mineral Facts and Problems, U.S. Department of Interior, Bureau of Mines, Bulletin 671 (1980). Numbers refer to a 100% cadmium basis.

- Primary copper smelting (SIC 3331)
- Primary lead smelting (SIC 3332)
- Sludge incineration

Other Sources

- Fuel oil combustion
- Coal combustion
- Municipal refuse incineration (SIC 4953)
- Iron and steel manufacturing (SIC 3312)
- Secondary lead smelting (SIC 3340)

3.2 Water Releases (CONTACT: Michael Slimak, FTS 426-2503)

Significant Sources

- Electroplating operations
- POTW pass-through water

3.3 Land Releases

Significant Sources

- Phosphate fertilizer application
- POTW sludge application

TABLE 2: CADMIUM MATERIALS BALANCE (kkg/yr)

	<u>AIR</u>	<u>WATER</u>	<u>LANDFILL</u>	<u>LANDSPREAD</u>	<u>POTW</u>	<u>MUNICIPAL REFUSE</u>
Zn/Pb Mining and Beneficiation	0 (V)	8 (W)a	250 (V)	-	-	-
Zn/Cd Smelting	7(G)b	5 (V)c	- (V)	-	-	-
Electroplating e	-	163 (W)	42 (W)	-	310 (W)	1225 d
Batteries f	1 (V)	1 (V)q	9 (V)	-	2 (V)	827 d
Pigment	10 (V)	1 (V)	17 (V)	-	2 (V)	519 d
Plastic	3 (V)	-	-	-	5 (V)	456 d
Pesticide	-	-	-	9 (A,S)	-	-
Other Cd Products	N	N	N	N	N	118 d
Iron and Steel	14 (G)	8 (W)	400 (Y)	-	-	-
Primary Non-Ferrous/Non-Zn	218 (G)	1 (V)	-	-	-	-
Secondary Non-Ferrous	2 (V)	- (V)	1 (W)	-	-	-
Zn Products h	-	N	N	-	g	N
Printing/Photography	-	-	N	-	<80 (W)i	N
Laundry & Car Wash	-	-	-	-	10 (W)	-
Coal Combustion	202 (G)	152 (V)	429 (V)	-	-	-
Coal Mining	-	45 (W)j	N	-	-	-
Oil Combustion	363 (G)	-	-	-	-	-
Gasoline Combustion	13 (E)	-	-	-	-	-
Lubricating Oil	1 (V)	N	N	-	-	N
Tire Wear	5 (V,E)	-	-	-	-	N
Phosphate Detergent	-	-	-	-	10 (V,W)	-
Phosphate Fertilizer	-	-	-	400 (W)	-	-
Urban Runoff s	-	115	-	-	11	-
Potable Water Supply t	-	-	-	-	41	-
Combustable Refuse k	-	-	-	-	-	420 k
POTW Effluent	-	308 m	-	-	-	-
POTW Sludge n	14 (G)	89	239	143	-	-
Municipal Refuse	38 (G)	-	3434 d	-	-	-
Totals	890	893 p	4821	552	475/800 r	3565
N = No Data						
- = Negligible						

TABLE 2: CADMIUM MATERIALS BALANCE (kkg/yr) (cont.)

Footnotes:

- a. Alternative estimate: 114 + 90 kkg/yr active + inactive mines (Y)
- b. Alternative estimates: 127 to air (V); 0.5 to water (W)
- c. Alternative estimate: 0.5 (W)
- d. By difference = Production less other identified releases
- e. Cycled to iron & steel or other industry = 216 (Y)
- f. Recycled = 89 (Y & V)
- g. Water pipe corrosion accounted for underwater supply
- h. Total Cd in Zn metal = 173 (Y), disposition unknown
- i. Alternative estimate = 11 (V)
- j. Alternative estimate = 0 (W)
- k. Excluding Cd pigments and plastics;
100 million kkg/yr combustible refuse X 14 ppm Cd (Campbell, 1976), less
pigments and stabilizers contribution.
- m. Influent 800 - sludge 492
- n. To air = 21% of sludge, 20% escapes emission controls
To water (ocean dump) = 18% of sludge
Landfill = 32% + captured emissions
Landspread = 29% (from EPA, OSW, 1979)
Total sludge quantity from Cook (1979)
- p. Excluding unknown quantity in rural runoff
- q. Scanty EGD data suggests a higher value
- r. Sum of known contributions, independently estimated POTW total influent
(derived from Sverdrup and Parcel (1977) data)
- s. Derived from Sullivan (1977): 6 ppb X 21 trillion liters/yr.
- t. Concentration from Battelle (1977)

Sources:

- (A) Arthur D. Little (1979)
- (S) SRI, Inc. (1979)
- (V) Versar (1979a)
- (W) Versar (1979b)
- (Y) Yost (1978)
- (E) EEA (1978)
- (G) GCA (1981)

Note: This table is a summary of the numerous cadmium mass balances assembled by OWRS, except for the air emissions which are more recent estimates from OAQPS (OAQPS, 1981).

4. EXPOSURE ROUTES

The major route of cadmium exposure in nonsmokers occurs through the food chain by soil contamination. The primary source of this contamination can be attributed to natural cadmium in the soil, phosphate fertilizers, cadmium contaminated sludge application, and air releases. Irrigation water, when taken from contaminated sources may also be a source of topsoil contamination. Although the contamination appears to be moderate in this country, the ability to create hotspots which result in substantial human risk has been observed in Japan where several routes combined to cause adverse human health effects (OWRS, 1980).

EPA has estimated that retention of 10 ug of cadmium in the body each day for 50 years would result in the critical concentration of 200 ppm in the kidney cortex. The 10 ug per day figure assumes a 38 year half-time of cadmium in the human body. For evaluating the health significance of cadmium exposures, EPA used 10 ug per day as a critical daily retention level. The total combined exposure from average levels in air, drinking water, and food result in a total daily retention of approximately 1 to 2 ug. Cigarette smoking can add about 1.5 ug/pack to this total. Thus, the general population is not expected to approach the critical retention level of 10 ug/day (ECAO, 1981). The various exposure routes are discussed in more detail below.

4.1 Air Exposure Routes (CONTACT: Rayburn Morrison, FTS 629-5519)

Analysis indicates that retention levels resulting from present and predicted future concentrations of cadmium in the ambient air are well below a kidney dysfunction level. Compared with the 10 ug critical level, average urban air results in a daily cadmium retention of less than 0.1 ug; the highest measured concentration (at a monitoring site near a currently out-of-compliance smelter) results in a daily retention of 2.4 ug; and the highest concentration predicted around any type of in-compliance cadmium source equates to a daily retention of less than 0.6 ug (OAQPS, 1981). Estimates of maximum anticipated annual average ambient cadmium concentrations around the primary sources indicate that very low concentrations should result if the sources, both existing and new, comply with current ambient air standards for particulate matter. These annual average concentrations were estimated to range from a high of about 0.13 ug/m³ for sewage sludge incinerators to as little as 0.002 ug/m³ for municipal incinerators. These levels are well below the ambient concentration of 2 ug/m³ which equates to a critical daily retention level of 10 ug (OAQPS, 1981).

Currently, regulation in State Implementation Plans and Federal regulations for new sources control the emissions of particulate matter from virtually all cadmium source categories, including sewage sludge incinerators, primary lead smelters, primary copper smelters, and municipal incinerators. In addition, state requirements for controlling emissions of lead are expected to be developed for some of the sources, and these requirements are expected to result in additional control of cadmium emissions.

4.2 Water Exposure

Drinking water contributes little to the average daily intake of cadmium. Community water supplies in the United States average about 1.3 ug/l. Sea waters have an average cadmium level of 0.1-0.15 ug/l. This is less than freshwater entering the sea and below the levels expected from solubility factors. Cadmium may be effectively removed by co-precipitation with or adsorption on clays, hydrous manganese oxide or phosphorites. Assuming a retention factor of about 6% for ingested cadmium, consumption of 2 liters of water containing 1.3 ug/l would result in retention of less than 0.2 ug per day (OWRS, 1980).

4.3 Other Exposure

Food

The major nonoccupational routes of human cadmium exposure are through food and tobacco smoke. Recent studies indicate that the average daily intake of cadmium is about 20 ug for teenage males. Other studies indicate that the daily intake of cadmium via food for individuals in the United States is comparable to that in other parts of the world. Daily retention of cadmium from an average intake of 20 ug/day would be about 1 ug/day, assuming a 6% retention factor (OWRS, 1980).

Balanced diets generally contain about 0.05 mg/kg of cadmium. Aquatic food species, (fish, crabs, oysters, and shrimps) bioconcentrate cadmium, as do visceral meats (liver, kidney and pancreas). Older animals generally have higher cadmium levels due to the cumulative nature of cadmium.

Tobacco

Tobacco in all forms contains appreciable amounts of cadmium. Smoking contributes to relatively high total body levels since the absorption of cadmium from the lung is greater than that from the gastrointestinal tract. Smoking 20 cigarettes per day results in the inhalation of about 3 ug of cadmium per day. Assuming a retention factor of 50%, smoking one pack of cigarettes a day results in the retention of about 1.5 ug of cadmium per day (OWRS, 1980; ECAO, 1981).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available in the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568 or Robin Heisler at FTS 382-3557.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. (EPACASR is scheduled to be added to CIS in early 1984.) For further information, contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information, contact Dr. Steve Heller at FTS 382-2424.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Doug Sellers at FTS 382-2320.

5.5 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is a sophisticated switching network based on heterogeneous distributed data base management and networking concepts. CSIN offers efficient access to on-line information resources containing data and information relevant to chemical substances, as well as information covering other scientific disciplines and subject matters. The purposes of CSIN are two-fold: first to meet the growing chemical data and information requirements of industry, academe, government (Federal and State), public interest groups, and others; and secondly to reduce the burden on the private and public sector communities when responding to complex Federal legislation oriented to chemical substances.

CSIN is not another data base. CSIN links many independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems". Users may converse with any or all systems interfaced by CSIN without prior knowledge of or training on these independent systems, regardless of the hardware, software, data, formats, or protocols of these information resources.

Information accessible through CSIN provides data on chemical nomenclature, composition, structure, properties, toxicity, production uses, health and environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, seven independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), Chemical Information System (CIS), CAS-On-Line, SDC's ORBIT, Lockheeds's DIALOG, Bibliographic Retrieval Service (BRS), and the US Coast Guard's Hazard Assessment Chemical System (HACS). For further information contact Dr. Sid Siegel at 202-395-7285.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 500 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. The clearinghouse listed 133 citations for cadmium. For further information, contact Irvin Weiss at FTS 382-5918.

6. REGULATORY STATUS (Current as of 9/83)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- o Section 311 - Cadmium acetate, cadmium bromide and cadmium chloride are designated as hazardous substances (40CFR116.4) and are subject to reporting requirements (40CFR117.3).
- o Sections 301, 304, 306, and 307 - Cadmium and its compounds are listed as priority pollutants (toxic pollutants, 40CFR401.15). Effluent limitations and/or pretreatment standards for cadmium have been issued for the following industries:

Electroplating and metal finishing	40CFR413,430
---------------------------------------	--------------

Inorganic chemicals (19 subcategories)	40CFR415
---	----------

Nonferrous metals (copper; lead; zinc)	40CFR421
---	----------

Ore mining and dressing (base and precious metals; ferroalloys)	40CFR440
---	----------

Porcelain enameling (steel; iron; aluminum; copper)	40CFR466
---	----------

Electrical and electronic components	40CFR469
---	----------

- o Section 403 - Ocean dumping of materials containing cadmium (except as a "trace" contaminant) is restricted (40CFR227.6 [a][3]).
- o Section 402 and 404 - Discharged toxic pollutants, such as cadmium, are controlled by permits under the National Pollutant Discharge Elimination System (NPDES). The Army Corps of Engineers issues permits for discharge of dredged or fill materials (40CFR122 to 125).

Safe Drinking Water Act (SDWA)

- o Section 1412 - A maximum contaminant level (MCL) of 0.01 mg/l for cadmium is in effect for community drinking water (40CFR141.11[b]).
- o Sections 1421 and 121 - An underground injection control (UIC) program protects underground sources of drinking water (40CFR146).

Requirements and criteria used by states incorporate hazardous wastes as defined by RCRA (40CFR261), including cadmium and its compounds. Permit procedures are given in consolidated permit regulations (40CFR122 to 124).

Resource Conservation and Recovery Act (RCRA)

- o Sections 1008(a)(3) and 4004(a) - The application of cadmium-bearing solid waste to land used for the production of food chain crops is regulated (40CFR257.3-5). A maximum contaminant level in ground water is also listed (40CFR257, App. I).
- o Section 3001 - Cadmium and its compounds are designated as hazardous constituents (40CFR261, App. VIII). Extractable cadmium also characterizes waste as hazardous (40CFR261.24). Non-specific sources of cadmium-containing hazardous wastes include electroplating operations (40CFR261.31, App. VII). Wastestreams from the following industries contain cadmium and are listed as specific sources of hazardous waste: iron and steel, and secondary lead (40CFR261.32, App. VII).
- o Sections 3002 to 3006 - Regulations for generators and transporters of hazardous waste and standards for treatment, storage, and disposal facilities are applicable (40CFR262 to 265). Permitting procedures are included in the consolidated permit regulations (40CFR122 to 124).

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- o Recommended procedures for the disposal of cadmium pesticides, residues, and containers (40CFR165.7 to .9).
- o Rebuttable presumption against registration (RPAR) and continued registration of cadmium pesticides (43FR151186).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- o Employee exposure to cadmium dust and fumes is limited by both eight-hour time-weighted averages (TWA) and acceptable ceiling concentrations (29CFR1910.1000).

DOT - Hazardous Materials Transportation Act

- o Regulations concern the listing, labeling, and shipping of hazardous materials, including cadmium compounds (40CFR171 and 172.101).

FDA - Federal Food, Drug and Cosmetic Act

- o Quality standards for bottled water include a maximum cadmium concentration of 0.01 mg/l (21CFR103.35[d][1]).
- o Cadmium is a regulated impurity in zinc methionine sulfate (21CFR172.399).

6.2 Proposed Regulations

6.2.1 EPA Programs

CWA

- o Effluent guidelines concerning cadmium have been proposed for the following industry point sources:

Inorganic chemicals	45FR49450
Porcelain enameling	46FR8860
Nonferrous metals (13 subcategories)	48FR7032
Pesticide Chemicals	47FR53394
Pharmaceuticals	47FR53584
Battery manufacturing	47FR51052

Comprehensive Environmental Response, Compensation, and Liability Act
(CERCLA or Superfund)

- o CERCLA provides for the liability, compensation, cleanup, and emergency response for the release of hazardous substances into the environment. This Act also deals with cleanup of hazardous waste disposal sites (42USC9601; PL-96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities (RQ), claims procedures, and the confidentiality of business records (46FR54032).
- o Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47FR10972). Adjustments to the statutory reportable quantities have been proposed; however, until an Agency assessment of the carcinogenicity and other effects is complete, a statutory RQ of one pound is applicable except for those cadmium compounds listed previously under Section 311 of the CWA (48FR23552).

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- Current OSHA occupational standards (29CFR1910.1000):

Cadmium fume	100 ug/m ³ (8-hr. TWA) 300 ug/m ³ (ceiling)
Cadmium dust	200 ug/m ³ (8-hr. TWA) 600 ug/m ³ (ceiling)
- NIOSH recommendation for occupational cadmium exposure limit.

	40 ug/m ³ (8-hr. TWA) 200 ug/m ³ (ceiling)
--	---

7.2 Water

- Hazardous spill rules specify the same reportable quantity for several cadmium compounds (40CFR117.3):

Cadmium acetate, cadmium bromide, cadmium chloride	100 lbs.
--	----------
- Effluent limitations for various industries:

	See Section 6.1.1 of this document for CFR citations.
--	---
- Maximum concentration level of total cadmium in drinking water (40CFR141.11[b]).

	10 ug/l
--	---------
- Water Quality Criteria (45FR79318)

Human Health	10 ug/l
Freshwater aquatic life	Varies with hardness
Saltwater aquatic life	4.5 ug/l (24 hr. avg.) 59 ug/l (max.)

7.3 Hazardous Waste

- Waste is hazardous if an extract exceeds the maximum EP toxicity level (40CFR261.24).

	1.0 mg/l
--	----------

7.4 Other Media

- FDA maximum for the level of cadmium in bottled water (21CFR103.35).

	10 ug/l
--	---------

*See Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL
(CONTACT: National Response Center, 800-424-8802 in Washington area 426-2675)

8.1 Hazards and Safety Precautions

Cadmium is a toxic material which may be fatal when inhaled or ingested. Fire will produce toxic combustion products. Runoff from fire control or dilution water may cause pollution. Some of these materials may burn but do not ignite readily.

Store in tightly closed containers in well-ventilated areas. Cadmium nitrate should be kept away from easily oxidized substances, sparks, flames, and highly heated surfaces.

8.2 First Aid

Move victim to fresh air; call emergency medical care. In case of contact with material, immediately flush skin or eyes with running water for 15 minutes.

8.3 Emergency Action

Spills

Avoid contact and inhalation of the spilled cargo. Stay upwind; notify local fire, air, and water authorities of the accident. Keep unnecessary people away. Use full protective clothing including NIOSH-approved rubber gloves and boots, safety goggles or face mask, hooded suit, and either a respirator whose canister is specifically approved for this material, or a self-contained breathing apparatus. Care must be exercised to decontaminate fully or dispose of all equipment after use.

OHM-TADS recommends the following action: dam the stream to reduce the flow and to retard dissipation by water movement. Dredging or bottom vacuum may be effective. Information on a specific cadmium compound can be found in the OHM-TADS data base of the Envirex Manual EPA 600/2-77-227.

Fire

Fire can be extinguished with water in flooding quantities or as a spray, foam, dry chemical, or carbon dioxide. If water or foam is used, contain flow to prevent spread of pollution, keep from drains and sewers. Remove container from fire area if you can do it without risk. Cool containers that are exposed to flames with water until well after the fire is out. For massive fire in cargo area, use unmanned hose holder or monitor nozzles. If this is impossible, withdraw from area and let fire burn.

8.4 Notification

Section 103(a) and (b) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 requires persons who release

hazardous substances into the environment in reportable quantities determined pursuant to Section 102 of the Act to notify the National Response Center (NRC): 800-424-8802 (Washington, D.C. 426-2675).

The following cadmium compounds are designated as hazardous under the CWA Section 311; all have reportable quantities of 100 lb.: cadmium, cadmium acetate, cadmium bromide, and cadmium chloride.

For technical assistance, call CHEMTREX (Chemical Transportation Emergency Center): 800-424-9300. Other sources of technical information are (1) the EPA's Oil and Hazardous Materials - Technical Assistance Data System (OHM-TADS) contained in the NIH-EPA Chemical Information System (CIS) which provides information pertinent to emergency spill response efforts, and (2) the CHRIS System which provides information on first aid, physical/chemical properties, hazard assessments, and response methods. Both systems can be accessed through NRC.

8.5 Disposal

Wastes that fail the EP toxicity test, 40 CFR (261.24), (EP extract cadmium concentration is greater than 1.0 mg/l), are subject to provisions of Subtitle C, the hazardous waste management standard.

The following waste streams are subject to subpart D regulations:

F006 - Generic wastewater treatment sludges from electroplating operations.

K061 - Emission control dust/sludge from electric furnace production of steel.

K069 - Emission control dust/sludge from secondary lead smelting.

K100 - Wastewater leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air (CONTACT: J. Walling, FTS 629-7954)

Cadmium in air is not a regulated pollutant. Therefore, no approved or reference procedure has been promulgated. Analyses for cadmium have been performed for a number of years, however, on particulate matter collected in the National Air Monitoring Stations (NAMS) network and its predecessor, the National Air Surveillance Network (NASN). More recently, analyses have been done for size fractionated particulates.

Hi-vol sampling is used for NAMS. Usual reference method sample handling precautions are needed. Filters are cut, extracted ultrasonically in a hot aqua regia, which after dilution is analyzed by optical emission spectrometry using plasma excitation. The discrimination limit is dependent on the particular filter and spectrometer used but is typically on the order of 10^{-3} ug Cd/m³ and reproducibility is usually within 15%. Accuracy is unknown, and interferences are a function of the specific instrument (wavelength monitored).

Dichotomous samplers can be used to obtain size fractionated atmospheric samples. Particulate loss from particulate coarse fraction samples is a problem. Using energy dispersive x-ray fluorescence for elemental analysis, the discrimination limit is on the order of 10^{-2} ug Cd/m³, while reproducibility is typically smaller than 10%; accuracy is not known.

9.2 Water (CONTACT: Theodore D. Martin, FTS 684-7312 or
Gerald D. McKee, FTS 684-7372)

Cadmium is a Clean Water Act 304(h) parameter and is listed as an inorganic priority pollutant. It is also a drinking water parameter with a maximum contaminant level of total cadmium set at 0.01 mg/l. The term "total cadmium" is defined as the sum of the concentrations of cadmium in both the dissolved and suspended fractions of the sample. Samples collected for the analyses of total cadmium are not filtered and must be preserved with nitric acid to pH < 2 as soon as possible, preferably at the time of collection. When a sample contains suspended material and is to be analyzed for total cadmium, a sample digestion step is required. When a colorimetric, stripping voltammetry, or chelation/extraction method is to be used, a sample digestion step is also required to ensure that the cadmium is in the proper chemical state and available for reaction.

There are a variety of approved methods for cadmium analysis. The most commonly used method is atomic absorption spectroscopy (AA). The analysis may be conducted using one of three different techniques: direct aspiration, chelation/extraction, or graphite furnace. For direct aspiration, a processed sample solution is aspirated into an air/acetylene flame for dissociation and absorption. The optimum concentration range for the 228.8 nm wavelength is 0.05 to 2 mg/l with an estimated detection limit of 0.005 mg/l. Chelation/extraction is used to concentrate and/or separate cadmium from

an interfering matrix. Either the PDCA/ CHCl_3 ^{1,2*} or APDC/MIBK^{3,4} methods can be used. Although cadmium can be extracted over a wide pH range, with the APDC/MIBK system the extracting time is critical (1 min.) and must be well controlled. Calibration standards must be treated in the same manner as the samples. Chelation/extraction can extend the direct aspiration working range downward from 0.05 mg/l to less than 0.005 mg/l. Interlaboratory precision and accuracy studies on 4 water samples containing 0.002 to 0.325 mg Cd/l analyzed by flame atomic absorption, gave relative standard deviations of $\pm 34\%$, to $\pm 4.7\%$. Recoveries at these levels were ranged from 78% to 98%.

The graphite furnace technique is also used for analyzing low concentrations of cadmium. To prevent volatilization before atomization, ammonium phosphate is added as a matrix modifier and the ashing temperature is limited to 500°C. For every matrix analyzed, verification is necessary to determine that method of standard additions is not required. The optimum range for graphite furnace methods (for 20 μl injection) is 0.5 to 10.0 $\mu\text{g/l}$ with an estimated detection limit of 0.1 $\mu\text{g/l}$. In an interlaboratory precision and accuracy study, where 31 laboratories participated and 2 water samples containing 1.7 and 17 $\mu\text{g Cd/l}$ were analyzed by AA-graphite furnace, the standard deviations were ± 0.41 and ± 3.0 , respectively. Recoveries at these levels were 108% and 99% respectively. In a single laboratory with concentrations of 2.5, 5.0, and 10.5 $\mu\text{g Cd/l}$ spiked in tap water, the standard deviations were ± 0.10 , ± 0.16 , and ± 0.33 , with recoveries of 95%, 99%, and 98%, respectively.

In the colorimetric method, cadmium reacts with dithizone in chloroform to form cadmium dithizonate. Cadmium is extracted at pH 2.8 and the absorbance of the pink dithizonate complex in chloroform is measured spectrophotometrically at 518 nm. No interference problems are reported. The analytical range for this method is 1 to 10 $\mu\text{g Cd}$ in the sample aliquot used for extraction. If 25 ml of sample is extracted, the minimum detectable concentration is 0.02 mg/l. In an interlaboratory precision and accuracy study with 44 participating laboratories using a synthetic sample with a concentration of 0.05 mg Cd/l, the reported relative standard deviation was $\pm 24.6\%$ with a recovery of 106%.

In the differential pulse anodic stripping voltammetry method (DPAS-voltammetry), the sample is first digested with nitric acid. The solution is then buffered with ammonium citrate to pH 3 and hydroxylamine is added to eliminate interference from ferric iron. After deposition onto a hanging mercury drop electrode at a constant potential, the cadmium is stripped back into solution using the differential pulse scanning mode. The current is measured and the cadmium concentration determined using the standard addition

*Numbers refer to references contained in the table at the end of this section.

technique. This method is applicable up to 0.1 mg/l cadmium, while the limit of detection is 0.001 mg/l. In an interlaboratory precision and accuracy study, where 7 laboratories participated and 3 water samples containing 0.01, 0.03, and 0.07 mg Cd/l were analyzed by DPAS-voltammetry, the standard deviations were ± 0.002 , ± 0.003 , and ± 0.01 , respectively. Recoveries at these levels were 103%, 91%, and 98%, respectively. In a single laboratory, the reported standard deviations for the same levels of concentration were ± 0.003 , ± 0.004 , and ± 0.01 , respectively.

In response to the improved state-of-the-art of multi-element analysis, a water/wastewater related method which includes cadmium has been promulgated by EPA (Federal Register, 44, p. 69559, December 3, 1979). The revised method (200.7) uses inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The atomic-line emission spectra is processed by computer to subtract background and to correct for any spectral interference. While the estimated instrument detection limit is 0.004 mg/l (at 226.5 nm), the optimum working range for cadmium by the ICP technique is considered to be from 0.01 mg/l to well above 100 mg/l. In an interlaboratory precision and accuracy study, where 7 laboratories participated and 2 quality control check samples containing 0.014 and 0.05 mg Cd/l were analyzed by ICP-AES, the relative standard deviations were $\pm 16\%$ and $\pm 12\%$, respectively. Recoveries at these levels were 93% and 96%, respectively. In a single laboratory at concentrations of 0.07 and 0.59 mg Cd/l, the relative standard deviations were $\pm 1.9\%$ and $\pm 1.8\%$ with recoveries of 100% and 98%, respectively.

The following table summarizes the approved method with appropriate references:

LIST OF APPROVED TEST PROCEDURES FOR TOTAL CADMIUM

	Reference Method No.			
	<u>EPA</u> ¹	<u>Std Methods</u> ³	<u>ASTM</u> ²	<u>USGS</u> ⁴
Digestion ⁵ followed by AA-direct aspiration	213.1	303A or 303B	D3557-78 (A or B)	I-3135-78 or I-3136-78
AA-graphite furnace	213.2	304	--	--
ICP-AES ⁶	200.7	--	--	--
DPAS-Voltammetry	--	--	D3557-78C	--
Colorimetric (Dithizone)	--	310B	--	--

1. "Methods for Chemical Analysis of Water and Wastes, 1979" EPA-600/4-79-020.
2. "Annual Book of Standards," Amer. Society for Testing and Materials, Part 31, Water.

List of Approved Test Procedures for Total Cadmium (continued)

3. "Standard Methods for the Examination of Water and Wastewater," 15th Edition.
4. "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments," U.S. Department of the Interior, Geological Survey, Open-file Report 78-679.
5. Sample digestion of the filtrate for dissolved metals, or digestion of the original sample solution for total metals may be omitted for AA (direct aspiration or graphite furnace) or ICP analyses provided the sample has a low COD and meets the following criteria: (a) visibly transparent, (b) no odor, (c) free of particulate matter following acidification.

Note: If the sample digestion procedure included in one of the other approved references is different than an EPA procedure, the EPA procedure must be used.

6. Inductively Coupled Plasma Optical Emission Spectrometric Method (ICP) for Trace Element Analysis of Water and Wastes; Method 200.7 published by U.S. EPA, EMSL-Cincinnati.

9.3 Solid Wastes (CONTACTS: T. Hanners, FTS 545-2140, W. Beckert, FTS 545-2137)

EPA regulations define a waste as hazardous if the concentration of cadmium in a specified extract of the waste, equals or exceeds 1.0 mg/l. The procedure is explained in detail in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (EPA, SW-846, 1980). The aqueous extract is analyzed by AA.

At present, no approved methods are available for determination of total cadmium content of wastes. Digestion procedures, similar to that described for soil analysis have been used for waste materials. Soil and sediment samples are prepared as outlined in "Interim Methods for Analysis of Elemental Priority Pollutants in Sludge," EPA-EMSL. Cinn. (1978). The sample is digested ($\text{HNO}_3/\text{H}_2\text{O}_2$) and analyzed for cadmium according to the AA methods detailed in Section 9.2 above.

9.4 Other Samples

The "NIOSH Manual of Analytic Methods" (2nd edition, Vol. 1, 1977) contains procedures for the analysis of cadmium in blood (Method 223) and urine (Method 224). Both procedures consist of digestion with an acid mixture followed by analysis using anodic stripping voltammetry. Volume 3 of the same NIOSH manual also provides procedures for analysis of cadmium dusts (Method S312) and fumes (Method S313) in air. These procedures use HNO_3 digestion of collection filters followed by AA analysis.

9.5 Quality Assurance (CONTACT: John Winter, FTS 684-7325)

ORD has a full range of quality assurance support available which includes the following items:

- Unknown performance evaluation samples
- Known quality control check samples

These are available to the Regions through the Quality Assurance Branch of EMSL-Cincinnati.

Quality control standards for air analysis for cadmium are under development. (CONTACT: J. Puzak, FTS 629-2188)

For hazardous waste analysis, quality assurance and certified samples are available from the National Bureau of Standards (telephone: 309-921-2045); samples include cadmium in coal fly ash (SRM 1633) and river sediment (SRM 1645).

REFERENCES

The major references used in the preparation of this document are listed below. EPA references are listed by EPA office of origin and the year of publication. For further information, refer to contacts given throughout this document or contact the relevant EPA offices listed at the end of this section.

- (ECAO, 1981) Health Assessment Document for Cadmium, EPA-600/8-81-023 Environmental Criteria and Assessment Office (1980).
- (Friberg, 1974) Cadmium in the Environment, L. Friberg M. Piscator, G. Nordberg, and T. Kjellstrom; 2nd edition, CRC Press (1974).
- (IARC, 1976) IARC Monograph, Vol. II, pp 39-74, World Health Organization (1976).
- (MERL, 1981) Effects of Sewage Sludge on the Cadmium and Zinc Content of Crops, EPA-600/8-81-003, Municipal Environmental Research Lab, Cincinnati, OH (1981).
- (Nriagu, 1980) Cadmium in the Environment, J.O. Nriagu, Ed., Wiley (1980).
- (OAQPS, 1981) Survey of Cadmium Emission Sources, EPA-450/3-81-013, Office of Air Quality Planning and Standards, (1981).
- (OHEA, 1983) Updated Mutagenicity and Carcinogenicity Assessment of Cadmium, EPA 600/8-83-025A, Draft, Office of Health and Environmental Assessment (1983).
- (ORNL, 1973) Cadmium the Dissipated Element, ORNL/NSF-EP-21, Oak Ridge National Laboratory (1973).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, Vol. I, Ch. 9, EPA-440/4-79-029a, Office of Water Regulations and Standards (1979).
- (OWRS, 1980) Ambient Water Quality Criteria for Cadmium, EPA-440/5-80-025, Office of Water Regulations and Standards (1980).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
---------------------------------	----------

Effluent Guidelines Division	426-2571
------------------------------	----------

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergenices call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information and Analysis Program

382-2249

Chlorinated Org. Solvents

CHLORINATED ORGANIC SOLVENTS: TRICHLOROETHANE, TETRACHLOROETHENE,
1,1,1-TRICHLOROETHANE, DICHLOROMETHANE, AND TETRACHLOROMETHANE

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-7
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-3
<u>Exposure</u>	4-1
Air Exposure	4-1
Water Exposure	4-2
<u>Data Bases</u>	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical in Commerce Information System (CICIS)	5-2
Chemical Substances Information Network (CSIN)	5-2
Graphic Exposure Modeling System (GEMS)	5-3
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-9
Other Actions	6-11
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Hazardous Waste	7-3
Other	7-3

<u>Spill or Other Incident Clean-Up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-2
Disposal	8-3
 <u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	 9-1
Air	9-1
Water	9-2
Solid Wastes	9-6
Other Samples	9-6
 <u>References and Office Contacts</u>	 R-1

CHLORINATED ORGANIC SOLVENTS: TRICHLOROETHENE, TETRACHLOROETHENE,
1,1,1-TRICHLOROETHANE, DICHLOROMETHANE, AND TETRACHLOROMETHANE

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-7
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-3
<u>Exposure</u>	4-1
Air Exposure	4-1
Water Exposure	4-2
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-1
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-5
Other Actions	6-8
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Hazardous Waste	7-2
Other	7-2

<u>Spill or Other Incident Clean-Up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-2
Disposal	8-2
 <u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	 9-1
Air	9-1
Water	9-2
 <u>References and Office Contacts</u>	 R-1

CHLORINATED ORGANIC SOLVENTS: TRICHLOROETHENE, TETRACHLOROETHENE,
1,1,1-TRICHLOROETHANE, DICHLOROMETHANE, AND TETRACHLOROMETHANE

Five chlorinated organic solvents are being extensively studied by several Agency program offices. These solvents include: trichloroethene (79-01-6), tetrachloroethene (56-23-5), 1,1,1-trichloroethane (71-55-6), dichloromethane (75-09-2), and tetrachloromethane (56-23-5). The information contained within is excerpted from the work-group's findings. General information pertaining to the chlorinated organic solvents is presented first, followed by specific information on the individual chemical where applicable. Further information can be obtained from Mr. Arnie Edelman, FTS 382-2249.

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Trichloroethene (TCE), tetrachloroethene (PCE), 1,1,1-trichloroethane, dichloromethane, and tetrachloromethane are all short-chain chlorinated aliphatic hydrocarbons. Physical/chemical properties characteristic of this class include: high volatility, non-flammability, good thermal stability, and in general low acute toxicity. Additionally, they are miscible with a wide variety of organic compounds. Relevant physical/chemical properties are listed in Table 1.

Because of their physical/chemical properties, these chemicals, with the exception of tetrachloromethane,* have found widespread use in a variety of industrial and consumer solvent applications. As a consequence of their use, these solvents are widely distributed throughout the environment.

1.2 Chemistry and Environmental Fate/Transport

As a consequence of use, approximately 90 percent of the chlorinated organic solvents are released directly to the atmosphere. Once in the troposphere, TCE and PCE react with hydroxyl radicals, via attack on the carbon-carbon double bond to yield phosgene and either dichloroacetyl chloride (from TCE) or trichloroacetyl chloride (from PCE). Dichloromethane and 1,1,1-trichloroethane also undergo photooxidation in the troposphere by hydroxyl radicals (OWRS, 1979). The photochemical oxidants which are produced in these reactions contribute to the formation of photochemical smog (NAS, 1977).

Approximately 1 percent of the dichloromethane and 15 percent of the 1,1,1-trichloroethane in the troposphere will be transported to the stratosphere where they will either undergo photodissociation by

* The use of tetrachloromethane as an industrial solvent has been on the decline because of the availability of more suitable and presumably safer substitutes.

TABLE 1. PROPERTIES OF THE CHLORINATED ORGANIC SOLVENTS

Chemical Name and Formula	CAS Number and Synonyms	Melting Point (°C)	Boiling Point (°C)	Water Density (20°/ 40°)	Vapor Pressure (torr)	Water Solubility (mg/l)	Flash- point (°C)	Log Octanol/ Water Parti- tion Coeffi- cient
Trichloroethene $\text{Cl}_2\text{C}=\text{CHCl}$	79-01-6 trichloroethylene	-73	87-90	1.46	58 (20°C)	1100 (20°C)	None	2.29
Tetrachloroethene $\text{Cl}_2\text{C}=\text{CCl}_2$	127-18-4 tetrachloroethylene perchloroethylene	-19	121	1.62	14 (20°C)	150-200 (20°C)	None	2.88
1,1,1-Trichloro- ethane $\text{H}_3\text{C}-\text{CCl}_3$	71-55-6 methyl chloroform	-30	74-76	1.34	96 (20°C)	480-4400 (20°C)	None	2.17
Dichloromethane CH_2Cl_2	75-09-2 methylene chloride	-95	40	1.33	362 (20°C)	13,200-20,000 (25°C)	None	1.25
Tetrachloromethane CCl_4	56-23-5 carbon tetrachloride	-23	77	1.59	90 (20°C)	785 (20°C)	None	2.64

higher energy ultraviolet light or be carried back to earth during the precipitation process. Tetrachloromethane is stable in the troposphere; the rate of photooxidation is extremely slow. As a consequence, it also diffuses into the stratosphere where it is photolytically degraded by high energy ultraviolet light or is carried back to the earth during the precipitation process. The resultant photodissociation products (chlorine atoms and other chlorine-containing free radicals) from these reactions are theorized to be involved in the series of reactions that contribute to the destruction of the ozone layer (OWRS, 1979; NAS, 1979).

Volatilization is the major transport process for the removal of the chlorinated organic solvents from surface water. The evaporative half-life for these chemicals from stirred water ranged from 15-30 minutes. Neither hydrolysis, oxidation, nor microbial degradation are important fate processes. These processes are slow compared to volatilization (OWRS, 1979).

All the chlorinated organic solvents have been measured in ground water and in ambient air*. If these chemicals are released into the soil, they are expected to move through the soil column to ground water. Sorbtion to soil is not a significant fate process (OWRS, 1979).

* Information received from OAQPS.

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACTS: Jerry Stara, FTS 684-7531;
Bill Lappenbush, FTS 472-6820)

2.1.1 Acute Toxicity

Dichloromethane: The primary health effects associated with acute exposure to dichloromethane are central nervous system (CNS) depression, cardiotoxic effects; and increased levels of carboxyhemoglobin (CoHb), which are a consequence of the metabolic transformation of dichloromethane to carbon monoxide (CO). The increased levels of CoHb in the blood interferes with oxygen transfer and transport.

CNS effects are related to the anesthetic properties of dichloromethane. The onset of these effects is generally rapid and temporary, normally subsiding within hours after cessation of exposure. However, in cases of acute human exposure, CNS effects have included death, unconsciousness, labored breathing, headache, lassitude, and nausea.

The observed cardiotoxic properties of dichloromethane include cardiodepression and cardiac sensitization. Several human studies have reported fatalities resulting from, or closely associated with, exposure to dichloromethane, in which myocardial infarction was diagnosed.

Hepatotoxicity has not been reported in any human case report, even those following fatal exposures.

The only evidence of human nephrotoxicity resulting from dichloromethane exposure was the finding of congested kidneys following a fatal exposure (OHEA, 1982a).

Tetrachloromethane: Tetrachloromethane is toxic to humans and animals following inhalation, ingestion or dermal administration. Exposure to tetrachloromethane primarily affects the CNS, liver, and kidneys. Tetrachloromethane has anesthetic properties.

Acute exposure to tetrachloromethane by ingestion or inhalation may result in fatal poisoning. Following ingestion, the patient experiences a burning sensation in the mouth, esophagus, and stomach. Soon the patient starts feeling dizzy, may suffer headache and become confused, semiconscious and delirious. Finally, consciousness is lost and the patient passes into a coma.

Ingestion of lesser amounts results in abdominal pain, nausea, and vomiting. Some patients develop hiccoughs. The tongue becomes coated. These symptoms are soon followed by diarrhea, which later may be followed by constipation and occasionally by gastric and intestinal hemorrhages which, in some cases, may also be seen in the mouth and pharynx. The patient can develop jaundice, the liver gets enlarged and tender, and this may be associated with ascites and generalized edema. Injury to kidney is also common. Some patients

complain of visual disturbances, and edema of the eyelids and develop hemorrhages of the sclerae.

Inhalation of low concentrations of tetrachloromethane may be restricted to such symptoms as moderate irritation of the eyes, moderate dizziness and headache, which disappear promptly upon discontinuation of exposure. In addition to the symptoms described above, effects from higher concentrations include nausea, loss of appetite, mental confusion, agitation, and the feeling of suffocation. At higher concentrations the patient may lose consciousness and develop fever and chills.

Dermal exposure causes a burning or stinging sensation followed by erythema, hyperemia, wheal formation and vesication (OHEA, 1982b).

TCE: Exposure to TCE is associated with neurological disorders, cardiovascular effects, and morphological damage to the liver and kidney.

Acute exposure to high concentrations ($>1,000$ ppm) of TCE via inhalation narcotizes the CNS, progressively depressing all functions of the brain from cortex to medulla. Short exposures (few minutes) result in headache, dizziness, nausea, vomiting, and uncoordination; longer exposures cause CNS depression and unconsciousness, in some cases death.

Exposure to low levels of TCE vapor can result in irritation of mucous membranes and impairment of psychophysiological functions. Exposures of 100 to 200 ppm TCE have caused eye and throat irritation. Inhibition of normal performance has been observed at concentrations as low as 100 ppm (8-hr. exposure) and is increasingly pronounced at 300-500 ppm.

Virtually no dose-response data for oral exposure of humans to TCE is available. Cases of poisoning from ingestion involved adverse effects on the heart or liver. However, liver damage was attributed to contamination of TCE with other substances since no damage occurred when pure TCE was ingested. The oral LD_{50} for humans has been reported to be 7,000 mg/kg body weight (OHEA, 1982c).

PCE: The immediate effect of acute exposure of humans to PCE is depression of the CNS. Acute exposure to high levels (approximately 4,000 ppm) may be fatal. Individuals, in controlled human studies, exposed to 100 ppm for up to seven hours have shown gross signs (decrements in task performance and coordination) of CNS depression and behavioral alterations.

While there are insufficient data to estimate the lowest level of PCE that would cause liver damage in humans upon acute or prolonged exposure, the evidence suggests that adverse effects upon the liver can occur at exposure levels that would cause only slight CNS depression. In animals, intermittent or prolonged exposure to PCE has been observed to result in both liver and kidney damage at levels exceeding 200 ppm.

The LD₅₀ values in rats and mice were determined to be 4,000 and 8,000 mg/kg respectively. Although PCE can be absorbed through unbroken skin, absorption through this route was estimated to be minor (OHEA, 1982d).

1,1,1-Trichloroethane: 1,1,1-Trichloroethane affects both the CNS and cardiovascular system (CVS). At levels of 1000 ppm, 1,1,1-trichloroethane produces cardiovascular effects in humans that include sensitization of the heart to spontaneous or catecholamine-provoked arrhythmias and hypotension. It is highly likely that myocardial depression occurs to some degree at much lower inhalation concentrations than has been previously thought.

Concentrations at levels as low as 350 ppm also produce adverse health effects. These effects include subjective symptoms of light-headedness, syncope, stuffiness, mild headache, nausea, and mild irritation of eye, nose, and throat. No significant abnormal blood chemistry or organ function tests have been noted. The most adverse effects are neurological symptoms, which have been diagnosed by subjects' impaired performance of cognitive and manual tasks (OHEA, 1982e).

2.1.2 Chronic Toxicity

Dichloromethane: The effects of low-level, long-term exposure are not well characterized. Experimental animal studies and evidence in humans provide limited information on the correlation between chronic exposure to dichloromethane and subsequent toxic effects. Interpretation of these data are further complicated by the fact that dichloromethane contains chemical impurities. Exposure to dichloromethane levels close to its threshold limit value (TLV) of 200 ppm have resulted in behavioral and psychological effects such as decrements in manual and mental performance. Decrements in eye-hand coordination and task-related response time have been associated with CoHb levels of 3 to 5 percent.

It has been reported that CoHb levels of 2.5 percent or greater can adversely affect individuals with angina pectoris or cardiovascular disease.

Dichloromethane has been shown to pass through the placenta and into the fetus. No clinical reports to date have shown an association between maternal exposure and congenital malformations; however, no epidemiology studies have been performed. There is some preliminary evidence to suggest behavioral teratogenic effects at low levels. More follow-up studies would be needed to clarify or confirm this evidence.

Dichloromethane has shown positive responses in both bacterial and yeast mutagenicity assays; information on the purity of the test compound is not as yet available.

There are no well-designed animal bioassays available that positively support the suggestive evidence of carcinogenic potential indicated by the bacterial mutagenic test results. The Dow Chemical Company

recently completed a two-year chronic toxicity and oncogenicity inhalation study of dichloromethane in rats and hamsters. A dose-response increase in salivary gland sarcomas in the male rats became statistically significant at the highest dose (3,500 ppm). There were also increases in benign mammary tumors in female rats at all dose levels (500, 1,500, and 3,500 ppm) and in male rats at the highest dose levels (3,500 ppm).

Two long-term animal bioassay studies are currently in progress at NTP (OHEA, 1982a).

Tetrachloromethane: Patients suffering from chronic inhalation poisoning by continued low exposures may complain of fatigue, lassitude, giddiness, anxiety, and headache. These patients suffer from paresthesias and muscular twitchings and show increased reflex excitability. They may be moderately jaundiced, have a tendency to hypoglycemia, and the liver may show fatty infiltration. Patients may complain of loss of appetite, nausea, and occasionally of diarrhea. In some cases, the blood pressure is lowered which is accompanied by pain in the kidney region, dysuria, slight nocturia, and has urine containing small amounts of albumin and a few red blood cells.

Burning of the eyes and, in a few instances, blurred vision are frequent complaints of those exposed. If these symptoms are not pronounced or of long standing, recovery usually takes place upon discontinuation of the exposure and if the proper treatment is received.

Tetrachloromethane has not been shown to be teratogenic; however, the potential exists for embryotoxicity, especially in males. Tetrachloromethane has produced distinct degenerative changes in testicular histology in male rats, eventually resulting in aspermatogenesis and functional male infertility. These effects occurred following intraperitoneal injection at relatively high doses. Unfortunately, low doses were not tested.

Studies on experimental animals indicate that this chemical is a carcinogen in three species: hamsters, mice, and rats. The International Agency for Research on Cancer (IARC) concluded that there is sufficient evidence that tetrachloromethane is carcinogenic in experimental mammals. There are suggestive case reports of liver cancer in humans. IARC states that "in the absence of adequate data on humans, it is reasonable, for practical purposes to regard tetrachloromethane as if it presented a carcinogenic risk to humans" (IARC, 1979).

TCE: The effects of low-level (50-500 ppm), long-term exposure are not well characterized. Reports of the toxicological consequences of industrial exposures are often sketchy, and there are few well-controlled epidemiological studies. Difficulties in delineating the toxic effects of trichloroethene are further compounded by chemical impurities and toxic decomposition products of trichloroethene. However, experimental studies in human volunteers provide some information about the relationship between chronic low-level exposure to

trichloroethene and toxic effects. Signs and symptoms of toxicity include dizziness, headache, fatigue, nausea, fainting spells, and other subjective responses that suggest a CNS origin. Dermal and eye irritation and intolerance to alcohol are among the better defined manifestations of exposure to trichloroethene. Behavioral and psychological effects, particularly as they affect manual and mental performance, have been reported at levels of 100 ppm (current TWA-TLV) in some, but not all, experimental and epidemiological studies. It is highly likely that the direct myocardial depressant effect, which is a serious health hazard for those with compromised or reduced cardiac reserve occurs at lower exposure concentrations than has been previously thought.

TCE has been associated with fetotoxicity in humans. However, these reports are not conclusive in establishing this association.

There is evidence that technical grade trichloroethylene (epoxide-stabilized) has carcinogenic activity, based on the increased incidence of hepatocellular carcinomas in exposed B6C3F1 mice, the positive mutagenic responses in bacteria and yeast, and the positive mutagenic response of bacteria to chloral hydrate, a metabolite found in both rats and man. Applying the International Agency for Research on Cancer criteria for animal studies, this level of evidence would be regarded as limited and not sufficient to provide a firm conclusion on its carcinogenic potential in humans (OHEA, 1982c).

However, the National Toxicology Program (NTP) recently completed a carcinogenesis bioassay of pure TCE by gavage in rats and mice. The preliminary draft report supports the carcinogenicity of pure TCE. (Carcinogenicity occurred in two species, which would cause it to be categorized as having sufficient evidence of carcinogenicity by the IARC criteria.) (OHEA, 1982c, NTP, 1982)

PCE: The data available from both human and animal exposures to PCE indicate that the CNS, liver and kidneys are adversely affected. Subjective complaints such as headache, fatigue, dizziness, and general intoxication have been reported after exposure to 100 ppm.

Both acute and chronic exposure situations have the potential to cause liver damage in humans. While there are insufficient data to estimate the lowest level of PCE that would cause liver damage upon acute or prolonged exposure, the evidence suggests that adverse effects upon the liver can occur at exposure levels that would cause only slight CNS depression. Since PCE has the potential to accumulate in lipid-rich body tissues and is only completely eliminated from the body several weeks after cessation of exposure, prolonged exposure may result in a greater body burden, subjecting the liver to a chronic insult at a given exposure concentration.

PCE has not been clearly demonstrated to cause point mutations in bacteria. There is suggestive information that PCE may be genetically active in yeast.

Two long-term animal bioassays have been performed to assess the carcinogenic potential of PCE. In one involving exposure of rats and mice to PCE by gavage, the National Cancer Institute (NCI) reported the induction of hepatocellular carcinomas in male and female mice. However, the dose levels used in the NCI study are levels that have been observed in other experiments to result in hepatotoxicity. Also, the PCE used contained epoxide stabilizers. In rats the resulting high mortality precluded any conclusions with regard to carcinogenic potential. In the second study, rats were exposed to PCE by inhalation. No evidence for carcinogenicity was reported, however, limitations in this study make it difficult to assess PCE's carcinogenic potential (OHEA, 1982d). NTP is currently completing a lifetime animal bioassay on purified PCE.

1,1,1-Trichloroethane: Very little information is available on low-level, long-term exposure to 1,1,1-trichloroethane.

Technical grade 1,1,1-trichloroethane has tested positive in several mutagenicity tests; however, this chemical contained small amounts of dioxane, a stabilizer, that may have contributed to the positive results.

NCI animal bioassays have not provided definitive evidence of carcinogenicity. An NTP lifetime animal bioassay using both rats and mice is currently nearing completion (OHEA, 1982e).

2.1.3 Absorption, Distribution, and Metabolism

The chlorinated organic solvents are readily absorbed through the lungs and gastrointestinal tract. Absorption through the skin occurs but at a much slower rate. Because of their physical/chemical properties, the chlorinated solvents are distributed to the fatty tissues. Tetrachloromethane is also found in high concentrations within the bone marrow. Dichloromethane, on account of its solubility in water, tends to distribute throughout all body fluids and tissues. These solvents readily cross the blood-brain barrier as witnessed by their narcotic effects. They can also cross the placenta and distribute within the developing fetus.

These chemicals are all metabolized to some extent before elimination from the body. The extent of metabolism varies among these chemicals and among species. The primary route of elimination is through the lungs. Dichloromethane is metabolized to carbon monoxide by the liver microsomes. Tetrachloromethane metabolism is thought to involve short-lived free radicals which either alkylate protein sulfhydryl groups or initiate peroxidative decomposition of lipids. Metabolites include chloroform, hexachloroethane, and carbon dioxide. These metabolites are thought to play a major role in the overall toxicity of tetrachloromethane.

The metabolism of both TCE and PCE probably involve an epoxide intermediate. The trichloroethylene oxide intermediate, an unsymmetrical epoxide, is less stable and more reactive toward cellular nucleophiles than the symmetrical tetrachloroethylene oxide

intermediate. The principal products of TCE metabolism are trichloroacetaldehyde, trichloroacetic acid, trichloroethanol, and trichloroethanol-glucuronide. PCE is metabolized to trichloroacetic acid as well as oxalic acid and trichloroacetyl chloride.

1,1,1-Trichloroethane is metabolized to only a small degree by mammals. The postulated metabolic pathway involves hydroxylation of 1,1,1-trichloroethane to trichloroethanol by cytochrome P-450 mixed function oxidase system. Other metabolites are trichloroacetic acid and trichloroethanol-glucuronide (OHEA, 1982a-e).

2.2 Environmental Effects

2.2.1 Aquatic Effects

Dichloromethane: The 48-hour LC₅₀ for Daphnia magna is 224,000 ug/l. There is little difference in sensitivity between Daphnia magna and bluegill towards dichloromethane. The 96-hour LC₅₀ for mysid shrimp is 256,000 ug/l. No information is available concerning the chronic toxicity of dichloromethane to freshwater aquatic life. (OWRS, 190a)

Tetrachloromethane: The available data for tetrachloromethane indicate that acute toxicity to freshwater aquatic life occurs at concentrations as low as 35,200 ug/l and would occur at lower concentrations among species that are more sensitive than those tested. No data are available concerning its chronic toxicity to sensitive freshwater aquatic life.

The available data for tetrachloromethane indicate that acute toxicity to saltwater aquatic life occurs at concentrations as low as 50,000 ug/l and would occur at lower concentrations among species that are more sensitive than those tested. No data are available concerning the chronic toxicity of tetrachloromethane to sensitive saltwater aquatic life (OWRS, 1980b).

TCE: No data on the effects of TCE on freshwater aquatic life were published prior to 1978, and consequently the data base is quite limited. The available data for TCE indicate that acute toxicity to freshwater aquatic life occurs at concentrations as low as 45,000 ug/l and would occur at lower concentrations among species that are more sensitive than those tested. No data are available concerning the chronic toxicity of TCE to sensitive freshwater aquatic life but adverse behavioral effects occur to one species at concentrations as low as 21,900 ug/l.

The available data for TCE indicate that acute toxicity to saltwater aquatic life occurs at concentrations as low as 2,000 ug/l and would occur at lower concentrations among species that are more sensitive than those tested.

There was a 50 percent decrease in ¹⁴C uptake by the alga Phaeodactylum tricornutum at a concentration of 8,000 ug/l. Erratic swimming,

uncontrolled movement, and loss of equilibrium have been observed in sheepshead minnows and grass shrimp after several minutes' exposure to 20,000 and 2,000 ug/l, respectively. No other data for saltwater organisms were found.

No data are available concerning the chronic toxicity of TCE to sensitive saltwater aquatic life (OWRS, 1980c).

PCE: The available data for PCE indicate that acute and chronic toxicity to freshwater aquatic life occur at concentrations as low as 5,280 and 840 ug/l, respectively, and would occur at lower concentrations among species that are more sensitive than those tested.

The data base for freshwater organisms exposed to PCE indicates that the rainbow trout is most sensitive and the bluegill and fathead minnow are about as sensitive as Daphnia magna. An embryo-larval test has been conducted with the fathead minnow and the ratio between the acute and chronic values for this species is 16. The data for an alga indicate that it is much more resistant than the fishes and cladoceran. Compared to the dichloroethenes and trichloroethene (TCE), tetrachloroethene (PCE) is more acutely toxic to fish and invertebrate species.

The available data for PCE indicate that acute and chronic toxicity to saltwater aquatic life occurs at concentrations as low as 10,200 and 450 ug/l, respectively, and would occur at lower concentrations among species that are more sensitive than those tested.

Acute and chronic tests have been conducted with the mysid shrimp and the acute value is 23 times the chronic value which result suggests a substantial accumulative chronic toxicity. The saltwater alga, Skeletonema costatum, is much more resistant than the mysid shrimp, and the alga, Phaeodactylum tricornutum, has a resistance comparable to that for the mysid shrimp (OWRS, 1980d).

1,1,1-Trichloroethane: The 48-hour LC₅₀ value for Daphnia magna was greater than the highest exposure concentration, 530,000 ug/l. The 96-hour LC₅₀ value for bluegill was 69,700 ug/l. No freshwater invertebrate species or saltwater organisms have been tested under chronic exposure conditions (OWRS, 1980e).

2.2.2 Other Effects

The available data indicate that the bluegill can bioconcentrate the chlorinated solvents to a limited extent. The highest factor obtained, 49, was for PCE. However, the biological half-life was less than one day. These results suggest that no residue problem will occur at concentrations that are not directly toxic to aquatic life (OWRS, 1980a-e).

3. ENVIRONMENTAL RELEASE

The uses of the chlorinated organic solvents and their releases to the environment are summarized in Tables 2 and 3. As shown in Table 2, these chlorinated organic chemicals, with the exception of tetrachloromethane, have found widespread use for a variety of solvent applications, most notable metal cleaning/degreasing. As a consequence of their use and as a function of their physical/chemical properties, these chemicals eventually reach the atmosphere. Table 3 quantifies these environmental releases. The figures in this table refer to initial release, not to their short-term or long-term environmental sink. Media transfer is expected to occur over time.

3.1 Air Releases* (CONTACT: Karen Blanchard, FTS 629-5519)

(It should be noted that the largest environmental releases do not necessarily contribute to the highest concentrations found in ambient air around a particular stationary source.)

Dichloromethane:

Significant Sources

The following are the sources contributing the highest concentrations of dichloromethane to the ambient air:

- Metal cleaning operations (widely scattered industries, SIC groups 25 and 33-39), and paint stripping operations.
- Chemical industries producing dichloromethane or using it as an intermediate (SIC 2869). Dichloromethane is produced at 7 plants located in West Virginia, Texas, Louisiana, Kentucky, and Kansas.

Other Sources

- Widely scattered industries or households using paint or varnish removers containing dichloromethane solvent.
- It is used as a chemical intermediate in the manufacture of various drugs, dyes, and perfumes, and in the dewaxing of oils. It is also used as a decaffeinating agent for coffee and as a foaming agent for flexible polyurethane foams. In 1978 approximately 5 percent of production was used as a solvent in plastics processing. About 17 percent was used as a vapor depressant in aerosols and represents the third largest end use. In these applications the chemical is eventually released to the atmosphere.

* Information supplied by OAQPS.

TABLE 2. USES OF THE CHLORINATED ORGANIC SOLVENTS, 1978 (kkg/yr)

Non-Consumptive Uses and Percent	Tetrachloro- methane	1,1,1-Trichloro- ethane	Dichloro- methane	PCE	TCE	<u>TOTALS</u>
Adhesives	--	19,800 (8%)	--	--	--	19,800
Aerosols	--	20,000 (8%)	40,500 (17%)	--	--	60,500
Dry Cleaning Solvent	--	--	--	168,000 (61%)	--	168,000
Foam Blowing Agent	--	--	11,900 (5%)	--	--	11,900
Grain Fumigant	13,300 (4%)	--	--	9,500 (3%)	--	22,800
Identified Solvent Uses	2,500 (1%)	--	--	--	--	2,500
Intermediate	293,000 (87%)	--	--	--	--	293,000
Metal, Cleaning/ Degreasing	--	187,000 (76%)	52,000 (22%)	53,900 (20%)	110,000 (89%)	402,900
Miscellaneous Solvent Uses and Other Applications	28,800 (8%)	--	49,400 (21%)	--	13,600 (11%)	91,800
Miscellaneous/ Other Uses	100 (<1%)	20,700 (8%)	--	22,200 (8%)	--	43,000
Paint Removers	--	--	71,400 (30%)	--	--	71,400
Pharmaceutical Solvent	--	--	10,000 (5%)	--	--	10,000
Textile Processing	--	--	--	22,200 (8%)	--	22,200

Source: Compiled by the Agency-wide Solvents Workgroup #2.

**TABLE 3. RELEASE OF THE CHLORINATED ORGANIC SOLVENTS
TO THE ENVIRONMENT (kkg/yr)***

	AIR	LAND	WATER
Dichloromethane			
Production	280	10	30-60
Paint removers	61,200	8,800	1,400
Metal degreasing	43,600	6,100	1,000
Aerosols	36,700	3,800	--
Foam blowing agent	10,700	1,200	--
Pharmaceutical solvent	5,300	2,200	460
Miscellaneous solvent uses	41,900	5,900	760
Total	199,680 (41%)	28,010 (58%)	3,665 (1%)
Tetrachloromethane			
Production	1,300-1,900	110	50
Grain fumigant	12,000	<1	<1
Intermediate	480	5	<1
Identified solvent uses	1,400	5	110
Miscellaneous	24,400	<10	200
Total	39,880 (99%)	130 (<1%)	360 (1%)
Trichloroethene			
Production	300	--	40
Metal degreasing	92,400	12,800	2,200
Other solvent uses	11,400	1,600	270
PVC chain terminator	130	--	--
Total	104,230 (86%)	14,400 (12%)	2,510 (2%)
Tetrachloroethene			
Production	420-1,030	--	30
Dry cleaning	143,000	25,200	<10
Metal degreasing	45,300	6,300	1,100
Grain fumigant	9,500	--	--
Textile processing	14,300	6,000	290
Miscellaneous	18,300-18,500	3,200-3,300	120-380
Total	231,275 (84%)	40,750 (15%)	1,680 (1%)
1,1,1-Trichloroethane			
Production	830	<1	<1
Metal degreasing	157,000	21,800	3,700
Aerosols	18,100	1,900	--
Adhesives	17,400	920	330
Miscellaneous	17,600	2,300	370
Total	210,930 (87%)	26,920 (11%)	4,400 (2%)

*1978

Source: Compiled by the Agency-wide Solvents Workgroup #2.

Tetrachloromethane:

Significant Sources

The following are the sources which contribute the highest concentrations of tetrachloromethane to the ambient air. They are located in West Virginia, Texas, Georgia, Louisiana, Kentucky, Kansas, Alabama, Illinois, New Jersey, California and Michigan.

- Tetrachloromethane production (SIC 2869)
- Fluorocarbon production (SIC 2869)

Other Sources

Scattered industrial users of end products containing tetrachloromethane solvents such as oil, wax and fat extractants, inks, stains, paints, and lacquers. Few end products will be used in sufficient volume to contribute significant pollution to the ambient air. Tetrachloromethane is being phased out of most of these applications.

TCE:

Significant Sources

The following are the sources contributing the highest concentrations of TCE to the ambient air:

- Chemical industries producing TCE or using it as an intermediate (SIC 2869). The three plants producing this chemical are located in Texas and Louisiana.
- Metal cleaning operations (various widely scattered industries, SIC groups 25 and 33-39). In 1978, 89 percent of the TCE produced was used for metal cleaning, but there is a trend toward substituting other chemicals (such as 1,1,1-trichloroethane) which contribute less to ozone formation.

Other Sources

TCE is used in dry cleaning establishments for removing grease spots. It is also used as a solvent base for adhesives, sealants, lubricants, and dip-painting processes, but these applications account for only 4 percent of total production.

PCE:

Significant Sources

The following are the sources contributing the highest concentrations to the ambient air.

- Dry cleaning establishments (SIC 7215, 7216, and 7218)
- Chemical industries producing PCE or using PCE as an intermediate (SIC 2869). PCE is produced at ten facilities located in California, Kansas, Kentucky, Louisiana, and Texas.
- Metal cleaning operations (various industries, SIC groups 25 and 33-39).

Other Sources

PCE is used for processing in some of the 2,500 textile processing facilities across the United States, accounting for less than 7 percent of total PCE consumption.

1,1,1-Trichloroethane:

Significant Sources

The following are the sources contributing the highest concentrations of 1,1,1-trichloroethane to the ambient air.

- Metal cleaning operations (widely scattered industries, SIC groups 25 and 33-39). This application constituted 63 percent of the 1978 total production.
- Chemical industries producing 1,1,1-trichloroethane (SIC 2869). The four plants producing this chemical are located in Texas and Louisiana.

Other Sources

1,1,1-Trichloroethane is used as a formulation and vehicle solvent in a wide variety of consumer products, such as adhesives, nonflammable paints, urethane coatings, and other sealants. It is also used as an extraction solvent in nonfood and drug formulations, as a fabric and drain cleaner, and as a lubricant and coolant in cutting oils. Aerosol formulations represented 8 percent of production in 1978.

3.2 Water Releases:

- Metal degreasing operations

4. EXPOSURE ROUTES (CONTACT: Mike Callahan, FTS 382-3873)

For all solvents, consumption of drinking water, inhalation of ambient air and air in certain occupational settings can result in the highest exposures. Food consumption may also be an important exposure route. Preliminary U.S. data suggest the highest solvent levels in foods appear to be trichloroethene in beverages (especially colas) and oils and fats (such as margarine). The activities responsible for inhalation exposures are primarily production, metal degreasing, and dry cleaning. The most severe drinking water exposures can be attributed to ground water contamination from disposal activities. At this time, the source of TCE in food has not been determined.

4.1 Air Exposure* (CONTACT: Karen Blanchard, FTS 629-5519)

Dichloromethane:

In addition to occupational exposure, persons living near chemical plants using dichloromethane may be exposed to it. Exposure may also occur at industrial degreasing operations or in plastics processing. Other exposures may be due to the use of paint remover or aerosols.

Tetrachloromethane:

Besides exposure in the workplace, persons living near tetrachloromethane or fluorocarbon production facilities are estimated to be the most exposed.

TCE:

Persons living near chemical plants using or producing this chemical may be exposed to TCE in the ambient air. Also the general population living near degreasing operations may be exposed to low concentrations.

PCE:

In addition to occupational exposures, persons living near dry cleaning establishments, metal cleaning operations, or certain chemical plants may be exposed to this chemical.

1,1,1-Trichloroethane:

Unnecessary exposure may occur at metal cleaning facilities, if improperly operated. Persons living near chemical plants producing this chemical or near degreasing operations may be exposed to 1,1,1-trichloroethane in the ambient air.

* Supplied by OAQPS.

4.2 Water Exposure (CONTACT: Bill Coniglio, FTS 382-3035
Michael Slimak, FTS 426-2503)

The chlorinated organic solvents have been found in both surface and ground water. The levels found in contaminated surface water are usually in the low ppb range. However, a small percentage of ground water supplies have been found to be contaminated by these chemicals at much higher concentrations (i.e., 100-1,000 ppb). Contamination of ground water to some degree has been detected in about 10 percent of the sites examined. This contamination is most likely the result of improper disposal of hazardous waste, industrial activities and/or sub-surface disposal system discharges.

5. DATA BASES

5.1 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. For further information, contact Jim Cottrell at FTS 382-3546.

CIS contains numeric, textual, and bibliographic information in the areas of toxicology, environment, regulations, and physical/chemical properties. Several of these data bases are described below.

5.1.1 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information.

EPACASR is now available on CIS for internal use by EPA personnel and is expected to be accessible from a public CIS account in the near future. The publication and computer tapes are also available through the National Technical Information Service (NTIS). For FTS-382-3626.

5.1.2 Industry File Indexing System (IFIS)

IFIS is an on-line system which contains information relating to the regulation of chemicals by EPA through industry-specific legislation. IFIS enables the user to determine, for any particular industry, which chemicals are used and produced and how these chemicals are regulated. IFIS is currently available on CIS for internal use by some EPA personnel and is expected to be accessible from a public CIS account soon. For more information on IFIS, contact Daryl Kaufman at FTS 382-3626.

5.1.3 Scientific Parameters in Health and the Environment, Retrieval and Estimation (SPHERE)

SPHERE is being developed by the EPA Office of Toxic Substances as a system of integrated data bases, each representing a compilation of extracted scientific data. The system is being released to the public in stages as part of CIS, and the accessibility of component data bases should be confirmed with the contact given below. The components currently available (either through public CIS accounts or

the internal EPA system) include: DERMAL, which provides quantitative and qualitative health effects data on substances admitted to humans and test animals via the dermal route; AQUIRE, a component containing aquatic toxicity data for about 2,000 chemicals; GENETOX, a mutagenicity data base; ISHOW, and ENVIROFATE, both of which are compilations of physical/chemical parameters useful in assessing environmental fate and transport. For more information contact Paula Miles, FTS 382-3760.

5.1.4 Oil and Hazardous Materials Technical Assistance Data System (OHMTADS)

OHMTADS is a data base created by EPA to aid spill response teams in the retrieval of chemical-specific response information. The file currently contains data for approximately 1,200 chemicals including physical/chemical, biological, toxicological, and commercial information. The emphasis is on harmful effects to water quality. OHMTADS is available to the public through CIS.

5.1.5 Chemical Evaluation Search and Retrieval System (CESARS)

CESARS provides detailed information and evaluations on a group of chemicals of particular importance in the Great Lakes Basin. CESARS was developed by the State of Michigan with support from EPA's Region V. Presently, CESARS contains information on 180 chemicals including physical-chemical properties, toxicology, carcinogenicity, and some aspects of environmental fate. Information for most chemicals is extensive and consists of up to 185 data fields. CESARS is accessible through public CIS accounts.

5.2 Chemicals in Commerce Information System (CICIS)

CICIS is an on-line version of the inventory compiled under the authority of TSCA. This law required manufacturers of certain chemicals (excluding food products, drugs, pesticides, and several other categories) to report production and import data to EPA. CICIS contains production volume ranges and plant site locations (for 1977) for over 58,000 chemical substances. There is also a Confidential Inventory in which data for some chemicals are claimed confidential and are not available in the public inventory. A version of CICIS (TSCA Plant and Production, or TSCAPP) is now accessible through CIS. For more information contact Geri Nowak at FTS 382-3568.

5.3 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is not another data base, but rather a sophisticated switching network. CSIN links many independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems." Users may converse with any or all systems interfaced by CSIN without training on these independent systems, regardless of the hardware, software, data formats, or protocols of these information resources.

Information accessible through CSIN includes data on chemical nomenclature, composition, structure, properties, toxicity, production uses, environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, twelve independent information resources are accessible through CSIN, including: National Library of Medicine (NLM); Chemical Information System (CIS); CAS-On-Line; SDC's ORBIT; Lockheeds's DIALOG, and the Bibliographic Retrieval Service (BRS). For further information contact Dr. Sid Siegel at FTS 395-7285.

5.4 Graphical Exposure Modeling System (GEMS)

EPA has developed GEMS, an interactive computer system, to provide a simple interface to environmental modeling, physiochemical property estimation, statistical analysis, and graphical display capabilities. GEMS is being developed for use by the Office of Toxic Substances to support integrated exposure/risk analyses. The system provides environmental analysts who are unfamiliar with computer programming with a set of sophisticated tools to undertake exposure assessments. For information about the system and the current accessibility of GEMS, contact Bill Wood at FTS 382-3928.

6. REGULATORY STATUS (Current as of 5/84)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Air Act (CAA)

- o Section 111 - New source performance standards have been promulgated to control fugitive emissions from the manufacture of volatile organic chemicals (VOC's) from new process units within the synthetic organic chemicals manufacturing industry. Chemicals listed as VOC's include the following: (40 CFR 60.489(a)).
 - Carbon tetrachloride,
 - Dichloromethane,
 - Perchloroethylene,
 - 1,1,1-trichloroethane, and
 - Trichloroethylene (40 CFR 60.480-.489).

Clean Water Act (CWA)

- o Section 311(b)(2)(A) - Carbon tetrachloride and trichloroethylene are designated hazardous substances (40 CFR 116, Table 116.4A). General provisions, reportable quantities, and notification requirements for discharges of hazardous substances to navigable waters (40 CFR 117).
- o Sections 318, 402, and 405(a) - National Pollutant Discharge Elimination System (NPDES) permitting requirements (40 CFR 122). Permit applicants must report quantitative data for toxic pollutants based on gas chromatographic and mass spectroscopic analyses for the following:
 - Carbon tetrachloride,
 - Methylene chloride,
 - Perchloroethylene,
 - 1,1,1-trichloroethane, and
 - Trichloroethylene-(40 CFR 122, App. D).

Other permitting requirements are covered in 40 CFR 123 and 40 CFR 124; NPDES standards and criteria are covered in 40 CFR 12 .

- o Sections 301, 304, 306, 307, and 316 - Designated as toxic pollutants (40 CFR 401.15):
 - Carbon tetrachloride,
 - 1,1,1-trichloroethane,
 - Dichloromethane,
 - Tetrachloroethylene, and
 - Trichloroethylene.

Accordingly, effluent limitations, new source performance standards, or standards of performance for new and existing sources have been promulgated for sections of the following industries:

- Electroplating¹ (40 CFR 413.02(i)),
- Iron and steel manufacturing² (40 CFR 420.02(p)) Subpart J,
- Steam electric power generating (40 CFR 423, App. A),
- Metal finishing¹ (40 CFR 433.11(e)),
- Coil coating³ (40 CFR 465.02(j)),
- Aluminum forming⁴ (40 CFR 467.02(p)),
- Copper forming⁵ (40 CFR 468.02(r)), and
- Electrical and electronic components¹ (40 CFR 469.12(a)).

Safe Drinking Water Act (SDWA)

- o Part C, Sections 1421, 1423, 1424, 1431, and 1450 - Chlorinated solvents are designated as hazardous wastes (40 CFR 144) as defined in 40 CFR 261.3 and are subject to requirements covered in the Underground Injection Control Program (UIC) (40 CFR 144) to protect underground sources of water.

Resource Conservation and Recovery Act (RCRA)

- o Sections 1006, 2002, 3001-3007, 3010, and 7004 - General provisions of the hazardous waste management system (40 CFR 260).
- o Sections 1006, 2002(a), 3001, and 3002 - Procedures for the identification and listing of hazardous wastes:
 - Designated as hazardous waste from nonspecific sources are wastes F001; spent halogenated solvents used in degreasing: perchloroethylene, trichloroethylene, dichloromethane, 1,1,1-trichloroethane, carbon tetrachloride, and sludges from the recovery of these solvents; F002; spent halo-

¹Controls carbon tetrachloride, 1,1,1-trichloroethane, dichloromethane, tetrachloroethylene, and trichloroethylene by limiting total toxic organics (TTO's).

²Controls perchloroethylene only.

³Controls 1,1,1-trichloroethane, dichloromethane, and perchloroethylene by limiting TTO's.

⁴Controls perchloroethylene and trichloroethylene by limiting TTO's.

⁵Controls 1,1,1-trichloroethane, dichloromethane, and trichloroethylene by limiting TTO's.

generated solvents: perchloroethylene, dichloromethane, trichloroethylene, 1,1,1-trichloroethane, and the still bottoms from the recovery of these solvents, and F024; wastes including, but not limited to, distillation residues, heavy ends, tars and reactor cleanout wastes from the production of chlorinated aliphatic hydrocarbons, having carbon content from one to five, utilizing free radical catalyzed processes (40 CFR 261.31).

- Designated as hazardous wastes from specific sources are:
 - K009 and K010: Distillation bottoms and side cuts from the production of acetaldehyde from ethylene (40 CFR 261.32); Basis for listing K009, K010: dichloromethane (App. VII),
 - K016: Heavy ends or distillation residues from the production of carbon tetrachloride (40 CFR 261.32); Basis for listing K016: carbon tetrachloride and perchloroethylene (App. VII),
 - K019: Heavy ends from the distillation of ethylene dichloride in EDC production (40 CFR 261.32); Basis for listing K019: 1,1,1-trichloroethane, perchloroethylene, carbon tetrachloride, and trichloroethylene (App. VII),
 - K020: Heavy ends from the distillation of vinyl chloride in VC monomer production (40 CFR 261.32); Basis for listing K020: same as K019 (App. VII),
 - K021: Aqueous spent antimony catalyst waste from fluoromethanes production (40 CFR 261.32); Basis for listing K021: carbon tetrachloride (App. VII),
 - K018: Heavy ends from the fractionation column in ethyl chloride production (40 CF 261.32); Basis for listing K018: trichloroethylene (App. VII),
 - K028: Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane (40 CFR 261.32); Basis for listing K028: 1,1,1-trichloroethane (App. VII),
 - K029: Waste from the product steam stripper in the production of 1,1,1-trichloroethane (40 CFR 261.32); Basis for listing K029: same as K028,
 - K073: Chlorinated hydrocarbon waste from the purification step of the diaphragm cell process using graphite anodes in chlorine production (40 CFR 261.32); Basis for listing K096: 1,1,1-trichloroethane (App. VII).

- Commercial chemical products, manufacturing chemical intermediates, or off specification commercial chemical products, when discarded, are identified as hazardous toxic wastes unless otherwise designated and are subject to the small quantity exclusion (for generators) defined in 40 CFR 261.5(a) and (f) are:

- U211: Carbon tetrachloride,
- U080: Dichloromethane,
- U226: 1,1,1-trichloroethane (methyl chloroform),
- U210: Perchloroethylene, and
- U228: Trichloroethylene.

The above chlorinated solvents are listed in 40 CFR 261.33(f).

- Listed as hazardous constituents (40 CFR 261, App. VIII):
 - 1,1,1-Trichloroethane,
 - Dichloromethane,
 - Carbon tetrachloride,
 - Trichloroethylene, and
 - Perchloroethylene.
- o Sections 3002 to 3006 - Wastes identified as hazardous under Section 3001 are subject to a "cradle to grave" management system. Standards are established for generators of hazardous waste for hazardous waste determination (40 CFR 262.11); packaging, labeling, and marking (40 CFR 262.30-.34); recordkeeping and reporting (40 CFR 262.40-.43). Standards for transporters of hazardous waste are covered under 40 CFR 263. Additional control standards covering treatment, storage, and disposal facilities (40 CFR 264 and 265). Permit procedures are included in the consolidated permit regulations covered in 40 CFR 122 to 124.

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- o Sections 2-12, 19, 21, and 25 - 1,1,1-Trichloroethane is designated as an inert ingredient when used as a diluent in antimicrobial products unless determined to be otherwise by the Agency (40 CFR 162.60(d)).

Toxic Substances Control Act (TSCA)

- o Section 8(a) - Requirements for the submittal of preliminary assessment reporting apply to:
 - Carbon tetrachloride and
 - 1,1,1-trichloroethane

(40 CFR 712.30(d)).

- o Section 8(d) - Requirements for the submission of lists and copies of health and safety studies apply to:

- Carbon tetrachloride,
- 1,1,1-trichloroethane

(40 CFR 716).

Federal Food, Drug, and Cosmetic Act (FFDCA) - Administered by EPA

- o Section 409 - Carbon tetrachloride may be used as a fumigant in or on grain-mill machinery.
(21 CFR 193.225(a))

- o Section 409 - The use of carbon tetrachloride with carbon disulfide or ethylene dichloride with or without pentane as a pesticide. (21 CFR 193.230(a)(1))

- o Section 408(d)(2) - 21 U.S.C. 346a(d)(2)

- The following are exempted from the requirement of a pesticide tolerance: tetrachloroethylene; when used as a solvent or cosolvent at a level of not more than 0.6 percent of the pesticide formulation and 1,1,1-trichloroethane; when used as a solvent or cosolvent, and when applied to growing crops or to raw agricultural commodities after harvest (40 CFR 180.1001(c)): dichloromethane; when used as a solvent or cosolvent in pesticide formulations applied to growing crops only (40 CFR 180.1001(d)): dichloromethane, tetrachloroethylene, and 1,1,1-trichloroethane, (not more than 25 percent), when used as solvents or cosolvents in pesticide formulations applied to animals (40 CFR 180.1001(e)).
- The following are exempted from the requirement of a tolerance for residues, when used as a fumigant after harvest on the grains, barley, corn, oats, popcorn, rice sorghum (milo), wheat; and when used in the post-harvest fumigation of citrus fruits:¹
 - Carbon tetrachloride (40 CFR 180.1005),
 - Dichloromethane (40 CFR 180.1010),
 - 1,1,1-trichloroethane (40 CFR 180.1012).

¹Dichloromethane and 1,1,1-trichloroethane only.

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- o General industry standards for employee exposure to air contaminants in the workplace (29 CFR 1910.1000).
 - 1,1,1-trichloroethane (methyl chloroform), Table Z-1,
 - Carbon tetrachloride (Table Z-2),
 - Dichloromethane (Table Z-2),
 - Tetrachloroethylene, (Table Z-2),
 - Trichloroethylene (Table Z-2).
- o Regulations establishing employee access to exposure and medical records which contain any information concerning that employee's exposure to any harmful physical agents or toxic substances; the latter of which are listed in the latest printed edition of RTECS or are regulated by any Federal law or rule due to a hazard to health (29 CFR 1910.20).

FDA - Federal Food, Drug, and Cosmetic Act

- o The use of dichloromethane as a diluent in color additive inks for marking fruit and vegetables (21 CFR 73.1(b)(1)(ii)).
- o Solvents permitted to be used as food-grade extractants in the preparation of the exempt color additive annatto extract (21 CFR 73.30(a)(1)(ii)):
 - Dichloromethane and
Trichloroethylene.
- o Solvents permitted to be used as extractants in the preparation of the exempt color additive paprik oleoresin (21 CFR 73.345(a)(1)), and turmeric oleoresin (21 CFR 73.615(a)(1)):
 - Dichloromethane and
Trichloroethylene.
- o Solvents permitted to be used as extractants in the manufacture of modified hops extract for beer (21 CFR 172.560(b)(3-6)):
 - Dichloromethane and
Trichloroethylene.
- o Sections 409, 701 (21 U.S.C. 348, 371) - Tetrachloromethane (carbon tetrachloride) is permitted as a substance from which anti-offset powders for use as components of paper and paperboard intended for use in food manufacturing process (21 CFR 176.130(c)), and as a component of uncoated and coated paperboard that contacts dry food (21 CFR 176.180(b)(2)).

- o Sections 201(s), 409 (21 U.S.S 321(s), 348) - Dichloromethane (methylene chloride) is accepted as an optional adjuvant substance which may be used in the production of polycarbonate resins intended for use in food manufacturing processes (21 CFR 177.1580(b)).
- o Trichloroethylene is permitted to be used as a chain transfer agent in the production of vinyl chloride-hexene-1 copolymers as components of articles intended for use in contact with food (21 CFR 177.1960(a)).
- o Tetrachloroethylene is approved for use as an adjuvant in the manufacture of foamed plastics intended for use in contact with food; when it is used as a blowing agent adjuvant in polystyrene at a level not exceeding 0.3 percent by weight (21 CFR 178.3010).
- o Sections 201-902 - Guidelines for aerosol drug products for human use that contain 1,1,1-trichloroethane (21 CFR 310.507).
- o Sections 409 and 701 - Approves for the use as components of adhesives, the following:
 - Carbon tetrachloride,
 - Dichloromethane,
 - Tetrachloroethylene,
 - Trichloroethylene, and
 - 1,1,1-trichloroethane (21 CFR 175.105).
- o Tolerances for residues of trichloroethylene resulting from its use as a solvent in the manufacture of certain foods (21 CFR 173.290). The foods and tolerances are presented in Section 7.4.
- o Section 409 - Approves dichloromethane (methylene chloride) for use as a secondary food additive in foods for human consumption (21 CFR 173.255). The permissible levels and foods are presented in Section 7.4.
- o Section 409 and 701 - Approves the use of tetrachloroethylene as an indirect food additive, adjuvant, production aid or sanitizer (21 CFR 178.3010).

CPSC - Federal Hazardous Substances Act

- o Section (2)(g)(1)(B) - Tetrachloromethane (carbon tetrachloride) and mixtures containing it (including CCl₄ and mixtures containing it in fire extinguishers) declared banned from interstate commerce (16 CFR 1500.17(2)).
- o Section (2)(F)(2) - Visual novelty devices containing no more than 105 ml of tetrachloroethylene are exempt from the labeling requirements of Title 21 Part 1500.121(a). (21 CFR 1500.83(31)(i-ii)).

DOT - Hazardous Materials Transportation Act

- o Regulations and procedures for the packaging requirements for transportation of hazardous materials via rail, air, vessel, and over public highways (49 CFR 172.101 and .102, 173, 174, 175, 176, and 177). Chemicals subject to these provisions are:
 - Carbon tetrachloride,
 - Dichloromethane,
 - 1,1,1-trichloroethane,
 - Perchloroethylene, and
 - Trichloroethylene.

DOT/Coast Guard - Port and Tanker Safety Act

- o Regulation pertaining to compatibility of bulk liquid hazardous materials on tank vessels (46 CFR 150, Subpart A).
 - Carbon tetrachloride,
 - Dichloromethane,
 - Trichloroethylene, and
 - Perchloroethylene.
- o Interim regulations governing foreign flag vessels carrying certain hazardous cargoes in U.S. waters (46 CFR 154a).
 - Carbon tetrachloride,
 - Dichloromethane.

DOT/Coast Guard - Port and Tanker Safety Act/Dangerous Cargoes Act

- o Regulations and standards for unmanned barges carrying certain bulk dangerous cargoes (46 CFR 151).
 - Carbon tetrachloride,
 - Dichloromethane,
 - Tetrachloroethylene, and
 - Trichloroethylene.
- o Regulations and standards for self-propelled shipping vessels carrying hazardous liquids (46 CFR 153, Table 1).
 - Carbon tetrachloride,
 - Dichloromethane,
 - Tetrachloroethylene, and
 - Trichloroethylene.

6.2 Proposed Regulations

6.2.1 EPA Programs

CAA

- o Section 111 - EPA has proposed new source performance standards to limit emissions of volatile organic carbons (VOC's) from new, modified, and reconstructed air oxidation facilities within the synthetic organic chemicals manufacturing industry (48 FR 48932, October 21, 1983); and for VOC emissions from the synthetic organic chemicals manufacturing industry distilling operations (48 FR 57538, December 30, 1983).

EPA has also proposed new source performance standards to limit emissions of VOC's from new, modified, and reconstructed petroleum solvent dry cleaning facilities installed at any petroleum dry cleaning plant which consumes more than 7,800 liters (4,700 gallons) of petroleum solvent annually (47 FR 56118, December 14, 1982).

CWA

- o Sections 301, 304, 306, 307, and 501 - EPA has proposed to establish effluent guidelines, new source performance standards (NSPS) and performance standards for new and existing sources (PSNS and PSES) for the organic chemicals and plastics and synthetic fibers point source category (40 CFR 414 and 416) by regulating the following: (48 FR 11852, March 21, 1983).

- Carbon tetrachloride,
- 1,1,1-trichloroethane,
- Dichloromethane, and
- Trichloroethylene.

- o Proposed effluent guidelines, NSPS, PSNS, and PSES for pesticide chemicals manufacturing (40 CFR 455) by regulating the following:

- Carbon tetrachloride,
- Dichloromethane.

(47 FR 54010, November 30, 1982).

SDWA

- o Section 1412 - EPA has proposed regulations establishing Recommended Maximum Contaminant Levels (RMCLs) for the following volatile synthetic organic chemicals (VOCs) in drinking water: (49 FR 24330, June 12, 1984).

- Carbon tetrachloride,
- 1,1,1-trichloroethane,

- Tetrachloroethylene, and
- Trichloroethylene.

RCRA

- o Section 3001 - EPA is proposing to establish as a toxic hazardous waste stream, F025; light ends, spent filters and filter aids, and spent dessicant wastes from the production of chlorinated aliphatic hydrocarbons having carbon content from one to five, utilizing free radical catalyzed processes. The hazardous constituents for which the waste stream is listed include:

- Carbon tetrachloride,
- Dichloromethane,
- 1,1,1-trichloroethane,
- Tetrachloroethylene, and
- Trichloroethylene.

(49 FR 5315, February 10, 1984)

TSCA

- o Section 4(a) - EPA has withdrawn the proposed health and environmental effects testing requirements for the following:

- Methylene chloride and
- 1,1,1-trichloroethane

(49 FR 25009 and 25013, June 19, 1984).

Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)

CERCLA provides for the liability, compensation, clean-up and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites (42 USC 9601; PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities (RQ), claims procedures, and the confidentiality of business records (46 FR 54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47 FR 10972).

The chemicals listed below are designated hazardous substances under CERCLA and will be subject to regulations developed under Superfund. EPA has proposed adjustments to many of the RQ's established under CERCLA and the CWA (48 FR 23552):

- Carbon tetrachloride,
- Perchloroethylene,
- Dichloromethane,

- 1,1,1-trichloroethane, and
- Trichloroethylene.

6.3 Other Actions

Public Health Service (PHS) - National Toxicology Program (NTP)

- o Published FY '84 plans for the testing of tetrachloroethylene to determine mutagenicity in L5178Y mouse lymphoma cells (Chemical Regulation Reporter, May 4, 1984, page 170).
- o Carbon tetrachloride is cited as a substance that may reasonably be anticipated to be a carcinogen (Third Annual Report on Carcinogens, Summary, September 1983, page 38).
- o Published FY '83 plans for testing 1,1,1-trichloroethane for cytogenetic effects in Chinese Hamster ovary cells (48 FR 17246, April 21, 1983); and for testing perchloroethylene for heritable genetic effects in Drosophila in FY '82 (48 FR 17247).

EPA

- o Announced availability of Draft Health Assessment Document for perchloroethylene (49 FR 10575, March 21, 1984).

EPA - CWA

- o Section 304(g) - Standard analytical test procedures are established for chlorinated organics (40 CFR 136) as defined in Sections 401 and 403 of Title 40.
- o Section 311(c)(2) - A methodology for rating uncontrolled hazardous waste sites by establishing quantity and waste characteristics determination parameters is set (40 CFR 300, Subpart H, Appendix A and Tables 4-5).

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- o OSHA Standard for workplace exposure to the solvents in air (29 CFR 1910.1000, Tables Z-1 and Z-2).

TWA Acceptable
8-hr. avg. ceiling

Dichloromethane	500 ppm	1,000 ppm
Carbon tetrachloride	10 ppm	25 ppm
Perchloroethylene	100 ppm	200 ppm
Trichloroethylene	100 ppm	200 ppm
1,1,1-Trichloroethane	350 ppm	N/A

- o American Conference of Governmental and Industrial Hygienists (ACGIH)

Recommended threshold limit values for 1980:

	TWA	STEL (tentative)
Dichloromethane	200 ppm	250 ppm
Carbon tetrachloride	10 ppm	20 ppm
Perchloroethylene	100 ppm	150 ppm
Trichloroethylene	100 ppm	150 ppm
1,1,1-Trichloroethane	350 ppm	450 ppm

7.2 Water

Water Quality Criteria (45 FR 79318)

Freshwater aquatic life (acute except where indicated):

Dichloromethane	11,000 µg/l
Carbon tetrachloride	35,200 µg/l
Trichloroethylene	45,000 µg/l
Tetrachloroethylene	5,280 µg/l
	840 µg/l (chronic)
1,1,1-Trichloroethane	18,000 µg/l

Saltwater aquatic life (acute except where indicated)

Dichloromethane	12,000 µg/l
Carbon tetrachloride	6,400 µg/l (chronic)
	50,000 µg/l
Trichloroethylene	2,000 µg/l

* See Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

Tetrachloroethylene	10,200 ug/l	
	450 ug/l	(chronic)
1,1,1-Trichloroethane	31,200 ug/l	

- o Water Quality Criteria for the Protection of Human Health corresponding to a 10^{-5} lifetime cancer risk by ingestion of contaminated water and contaminated aquatic organisms^a and contaminated aquatic organisms only:^b

Criteria Limits

- Dichloromethane	1.9 ug/l ^a	157 ug/l ^b
- Carbon tetrachloride	4.0 ug/l ^a	69.4 ug/l ^b
- Perchloroethylene	8 ug/l ^a	88.5 ug/l ^b
- Trichloroethylene	27 ug/l ^a	807 ug/l ^b

- o Water Quality Criteria for the protection of human health by ingestion of water and contaminated aquatic organisms (noncarcinogenic risk)

- 1,1,1-Trichloroethane 18,400 ug/l

- o Designated as hazardous substances under Section 311 of the CWA, notification is required if discharges exceed the following:

Carbon tetrachloride	5,000 lbs
Trichloroethylene	1,000 lbs

(40 CFR 117.3) the proposed regulation is the same (48 FR 23577 and 23595).

- o The Office of Drinking Water has issued Health Advisories; the Suggested No Adverse Response Levels (SNARLs) are:

Dichloromethane	13,000 ug/l (one day)
	1,300 ug/l (ten days)
	150 ug/l (chronic)
Carbon tetrachloride	200 ug/l (one day)
	20 ug/l (ten days)
Trichloroethylene	2,000 ug/l (one day)
	200 ug/l (ten days)
	75 ug/l (chronic)

Tetrachloroethylene 2,300 ug/l (one day)
 175 ug/l (ten days)
 20 ug/l (chronic)

1,1,1-Trichloroethane 1,000 ug/l (chronic)

- o Draft - Office of Drinking Water ANPRM Potential Maximum Contaminant Levels (PMCLs), (47 FR 9351).

Carbon tetrachloride 5-500 µg/l

Trichloroethylene 5-500 µg/l

Perchloroethylene 5-500 µg/l

1,1,1-Trichloroethane 1,000 µg/l

- o Proposed RMCLS (49 FR 24352) are zero for the following VOCs:

Carbon tetrachloride,

Tetrachloroethylene, and

Trichloroethylene.

The proposed RMCL for 1,1,1-trichloroethane is
0.2 mg/l (49 FR 24352).

7.3 Hazardous Waste

- o The chlorinated organic solvents are listed as toxic waste and are subject to the small quantity exclusion; any disposal of more than 1,000 kg per month of hazardous waste is subject to RCRA regulations (40 CFR 261-33(f)).

7.4 Other

- o FDA tolerance levels of solvents in food.

Dichloromethane (21 CFR 173.255)

Extractant for spice
oleoresins (if other
chlorinated solvents
are present, total
residue must be less
than 30 ppm)

30 ppm

Hops extractant; the limit is 2.2% provided than the hops extractant is added before the beer production process

Extractant for removal of caffeine from coffee

ground coffee	10 ppm (residue)
---------------	------------------

instant coffee	10 ppm (residue)
----------------	------------------

Trichloroethylene (21 CFR 173.290)

Extractant for spice oleoresins (if other chlorinated solvents are present, total residue must be less than 30 ppm)	30 ppm
---	--------

Extractant for removal of caffeine from coffee

Decaffeinated ground coffee	10 ppm (residue)
-----------------------------	------------------

Decaffeinated soluble (instant) coffee	10 ppm (residue)
--	------------------

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL
(CONTACT: National Response Center, 800-424-8802; in Washington area, 426-2675)

8.1 Hazards and Safety Precautions

The combustion products of these chlorinated organic solvents are highly toxic and may be fatal if inhaled, swallowed or absorbed through the skin. Contact may cause burns to skin and eyes. Runoff from fire control or dilution water may cause pollution.

Store in cool, dry, well-ventilated area.

8.2 First Aid

Move victim to fresh air; call emergency medical care. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact with material, immediately flush skin or eyes with running water for 15 minutes. Speed in removing material from skin is of extreme importance. Remove and isolate contaminated clothing and shoes. Keep victim quiet and maintain normal body temperature. Effects may be delayed; keep victim under observation.

8.3 Emergency Action

Avoid contact and inhalation of the spilled cargo. Stay upwind; notify local fire, air, and water authorities of the accident. Keep unnecessary people away. Wear "acid" goggles and use self-contained (positive pressure) breathing apparatus and special protective clothing.

It should be noted that PVC and natural rubber should not be used. Use Neoprene for protective clothing. Do not use closed-circuit rebreathing system employing soda lime or other carbon dioxide absorber because of formation of toxic compounds capable of producing cranial nerve paralysis. Equipment should not be iron or metal, susceptible to hydrogen chloride.

OHM-TADS recommends the following action: seek professional environmental engineering assistance through EPA's Environmental Response Team (ERT), Edison, NJ, 24-H at 201-321-6660. Contain and isolate spill by using clay/bentonite dams, interceptor trenches, or impoundments. Construct swale to divert uncontaminated portion of watershed around contaminated portion. Seek professional help to evaluate problem; implement containment measures and conduct bench scale and pilot scale tests prior to full scale decontamination program implementation. Density stratification and impoundment--remove product from bottom layer by pumping through manifold or polyethylene rope mop collection or remove clarified upper portion by skimmers or siphon. Treatment is required for both clarified and concentrated product fractions. Treatment alternatives include powdered activated carbon, granular activated carbon, and biodegradation. Treatment alternatives for contaminated soils include well point collection and treatment of leachates as for contaminated waters, bentonite/cement injection to

immobilize spill. Contaminated soil residues may be packaged for disposal.

Although these chemicals are not flammable, high temperature can cause decomposition which can produce very toxic decomposition products (i.e., phosgene, hydrogen chloride, etc.).

Remove container from fire area if it can be done without risk. Cool containers that are exposed to flames with water from side until well after the fire is out. Fight fire from maximum distance.

8.4 Notification and Technical Assistance

Section 103(a) and (b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 require persons who release hazardous substances into the environment in reportable quantities determined pursuant to Section 102 of the Act to notify the National Response Center (NRC): 800-424-8802 (Washington, D.C. 426-2675).

All the chlorinated organic solvents are designated as hazardous under CERCLA. Their reportable quantities are as follows: dichloromethane (100 lbs.), tetrachloromethane (5000 lbs.), TCE (1000 lbs.), PCE (100 lbs.), and 1,1,1-trichloroethane (100 lbs.). EPA has proposed an adjustment of the RQ to 1 lb. for dichloromethane, PCE, and 1,1,1-trichloroethane (Federal Register, May 25, 1983, p. 23587, 23594, and 23595).

For technical assistance, call CHEMTREX (Chemical Transportation Emergency Center): 800-424-9300. Other sources of technical information are: (1) the EPA's Oil and Hazardous Materials Technical Assistance Data System (OHMTADS) contained within the NIH-EPA Chemical Information System (CIS) which provides information pertinent to emergency spill response efforts, and (2) the CHRIS System which provides information on first aid, physical/chemical properties, hazard assessments, and response methods. Both systems can be accessed through NRC.

8.5 Disposal

The chlorinated organic solvents are subject to Subpart D regulation under RCRA only if 1000 kg of the commercial product is disposed of in one month (40 CFR 261.33).

The following nonspecific and specific wastestreams, which contain one or more of the solvents, are also subject to RCRA regulations (40 CFR 261.31 and 261.32).

- (1) The spent halogenated solvents used in degreasing; PCE, TCE, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and sludges from the recovery of these solvents (F001).
- (2) The spent halogenated solvents; PCE, TCE, methylene chloride, 1,1,1-trichloroethane and the still bottoms from the recovery of these solvents (F002).

- (3) Wastes including, but not limited to, distillation residues, heavy ends, tars, and reactor cleanout wastes from the production of chlorinated aliphatic hydrocarbons, having carbon content from one to five, utilizing free radical catalyzed processes (F024).
- (4) Distillation bottoms from the production of acetaldehyde from ethylene (K009).
- (5) Distillation side cuts from the production of acetaldehyde from ethylene (K010).
- (6) Heavy ends or distillation residues from the production of carbon tetrachloride (K016).
- (7) Heavy ends from the fractionation column in ethyl chloride production (K018).
- (8) Heavy ends from the distillation of ethylene dichloride in EDC production (K019).
- (9) Heavy ends from the distillation of vinyl chloride in VC monomer production (K020).
- (10) Aqueous spent antimony catalyst waste from fluoromethanes production (K021).
- (11) Spent catalyst from the hydrochlorinator reactor in the Production of 1,1,1-trichloroethane (K028).
- (12) Waste from the product steam stripper in the production of 1,1,1-trichloroethane (K029).
- (13) Chlorinated hydrocarbon waste from the purification step of the diaphragm cell process using graphite anodes in chlorine production (K073).

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

- 9.1. Air (CONTACT: Robert Jungers for PCE, FTS 629-2331; Joseph F. Walling for the other solvents, FTS 629-7954).

PCE is not a criteria air pollutant; therefore, no Agency-approved or reference procedure is available. A procedure using charcoal for sampling and gas chromatography with flame ionization detectors (FID) and/or electron capture detectors (ECD) for analysis has been used for ambient monitoring around metal degreasing and commercial dry cleaning facilities ("Development of a Measurement Method for Perchloroethylene in Ambient Air," RTI/1507/10-01F, March 1979). Confirmation analysis is made using gas chromatography for component separation and mass spectrometry for analysis.

The method was evaluated in coin-operated dry cleaning establishments and in the peripheral ambient atmosphere. Indoor concentrations of PCE ranging from 100 ppb to 10,000 ppb, were collected for eight hours at a sampling rate of 60 cm³/min. Outdoor (ambient) concentrations of PCE ranging from less than 1 ppb to 30 ppb, were collected for 24 hours at a sampling rate of 230 cm³/min.

The total method precision determined by analysis of replicate field samples ranged from 12.2 percent to 18.1 percent relative standard deviation. The laboratory method precision determined by replicate analyses of samples ranged from 1.43 percent to 6.57 percent relative standard deviation. The average percent PCE recovery efficiency, at the 95 percent confidence interval, of quality control spiked sample analyses ranged on inside samples from 86.4 ± 10.2 to 98.5 ± 2.9 and on outside samples from 60.1 ± 1.9 to 84.6 ± 8.9.

The quality assurance program for this evaluation consisted of the following:

- o Triplicate samples were collected at selected sites to determine field method precision.
- o Samples were distributed to three laboratories to detect possible bias.
- o External QA spiked samples were distributed to determine accuracy of analysis.

Like PCE, dichloromethane, tetrachloromethane, TCE, and 1,1,1-trichloroethane are not criteria air pollutants; therefore, no Agency-approved or reference procedure is available.

A procedure using Tenax adsorbent for sampling and gas chromatography/mass spectrometry (GC/MS) for analysis has been used but little is known about the precision and accuracy of the procedure. GC/MS requires special expertise and expensive, sophisticated equipment. For these reasons, monitoring for one compound alone using the Tenax GC/MS procedure is rarely cost-effective and the approach is most suitable when monitoring for an array of volatile compounds is desired.

The preparation of Tenax suitable for sampling is demanding. Tenax background is a problem that must be addressed. Precautions about permissible maximum air volumes, sampling rates and ambient temperatures during sampling must be observed and these, in turn, govern allowable sampling times.

Detection limits and accuracy are not known; reproducibility is estimated to be 50-100 percent. Quality assurance materials composed of blank Tenax sampling cartridges spiked with known amounts of solvent can be prepared and must be used in any monitoring program.

9.2 Water (CONTACT: Thomas Bellar, FTS 684-7311 or
James Lichtenberg, FTS 684-7308)

The chlorinated organic solvents are all parameters under Section 304(h) of the Clean Water Act. Information has been supplied on all the chlorinated solvents except 1,1,1-trichloroethane. However, the analytical procedures should be analogous.

There are several approved and proposed gas chromatographic procedures for the analysis of the chlorinated solvents in natural, waste, and drinking waters.

The primary differences between the methods are the extraction procedure and the means of injecting the extracts into the gas chromatograph. Mass spectrometry and halogen specific detectors are normally used to improve qualitative accuracy.

Direct Aqueous Injection EPA # Method 8 ⁽¹⁾
ASTM # D 2908-74 ⁽²⁾

Major Equipment Required: Gas chromatograph

One to 5 ul of the neat sample is injected directly into the gas chromatograph. The method detection limit is approximately 1 mg/l when mass spectrometry, flame ionization or halogen specific detectors are used. For nickel-63 electron capture detectors the method detection limit is approximately 1 µg/l.

Liquid-Liquid Extraction EPA # 501.2 ⁽³⁾
ASTM - To be included in the 1981
Annual Book of ASTM Standards

Major Equipment Required: Gas chromatograph

A small volume of sample is extracted once with a low boiling water insoluble solvent, such as pentane. Sample/solvent ratios of 5:1 are commonly used. One to five ul of the extract is then injected into a gas chromatograph equipped with an electron capture detector. The method detection limit is approximately 1.0 ug/l.

Purge and Trap EPA # 601, ⁽⁴⁾625, ⁽⁴⁾502.1, ⁽⁵⁾
ASTM # D-3871-79 ⁽⁶⁾
Standard Methods - included in the 15th Edition

Major Equipment: Gas chromatograph and purge and trap apparatus. Five ml of the aqueous sample is placed into a purging device. The solvent and other volatile water insoluble organic compounds are transferred from the aqueous phase to the gas phase. The volatilized compounds are swept from the purging device by the purge gas and are trapped in a short column containing a suitable sorbent. After a predetermined period of time the trapped compounds are thermally desorbed and backflushed into a gas chromatograph equipped with a mass spectrometer, flame ionization or a halogen specific detector.

The method detection limit for the mass spectrometer (full scan) and for the flame ionization detector is approximately 1 µg/l. For a carefully optimized halogen specific detector method, detection limits as low as 20 ng/l have been achieved.

Samples are collected in narrow-mouth screen-cap bottles with TFE fluorocarbon seals. Samples are stored head-space free at 4°C in the dark. Sodium thiosulfate is normally used to remove free residue chlorine. Spiked river water samples have been stored for up to 27 days under these conditions with no apparent losses.

Single laboratory test data on simple spiked matrices have been collected by EPA. Intralaboratory accuracy and precision and method detection limit data are currently being collected. Quality control and performance evaluation samples (methanolic concentrates containing solvent to be spiked into water) are available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, USEPA, Cincinnati, Ohio 45268.

References for Water Analysis

1. "A Method for Organochlorine Solvents in Industrial Effluents." National Pollutant Discharge Elimination System Appendix A, Federal Register 38, No. 7S Pt. II.
2. "Standard Test Method for Measuring Volatile Organic Matter in Water by Aqueous - Injection Gas Chromatography," Annual Book of ASTM Standards, 1980, Part 31, Water, ASTM D-2908-74.
3. Federal Register, Thursday, November 29, 1979, Volume 44. No. 231, 40 CFR, Appendix C - Parts I and II.
4. Federal Register, Monday, December 3, 1979, Volume 44, No. 233, 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants.
5. "The Determination of Halogenated Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method." Method 502.1, September 1980, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
6. "Standard Test Methods for Measuring Purgeable Organic Compounds in Water Using Headspace Sampling," ASTM D-3871-79, Part 31, Water, Annual Book of ASTM Standards, 1980.

LIST OF PROCEDURES FOR DICHLOROMETHANE

Method	Type	MDL	Recovery ^a (%)	Standard Deviation (%)	Status
EPA 624	P&T	2.8	66-82	46-66	Proposed
EPA 601	P&T	0.25 ug/1	90.7	4.6	Proposed
EPA 502.1	P&T	ND	84	12	Proposed
EPA 501.2	LLE	ND	ND	ND	Untested
EPA 8	DAI	1 mg/1	ND	ND	Official ^b
Standard Methods	P&T	ND	ND	ND	Untested
ASTM D-2098-74	DAI	ND	ND	ND	Untested
ASTM-D-3871-79	P&T	ND	ND	ND	Untested

P&T = Purge and Trap

LLE = Liquid/Liquid Extraction

DAI = Direct Aqueous Injection

Status - As of March 1981.

^a Single laboratory recovery from spiked reagent water or wastewater.

^b Official for the analysis of organohalides in wastewater.

LIST OF PROCEDURES FOR TETRACHLOROMETHANE

Method	Type	MDL	Recovery ^a (%)	Standard Deviation (%)	Status
EPA 624	P&T	2.8 ug/1	91	23	Proposed
EPA 601	P&T	0.12 ug/1	88	26	Proposed
EPA 502.1	P&T	<0.1 ug/1	90	7	Proposed
EPA 501.2	LLE	<1 ug/1	ND	ND	Untested
EPA 8	DAI	1 mg/1	ND	ND	Official ^b
Standard Methods	P&T	ND	ND	ND	Untested
ASTM D-2098-74	DAI	ND	ND	ND	Untested
ASTM-D-3871-79	P&T	ND	ND	ND	Untested

P&T = Purge and Trap

LLE = Liquid/Liquid Extraction

DAI = Direct Aqueous Injection

Status - As of March 1981.

^a Single laboratory recovery from spiked reagent water or spiked wastewater.

^b Official for the analysis of organohalides in wastewater.

LIST OF PROCEDURES FOR TRICHLOROETHENE

Method	Type	MDL	Recovery ^a (%)	Standard Deviation (%)	Status
EPA 624	P&T	1.9 ug/1	106-110	14-22	Proposed
EPA 601	P&T	0.1	96	14	Proposed
EPA 502.1	P&T	ND	94	6.0	Proposed
EPA 501.2	LLE	ND	ND	ND	Untested
EPA 8	DAI	1 mg/1	ND	ND	Official ^b
Standard Methods	P&T	ND	ND	ND	Untested
ASTM D-2098-74	DAI	ND	ND	ND	Untested
ASTM-D-3871-79	P&T	ND	ND	ND	Untested

P&T = Purge and Trap

LLE = Liquid/Liquid Extraction

DAI = Direct Aqueous Injection

Status - As of March 1981.

^a Single laboratory recovery from spiked reagent water or wastewater.

^b Official for the analysis of organohalides in wastewater.

LIST OF PROCEDURES FOR TETRACHLOROETHENE

Method	Type	MDL	Recovery ^a (%)	Standard Deviation (%)	Status
EPA 624	P&T	4 ug/1	97-99	13-26	Proposed
EPA 601	P&T	.03 ug/1	97	16	Proposed
EPA 502.1	P&T	ND	90	10	Proposed
EPA 501.2	LLE	ND	ND	ND	Untested
EPA 8	DAI	1 mg/1	ND	ND	Official ^b
Standard Methods	P&T	ND	ND	ND	Untested
ASTM D-2098-74	DAI	ND	ND	ND	Untested
ASTM-D-3871-79	P&T	ND	ND	ND	Untested

P&T = Purge and Trap

LLE = Liquid/Liquid Extraction

DAI = Direct Aqueous Injection

Status - As of March 1981.

^a Single laboratory recovery from spiked reagent water or wastewater.

^b Official for the analysis of organohalides in wastewater.

9.3 Solid Waste

The chlorinated organic solvents being discussed may be determined as described by Method 8010 in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (Office of Solid Waste and Emergency Response, July 1982, SW-846, Second Edition). Method 8010 is used to determine the concentration of various halogenated volatile organic compounds in groundwater, liquid, and solid matrices.

Specifically, Method 8010 provides cleanup and GC conditions for the detection of halogenated volatile organic compounds including the compounds under discussion. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a halide-specific detector (HSD). The estimated method detection limits using the purge-and-trap procedure for the various chlorinated organic solvents being discussed are as follows: 0.12 ug/l for trichloroethene and tetrachloromethane, .03 ug/l for tetrachloroethene and 1,1,1-trichloroethane, and .10 ug/l for dichloromethane.

9.4 Other Samples

The methods used for the analysis of these chlorinated organic solvents in environmental and other samples are summarized in an IARC Monograph (IARC, 1979). The determination is made most frequently by using GC in conjunction with one of several available detectors.

REFERENCES

The major references used in the preparation of this document are listed below. EPA documents are referenced by the EPA office of origin and the year of publication. For further information refer to the contacts given throughout this document or contact the EPA Program Offices listed in the next section.

- (IARC, 1979) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 20, International Agency for Research on Cancer, World Health Organization, Lyon (1979).
- (NAS, 1977) Ozone and Other Photochemical Oxidants, National Academy of Science, Washington, D.C. (1977).
- (NAS, 1979) Stratospheric Ozone Depletion by Hydrocarbons: Chemistry and Transport, National Academy of Sciences, Washington, D.C. (1979).
- (NTP, 1982) NTP Technical Report on the Carcinogenesis Bioassay of Trichloroethylene in F344/N Rats and B6C3F1/N Mice (Gavage Study) National Toxicology Program (1982).
- (OHEA, 1982a) Health Assessment Document for Dichloromethane (Methylene Chloride), Draft, EPA-600/8-82-004, Office of Health and Environmental Assessment (1982).
- (OHEA, 1982b) Health Assessment Document for Carbon Tetrachloride, draft, EPA-600/8-82-001, Office of Health and Environmental Assessment (1982).
- (OHEA, 1982c) Health Assessment Document for Trichloroethylene, Draft, EPA-600/8-82-006, Office of Health and Environmental Assessment (1982).
- (OHEA, 1982d) Health Assessment Document for Tetrachloroethylene (Perchloroethylene), Draft, EPA 600/8-82-003, Office of Health and Environmental Assessment (1982).
- (OHEA, 1982e) Health Assessment Document for 1,1,1-Trichloroethane (Methyl Chloroform), Draft, EPA 600/8-82-003, Office of Health and Environmental Assessment (1982).
- (OWRS, 1979) Water-Related Fate of 129 Priority Pollutants, Vol. II, EPA-440/4-79-029b, Office of Water Regulations and Standards (1979).
- (OWRS, 1980a) Ambient Water Quality Criteria for Halomethanes, EPA 440/5-80-051, Office of Water Regulations and Standards (1980).
- (OWRS, 1980b) Ambient Water Quality Criteria for Carbon Tetrachloride, EPA 440/5-80-026, Office of Water Regulations and Standards (1980).

- (OWRS, 1980c) Ambient Water Quality Criteria for Trichloroethylene,
EPA 440/5-80-077, office of Water Regulations and Standards
(1980).
- (OWRS, 1980d) Ambient Water Quality Criteria for Tetrachloroethylene, EPA
440/5-80-073, Office of Water Regulations and Standards
(1980).
- (OWRS, 1980e) Ambient Water Quality Criteria for Chloroethanes, EPA
440/5-80-029, Office of Water Regulations and Standards
(1980).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-4173 (919-541-4173)

Carcinogen Assessment Group	382-7341
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	382-7571
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality and Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	382-7051
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
------------------------------	----------

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Information Management Division 382-3749

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division
Research Triangle Park, NC 629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division 382-7575

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division 755-0100

Effluent Guidelines Division 382-7120

Office of Solid Waste (OSW)

Permits and State Programs Division 382-4746

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division 382-2182
Hazardous Site Control 382-2443

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II 340-6635 (201-321-6635)

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis
Research Triangle Park, NC 629-2454 (919-541-2454)

Water Analysis
Cincinnati, OH 684-7311 (513-684-7311)

Waste Analysis
Las Vegas, NV

545-2137 (702-798-2137)

Office of Monitoring Systems
and Quality Assurance

382-5767

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Chemical Coordination Staff

Chemical Information
and Analysis

382-3375

Chloroform

CHLOROFORM

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-3
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-1
Land Releases	3-1
<u>Exposure</u>	4-1
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-1
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2
Other Actions	6-3
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Hazardous Waste	7-1
Other	7-2

<u>Spill or Other Incident Clean-up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-2
Disposal	8-2
 <u>Sampling and Acceptable Analytical Techniques</u>	 9-1
Air	9-1
Water	9-1
Solid Waste	9-3
 <u>References and Office Contacts</u>	 R-1

CHLOROFORM

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

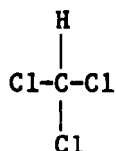
1.1 Properties (OWRS, 1980)

At standard temperatures and pressures, chloroform is a clear, colorless, volatile liquid with a pleasant, etheric, non-irritating odor and sweet taste.

Synonyms: formyl trichloride; methane trichloride; methenyl chloride; methenyl trichloride; methyl trichloride; trichloroform.

CAS Number 67-66-3

Formula CHCl_3



Molecular Weight 119.4

Melting Point ($^{\circ}\text{C}$) -63.5

Boiling Point ($^{\circ}\text{C}$) 61.2

Vapor Pressure (25°C) 190 torr

Water Solubility (25°C) 7800 mg/l

Log Octanol-Water Partition
Coefficient 1.95

1.2 Chemistry and Environmental Fate/Transport

Chloroform is released to the atmosphere directly and by volatilization from the aquatic environment and soil surfaces. Once it is in the troposphere, its estimated lifetime is reported to be 2-3 months. Reaction with hydroxyl radicals appears to be the primary degradation mechanism. Photochemical degradation is not expected to be an important pathway. Removal from the atmosphere by rainout is also considered unlikely because the high vapor pressure of chloroform indicates that an insignificant fraction will be associated with water droplets or dust particles.

Volatilization is the predominant pathway for removal of chloroform from the aquatic environment. One study reported that the half-life

for evaporation of chlorine from a stirred aqueous solution was approximately 20 minutes. Hydrolysis does not appear to be rapid enough to compete with volatilization as a removal mechanism. Biodegradation and bioaccumulation in the aquatic environment are probably not important fate pathways. The extent to which adsorption competes with volatilization is uncertain due to a lack of data in this area, although volatilization is likely to predominate.

Little information is available on the fate of chloroform in soils and sediment. Volatilization is probably the dominant pathway from surface soils. Evidence does suggest, however, that migration to ground water might also occur (OWRS, 1980).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACT: Jerry Stara, FTS 684-7531)

2.1.1 Acute Toxicity (OWRS, 1980)

The acute toxicity of chloroform in experimental animals is species-, strain-, sex-, and age-dependent. Oral LD₅₀ values range from 119 mg/kg to 2,000 mg/kg with indications of renal and hepatic necrosis.

Most human toxicologic observations on chloroform have been made as a result of its use as a general anesthetic, a practice which has been discontinued. There are many documented fatalities from chloroform-induced anesthesia. Ingestion of 120 ml of chloroform has been survived, but serious illness occurred in another individual after ingestion of only 5 ml.

Signs of chloroform poisoning in humans include a characteristic sweetish odor on the breath, dilated pupils, cold and clammy skin, initial excitation alternating with apathy, loss of sensation, abolition of motor functions, prostration, unconsciousness and eventual death. Liver and renal damage have been found.

Acute dermal exposure to chloroform may result in hyperemia, erythema, irritation and destruction of the epithelium. Eye contact produces burning, redness of conjunctival tissue and possible damage to the corneal epithelium.

2.1.2 Chronic Toxicity

Worker exposure to concentrations of chloroform of over 112 mg/m³ have been reported to result in depression, ataxia, flatulence, irritability, and liver and kidney damage (ORNL, 1978; OWRS, 1980a). Based on evidence that chloroform is carcinogenic in mice and rats, IARC states that it is reasonable to regard the substance as though it presents a carcinogenic risk to humans (IARC, 1979).

2.1.3 Absorption, Distribution and Metabolism (OWRS, 1980)

Chloroform is rapidly absorbed through the lungs if inhaled, through the gastrointestinal tract if ingested, and, to a lesser extent, through intact skin. With some species variation, chloroform is partially excreted unchanged and partially metabolized to carbon dioxide and unidentified urinary metabolites in mice, rats, monkeys and humans.

An average chloroform concentration of 51 ug/kg was detected in samples of body fat taken from eight subjects between 48 and 82 years of age. Concentrations of 1.0 ug/kg to 10 ug/kg were present in kidney, liver, and brain tissues.

2.2 Environmental Effects (Contacts: John Gentile, FTS 838-4843)

2.2.1 Aquatic Effects

Freshwater - Available data for chloroform indicate that acute toxicity to freshwater life occurs at concentrations as low as 28.9 mg/ml. Twenty-seven-day LC₅₀ values indicate that chronic toxicity occurs at concentrations as low as 1.2 mg/l and could occur at lower concentrations among species or other life stages that are more sensitive than the earliest life cycle stage of the rainbow trout (ORNL, 1978).

Saltwater - The lowest reported 96-hour LC₅₀ value for a marine organism is 28 mg/l for the dab (*Limanda* sp). The 96-hour LC₅₀ for the pink shrimp is 81.5 mg/l (OWRS, 1980).

2.2.2 Other Effects

Plants - Studies show that abnormal mitosis has occurred in cells exposed to chloroform concentrations of 0.025%. Toxic effects also occur at this level. Concentrations greater than 0.25% have been shown to be lethal (ORNL, 1978).

Microorganisms - Chloroform is not particularly susceptible to degradation by microorganisms. It is a powerful inhibitor and has been used for sterilization purposes. One study indicates that extremely low concentrations of chloroform can severely limit digestion of sewage sludge (ORNL, 1978).

3. ENVIRONMENTAL RELEASE

Information on sources and amounts of chloroform released to the environment varies. For instance, a comparison of two studies reveals air emissions estimates in 1978 of 19,200 kkg (OWRS, 1980) and 11,100 kkg (OAQPS, 1980). In general, present knowledge of releases due to the activities of man is sketchy. There is also some question about the relative importance of natural versus anthropogenic sources. Materials balances, therefore, are tentative. The releases listed in the table below are taken from a report prepared by the Office of Water Regulations and Standards (OWRS, 1980).

3.1 Air Releases

<u>Source of Release</u>	<u>Amount (kkg)</u>
Pulp and Paper Bleaching	12,100
Chlorination of Water	3,245
Pharmaceutical Extractions	1,525
Automobile Exhausts	965
Atmospheric Decomposition of Trichloroethylene	450
Chloroform Production	370
Production of Vinyl Chloride Monomer	187
Transportation & Storage Loss	177
Production of F-22	150
Use of Chloroform as a Fumigant	38

3.2. Water Releases

<u>Source of Release</u>	<u>Amount (kkg)</u>
Pulp and Paper Bleaching	400
Pharmaceutical Extractions	275
Chlorination of Water	221
Chloroform Production	14
Production of Vinyl Chloride Monomer	2

3.3 Land Releases

<u>Source of Release</u>	<u>Amount (kkg)</u>
Pharmaceutical Extractions	290
Production of Vinyl Chloride Monomer	200

4. EXPOSURE (CONTACT: Mike Slimak, FTS 426-2503)

The chlorination of drinking water represents the largest source of human exposure to chloroform in the United States, generally ranging from 0.02 - 0.2 mg/day. Although data are scarce, maximum exposure due to ingestion of food has been estimated at 0.04 mg/day. In general, inhalation exposure is thought to be low; however, somewhat higher exposures are expected in industrialized and urban areas. Another exposure route that may be of significance is absorption of chloroform through the skin. Swimmers may receive up to 1.1 mg/day via this route (OWRS, 1980).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available on the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purpose of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. For further information contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information contact Delores Evans at FTS 382-3546 or Irv Weiss at FTS 382-3524.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Delores Evans at FTS 382-3546 or Ingrid Meyer at FTS 382-3773.

5.5 Chemical Substances Information Network (CSIN)

The prototype CSIN, operational since November 1981, has been developed by merging the technologies of computer networking and distributed data base management. CSIN is not another data base, but a library of systems. Through the CSIN front-end intermediary management computer, the user may access and use independent and autonomous information resources which are geographically scattered, disparate for data and information content, and employ a variety of types of computer hardware, software, and protocols. Users may converse in and among multiple systems through a single connection point, without knowledge of or training on these independent systems.

Presently, six independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), CIS, EPA-CICIS, CAS-On-Line, SDC-orbit, and two files of Dialog: CRGS and TSCA Inventory. The CSIN management computer allows the user to create, retrieve, store, or manipulate data and queries. This eliminates the need for re-entering long lists of chemical identifiers or other information elements which are part of the original query or which have been identified and acquired from one or more of the CSIN resources. For further information contact Dr. Sid Siegal at FTS 382-2256.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 475 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained by offices within EPA. For further information, contact Charlene Sayers at FTS 755-9112.

The following data bases contain information on chloroform:

Consolidated Permits Program-Application Form 1,2b,2c
Data Collection Portfolio for Industrial Waste Discharges
Distribution Register of Organic Pollutants in Water
Drinking Water
Effluent Guidelines GC/MS Screening Analysis Data Base
Energy and Mining Point Source Category Data Base
Federal Facilities Information System
Fine Particle Emissions Information System
Food Industry Group
Fugitive Emissions Information System
Gaseous Emissions Data System
Hazardous Waste Data Management System
Hazardous Waste Site Tracking System
Hemlock, Michigan Environmental Samples
Hewlett-Packard
Humacao Ambient Data Base
IFB Organics Data Base
Indicator Fate Study
Industrial Process Evaluations
Innovative Technology, Timber Industry Effluent Guidelines

Inorganic Chemicals Industry Regulation Record
 LiParl Landfill
 Liquid Effluents Data System
 Listing of Organic Compounds Identified in Region IV
 Love Canal Data Handling System
 Method Validation Studies of Priority Pollutants
 National Electronic Injury Surveillance System
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Permit Compliance
 Nationwide Urban Runoff Program
 Needs Survey
 New York Bight Ocean Monitoring Program
 Organic Chemicals/Plastics Industry
 Organic Transport thru Soil
 Ozone and its Precursors Data Base--Houston/Los Angeles
 Ozone and its Precursors Data Base--Midwest/Boston
 Paint and Ink Analytical Data
 Permit Compliance System
 Pesticide Incident Monitoring System
 Pesticide Product Information System
 Pharmaceutical Screening/Verification Data Base
 Precision and Accuracy for Screening Protocols
 Priority Pollutants-Region I
 Priority Pollutants-Region III
 Publicly Owned Treatment Works (POTW) Analytical Data
 Publicly Owned Treatment Works (POTW) Quality Control
 Puerto Rico Reservoirs
 Regional Toxics Monitoring Program
 Resource Conservation and Recovery Act (RCRA)-Hazardous Waste Site
 Inspections
 Screening Sampling Program
 Select Hazardous Chemicals-Ambient
 Sources of Toxic Pollutants Found in Influent to Sewage Treatment
 Plants
 Spill Prevention Control and Countermeasure
 System for Consolidated Permitting and Enforcement Data Base
 Textile Industry BAT Study-Toxic Sampling Data
 Toxics Monitoring
 U.S. Virgin Islands-St. Thomas, St. Croix
 Verification Data Base
 Verification Sampling Program
 Waste Characterization Data Base
 Water Enforcement Regional System
 Water Quality Information System
 Wisconsin Power Plant Impact Study Data Center

6. REGULATORY STATUS (Current as of 4/15/82)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Air Act (CAA)

Chloroform is not regulated directly as an air pollutant.

Clean Water Act (CWA)

- Toxic Pollutant Effluent Standards - Pursuant to Section 307(a)(1) of the Federal Water Pollution Control Act (FWPCA), chloroform is listed as a toxic pollutant (40CFR401.15). As such, it is subject to effluent limitations reflecting the "best technology economically achievable" (BAT). Effluent limitations for chloroform have not been promulgated, however.
- Designation of Hazardous Substances and Reportable Quantities - Chloroform has been designated as a hazardous substance under Section 311(b)(2)(A) of the FWPCA (40CFR116.4). A reportable quantity has been established; any discharge into navigable waters in excess of the reportable quantity must be brought to the attention of the Coast Guard (40CFR117.21), and the discharger is subject to clean-up liability and civil penalties (40CFR117.22-23).

Safe Drinking Water Act (SDWA)

- Maximum Contaminant Levels - National Interim Primary Drinking Water regulations for total trihalomethanes (TTHMs; a combination of chloroform and three other trihalogenated methanes) apply to community water systems which serve 10,000 individuals or more and which add a disinfectant as part of their treatment process. For such systems, the maximum contaminant level (MCL) for TTHMs is 0.10 mg/l (40CFR141.12). This restriction takes effect for large water systems (greater than 75,000 customers) on November 29, 1981, and for all regulated systems by November 29, 1983.
- Underground Injection Control - The Safe Drinking Water Act requires EPA to promulgate minimum requirements for State programs to protect underground drinking water sources from contamination due to pollutants injected into wells. Technical requirements and criteria can be found at 40CFR part 146. In a State with an approved UIC program, underground injection of chloroform-containing wastes designated as hazardous wastes under RCRA cannot occur without a permit.

Resource Conservation and Recovery Act (RCRA)

Wastes identified as hazardous under Section 3001 of RCRA are subject to a "cradle-to-grave" management system which encompasses generation, transportation and treatment, storage or disposal. Chloroform is identified as a hazardous toxic waste under 40CFR261.33(f) if it is a discarded commercial chemical product or manufacturing intermediate, off-specification commercial product or manufacturing intermediate, or contained in clean-up residue resulting from a spill of chloroform in the form of a commercial product or manufacturing intermediate. An exclusion for those who generate less than 1,000 kg/month of these wastes is available.

Chloroform is also identified as a toxic constituent of the following wastes listed as hazardous under 40CFR261.32:

- (1) Distillation bottoms from the production of acetaldehyde from ethylene;
- (2) Distillation side cuts from the production of acetaldehyde from ethylene;
- (3) Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production;
- (4) Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production;
- (5) Aqueous spent antimony catalyst waste from fluoromethanes production;
- (6) Waste from the product stream stripper in the production of 1,1,1-trichloroethane; and
- (7) Chlorinated hydrocarbon wastes from the purification step of the diaphragm cell process using graphite anodes in the production of chlorine.

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

On April 6, 1976, (41FR14588), pursuant to the procedures set forth in 40CFR162.11, a Notice of Rebuttable Presumption Against Registration (RPAR) was issued for pesticide products containing chloroform. Under 40CFR162.11 the RPAR was triggered when chloroform was found to meet or exceed EPA's oncogenic risk criterion.

The RPAR on chloroform may be rebutted by showing that it "will not concentrate, persist or accrue to levels in man or the environment likely to result in any significant chronic adverse effects" or that the risk criteria determination was in error (40CFR162.11). In addition, the registrant may submit evidence that the benefits of the pesticide outweigh the risk (40CFR162.11).

Marine Protection, Research and Sanctuaries Act (MPRSA)

Section 102(a) of the Marine Protection, Research and Sanctuaries Act authorizes the Administrator of EPA to issue ocean dumping permits if such dumping will not degrade or endanger human health, welfare, or amenities, or the marine environment, or economic potential. The Agency has promulgated criteria to which permitted dumping operations must adhere. Major provisions which affect the disposal of chloroform are:

- A prohibition on dumping organohalogens, mercury, and cadmium compounds except as "trace contaminants" (40CFR227.6).
- A prohibition on dumping known or suspected carcinogens, mutagens, and teratogens (40CFR227.6).

However, chloroform is not mentioned in the regulations, and it appears that if any control over its disposals exists, it is exercised on a case-by-case basis when disposers apply for ocean dumping permits.

6.1.2 Programs of Other Agencies

Occupational Safety and Health Administration (OSHA)

Section 6(a) of OSH Act requires the Secretary of Labor to adopt as mandatory any national consensus standard or established Federal standard relating to employee health and safety. OSHA has adopted the Threshold Limit Value established by the American Conference of Government Industrial Hygienists. OSHA limits the concentration of chloroform in workplace air to a ceiling value of 50 ppm, or 240 mg/m³ (29CFR1910.1000)

Food and Drug Administration (FDA)

FDA has banned chloroform as an ingredient (active or inactive) in any human or animal drug or any cosmetic product, except in residual amounts resulting from the manufacturing process (21CFR310.513, 510.413 and 700.18 respectively).

Department of Transportation (DOT)

Pursuant to the Hazardous Materials Transportation Act, the Department of Transportation has promulgated rules governing the transporters of hazardous materials. The rules require that shippers and transporters of hazardous materials (as defined in 49CFR172.101) adhere to standards for containing, packaging and labeling such materials and for maintaining manifests and documentation (49CFR171-177). Amendments to the rules were promulgated on May 22, 1980, (45FR34560), which add to the Hazardous Materials Table the hazardous substances and hazardous wastes regulated by EPA (40CFR116 and 262, respectively). Further provisions were added requiring transporters to notify the appropriate Federal agency of any discharges

of hazardous wastes and hazardous substances (49CFR171.16, 171.17). The revised Hazardous Materials Table, published as 49CFR172.101, includes chloroform.

6.2 Proposed Regulations

6.2.1 EPA Programs

Clean Air Act

- No proposed regulations address chloroform directly. Proposed New Source Performance Standards for the Synthetic Organic Chemicals Manufacturing Industry (46FR1136) would regulate volatile organic compounds (VOC), however. If promulgated, this regulation could affect emission of chloroform (OTI, 1981).

Clean Water Act

- Best Available Technology (BAT) and New Source Performance Standards (NSPS) would impose effluent limitations on concentrations of chloroform in waste water for 10 subcategories of the Pulp, Paper and Paperboard and Builder's Paper and Board Mills point source categories (46FR1430).

6.2.2 Programs of Other Agencies

FDA - Food and Drug Administration

- FDA has proposed a ban on the use of chloroform as a component of food-contact articles and the listing of chloroform as a substance prohibited from use in human food under Section 409(c)(3)(A) of the Federal Food Drug and Cosmetic Act (Food Additives - the Delaney Clause) 41FR15029.

6.3 Other Actions

Clean Water Act - Water Control Criteria - While Water Quality Criteria published pursuant to Section 304(a)(1) of the FWPCA do not have regulatory force, they are used in establishing individual effluent limitations for point source discharge permits under Section 402 (NPDES permits) and best management practices for non-point sources under Section 208. Water Quality Criteria for chloroform are based on protection of human health and are calculated parametrically on the basis of various expected levels of incremental cancer risk resulting from ingestion of a) aquatic organisms only and b) aquatic organisms plus water (OWRS, 1980a).

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) - CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the clean-up of hazardous waste disposal sites (42USC9601; PL 96-510). EPA is

developing regulations concerning the designation of hazardous substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46FR54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47FR10972). Hazardous substances as defined by Section 101(14) of CERCLA include: hazardous wastes designated under Section 3001 of the RCRA; hazardous air pollutants regulated under Section 112 of the CAA; water pollutants listed under Sections 307 and 311 of the CWA (and also any substances regulated in the future under Section 7 of TSCA and Section 102 of CERCLA). Therefore, chloroform is a hazardous substance under CERCLA and will be subject to regulations developed under Superfund.

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air - None

7.2 Water

- Water Quality Criteria (OWRS, 1980a)

Aquatic Life

- Freshwater Species

Acute Toxicity: 28,900 ug/ml
Chronic Toxicity: 1,240 ug/ml

- Saltwater Species - None

Human Health

For the maximum protection of human health from the potential carcinogenic effects due to exposure of chloroform through ingestion of contaminated water and contaminated aquatic organisms, the ambient water concentrations should be zero based on the non-threshold assumption for this chemical. However, zero level may not be attainable at the present time. Therefore, the levels which may result in incremental increase of cancer risk over the lifetime are estimated at 10^{-5} , 10^{-6} , and 10^{-7} . The corresponding recommended criteria are 1.90 ug/l, 0.19 ug/l, and 0.019 ug/l, respectively. If the above estimates are made for consumption of aquatic organisms only, excluding consumption of water, the levels are 157 ug/l, 15.7 ug/l, and 1.57 ug/l, respectively.

- Reportable Quantity Under Section 311 of the Clean Water Act (40CFR117)

The reportable quantity for spilled chloroform has been set at 5,000 pounds. EPA has proposed to lower this amount to 100 pounds (45FR46097). Discharge of chloroform into the navigable waters of the United States or adjoining shorelines in excess of the reportable quantity must be brought to the attention of the Coast Guard.

- Maximum Contaminant Level Under the Safe Drinking Water Act (40CFR141.12)

Restrictions on total trihalomethanes (TTHMs); a combination of chloroform and three other trihalogenated methanes apply to community water systems which serve 10,000 individuals or more and which add a disinfectant as part of the treatment process. For such systems, the maximum contaminant level (MCL) for TTHMs is 0.10 mg/l.

* See Appendix A for a discussion of the derivation, uses, and limitations of these Criteria and Standards.

7.3 Hazardous Waste

Generation as waste in one month of 1,000 kilograms or more of chloroform in the form of a commercial chemical product, manufacturing chemical intermediate, off-specification product or clean-up residue resulting from a spill of the above, is subject to the hazardous waste regulations promulgated under RCRA.

7.4 Others

- **Transportation - Reportable Quantities**

Under regulations promulgated pursuant to the Hazardous Materials Transportation Act, 5,000 pounds or more of chloroform is a reportable quantity. If a quantity of chloroform equaling or exceeding that amount is offered for transportation in one package, or transport vehicle when the material is not packaged, that fact must be noted on shipping papers and displayed on packages.

- **Workplace**

- OSHA limits the concentration of chloroform in workplace air to a ceiling value of 50 ppm or 240 mg/m³ (29CFR1910.1000).
- The American Conference of Government Industrial Hygienists has revised their TLV to 10 ppm (approximately 50 mg/m³) on an 8-hour time-weighted average basis.
- NIOSH recommended a standard that limited workplace concentrations to 10 ppm on a 10-hour time-weighted average basis, with a 10-minute maximum of 50 ppm. NIOSH also recommended that chloroform, when used as an anesthetic, be limited to an airborne concentration of 2 ppm.

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL
(CONTACT: National Response Center, 800-424-8802; in the Washington area, 426-2675)

8.1 Hazards and Safety Precautions (SAX, 1979; ITII, 1980)

Highly toxic by inhalation. Slightly flammable but will burn on prolonged exposure to flame or high temperature (combustion products are highly toxic). Reacts violently with (acetone + a base), Al, disilane, Li, Mg, nitrogen tetroxide, K, (perchloric acid + phosphorus pentoxide), (KOH + methanol), K-tert-butoxide, Na, (NaOH + methanol), sodium methylate.

Protect containers from damage. Store in a dark place away from direct sunlight and moisture. When handling, use safety glasses, self-contained breathing apparatus, protective clothing. Note: PVC and rubber are unsuitable materials for protective clothing.

8.2 First Aid (SAX, 1979; ITII, 1980)

If chloroform has been ingested, or there has been substantial over-exposure, the following antidotes may be applied: emetics, stomach syphon, friction, cold douche, fresh air, strychnine (hypodermically--from 1/120 to 1/60 grain), rubefacients, artificial respiration. Wash eyes with abundant water. Contaminated areas of the body should be washed clean with soap and water.

8.3 Emergency Action (DOT, 1980)

Do not touch spilled material. Use water spray to reduce vapors. For small spills, take up with absorbent material then flush area with water. For large spills, dike far ahead.

8.4 Notification and Technical Assistance

Section 103 of the "Superfund" Act requires persons who release hazardous substances into the environment in reportable quantities to notify the National Response Center at 800-424-8802 (in the Baltimore-Washington, D.C. area, call 800-426-2675). The reportable quantity for chloroform is 5,000 pounds.

For technical assistance, call CHEMTREC (Chemical Transportation Emergency Center) at 800-424-9300. Another source of information is the Oil and Hazardous Materials Technical Assistance Data System (OHM-TADS) contained in the NIH/EPA Chemical Information System (CIS) (See Section 5.3).

8.5 Disposal

A person who generates 1,000 kg or more per month of chloroform defined as a hazardous waste (discarded commercial product, off-spec product, manufacturing intermediate and clean-up residues of same) is subject to the RCRA hazardous waste regulations on treatment, storage and disposal.

The following specific waste streams, which contain chloroform, are also subject to the hazardous waste regulations.

- (1) Distillation bottoms from the production of acetaldehyde from ethylene;
- (2) Distillation side cuts from the production of acetaldehyde from ethylene;
- (3) Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production;
- (4) Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production;
- (5) Aqueous spent antimony catalyst waste from fluoromethanes production;
- (6) Waste from the product stream stripper in the production of 1,1,1-trichloroethane; and
- (7) Chlorinated hydrocarbon wastes from the purification step of the diaphragm cell process using graphite anodes in the production of chlorine.

9. SAMPLING AND ACCEPTABLE ANALYTICAL TECHNIQUES

9.1 Air (CONTACT: Joseph F. Walling, FTS 629-7954)

Chloroform is not regulated as an air pollutant. Therefore, no Agency or reference procedures exist. Although measurements of this pollutant have been made and reported, there are no well-documented method descriptions available for quantitative measurements in ambient air. Therefore, monitoring for this pollutant must be approached with great caution.

A procedure using Tenax adsorbent for sampling and gas chromatography/mass spectrometry (GC/MS) for analysis has been used but little is known about the precision and accuracy of the procedure. GC/MS requires special expertise and expensive, sophisticated equipment. For these reasons, monitoring for one compound alone using the Tenax GC/MS procedure is rarely cost effective and the approach is most suitable when monitoring for an array of volatile compounds is desired.

The preparation of Tenax suitable for sampling is demanding. Tenax background is a problem that must be addressed. Precautions about permissible maximum air volumes, sampling rates and ambient temperatures during sampling must be observed and these, in turn, govern allowable sampling times.

Detection limits and accuracy are not known; reproducibility is estimated to be 50-100 percent. Quality assurance materials composed of blank Tenax sampling cartridges spiked with known amounts of chloroform can be prepared and must be used in any monitoring program.

9.2 Water (CONTACT: Thomas Bellar, FTS 684-7311 or
James Lichtenberg, FTS 684-7308)

There are several approved and proposed gas chromatographic procedures for the analyses of chloroform in natural, waste and drinking waters. The primary difference between the methods is the extraction procedure and the means of injecting the extracts into the gas chromatograph. Mass spectrometry and halogen-specific detectors are normally used to improve qualitative accuracy.

- Direct Aqueous Injection for Wastewater EPA # Method 8 (1a)*
ASTM # D-2908-74 (2a)

Major Equipment Required: Gas chromatograph

One to 5 ul of the neat sample is injected directly into the gas chromatograph. The method detection limit is approximately 1 mg/l when mass spectrometry, flame ionization or halogen-specific detectors are used. For nickel-63 electron capture detectors the method detection limit is approximately 1 ug/l. Direct aqueous injection techniques are not acceptable for the analysis of chloroform in drinking water.

*Superscripts refer to references at the end of this subsection.

- Liquid-Liquid Extraction EPA # 501.2(3a)
ASTM - To be included in the 1981
Annual Book of ASTM Standards

Major Equipment Required: Gas chromatograph

A small volume of sample is extracted once with a low boiling, water insoluble solvent such as pentane. Sample/solvent ratios of 5:1 are commonly used. One to 5 ul of the extract is then injected into a gas chromatograph equipped with an electron capture detector. The method detection limit is approximately 0.5 ug/l.

- Purge and Trap EPA # 601,(4a) 625,(4a) 502.1,(5a) 501.1 (3a)
ASTM # D-3871-79(6a)
Standard Methods - To be included in the
15th Edition

Major Equipment: Gas chromatograph and purge and trap apparatus.

Five ml of the aqueous sample is placed into a purging device. Chloroform and other volatile, water insoluble organic compounds are transferred from the aqueous phase to the gas phase. The volatilized compounds are swept from the purging device by the purge gas and are trapped in a short column containing a suitable sorbent. After a predetermined period of time, the trapped compounds are thermally desorbed and backflushed into a gas chromatograph equipped with a mass spectrometer, flame ionization or a halogen-specific detector.

The method detection limit for the mass spectrometer (full scan) and the flame ionization detector is approximately 1 ug/l. For a carefully optimized halogen-specific detector method, detection limits as low as 20 ng/l have been achieved.

Samples are collected in narrow-mouth screen-cap bottles with TFE fluorocarbon seals. Samples are stored head-space free at 4°C in the dark. Sodium thiosulfate must be used to remove free residue chlorine. Spiked water samples have been stored for up to 14 days under these conditions with no apparent losses.

Single laboratory test data on simple spiked matrices have been collected by EPA. Intralaboratory accuracy and precision and method detection limit data are currently being collected. Quality control and performance evaluation samples (methanolic concentrates containing chloroform to be spiked into water) are available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, USEPA, Cincinnati, Ohio 45268.

References

- 1a. "A Method for Organochlorine Solvents in Industrial Effluents." National Pollutant Discharge Elimination System Appendix A, Federal Register 38, No. 7S Pt. II.
- 2a. "Standard Test Method for Measuring Volatile Organic Matter in Water by Aqueous - Injection Gas Chromatography," Annual Book of ASTM Standards, 1980, Part 31, Water, ASTM D-2908-74.
- 3a. Federal Register, Thursday, November 29, 1979, Volume 44. No. 231, 40CFR, Appendix C - Parts I and II.
- 4a. Federal Register, Monday, December 3, 1979, Volume 44, No. 233, 40CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants.
- 5a. "The Determination of Halogenated Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method," Method 502.1, September 1980, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
- 6a. "Standard Test Method for Measuring Purgeable Organic Compounds in Water Using Headspace Sampling," ASTM D-3871-79, Part 31, Water, Annual Book of ASTM Standards, 1980.

LIST OF PROCEDURES FOR CHLOROFORM

Method	Type	MDL	Recovery ^a (%)	Standard Deviation (%)	Status
EPA 624	P&T	1.6	90	18	Proposed
EPA 601	P&T	0.05 ug/l	98	7.5	Proposed
EPA 502.1	P&T	<1 ug/l	ND	ND	Proposed
EPA 501.2	LLE	<1 ug/l	106-110	5.3-9.8	Official ^b
EPA 8	DAI	1 mg/l	ND	ND	Official ^c
Standard Methods	P&T	ND	ND	ND	Untested
ASTM D-2098-74	DAI	ND	ND	ND	Untested
ASTM D-3871-79	P&T	ND	99-121	ND	Untested
EPA 501.1	P&T	<1 ug/l	88-100	0.14-7.9	Official ^b

P&T = Purge and Trap

LLE = Liquid/Liquid Extraction

DAI = Direct Aqueous Injection

Status - As of March 1981.

^a Single laboratory recovery from spiked reagent water or wastewater.

^b Official for the analysis of chloroform in drinking water.

^c Official for the analysis of organohalides in wastewater.

9.3 Solid Waste (CONTACT: Michael Hiatt, FTS 545-2118 or
Werner F. Beckert, FTS 545-2118)

Chloroform is a volatile priority pollutant that is determined in water according to Method 601 (44FR69468, gas chromatography with electron capture detector - GC/EC) or Method 624 (44FR69532, gas-chromatography/mass spectroscopy - GC/MS). No approved method for the determination of chloroform in soil, sediment or hazardous waste has been published. The commonly used analytical technique for the determination of volatile priority pollutants is GC/MS.

Sediments may be stored as long as 60 days when kept at 4°C and tightly sealed (1b).^{*} The container should be a glass septum vial with an unpierced teflon-lined septum. However, it is desirable to analyze samples as soon as possible, preferably within seven days since the septum vial seals are difficult to insure. When improperly sealed, the samples are easily cross-contaminated during storage by other stored samples or solvents used in laboratory operations. It has been found that 10 g blank sediment sealed in a septum vial and stored for several days in a freezer, which was situated in a sample preparation laboratory, has been contaminated with methylene chloride to a level of 200 ppb.

GC/MS quantitation is done using bromochloromethane as the internal standard for both capillary and packed columns. Chloroform is completely separated in the GC column from the other volatile priority pollutants. Quantitation is done by peak height or using the area of mass 83 m/e. The recommended reverse library identification masses are 47, 48, 49, 83, 85, and 87 m/e. Identification should be confirmed by a NBS forward library search.

Four sample preparation techniques that are applicable to GC/MS are: head space analysis, solvent extraction (2b), modified purge and trap (3b & 4b), and vacuum extraction (5b).

Head space analysis is not recommended since the precision is very poor for spike recoveries and is suspected to be analyst-dependent.

The solvent extraction is done by shaking 1 ml n-hexadecane with 1 g of sample in a 1-ml septum vial. The injection aliquot is removed directly from the vial after 30 seconds of mixing and injected splitless into a capillary column. The solvent extraction technique is recommended only for ppm or greater concentrations. A standard deviation of 1.4% at 10 ppm has been reported for this method.

One modified purge and trap technique (3b) desorbs the volatile compounds from the sample by heating the sample to 110°C while sweeping with helium carrier gas that is subsequently passed through 5 ml of water. The carrier gas then passes through a Tenax-silica gel trap which absorbs the volatile organics. The volatiles are desorbed from the trap by heating and passed through a GC column. Sample

^{*}Superscripts refer to references at the end of this subsection.

preparation generally takes less than 30 minutes. Recoveries are reported to be 77% at 26 ppb with a 35% precision. This method has been tested for the ppb range.

In another modified purge and trap technique (4b), which was used in the Love Canal Study, the sample is diluted with water and the resultant slurry is purged. A standard deviation of 19% has been reported for this method at the 20 ppb range with a recovery of 88%.

With the vacuum extraction technique (5b), the volatiles are extracted from the sample using a vacuum. The extracted volatiles are collected in a liquid-nitrogen-cooled trap. After extraction, 5 ml of water are added to the extract and the sample analyzed as a 5-ml water sample using Method 624. The precision at 25 ppb is 11% with a 102% recovery. The total sample preparation takes approximately 36 minutes.

Standards can be obtained from Radian Corporation or EMSL-Las Vegas (see Contact). Supelco supplies diluted standards but the concentrations are not verified. Standard solutions may also be prepared in the laboratory from reagent-grade chloroform to the appropriate dilution using methanol.

Periodic performance evaluations with samples that include chloroform are carried out by EMSL/CIN (Water Supply and Water Pollution Studies).

- 1^b. Memorandum Report, March 12, 1981, entitled "Holding Time for Purgeable Love Canal Soil and Sediment Samples," Dennis L. Forest to William L. Budde, EMSL-CIN.
- 2^b. I. R. DeLeon, et al., "Rapid Gas Chromatographic Method for the Determination of Volatile and Semivolatile Organochlorine Compounds in Soil and Chemical Waste Disposal Site Samples," *Journal of Chromatographic Science*, 18:85-88 (1980).
- 3^b. David N. Speis, "Determination of Purgeable Organics in Sediment Using a Modified Purge and Trap Technique," Protocol, U.S. EPA, Region II, Edison, New Jersey, October 10, 1980.
- 4^b. Quality Assurance Plan, Love Canal Study (unpublished).
- 5^b. Michael H. Hiatt, "Analysis of Fish and Sediment for Volatile Priority Pollutants." Submitted for publication to *Analytical Chemistry*.

REFERENCES

The major refernces used in preparation of this document are listed below. EPA references are listed below. EPA references are listed by the EPA office of origin and the year of publication. For additional information, refer to contacts given throughout this document or contact the EPA offices listed below.

- (DOT, 1980) Hazardous Materials: 1980 Emergency Response Guidebook.
U.S. Department of Transportation, 1980.
- (IARC, 1979) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 20, International Agency for Research on Cancer, World Health Organization, October 1979.
- (ITII, 1980) Toxic and Hazardous Industrial Chemicals Safety Manual.
International Technical Information Institute, 1980.
- (OAQPS, 1980) Human Exposure to Atmospheric Concentrations of Selected Chemicals. Prepared for the Office of Air Quality Planning and Standards by Systems Applications, Inc., March 1980.
- (ORNL, 1978) Environmental and Health Aspects of Selected Organohalide Compounds: An Information Overview. Oak Ridge National Laboratory, July 1978.
- (OTI, 1981) Integrated Multimedia Control Alternatives: Phase I Case Study - Chloroform. Draft report prepared by Abt Assoc. for the Office of Toxics Integration, June 1981.
- (OWRS, 1980) An Exposure and Risk Assessment for Trihalomethanes. Final Draft Report, Office of Water Regulations and Standards, November 1980.
- (OWRS, 1980a) Ambient Water Quality Criteria for Chloroform, Office of Water Regulations and Standards, EPA 440/5-80-033, October 1980.
- (SAX, 1979) Dangerous Properties of Industrial Chemicals, N. Irving Sax, 5th ed., 1979.

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
---------------------------------	----------

Effluent Guidelines Division	426-2571
------------------------------	----------

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergenices call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information and Analysis Program

382-2249

CHROMIUM

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-4
<u>Environmental Release</u>	3-1
<u>Exposure Routes</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
Other Exposure Routes	4-1
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-4
Other Actions	6-5
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-2
Other	7-2

<u>Spill and Other Incident Cleanup/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-2
<u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	9-1
Air	9-1
Water	9-1
Solid Wastes	9-3
Other Samples	9-3
<u>References and Office Contacts</u>	R-1

CHROMIUM

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Chromium is a common metallic element present in low concentrations throughout the environment. While there is no significant domestic mining of chromite ore (the predominant chromium-bearing mineral), about 1.2 billion lbs. (540×10^3 metric tons) of chromite ore and 320 million lbs. (145×10^3 metric tons) of chromium ferroalloy were imported for consumption in 1982. Chromium is widely used as an alloying element in stainless steel and heat-resistant materials; chromium compounds are also used in pigments, metal finishing, and leather tanning. Very little chromite ore is processed to chromium metal, but rather most is used in intermediate forms such as ferrochrome, sodium dichromate, and chromium trioxide. Table 1 summarizes the properties and uses of a variety of chromium compounds (IARC, 1980).

1.2 Chemistry and Environmental Fate/Transport

Although chromium can exist in a variety of oxidation states, the hexavalent (+6) and trivalent (+3) forms are the most significant. Hexavalent chromium, such as dichromate, is a strong oxidizing agent and readily reacts with reducing agents and organic matter to produce the more stable trivalent form. The foremost characteristic of trivalent chromium is the tendency to form relatively inert complexes and insoluble compounds. Chromium has its greatest industrial applications in the +6 state due to its oxidizing properties and its ability to form soluble colored salts (OWRS, 1980; ORNL, 1978).

Chromium is released into the atmosphere mainly from processes in the chromium industry, such as ore refining, and from inadvertent sources, such as coal combustion. Chromium is emitted and transported primarily in particulate form and removal occurs by fallout and precipitation. The chemical form of chromium in air depends on its source. While chromium from metallurgical production is usually in the trivalent or metallic state, hexavalent chromium may be released in dusts during chromate production and in the form of chromic acid aerosols from plating processes (ORNL, 1978).

Most aqueous chromium in excess of background levels originates from direct and indirect industrial discharges. Chromium is one of the most commonly detected priority pollutants in sewage and industrial wastewater. Trivalent chromium is very insoluble and tends to accumulate in the sediments in the form of oxides or hydroxides. The hexavalent form (i.e., chromates) tends to remain in solution due to its high water solubility and resistance to adsorption. Interconversion between the two oxidation states does not occur under most environmental conditions. Apparently, hexavalent chromium must diffuse into anaerobic sediments in order to undergo reduction to the trivalent form and thus accumulate in the sediment. Photolysis and volatilization are not

TABLE 1: PROPERTIES OF CHROMIUM COMPOUNDS

Chemical Name and Formula	CAS Number and Synonyms	Oxidation State	Transition Points (°C)	Water Solubility (per liter)	Uses
Chromium Cr	7440-47-3 chrome.	0	mp: 1857 bp: 2672	insol.	In alloys for strength, hardness and corrosion resistance.
Ferrochromium	11114-46-8 Chromium alloy, Cr, C, Fe, N, Si; ferrochrome.	0	--	insol.	In stainless and heat resistant steels and alloys.
Chromite ore $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$	1308-31-2 Chromite mineral [Cr_2FeO_4]; chrome ore; chromite.	+3	--	--	Common mineral forms also contain Al, Mg, and other metals.
Chromic oxide Cr_2O_3	1308-38-9 Chromium oxide [Cr_2O_3]; chromium trioxide.	+3	mp: 2435 bp: 4000	insol.	In pigments in glass, ceramic polymers, and paints; also a brick component.
Chromic chloride CrCl_3	10025-73-7 chromium chloride [CrCl_3].	+3	mp: 1150 bp: decomposes at 1300	585g (hydrated)	Limited use in dyes.
Chromium trioxide CrO_3	1333-82-0 Chromic acid; chromium oxide [CrO_3].	+6	mp: 196 bp: decomposes	625g (20°)	Corrosion inhibitor in chrome plating and an oxidizing agent.

TABLE 1: PROPERTIES OF CHROMIUM COMPOUNDS (cont.)

Chemical Name and Formula	CAS Number and Synonyms	Oxidation State	Transition Points (°C)	Water Solubility (per liter)	Uses
Lead Chromate PbCrO_4	7758-97-6 Chromic acid [H_2CrO_4], lead (2+) salt (1:1).	+6	mp: 844 bp: decomposes	0.58mg (25°)	Yellow orange pigments for paints, inks, and resins.
Sodium Chromate Na_2CrO_4	7775-11-3 Chromic acid, [H_2CrO_4], di- sodium salt.	+6	mp: 792 bp: decomposes	873g (30°)	In tanning and as a preservative; an intermediate for other chromium compounds.
Sodium Dichromate $\text{Na}_2\text{Cr}_2\text{O}_7$	10588-01-9 Chromic acid [$\text{H}_2\text{Cr}_2\text{O}_7$] disodium salt.	+6	mp: 357 bp: decomposes at 400°	2380g (0°)	An intermediate for many chromium compounds; used in tanning and as corrosion inhibitor.

Source: (IARC, 1980).

important transformation processes for chromium in water (OWRS, 1979; OWRS, 1981).

Most chromium naturally present in soils is in an insoluble state in adsorbed, mineral, or precipitated forms. In most cases, chromium in soil is relatively immobile and is unavailable for uptake by plants. Wind action and weathering can transport chromium-bearing soils to the atmosphere. The chromium content of soils may be increased by application of phosphate fertilizers and sludges. Chromium precipitated from wastewaters and municipal wastes is often disposed of in landfills, and leaching could potentially result in contamination of groundwater. However, leachate is not expected to contain significant amounts of chromium unless the landfill is subject to acidic conditions which would solubilize and mobilize a portion of the chromium (ORNL, 1978).

2. EFFECTS INFORMATION

2.1 Health Effects (Contacts: Lester Grant, FTS 629-4172; Si Duk Lee, FTS 629-4159)

2.1.1 Acute Toxicity

Chromium is generally accepted to be an essential element in humans. The amount of chromium needed to produce toxic effects is several orders of magnitude higher than the dose needed to relieve symptoms of chromium deficiency. Because of their insolubility, trivalent chromium compounds are relatively nontoxic when given orally. Hexavalent chromium compounds are strong oxidizing agents and are highly irritating to tissues (ORNL, 1978).

The lethal oral dose in humans from the various forms of hexavalent chromium has been estimated to be in the range of 1.5 to 16g. High oral doses of hexavalent chromium can lead to kidney damage; tubular necrosis has often been observed in humans following massive accidental or deliberate exposures. Renal lesions have also been reported in animals; a single subcutaneous dose (15mg/kg) of potassium dichromate led to changes in renal tubules and increases in chemical levels in the urine that were indicative of renal damage (IARC, 1980).

Acute human exposure to high concentrations of chromic acid via inhalation results in severe damage to deep pulmonary structures. Similar damage including bronchitis and pneumonia developed in cats acutely exposed to dichromate (11-23 mg/kg). Acute skin exposure to chromate dusts or solutions may result in the development of ulcers, especially if a break in the skin is present. Acute systemic effects of hexavalent chromium compounds are rare in humans and generally result from deliberate exposure (ECAO, 1983).

2.1.2 Chronic Toxicity

Long-term exposures to relatively high dietary levels of chromium have been studied extensively in animals. Although increases in chromium concentrations were reported in the liver, spleen, and kidneys, few adverse effects were noted in most cases. Thus, few systemic changes are expected from moderately elevated oral exposure to chromium (OWRS, 1980).

After a review of the toxicity data, EPA used a one-year feeding study in rats to estimate an acceptable daily intake (ADI) for hexavalent chromium. A well-defined, no-observable-effect-level (NOEL) of 2.5 mg/kg per day in rats was divided by a safety factor of 1000 to give an ADI for a 70kg man of 0.18 mg/day. Several studies are also available that give dose levels for trivalent chromium in animals with no evidence of toxicity (NOEL). No effects were noted in a two-year study with rats fed up to 5% trivalent chromium in their diet. This translates into a NOEL of about 5.1 g/kg per day and, using a safety factor of 1000, EPA calculated an ADI of 357 mg of trivalent chromium for a 70 kg adult (OWRS, 1980). Note that these ADI calculations refer only to oral routes of exposure.

Occupational exposures to airborne hexavalent chromium compounds give rise to severe nasal irritation and to corrosive action in the nasal passage (septum perforation). Bronchitis, bronchial asthma, and an obstructive respiratory syndrome have all been reported in workers exposed to hexavalent chromium compounds at concentrations as low as 0.12 mg/m^3 . In animal studies, lifetime inhalation exposure to calcium chromate (13 mg/m^3) resulted in lung damage and ulceration of the stomach and intestinal membranes. Dermal contact with chromic acid, chromate dusts, or chromate solutions results in development of primary dermatosis in workers. An eczmoid dermatitis, which is considered an allergic reaction to chromate, may develop from skin contact to much lower concentrations of hexavalent chromium compounds. Sensitization may take place in a few days or over the course of several years (ECAO, 1983).

Carcinogenicity, Mutagenicity, and Teratogenicity - The carcinogenicity of various chromium compounds has been well documented in humans. Several studies of the chromate production industry have demonstrated a large excess risk of lung cancer. Studies of the chromate pigment industry also suggest a similar risk of lung cancer. Although the available epidemiological evidence does not permit a clear distinction between the relative carcinogenicity of different chromium compounds, exposure to a mixture of hexavalent compounds apparently carries the greatest risk (IARC, 1980).

Except for experiments showing sarcoma production at implantation or injection sites, the evidence for cancer production by chromium in experimental animals is not convincing. Attempts to produce lung cancers in animals by feeding or inhalation exposure to chromium have not been very successful. Positive results were obtained, however, by intrabronchial, intrapleural, intramuscular, or subcutaneous injection of hexavalent chromium compounds. These studies provide sufficient evidence for the carcinogenicity of several chromium compounds in animals. This work also indicates that all hexavalent forms of chromium are likely to be carcinogenic, but that the degree is modified by the solubility of the specific compounds. Thus, the animal studies suggest that hexavalent chromium is the etiologic agent in chromium-related cancer in humans (ECAO, 1983; IARC, 1980).

Most occupational epidemiological studies do not show an excess risk of cancer at sites other than the respiratory tract; some studies suggest that exposure to chromium compounds may lead to an increased risk of gastrointestinal cancer, but this has not been firmly established. Attention must be drawn to the fact that most occupational exposures involve airborne chromium concentrations which are quite high. In addition, the specific carcinogens responsible for the increased incidences of cancer in various industries have not been fully identified. It is also possible that chromium may possess cocarcinogenic properties, especially at high levels of exposure (OWRS, 1980).

Evidence has accumulated in recent years to show that chromium compounds possess the ability to cause cell transformations and mutations. Hexavalent chromates are mutagenic in E. coli and Salmonella and also affect DNA repair in bacteria. Chromates appear to be direct-acting mutagens and do not require activation by microsomal fraction. In fact, several studies indicate that sodium dichromate is deactivated as a mutagen in the Salmonella system in the presence of liver microsomes. Trivalent chromium salts appear to be either nonmutagenic or very weakly mutagenic in bacterial systems. Hexavalent chromium is mutagenic in yeast, and soluble hexavalent salts induce in vitro morphological transformations and chromosomal aberrations in mammalian cells. Chromosomal aberrations are also found in exposed workers (ECAO, 1983).

Little evidence exists for fetal damage that is directly attributable to chromium. While trivalent chromium in the form of natural complexes obtained from yeast can readily cross the placental barrier, simple inorganic chromium compounds do not. Although embryonic abnormalities were observed in the chick when hexavalent chromium was injected directly into the yolks of eggs, the significance to normal routes of exposure to chromium is questionable (OWRS, 1980). Teratogenic effects were detected in hamsters following single intravenous doses of 5 mg/kg CrO_3 and in mice following a single intraperitoneal injection of 15 mg/kg CrCl_3 during the critical period of gestation. The most common findings were cleft palate and hydrocephaly. Note that these teratogenic effects were observed at doses that were toxic to the mother (ECAO, 1983).

2.1.3 Absorption, Distribution, and Metabolism

Less than 1% of trivalent chromium is absorbed from the gastrointestinal (GI) tract of animals, whereas chromates are absorbed at a rate of 3-6% in rats. In humans, hexavalent chromium is absorbed from the GI tract at a rate of about 2% (IARC, 1980). The ability of GI juices to reduce hexavalent chromium to the trivalent form may decrease any differences between the two valence states in absorption efficiency or toxic effects after ingestion. Compounds of chromium also penetrate the skin fairly readily in the hexavalent form, while trivalent chromium reacts directly with epithelial and dermal tissues. In animal studies, water-soluble chromates disappeared rapidly from the lungs into circulation, whereas trivalent chromium did not. Workers exposed to primarily hexavalent chromium also absorbed chromium rapidly via the respiratory tract (IARC, 1980; OWRS, 1980).

Normally in humans the highest concentration of chromium is found in the lungs, and pulmonary levels tend to rise with age while the chromium content in other tissues falls. Apparently, the lung obtains most of the chromium from the air, not from oral exposure, and pulmonary chromium is not in complete equilibrium with other body pools of chromium. Once absorbed, the three major accumulation and clearance organs are the liver, spleen, and bone marrow (OWRS, 1980).

Chromium circulates in the blood bound primarily to plasma proteins. The half-life of chromium in plasma is relatively short, and cells tend to accumulate the metal. Chromium penetrates the cells in the hexavalent state and reacts with cell constituents (such as hemoglobin in red blood cells). Thus, within the cell, hexavalent chromium is reduced to the trivalent form which cannot exit the cell. This lack of chromium equilibrium between plasma and cells renders invalid the use of blood levels as exposure indicators. In general, the reduction of hexavalent chromium to the trivalent form and the subsequent reaction of Cr^{+3} with organic molecules of biochemical importance explain, in large part, the biological reactivity of chromium (OWRS, 1980). In rats, three main components of elimination have half-lives of 0.5, 5.9, and 83 days. Urinary excretion is the major route of elimination (ORNL, 1978).

Chromium is necessary for glucose and lipid metabolism and for utilization of amino acids in several mammalian systems. It is also important in the prevention of chronic diseases such as mild diabetes and atherosclerosis in humans. In addition, nucleic acids normally contain high chromium concentrations and the trivalent form may play a role in maintaining the configuration of the RNA molecule (ORNL, 1978).

2.2 Environmental Effects

2.2.1 Aquatic Effects

Chromium toxicity to aquatic organisms varies with pH, hardness, temperature, species, and the chemical form of chromium. Although hexavalent chromium is often considered the greater hazard, the bioassay data as a whole indicate no substantial overall differences in the aquatic toxicity of the two forms. Trivalent chromium appears to be more toxic in fish, while the hexavalent compounds are more toxic for invertebrates (OWRS, 1981; OWRS, 1980).

The lowest observed acute or chronic values in fish and invertebrates are 44 to 66 ug/L for trivalent and 47 ug/L for hexavalent chromium. For hexavalent chromium, Water Quality Criteria have been set for freshwater life. The acute criterion (21 ug/L) was determined primarily from effects on the invertebrate Gammarus which is nearly 50-fold more sensitive than the next most sensitive species. The chronic criterion for hexavalent chromium (0.29 ug/L) is almost 500-fold lower than the chronic value for rainbow trout, the most sensitive of three species tested for chronic effects (OWRS, 1981).

3. ENVIRONMENTAL RELEASE

In 1979 total domestic consumption of chromium was 540×10^3 metric tons; metallurgical usage constituted 61% of consumption, while chemical and refractory uses totaled 21% and 18%, respectively. The greatest use by far of chromium is in the production of wrought stainless and heat resistant steels. Major chemical uses are in the production of pigments, metal finishing, and leather tanning (ECAO, 1983).

Table 2 summarizes the major sources of emissions of chromium to the atmosphere; approximately 16,500 metric tons/yr are estimated to be emitted after controls (for the year 1970). The major sources are from different aspects of the chromium industry (ore refining, chemical processing, refractory processing, and metallurgical processing) and inadvertent sources (coal and oil combustion, incineration, and asbestos mining). Ferrochromium production during refining is apparently the major source of atmospheric emissions (68%). The more populated, industrial areas of the United States receive the most emissions, especially the Great Lakes area and the East Coast regions (Contact: Dave Patrick, FTS 629-5645).

POTWs discharge about 1,000 metric tons of chromium a year to water, nearly all of which originates from indirect industrial discharge. POTW influent is estimated to be approximately 8,000 metric tons/yr. Based on limited data, the Metal Finishing and Leather Tanning industries appear to contribute the most to POTW influents. Industry also discharges about 850 metric tons/yr directly to surface waters, most of which is generated by Coal Mining, Metal Finishing, Nonferrous Metals, Organic Chemicals, Pulp and Paper, and Iron and Steel. Chromium is one of the three or four most commonly detected priority pollutants in sewage and industrial wastewater (OWRS, 1981) (Contact: Mike Slimak, FTS 382-7051).

Although chromium in urban runoff is significant (perhaps up to 1000 metric tons/yr), most chromium in excess of rural background levels appears likely to originate from industrial releases. The amount of chromium disposed of on land is probably a large portion of total use, but the quantity has not been estimated (OWRS, 1981).

TABLE 2. SOURCES AND ESTIMATES OF UNITED STATES
ATMOSPHERIC CHROMIUM EMISSIONS IN 1970^a

Source	Chromium Emissions, metric tons/year
Industrial Sources:	
ferrochromium refining	11,200
steel and alloy	595
material handling	750
chemical processing	106
refractory	1,650
Inadvertent Sources:	
coal combustion	1,420
oil combustion	336
cement production	254
incineration	143
Total	16,500

^aSource: (ORNL, 1978); controlled emissions.

4. EXPOSURE

Food is apparently the major route of exposure to chromium for the general population. The oral routes of exposure are not expected to lead to harmful levels of chromium in the body when exposure involves the low levels normally present in food and water. In fact, the average American may actually suffer from mild chromium deficiency. However, exposure to airborne chromium may pose special risks both because the lungs tend to retain the element, and also because of the carcinogenic hazard posed by inhaled hexavalent chromium (OWRS, 1980).

4.1 Air Exposure

The majority of chromium in the atmosphere is probably in the trivalent or metallic state. However, chromium released during chrome production, chrome plating, and cooling tower drifts (chromate salts are often used in cooling towers as a corrosion inhibitor) may be in the more toxic hexavalent form. Air levels near a cooling tower were measured to be about 50 ng/m³ up to 660 ft. from the tower. (ECAO, 1983).

Data concerning levels of total chromium in ambient air are available from the EPA's National Aerometric Data Bank. According to the available data obtained during the 1977 to 1980 period, the mean chromium concentration for urban areas ranged from 0.0052 ug/m³ (i.e., background) to 0.16 ug/m³; the highest level (24 hour average) was 2.5 ug/m³. Specific industrial sources such as power plants, incinerators, and iron and steel plants may significantly increase atmospheric levels in certain areas (ECAO, 1983).

4.2 Water Exposure

Although chromium is a widely distributed element, high levels are not naturally found in surface or groundwater. The amounts of chromium found in these waters are usually related to anthropogenic sources. The chromium concentration in various United States drinking water supplies has been measured in several studies. In a recent survey (1974 to 1975) of 3834 tap waters from 35 representative locations only 28% of the areas monitored had chromium levels above the detection limit (0.1 ug/L). The range in this study was 0.4 to 8 ug/L and the average value was 1.8 ug/L (ECAO, 1983). Assuming a typical concentration of 2 ug/L, ingestion of 2 liters per day of water would lead to the uptake of only 0.2 ug/day based on an absorption factor of 5% (OWRS, 1981).

4.3 Other Exposure Routes

The chromium content of a variety of foods has been determined. Foods with the highest mean concentrations are canned fruits (0.51 ppm), seafoods (0.47 ppm), meats and fish (0.23 ppm), frozen or fresh vegetables (0.23 ppm), and grains and cereals (0.22 ppm). The most recent (1979) diet study conducted by FDA-USDA indicated that the chromium intake from the typical American diet was 62 ± 28 ug/day and 89 ± 56 ug/day respectively, for diets with high (43%) and low (25%)

fat content (ECAO, 1983). Older estimates for dietary intake of chromium ranged from 50 to 280 ug/day (OWRS, 1980). Assuming 5% absorption of ingested chromium, uptake from food containing 90 ug of chromium would be 4 to 5 ug/day (OWRS, 1981).

Chromium has been determined to be a component of cigarette tobacco. Tobaccos grown in the United States have been found to have a chromium content of 0.24 to 6.3 ppm. However, the amount actually inhaled during smoking has not been determined (IARC, 1980).

NIOSH estimated that 175,000 workers in 104 occupations are potentially exposed to hexavalent chromium. Chromium and its compounds are found in several types of industrial activity including: (1) the metallurgical industry, particularly chromium extraction, ferro-alloy production, and chromium plating; (2) the manufacture of refractory materials, such as bricks, glass, ceramics, and certain metals; and (3) the pigment, paint, dyeing, and tanning industries (IARC, 1980).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available on the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568 or Robin Heisler at FTS 382-3557.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemized NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. (EPACASR is scheduled to be added to CIS in 1984.) For further information contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information contact Dr. Steve Heller at FTS 382-2424.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact (Doug Sellers) at FTS 382-2320.

5.5 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is a sophisticated switching network based on heterogeneous distributed data base management and networking concepts which were only theory less than a decade ago. CSIN offers efficient and effective access to on-line information resources (systems) containing data and information relevant to chemical substances, as well as information covering other scientific disciplines and subject matters. The purposes of CSIN are two-fold; first to meet the growing chemical data and information requirements of industry, academe, government (Federal and State), public interest groups, others, and secondly to reduce the burden on the private and public sector communities when responding to complex Federal legislation oriented to chemical substances.

CSIN is not another data base. CSIN links many independent and antonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems". Users may converse with any or all systems interfaced by CSIN (see Table 1) without prior knowledge of or training on these independent systems, regardless of the hardware, software, data, formats, or protocols of these information resources.

Information accessible through CSIN provides data on chemical nomenclature, composition, structure, properties, toxicity, production uses, health and environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. CSIN provides more data, information, and processing capabilities than could practicably or cost effectively be included in as single centralized data base. Users may now converse in and among multiple systems through a single connection point -- CSIN.

Currently, seven (7) independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), Chemical Information System (CIS), CAS-On-Line, SDC's ORBIT, Lockheeds's DIALOG, Bibliographic Retrieval Service (BRS), and the US Coast Guard's Hazard Assessment Chemical System (HACS). Since November of 1981 the CSIN support contractor has trained over 400 users from the public and private sectors, representing over 100 different organizations.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 500 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. The clearinghouse listed 120 citations for chromium. For further information, contact Irvin Weiss at FTS 382-5918.

6. REGULATORY STATUS (Current as of 7/83)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Air Act (CAA)

- o Section 111 - New Source Performance Standards have been issued covering particulate emissions from ferroalloy production facilities (40 CFR 60.260-.262). Although chromium emissions are not directly controlled, particulate chromium is indirectly limited by this NSPS. Most other source categories are also controlled to some extent by existing State or Federal requirements for particulate matter.

Clean Water Act (CWA)

- o Sections 301, 304, 306, and 307 - Chromium and its compounds are listed as priority pollutants (toxic pollutants, 40 CFR 401.15). Effluent limitations, pretreatment standards, and new source performance standards have been issued for sections of the following industries:
 - o Textile (40 CFR 410, Subparts A-B and D-G)
 - o Electroplating (40 CFR 413, Subparts A-B and D-H)
 - o Inorganic chemicals (40 CFR 415, Subparts L, Q, V, W, AH, AL, and BB)
 - o Petroleum refining (40 CFR 419, Subparts A-E)
 - o Iron and steel manufacturing (40 CFR 420, Subparts T and W-Z)
 - o Non-ferrous metals (40 CFR 421)
 - o Steam electric power generating (40 CFR 423, Subparts A-C)
 - o Ferroalloy manufacturing (40 CFR 424, Subparts A-C and G)
 - o Leather tanning and finishing (40 CFR 425, Subparts A-F)
 - o Rubber manufacturing (40 CFR 428, Subpart J)
 - o Timber products (40 CFR 429, Subparts G and H)
 - o Pulp, paper, and paperboard mills (40 CFR 430 and 431)
 - o Electroplating and metal finishing (40 CFR 433)
 - o Ore mining and dressing (40 CFR 440)
 - o Paint formulation (40 CFR 446)
 - o Ink formulation (40 CFR 447)
 - o Battery manufacturing (40 CFR 461)
 - o Metal molding and casting (40 CFR 464)
 - o Aluminum forming (40 CFR 467)
 - o Copper forming (40 CFR 468)
- o Section 311 - The following chromium compounds have been designated as hazardous materials and are subject to reportable quantity rules for discharges exceeding 1,000 lbs (40 CFR 116.4 and 117.3):
 - o Ammonium chromate
 - o Calcium chromate
 - o Chromic acetate

- o Chromic acid
 - o Chromic sulfate
 - o Chromous chloride
 - o Lithium chromate
 - o Potassium bichromate
 - o Potassium chromate
 - o Sodium chromate
 - o Sodium bichromate
 - o Strontium chromate
- o Sections 402 and 404 - Discharge of toxic pollutants such as chromium are controlled by permits required under the National Pollutant Discharge Elimination System (NPDES). Permits for discharge of dredged or fill materials are issued by the Army Corps of Engineers (40 CFR 122 to 125).

Safe Drinking Water Act (SDWA)

- o Section 1412 - Establishes a maximum contaminant level (MCL) for chromium in drinking water supplies (40 CFR 141.11).
- o Sections 1421 to 1424 - Establishes an underground injection control (UIC) program to protect underground sources of drinking water (40 CFR 146).

Resource Conservation and Recovery Act (RCRA)

- o Sections 1008(a)(3) and 4004(a) - Establishes a safe level for chromium in ground water (40 CFR 257, App. I).
- o Section 3001 - Chromium and its compounds are designated as hazardous constituents (40 CFR 261, App. VIII). Extractable chromium also characterizes waste as hazardous (40 CFR 261.24). Non-specific sources of chromium-containing hazardous wastes include electroplating operations (40 CFR 261.31, App. VII). Waste streams containing chromium from the following industries are listed as specific sources of hazardous waste: pigment production, ink formulation, production of iron and steel, and petroleum refining (40 CFR 261.32, App. VII). Calcium chromate is designated as a toxic waste (U032) when it is discarded or intended to be discarded as a commercial product or off-specification species. Container residues and spill residues are also included.
- o Sections 3002 to 3006 - Hazardous wastes containing chromium are subject to further control under RCRA. Regulations cover generators (40 CFR 262) and transporters (40 CFR 263) of such waste; and treatment, storage, and disposal facilities are subject to interim standards (40 CFR 264 and 265). Hazardous waste-permitting procedures are included in the consolidated permit regulations (40 CFR 122 to 124).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- o General industry standards for workplace exposure to air contaminants (29 CFR 1910.1000):
 - o Chromic acid and chromates
 - o Soluble chromic and chromous salts
 - o Metal and insoluble salts
- o Regulations also cover respiratory protection from chromium dust (29 CFR 1915.152) and ventilation requirements for welding, cutting, or heating chromium-bearing metals (29 CFR 1915.51 and 1926.353).

FDA - Food, Drug, and Cosmetic Act

- o Maximum quantity of chromium-cobalt-aluminum oxide as coloring agent in surgical sutures (21 CFR 73.1015).
- o Minimum amount of chromium oxide in chromium hydroxide green coloring agent used in externally applied drugs (21 CFR 73.1326) and cosmetics (21 CFR 73.2326).
- o Minimum amount of chromium oxide in chromium oxide coloring agent used in externally applied drugs (21 CFR 73.1327) and cosmetics (21 CFR 73.2327).
- o Maximum level of chromium as an impurity in food coloring FD&C Blue No. 1 (21 CFR 74.101), FD&C Green No. 3 (21 CFR 74.203), drug coloring D&C Blue No. 4 (21 CFR 74.1104) and cosmetic coloring D&C Blue No. 4 (21 CFR 74.2104).
- o Standard for bottled water (21 CFR 103.35).
- o Regulated under 21 CFR 175.105 for packaging adhesives; 21 CFR 176.160 and 21 CFR 176.180 for packaging; 21 CFR 177.2600 for rubber products; 21 CFR 178.3120 in paper and paperboard manufacture; 21 CFR 178.3290 for release agents in food packaging; 21 CFR 181.30 for use in waxed paper and paperboard.

MSHA - Mine Safety and Health Act

- o Performance requirements for respirators (30 CFR 11.130-140):
 - o Chromium
 - o Chromic acid

DOT - Hazardous Materials Transportation Act

- o Listed as a hazardous material (49 CFR 172.101):
 - o Chromic acid
 - o Chromic fluoride
 - o Chromium oxychloride
 - o Chromic anhydride
 - o Chromic sulfate
 - o Chromic acetate
 - o Chromium
 - o Chromous chloride
- o Specifications for packaging (49 CFR 173.164 and 49 CFR 173.247):
 - o Chromic acid
 - o Chromium oxychloride

6.2 Proposed Regulations

6.2.1 EPA Programs

CWA

- o Sections 54, 204, 208, 301, 304, 307, 308, 309, 402, 405, and 501 - General pretreatment regulations for a wide variety of existing and new sources (47 FR 42698).
- o Section 403 - Ocean discharge criteria (45 FR 9549).
- o Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund)
- o CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites. (42 USC 9601; PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities (RQ), claims procedures, and the confidentiality of business records (46 FR 54032).
- o Chromium compounds are hazardous substances under CERCLA and will be subject to regulations developed under Superfund. Although EPA has proposed adjustments to many of the RQs established under CERCLA and the CWA, RQs for chromium compounds are still under development (48 FR 23552).

Atomic Energy Act

- o Section 206(a) - Proposed disposal standards for uranium mill tailings; limit on chromium leakage (46 FR 2556).

6.2.2 Other Programs

OSHA

- o Sections 6(b) and 8(g)(2) - Proposed standard requires employers to identify hazardous materials in the workplace (46 FR 4412).

6.3 Other Actions

CAA

- o Although OAQPS has not yet proposed regulations, chromium is considered a high assessment priority. An exposure assessment has been completed and a source assessment is undergoing revision. A regulatory decision is currently scheduled for early FY 1985 (Contact: Dave Patrick, FTS 629-5645).

NIOSH - Occupational Safety and Health Act

- o Request for information on data pursuant to the development of a criteria document for chromic acid.

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- o Current OSHA occupational standards (29 CFR 1910.1000):

Soluble chromic and chromous salts	500 ug/m ³	(8-hr. TWA)
Chromium and insoluble salts	1,000 ug/m ³	(8-hr. TWA)
Chromic acid and chromates	100 ug/m ³	(ceiling)

- o NIOSH recommendations for occupational exposure limits:

Chromic acid	50 ug CrO ₃ /m ³	(8-hr. TWA)
	100 ug CrO ₃ /m ³	(ceiling)

Carcinogenic chromium** (VI)	1 ug/m ³
---------------------------------	---------------------

Chromium (VI)	25 ug/m ³	(8-hr. TWA)
	50 ug/m ³	(ceiling)

- o American Conference of Government Industrial Hygienists (ACGIH) threshold limit values (TLV) based on an 8-hour time-weighted average:

Chromium metal, Chromium II compounds, and Chromium III compounds	0.5 mg/m ³
---	-----------------------

Chromium VI compounds and Chromite ore processing	0.05 mg/m ³
---	------------------------

Tert-Butyl Chromate, as CrO ₃ (skin)	0.1 mg/m ³
--	-----------------------

7.2 Water

- o Various chromium compounds are designated as hazardous substances under Section 311 of the CWA and have reportable quantities for spills defined as over 1,000 lbs (40 CFR 117.3). See Section 6.1.1 of this document for compounds listed.

*See Appendix A for a discussion of derivation, uses, and limitations of these criteria and standards.

**Certain forms of chromium (VI) have been found to cause increased respiratory cancer among workers; other forms are currently labeled non-carcinogenic by NIOSH.

- o Maximum Contaminant Level (MCL) 50 ug/1
for total chromium in drinking
water (40 CFR 141.11) and ground
water (40 CFR 257, App. I).

- o Water Quality Criteria (45 FR 79318)

Freshwater aquatic life:

Chromium III	44 ug/1 (chronic)
Chromium VI	0.29 ug/1 (24-hr. average)
	21 ug/1 (ceiling)

Saltwater aquatic life:

Chromium III	10,300 ug/1 (acute)
Chromium VI	18 ug/1 (24-hr. average)
	1,260 ug/1 (ceiling)

Human health (values refer to non-carcinogenic criteria levels associated with ingestion of contaminated aquatic organisms and drinking water except where indicated):

Chromium III	170 mg/1
	3,433 mg/1 (ingestion of aquatic organisms only)
Chromium VI	50 ug/1

7.3 Other

- o Solid waste is considered 5.0 mg/1
hazardous if the concentration
of chromium equals or exceeds
this maximum for extractable
chromium (40 CFR 261.24).
- o Numerous FDA regulations set limits on levels of chromium permitted in coloring agents. See Section 6.1.2 for CFR citations.
- o FDA maximum concentration level of 0.05 mg/1 total chromium in bottled water (21 CFR 103.35).

8. SPILL OR OTHER INCIDENT CLEANUP/DISPOSAL

8.1 Hazards

The toxicity and hazardous properties of chromium compounds vary widely. In general, the hexavalent chromate salts and chromic acid are the most hazardous due to their irritative and corrosive action on skin, mucous membranes, GI tract, and the respiratory tract. In addition, hexavalent chromium compounds are recognized as having carcinogenic potential when inhaled. Chromate salts are strong oxidizing agents and may react violently with other chemicals and organic matter. Chromic acid (CrO_3) reacts so vigorously that it may ignite on contact with compounds such as acetic acid and alcohol, and organic materials such as cloth or wood.

Protective clothing should be worn during clean-up to prevent skin contact with solids or liquids containing chromic acid or chromates. Areas in which exposure to carcinogenic hexavalent chromium may occur should be identified and access should be limited.

8.2 First Aid

Acute poisoning by ingestion of chromates is manifested by dizziness, thirst, abdominal pain, vomiting, and shock. Use of dimercaprol has been suggested as treatment. Emergency treatment includes the immediate administration of large amounts of water; afterwards try to induce vomiting. Skin or eye exposure should be followed by thorough washing with water. Contaminated clothing must be removed immediately. In case of inhalation exposure, move the victim to fresh air and perform artificial respiration if necessary.

8.3 Emergency Action

Unnecessary people and people not wearing protective equipment and clothing should be restricted from spill areas. If chromic acid or chromates are spilled, the area should be ventilated, and the material collected for disposal. Solutions should be absorbed with vermiculite, sand, or similar material. Fires can be extinguished with water, spray, or foam. Note that a few chromium compounds (chromium oxychloride, chromosulfuric acid) may react violently with water. Fire may also produce toxic gases from the decomposition of chromium compounds.

8.4 Notification and Technical Assistance

Section 103(a) of CERCLA (Superfund) requires notification of the National Response Center (NRC; 800-424-8802; in Washington, D.C., 426-2675) if releases exceed reportable quantities (RQ). At present, Section 102 of CERCLA sets a statutory RQ of 1 pound for hazardous substances except those for which RQs have been established previously under Section 311 of the CWA. Thus, until and unless adjustments of the RQs are promulgated, the CWA RQs of 1000 lbs. are in effect for a number of chromium compounds (see section 6.1.1 of this document).

For technical assistance call CHEMTREC (800-424-9300) or EPA's Environmental Response Team (ERT), Edison, NJ (201) 321-6660. Further information may be obtained from the Division of Oil and Special Materials (1-202-245-3045).

The Center for Disease Control (CDC) has developed a manual ("A System for Prevention, Assessment, and Control of Exposure and Health Effects from Hazardous Sites") in order to help State health departments in efforts related to hazardous wastes and substances. The manual includes procedures for inspection of hazardous waste sites, monitoring and analysis of hazardous substances (including chromium), assigning priorities to various sites, and conducting health studies. Sources of information and assistance related to these tasks are also given (Contact: Kathy Deck, FTS 236-4100).

8.5 Disposal

Generators of more than 1,000 kg of hazardous waste per month, or spill clean-up residues or debris resulting from clean-up are subject to regulation under RCRA. Such wastes include wastes that fail the EP (extraction procedure) toxicity test for chromium (40 CFR 261.24).

A variety of industrial wastestreams which contain chromium are also listed as hazardous (40 CFR 261.31 and 261.32), including sludges from electroplating (F006) and from chemical conversion of aluminum (F019). Specific source wastestreams which contain chromium are listed below by industry:

- Inorganic Pigments..... Wastewater treatment sludges and oven residue from the production of inorganic pigments.
- Petroleum Refining..... Dissolved air flotation (DAF) float, stop oil emulsion solids, heat exchanger bundle cleaning sludge, and API separator sludge from the petroleum refining industry.
- Iron and Steel..... Emission control dust/sludge from the primary production of steel in electric furnaces and spent pickle liquor from steel finishing.
- Secondary Lead..... Emission control dust/sludge and waste leaching solution from secondary lead smelting.
- Ink Formulation..... Washes and sludges from equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air

Although no EPA approved procedures have been issued for the analysis of chromium in air, a variety of procedures have been published. The NIOSH Manual of Analytical Methods contains several procedures which may be useful in analytical situations outside of the occupational environment. Method 351 in the NIOSH Manual (Volume 7) describes a general method for the analysis of trace elements, including chromium, by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in airborne material. A known volume of air is drawn through a mixed cellulose ester filter and the filters are treated ($\text{HNO}_3/\text{HClO}_4$) to ash the organic matrix and dissolve the elements. Analysis is accomplished by nebulization into an inductively coupled argon plasma and monitoring the emission spectra of the various elements. The working range is 5 to 2000 ug/m^3 in a 500 L sample (i.e., 2.5 to 1000 ug dissolved in a 10 mL sample solution). The instrumental detection limit for chromium is quite low (1.3 ng/mL of solution) which translates into a detection limit of about 0.03 ug/m^3 for a 500 L air sample. Multi-element spiked filters at 2.5 ug element/filler ashed and analyzed by this procedure yielded a relative standard deviation of approximately 5% for chromium and recoveries of chromium were essentially quantitative.

The NIOSH Manual also contains procedures for analysis of chromium in air by atomic absorption AA spectroscopy (Method 152, Vol. 1), colorimetry (Method 319, Vol. 6), a kinetic procedure (Method 182, Vol. 1), and methods to analyze for insoluble or soluble chromium compounds (Methods S323 and S352, Vol. 3). Among other techniques commonly used in the analysis of air particulates (collected on filters) is X-ray fluorescence (XRF). This method is particularly well suited to samples which have more-or-less homogeneous surfaces, such as filtered air particulates. XRF can distinguish between the oxidation states of chromium without pretreatment of the samples. Neutron activation analysis is also widely used to determine chromium levels due to its high sensitivity, ability for multi-element analyses, and the need for a minimum of processing prior to analysis. In ambient air, dusts and fumes of chromium compounds are usually collected by high volume samplers. Typical filter media have included cellulose, polyethylene, PVC, and glass fibers (ECAO, 1983).

9.2 Water

Chromium is listed under the Clean Water Act 304(h) as an inorganic priority pollutant. A drinking water standard has also been promulgated which lists a Maximum Contaminant Level (MCL) of 0.05 mg/L . The Agency-approved methods described below may be used for measuring both total and dissolved chromium; if dissolved chromium is to be measured, the sample must be filtered (0.45 micron membrane filter) prior to analysis. The sample (or filtrate) may be preserved with HNO_3 (pH 2); however if hexavalent chromium is to be determined (Method 218.4), the sample should not be preserved with acid, but rather filtered and a portion of the filtrate analyzed as soon as possible for hexavalent chromium.

The approved methods for chromium (Methods for Chemical Analysis, of Water and Wastes, 1979, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory) all utilize atomic absorption (AA) techniques for analysis. The direct aspiration procedure (Method 218.1) has an optimum working range of 0.5 to 10 mg/L and a detection limit of 0.05 mg/L.

For increased sensitivity, the sample may be concentrated by chelation of hexavalent chromium prior to analysis. To determine total chromium present (Method 218.3) the sample must first be treated with an oxidizing agent in order to convert trivalent chromium to the hexavalent form. Method 218.4 covers the determination of dissolved hexavalent chromium only, and thus, the sample is not oxidized prior to extraction. Both chelation methods utilize direct aspiration AA and have a working range of 1.0 to 25 ug/L.

When direct aspiration AA techniques do not provide adequate sensitivity, furnace techniques may be used (Method 218.2). In this procedure, hydrogen peroxide is added to convert all chromium to the trivalent state. The optimum concentration range is 5 to 100 ug/L and the detection limit is 1 ug/L. To insure valid data with furnace techniques, the sample matrix should be examined for interference effects.

EPA has also issued a method for multi-element analysis which can be used to determine chromium concentration in solution. (Federal Register 44, 69559, December 3, 1979). The method (200.7) uses inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The atomic-line emission spectra are processed by computer to correct for background and spectral interference. The estimated instrumental detection limit for chromium is 7 ug/L (at 267.7 nm).

Several methods for chromium analysis are also included in Standard Methods for the Examination of Water and Wastewater, 15th Edition, American Public Health Association (1980). Direct aspiration AA procedures (Methods 303A and 303B) are quite similar to EPA methods (218.1 and 218.3). A colorimetric method (Method 312B) based on the reaction of hexavalent chromium with diphenyl carbazide in acid solution is also included. (To determine total chromium, potassium chromate is used to convert all chromium to the hexavalent form.) The intense red violet color produced is monitored at 540 nm. This method may be used to analyze samples containing 0.5 to 50 mg of chromium per liter.

9.3 Solid Waste

Five approved methods for chromium analysis in wastes are given in Test Methods for Evaluating Solid Wastes - Physical Chemical Methods, EPA/SW-846, Office of Solid Waste (1982). Methods 7190, 7191 and 7197 are AA methods similar to water methods 218.1, 218.2, and 218.4 respectively. Method 7195 is a specific procedure for determining the level of hexavalent chromium in solution. This method is based on the separation of hexavalent chromium from solution by coprecipitation of lead chromate with lead sulfate. The hexavalent chromium is then reduced to the trivalent state and quantified by either flame or furnace AA. Method 7196 is a colorimetric procedure analogous to the procedure described in Standard Methods referenced in the water section (9.2) of this document.

Acid digestion procedures for the preparation of samples for analysis by flame and furnace AA are given in the solid waste document noted above (methods 3010 and 3020). These methods are applicable for aqueous samples, EP extracts, and certain nonaqueous wastes containing chromium. A method (3050) is also included to prepare sludge-type and soil samples for analyses by AA or ICP methods. A special method (3060) describes the alkaline digestion of waste samples for analysis for hexavalent chromium; the digestion is done under basic conditions to protect the chromium from reduction to the trivalent form.

9.4 Other Samples

Analytical methods for the detection of chromium have been summarized in an IARC monograph (IARC, 1980) and in several EPA publications (ECAO, 1983; ORNL, 1978). Sampling and analytical methods used to monitor air, water, and soil near industrial sites have been summarized in Environmental Monitoring Near Industrial Sites, Chromium (PB-271 881; 1977). Numerous references exist for the analyses of biological samples (IARC, 1980) and NBS has recently issued chromium certified materials for biological media (yeast, liver, plants).

REFERENCES

The major references used in preparation of this document are listed below. EPA references are listed by EPA office of origin and the year of publication. For further information refer to contacts given throughout this document or contact the relevant EPA offices listed at the end of this section.

- (ECAO, 1983) Health Assessment Document for Chromium, EPA-600/8-83-014A, External Review Draft, Environmental Criteria and Assessment Office (1983).
- (IARC, 1980) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 23, p. 205, International Agency for Research on Cancer, World Health Organization (1980).
- (ORNL, 1978) Reviews of the Environmental Effects of Pollutants:III. Chromium, EPA-600/1-78-023, Oak Ridge National Laboratory (1978).
- (OWRS, 1979) Water Related Environmental Fate of 129 Priority Pollutants, Vol. I, Chapter 10, EPA 440/4-79-029a, Office of Water Regulations and Standards (1979).
- (OWRS, 1980) Ambient Water Quality Criteria for Chromium, EPA-440/5-80-035, Office of Water Regulations and Standards (1980).
- (OWRS, 1981) Recommendations for Control of Environmental Hazards of Chromium, draft document, Office of Water Regulations and Standards (1981).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-4173 (919-541-4173)

Carcinogen Assessment Group	382-7341
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	382-7571
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality and Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	382-7051
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
------------------------------	----------

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Information Management Division 382-3749

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division
Research Triangle Park, NC 629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division 382-7575

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division 755-0100

Effluent Guidelines Division 382-7120

Office of Solid Waste (OSW)

Permits and State Programs Division 382-4746

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division 382-2182

Hazardous Site Control Division 382-2443

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II 340-6635 (201-321-6635)

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis
Research Triangle Park, NC 629-2454 (919-541-2454)

Water Analysis
Cincinnati, OH 684-7311 (513-684-7311)

Waste Analysis
Las Vegas, NV 545-2137 (702-798-2137)

Office of Monitoring Systems
and Quality Assurance

382-5767

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Chemical Coordination Staff

Chemical Information
and Analysis Group

382-3375

CHLORINATED PHENOLS

CHLOROPHENOLS

Table of Contents

	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-5
<u>Environmental Release</u>	3-1
<u>Exposure Routes</u>	4-1
Air Exposure	4-1
Water Exposure	4-2
Other Exposure Routes	4-2
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemicals Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2
Other Actions	6-3
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Other	7-2

<u>Spill or Other Incident Cleanup/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-2
<u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	9-1
Air	9-1
Water	9-1
Solid Waste	9-2
Other Samples	9-3
<u>References and Office Contacts</u>	R-1

CHLOROPHENOLS

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Chlorophenols are a family of compounds consisting of the phenol ring structure substituted with from one to five chlorine atoms. Chlorophenols are used as intermediates in the manufacture of dyes, herbicides, pesticides, pigments, and phenolic resins. Certain chlorophenols are also used directly as antimicrobial agents and preservatives. There are 19 different chlorophenols which differ in the degree or site of chlorination of the aromatic ring. Commercially, the most important compounds are: 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-CP), 2,4,5-trichlorophenol (2,4,5-TCP), and pentachlorophenol (PCP) (ECT, 1979; OWRS 1980a).

As shown in Table 1, the physical/chemical properties of chlorophenols vary according to chlorine content. The less chlorinated isomers are moderately volatile and water soluble while the highly chlorinated phenols are relatively nonvolatile and only sparingly soluble in water. The dissociation constants in Table 1 illustrate that increased chlorination also increases the acidity of the chlorophenol (ORNL, 1979).

1.2 Chemistry and Environmental Fate/Transport

Most chlorophenols are commercially synthesized by the chlorination of phenol. Other chlorophenols which have no commercial applications are produced to some extent as by-products during the synthesis of commercially important chlorophenols. Chlorinated dibenzo-p-dioxins may also be formed during the synthesis of chlorophenols. The highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) has been reported in commercial samples of 2,4,5-TCP and is carried as a trace contaminant in derived herbicides. While other chlorinated dioxins have been found in samples of tetra- and pentachlorophenol, the 2,3,7,8-TCDD isomer has not been reported. Chlorodibenzofurans have also been found as contaminants in various chlorophenol samples (ORNL, 1979).

Only a small fraction of environmental releases of chlorophenols is emitted to the atmosphere, primarily in the form of vapor from production processes. Little air monitoring has been done for these substances and the fate and persistence of chlorophenols in the atmosphere are not known. The detection of PCP in precipitation, however, indicates that this relatively non-volatile chlorophenol is present in the atmosphere and that it is removed by washout. While little or no evidence exists regarding degradation of chlorophenols in the atmosphere by photolysis or free radical oxidation, these are probably not significant removal pathways (OWRS, 1980e; OWRS, 1980f).

TABLE 1. PHYSICAL PROPERTIES OF CHLOROPHENOLS^a

Chemical Name	CAS Number	Melting Point (°C)	Boiling Point (°C)	Water Solubility (g/100g)	Vapor Pressure (torr)	Log P ^b	pK _a ^c
2-Chlorophenol	95-57-8	8.7	175	2.85 (20°C)	1 (12°C)	2.12-2.19	8.50
4-Chlorophenol	106-48-9	40-41	220	2.71 (25°C)	---	2.35-2.53	9.18
2,4-Dichlorophenol	120-83-2	43-33	210	0.45 (20°C)	1 (53°C)	3.06-3.30	7.68
2,4,5-Trichlorophenol	95-95-4	68	245-246	sl. sol.	1 (72°C)	3.72	7.43
2,4,6-Trichlorophenol	88-06-2	68	246	0.08 (25°C) ^d	1 (76°C)	3.62-4.05	7.42
2,3,4,6-Tetrachlorophenol	58-90-2	69-70	150 (15 torr)	0.01 (25°C)	1 (100°C)	4.10	5.38
Pentachlorophenol	87-86-5	190	310	0.0014 (20°C)	0.12 (100°C)	5.01-5.86	4.92

^a Data as summarized in (ORNL, 1979) or (OTS, 1980) unless otherwise noted.

^b Log octanol-water partition coefficients are the highest and lowest values reported in (Hansch, 1979).

^c pK_a = - log K_a, where K_a is the dissociation constant.

^d From (OWRS, 1979).

Chlorophenols enter the environment by discharge to water primarily by chemical producers. Chlorophenols may also be inadvertently produced during treatment of drinking water by chlorination of phenol and lower chlorophenols already present. Chlorophenols are removed from environmental waters by volatilization, sorption to sediments, biodegradation, or photodegradation. The relative importance of these processes is unclear due to a lack of experimental data (OWRS, 1980e).

The high vapor pressure of the lower chlorophenols suggests that volatilization plays a role in their dissipation from water. However, definitive data are not available and the relatively high water solubility of the less chlorinated phenols should inhibit volatilization. Biodegradation is probably the major route of removal of most chlorophenols from aquatic environments. However, due to the microbial toxicity of these compounds, ready degradation probably requires acclimated microorganisms. Based on octanol/water partition coefficients, adsorption onto organic matter appears to be important for the higher chlorophenols. For example, PCP and its metabolites are known to concentrate in sediment and to bioaccumulate in fish. While the anionic forms of the chlorinated phenols may undergo photochemical reactions in surface waters, other chemical reactions in water, such as hydrolysis and oxidation, are unlikely (OWRS, 1980f; ORNL, 1979).

The primary source of soil contamination by many chlorophenols is through application of herbicides; other chlorophenols enter the soil as impurities or breakdown products of several pesticides. Based on limited data, the mono-, di-, and trichlorophenols seem to be absorbed only weakly by soil particles, and the potential for seepage into groundwater exists. As in water, biodegradation plays a crucial role in the dissipation of chlorophenols from soil. Microbial degradation in soils is inhibited by the presence of a chlorine atom in the meta-position (ring position 3 or 5); limited data indicate that 2,4,5-TCP, 2,3,4,6-tetrachlorophenol, and PCP are more persistent. Even the most resistant isomers appear to biodegrade under appropriate conditions; however, the rate of removal depends on a variety of soil parameters and on the presence of acclimated microorganisms (ORNL, 1979).

2. EFFECTS INFORMATION

2.1 Health Effects

Various impurities have been found in commercial samples of chlorophenols which may have important toxicological implications. Of most concern are the polychlorodibenzodioxins (PCDD) and chlorodibenzofurans found in technical grade trichlorophenols and PCP. The highly toxic 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) has been found in 2,4,5-TCP samples at levels of 0.07 to 6.2 mg/kg; 2,3,7,8-TCDD has not been found in PCP or most other samples of chlorophenols sampled. Other PCDDs have also been found in chlorophenols, especially technical PCP; commercial PCP is reported to contain on the order of 1,000 ppm octachlorodibenzodioxin and 100 ppm hexachlorodibenzodioxin. Chlorinated dibenzofurans have also been reported in samples of trichlorophenols and PCP (IARC, 1979; OWRS, 1980f).*

2.1.1 Acute Toxicity

Except for PCP, most toxicological information on chlorophenols is derived from experiments with animals. Chlorophenols may be separated into two categories based on their acute toxic effects: (1) convulsive chlorophenols, including 2-CP and 2,4,6-TCP, and (2) nonconvulsive chlorophenols. Poisoning by chlorophenols in general is characterized by a marked rise in temperature and, in most cases, an initial increase in respiratory rate followed by a decreased rate and onset of coma. Poisoning by the convulsive chlorophenols can lead to convulsions, tremors and eventually coma. The most common symptoms in humans poisoned by acute (or chronic high-level) doses of PCP are general weakness, profuse perspiration, and weight loss. Chlorophenols are also irritating to the nose, throat, skin, and eyes (ORNL, 1979; OWRS, 1980e).

The toxic action of chlorophenols appears to involve the uncoupling of oxidative phosphorylation leading to serious metabolic disturbances. Increased chlorine content increases the potency of the chlorophenols in producing this effect and the acute toxicity of the higher chlorinated phenols (PCP, and tetrachlorophenols) is greater. In general, increased chlorination of phenol leads to a reduction of the convulsant action but an increase in the inhibition of oxidative phosphorylation (ORNL, 1979).

Oral LD₅₀ values for chlorophenols in rats range from 50 mg/kg for PCP to the gram-per-kilogram levels for the trichlorophenol isomers; the lowest reported oral lethal dose in humans is 29 mg/kg for PCP and 500 mg/kg for 2,4,6-TCP. Chlorophenols are also toxic when inhaled or absorbed through the skin. In the case of PCP, for example, the LD₅₀

*Information concerning the toxic effects of PCDDs may be found in the IARC monographs (Vol. 15, 1977), the Intermedia Priority Pollutant document on 2,3,7,8-TCDD, and references cited therein.

in rats for inhaled aerosol (11.7 mg/kg) and the dermal LD₅₀ (105 mg/kg) are both comparable to the oral LD₅₀ for rats (50 mg/kg) (OWRS, 1980e; OWRS, 1980f).

2.1.2 Chronic Toxicity

Symptoms of chronic toxicity are, in general, similar to those seen in acute poisonings. Chlorophenols do not accumulate in body tissues to the extent of more lipophilic chlorinated organics; consequently, chronic effects usually require relatively high levels of continuous exposure. While the long term effects of many of the chlorophenols have not been extensively studied, the limited information available suggests that most chlorophenols are of low-to-moderate toxicity (ORNL, 1979; OWRS, 1980e). More specific information on the chronic effects of individual chlorophenols is summarized below.

Monochlorophenols

Monochlorophenols have not been adequately tested for long term effects. Short term (3-week) feeding studies with 2-CP in rats (65 mg/kg every other day) showed altered function and histological degeneration of the liver. Rats exposed to 4-CP aerosols at levels of 2 mg/m³ for 6 hrs/day showed reversible weight loss and increased myoneural excitability, but temperature and blood parameters were not affected. Workers exposed to 4-CP are reported to have a significantly higher incidence of neurological disorders, including increased myoneural excitability (OWRS, 1980a; OWRS, 1980e).

The carcinogenic potential of monochlorophenols has not been tested by the oral route; 2-CP was found to be a promoter in the DMBA-induction of tumors on the skin of mice. Both 2-CP and 4-CP have shown some mutagenic potential; 4-CP was positive in a microorganism test and 2-CP caused increased chromosomal damage and deletions in mammalian cells. Adequate tests have not been done with 2-CP and 4-CP for teratogenic or reproductive effects (OWRS, 1980a; OWRS, 1980b).

2,4-Dichlorophenol

A chronic feeding study showed that mice fed 2,4-DCP at the level of 230 mg/kg/day for 6 months had a slight increase in histological abnormalities of the liver and a significantly depressed growth rate. In the same study, animals dosed with 100 mg/kg showed no apparent adverse effect. Based on this no-observable-effect-level (NOEL) of 100 mg/kg/day and a 1000-fold safety factor, EPA has estimated the Acceptable Daily Intake (ADI) for 2,4-DCP to be about 7 mg/day for a 70 kg human (OWRS, 1980c; OWRS, 1980e).

As part of the National Toxicology Program (NTP), 2,4-DCP is currently undergoing testing by NCI for possible carcinogenicity. The chemical has been found to be a promotor of DMBA-induced skin tumors on mice but was negative when examined for mutagenicity by the Ames Salmonella microsomal test. While the teratogenicity of 2,4-DCP has not been adequately examined, effects have been reported in rats following oral doses as low as 20 mg/kg (OWRS, 1980e).

2,4,5-Trichlorophenol

High chronic doses of 2,4,5-TCP have produced relatively minor damage to kidneys and liver in animals. Rats fed 2,4,5-TCP (99% pure) for 98 days at levels of 100 mg/kg/day had no apparent adverse effects. At 1000 mg/kg growth was slowed in females and at 3000 mg/kg reversible histopathologic changes in the liver and kidneys were observed. Using a NOEL of 100 mg/kg and an uncertainty factor of 1000, the ADI is estimated to be about 7 mg/day for a 70 kg human (OWRS, 1980a).

The carcinogenic potential of 2,4,5-TCP has not been demonstrated except as a promotor on the skin of mice. The Ames Salmonella mutagenicity test proved negative both with and without microsomal activation. No teratogenic effects of 2,4,5-TCP were observed at doses of 0.9 or 9 mg/kg/day (at 6-15 days gestation) in pregnant mice (OWRS, 1980a).

Adverse health effects have been seen in workers exposed to trichlorophenols contaminated with 2,3,7,8-TCDD. These effects (persistent chloracne, liver dysfunction, neuromuscular weakness, and porphyria) have been attributed to the 2,3,7,8-TCDD contaminant (IARC, 1979).

2,4,6-Trio chlorophenol

The National Cancer Institute (NCI) has completed an assessment of the carcinogenicity of 2,4,6-TCP in rats and mice. Male rats showed a significant increase in the incidences of lymphoma or leukemia when fed approximately 250 mg/kg/day (5000 ppm in diet) over two years. Statistically significant incidences of liver carcinomas or adenomas were observed in mice (both sexes) fed 2,4,6-TCP at a similar dietary level (equivalent to about 600 mg/kg/day). EPA has extrapolated the animal data using four dose-response models to estimate human dose response; the predicted excess lifetime cancer risk was estimated to be between about 10^{-7} and 30×10^{-6} for exposure to 20 ug of 2,4,6-TCP per day (OWRS, 1980e).

While 2,4,6-TCP gave a negative result in Ames Salmonella test for mutagenicity, a weak, but significant, mutagenic response was reported in yeast cultures. No evidence is available to judge the teratogenicity of 2,4,6-TCP (OWRS, 1980e). NTP testing for cytogenic effects (hamster ovary cells) yielded negative results in chromosome aberration and sister chromatid exchange tests.

2,3,4,6-Tetrachlorophenol

No long term toxicity studies are available for 2,3,4,6-TCP. Commercial tetrachlorophenol reportedly contains PCP (27%) and toxic impurities (chlorodibenzofurans and chlorodioxins) that may be of more concern. No other data pertinent to the carcinogenicity of 2,3,4,6-TCP is currently available. Tetrachlorophenol is reported to be nonmutagenic in the Ames test, both with and without microsomal activation. The chemical also did not induce teratogenic effects in rats at doses of 10 or 30 mg/kg given on days 6 through 15 of

gestation. However, tetrachlorophenol produced fetotoxic effects (subcutaneous edema and delayed ossification) in pregnant rats at doses of 10 and 30 mg/kg (OWRS, 1980a).

Pentachlorophenol

A long term (2-year) feeding study with purified PCP in rats showed some toxic effects (decreased weight gain, increased activity of selective serum enzymes, pigmentation accumulation in the liver and kidneys) at levels of 30 mg/kg PCP per day. The apparent NOEL from this study was 3 mg/kg/day for females and 10 mg/kg/day for male rats. No increases in tumor incidence were evident in this study. Using a NOEL of 3 mg/kg and applying a 100-fold uncertainty factor, EPA has calculated an ADI of about 2.1 mg for a 70 kg human. Another feeding study in rats over 8 months yielded an NOEL of 6 mg/kg/day based on clinical changes in enzymatic activities. Liver changes observed in other feeding studies with technical grade PCP have been attributed to toxic contaminants rather than PCP itself; long term dietary exposure to 20 mg/kg of technical grade PCP produced liver lesions, porphyria, and enhanced hepatic enzyme activity. (OWRS, 1980d).

The most serious effects of PCP may be its embryotoxicity and fetotoxic effects. PCP of both commercial and purified grades produced fetal anomalies in rats. Fetotoxic and teratogenic effects have been produced in rats following oral doses of 30 mg/kg/day of PCP during gestation. Purified PCP was somewhat more toxic than commercial grade PCP with respect to the incidence of fetal resorptions, growth retarded fetuses, and skeletal and soft tissue anomalies; these effects were more apparent when pregnant rats were dosed during early organogenesis. Comparable effects were not observed following a single but higher oral dose of PCP (OWRS, 1980f).

PCP has been shown to be mutagenic in a few test systems. Purified PCP was mutagenic in yeast cells; in mice, single high doses of PCP during gestation reportedly yielded significant changes in the hair coat color of mice offspring. PCP has produced negative mutagenic responses in tests with Drosophila fruit flies, and tests in microorganisms (bacteria and yeast) have yielded conflicting results. PCP was not found to be carcinogenic in long term studies in rats and mice. PCP also did not act as a promotor in skin tumor promotion studies with mice. PCP is currently undergoing further testing by the National Cancer Institute (OWRS, 1980f).

2.1.3 Absorption, Distribution and Metabolism

Information on the uptake and metabolism is derived mainly from studies on experimental animals. In general, absorption can occur via oral or dermal routes; respiratory absorption has also been confirmed for PCP. Chlorophenols given orally appear to be readily absorbed, metabolized, and excreted. Absorption efficiency by the dermal route varies widely; 2,3,4,6-TCP and PCP are readily absorbed through the skin, 2,4-DCP less readily, and the trichlorophenols are apparently not absorbed in toxic amounts. Based on the available data for PCP,

chlorophenols are transported in the blood. Analyses of human cases of fatal PCP poisoning show high PCP residues in the liver, kidney, and stomach, as well as in the blood (ORNL, 1979).

Little information is available on the metabolism of lower chlorophenols in mammals. Conjugation to form the sulfate or glucuronide salts is thought to be the major metabolic route for the less chlorinated phenols. The more extensive data on the fate of PCP in mammals indicates that conjugation with glucuronic acid is also the major pathway for PCP. PCP is also oxidized in mammals to produce tetrachlorohydroquinone and chloranil (tetrachloroquinone). Because urine levels of PCP are used to estimate PCP exposure in humans, analysis of urine should encompass these oxidation products (and conjugates) as well as PCP itself. In mammals the bulk of PCP administered appears to be excreted relatively rapidly, e.g., about 50% is excreted in 24 hours. However, excretion of residual PCP may take longer (OWRS, 1980f).

Note that exposure to other chlorinated organics can result in exposure to chlorophenols via metabolic degradation. For example, 2,4,6-TCP is the major metabolite of 1,3,5-trichlorobenzene in rabbits and 2,4-DCP is produced in mice from hexachlorocyclohexanes (OWRS, 1980e).

2.2 Environmental Effects

2.2.1 Aquatic Effects

The toxicity of chlorinated phenols to aquatic life varies widely and appears to be a function of the ring position and number of chlorine substituents. In general, the toxicity increases with increasing substitution, and in most cases, aquatic plants appear to be less sensitive than aquatic animals. Chlorinated phenols have also been shown to impair the flavor of fish at concentrations lower than levels which are toxic to aquatic organisms (OWRS, 1980a).

The limited information on the effects of chlorophenols on aquatic organisms indicates acute toxicity for fish at concentrations on the order of 0.1 to 10 mg/L. Reported LC_{50} 's for bluegill were 6.6, 2.02, and 0.32 mg/L, respectively, for 2-CP, 2,4-DCP, and 2,4,6-TCP. Daphnia were affected by these three chlorophenols at levels ranging from 2 to 11 mg/L. Chronic values for minnows were >3.9 mg/L, 0.37 mg/L and 0.72 mg/L for 2-CP, 2,4-DCP, and 2,4,6-TCP respectively. Toxicity tended to increase with the degree of chlorination (OWRS, 1980e).

The lowest effect level for freshwater aquatic organisms for PCP was 1 mg/L in algae. Salmon exhibited sublethal effects at 1.74 mg/L and rainbow trout had the lowest acute level (LC_{50} of 15.5 ug/L). LC_{50} 's for freshwater fish and invertebrate species ranged over two orders of magnitude. Marine organisms exhibited effects and levels as low as 38 mg/L for fish. For PCP, the toxicity increases with decreasing pH and, to a lesser degree, with decreasing hardness (OWRS, 1980f).

Few bioconcentration experiments have been undertaken for chlorophenols. Steady state bioconcentration factors (BCFs) for PCP in most aquatic organisms are reportedly low (390 or less). PCP is rapidly absorbed by fish but bioconcentration is low (11) because PCP is rapidly conjugated and excreted (OWRS, 1980d). A BCF of 214 has been measured for 2-CP and theoretical BCFs were calculated from octanol/water partition coefficients for 4-CP (41), 2,4-DCP (130), 2,4,6-TCP (380), 2,4,5-TCP (440), and 2,3,4,6-TCP (1100). These theoretical BCFs probably represent upper limits for uptake; the limited data available indicate that fish rapidly metabolize and excrete chlorophenols (OWRS, 1980a; OWRS, 1980e).

2.2.2 Other Effects

PCP has documented toxic effects of domestic animals and wildlife; toxic effects have been noted in swine, cattle, sheep, cats, and rabbits. Food animals can come into contact with wood treated with PCP; residues in food products of animal origin are the principle problem rather than overt toxicity to exposed animals. Problems related to poultry occur when sawdust or wood chips (from treated wood) containing PCP are used for bedding (litter). Fungi in the litter convert PCP and tetrachlorophenols to the corresponding anisole by methylation. The chicken absorbs the anisoles, resulting in a musty taint to meat and eggs. (ORNL, 1979).

3. ENVIRONMENTAL RELEASE (CONTACT: Mike Slimak, FTS 426-2503)

The production volume, uses, and releases of the individual chlorophenols are discussed below. Recent production data on most of these chemicals are proprietary and unpublished. In addition, releases could not be estimated in some cases due to insufficient information. More monitoring data are needed to properly assess the source and quantity of releases. In Table 2 the environmental compartments (air, land, or water) initially receiving and transmitting the compounds are identified. These annual release estimates were drawn from several sources (OWRS, 1980e; OWRS, 1980f; OTS, 1980) for different chlorophenols and may not be strictly comparable due to the use of differing assumptions and production data.

Quantification of indirect sources of chlorophenols in the environment is also quite difficult. Prime examples of indirect releases are chlorination of phenols present in water during industrial, POTW, and drinking water treatment processes and the environmental degradation of complex chlorinated organics (i.e., 2,4-D; 2,4,5-T, pesticides, and higher chlorophenols) into chlorophenols (OWRS, 1980e).

Monochlorophenols

The 2- and 4-chlorophenols are produced in low volume primarily through the chlorination of phenol. Production estimates are 8150 kkg for 2-CP in 1977 (OWRS, 1980e) and 9800 kkg for 4-CP in 1976 (OTS, 1980). Both 2-CP and 4-CP are used primarily as intermediates for production of higher chlorinated phenols. The 4-CP is also used in the production of other chemicals (quinizarin, dye intermediates, germicides) and as a denaturant for ethanol (OTS, 1980). While the data in Table 2 show that releases to water are by far the most important route of entry of the monochlorophenols into the environment, the amounts released are limited.

2,4-Dichlorophenol

2,4-Dichlorophenol is produced by chlorination of phenol or monochlorophenols. The major use of 2,4-DCP is in the manufacture of 2,4-dichlorophenoxyacetic acid (2,4-D) and related herbicides. For the purpose of a mass balance analysis, the production volume of 2,4-DCP was estimated to be about 14,000 kkg in 1977 (OWRS, 1980e).

As shown in Table 2, direct emissions of 2,4-DCP are predominantly aqueous and arise from the manufacture of 2,4-DCP and consumption via the production of 2,4-D. Use of the herbicide 2,4-D will result in the direct release to the land of 1-70 kkg of 2,4-DCP present as an impurity in commercial 2,4-D formulations (OWRS, 1980e). Of greater

potential significance, however, is the degradation of 2,4-D to 2,4-DCP in soils, which would result in a major source of land emissions. However, 2,4-DCP is expected also to degrade readily under conditions favorable to 2,4-D breakdown. Therefore, further information is needed to evaluate this point (OTS, 1980).

Trichlorophenols

The commercial synthesis of 2,4,6-TCP is readily accomplished by the direct chlorination of phenol. Production volume is difficult to estimate; a value of 0-16,000 kkg has been reported for 1977 (OWRS, 1980e). While 2,4,6-TCP has numerous potential direct uses (germicide, glue and wood preservative, anti-mildew treatment), the majority produced is used as feedstock for higher chlorophenols. Limited sampling data indicate that 2,4,6-TCP (as well as 2,4-DCP) has been detected in effluents from various industrial operations. For example, 2,4,6-TCP has been measured in effluents from pulp and paper mills, the timber industry (notably barking), the manufacture of paints and ink, and pesticide manufacturing. However, lack of sufficient data makes it virtually impossible to assess environmental emissions of 2,4,6-TCP (OWRS, 1980e).

2,4,5-TCP is synthesized by the hydrolysis of 1,2,4,5-tetrachlorobenzene. In the absence of direct data, production was estimated at 6500 kkg in 1976. Emissions due to production were estimated to be 94 kkg to water, 7 kkg to air, and 6 kkg to land in 1976. In several consumption processes total emissions were estimated to be significant but allocation to an environmental medium was not possible. 2,4,5-TCP or its sodium salt was used directly as a fungicide, preservative, or antimildew treatment. In 1976 it was estimated that a majority of the 2,4,5-TCP available was consumed in the production of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and derived herbicides. Subsequent restrictions on the use of these herbicides may have resulted in decreased production of 2,4,5-TCP, and therefore the potential for releases of 2,4,5-TCP should also be significantly reduced (OTS, 1980).

Tetrachlorophenols

Although the direct production of tetrachlorophenols in 1976 has been reported to be insignificant (OTS, 1980), production volume in 1977 for 2,3,4,6-tetrachlorophenol has been estimated to be from 0 to 19,000 kkg (OWRS, 1980e). Production quantities of 2,4,6-TCP and 2,3,4,6-TCP are interdependent; both are probably produced, and therefore the production of each is less than the maximum estimates given above. In the past, 2,3,4,6-TCP was used directly as a preservative. The compound is also found as a by-product in commercial PCP in concentrations ranging from 4 to 10% by weight. For this reason, releases of 2,3,4,6-TCP are expected to be similar

to those described for PCP below. Thus, releases have been estimated to be approximately 8 percent of those estimated for PCP (OTS, 1980).

Pentachlorophenol

Annual production of PCP has remained constant at approximately 20,000 kkg for over a decade; production in 1978 totaled 21,300 kkg (OWRS, 1980f). Most of the PCP consumed in the United States is produced domestically and only a small portion of domestic production is exported. Pentachlorophenol is manufactured via the complete chlorination of phenol using various catalysts. Over 80 percent of the PCP (and its salt, sodium pentachlorophenate) produced is consumed in the timber and plywood industry as a wood preservative for poles, lumber, fence posts, etc. Other significant uses of PCP or its salt are as an antimicrobial agent in paints and cooling tower waters, tanning, and textiles. In the past, PCP has also been used as a herbicide, both commercially and in home and garden applications.

Table 2 summarizes the releases of PCP to the environment for the year 1978. Although PCP is only moderately volatile, widespread use as a wood preservative and in cooling tower waters may result in significant release to the atmosphere. Home/garden use and herbicidal applications of PCP are thought to result in significant land releases. However, the estimates in Table 2 are based on limited information and other sources of PCP release are probably important. For example, the amount of PCP lost from treated wood (e.g., utility poles) through leaching and runoff could be quite large (OTS, 1980; OWRS, 1980f).

TABLE 2. ESTIMATED RELEASES OF CHLOROPHENOLS TO THE ENVIRONMENT (kg/yr)^{a,b}

	Air	Water	Land
2-Chlorophenol (8,150 kkg, 1977)^c			
Production	9	170	neg
Intermediate for higher chlorophenols	--	81	neg
Total	9	251	neg
4-Chlorophenol (9,900 kkg, 1976)^d			
Production	11	210	--
Intermediate for higher chlorophenols	9	180	--
Denatured Alcohol	--	96	--
Miscellaneous	1	182	--
Total	21	668	--
2,4-Dichlorophenol (14,000 kkg, 1977)^c			
Production	14.0	294	neg
2,4-D production	2.1	42	neg
Miscellaneous	--	--	1-70
Total	16.1	336	1-70
Pentachlorophenol (18,140 kkg, 1978)^c			
Production	50	--	--
Wood Preserving Industry	--	neg	74
Preserved Wood ^e	340	--	--
Cooling Towers	230	2.0	neg
Textiles/Rayons	--	3.0	9.0
Pulp and Paper Mills	--	5.0	--
Tanning Industry	--	2.0	6.0
Home and Garden ^e	--	--	600
Herbicide ^e	--	--	200
POTW	--	--	18
Total	620	12	907

^a Sources for the data are given for each chemical. Numbers in parentheses show estimated production volume in the year for which the mass balance was calculated.

^b Blanks indicate insufficient data.

^c (OWRS, 1980e).

^d (OTS, 1980).

^e Portions of these releases may enter other media other than those noted; however, insufficient data exist to properly apportion the estimated releases.

4. EXPOSURE

Except for PCP, little or no monitoring information exists for most chlorinated phenols. Crude estimates concerning the exposure of the general population to the lower chlorophenols (mono-, di-, and trichlorophenols) suggest human exposure is most likely due to food consumption, especially fish (OWRS, 1980e). Monitoring data showing the presence of PCP in various foods indicates that the major route of PCP exposure is also probably through food consumption. In the case of PCP, widespread use as a wood preservative can result in significant exposure via inhalation and dermal routes in both occupational settings and during home use (OWRS, 1980f; OPP, 1981).

PCP has been detected in human urine and tissue of occupational and non-occupational populations. In one study, 85 percent of the urine samples analyzed for the general population showed the presence of PCP (6.3 ug/L mean). Using reported urine PCP levels, exposure estimates (representing total body exposure from all routes) were calculated to be in the range of 10 to 17 ug/day per person for the general population and 1.5 to 4.4 mg/day for certain occupational settings (OWRS, 1980d).

The contaminants of chlorophenols may also influence the environmental impact of releases. The presence of polychlorinated dibenzo-p-dioxins (PCDDs) in these chemicals has been well established. The highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is apparently formed during the synthesis of 2,4,5-TCP and was detected in the past at levels of up to 10 mg/kg in the derived herbicide 2,4,5-T; levels of 2,3,7,8-TCDD in more recent samples of 2,4,5-T were reported to be below 0.1 ppm. Samples of trichlorophenols have also contained other PCDDs with 2 to 8 chlorine substituents. Only those dioxins with 6 to 8 chlorine atoms have been found in tetrachlorophenols and PCP. Numerous analyses have confirmed that 2,3,7,8-TCDD is not a contaminant in PCP (OWRS, 1980a).

More detailed information concerning human exposure to chlorophenols via specific exposure routes are given below.

4.1 Air Exposure

While the potential exists for exposure to airborne chlorophenols, especially during the use of products containing these compounds, little or no monitoring data exist on ambient atmospheric levels. Di- and trichlorophenols have been identified in gas condensates from municipal incinerators, but levels were not quantified.

Simple modeling techniques were used to estimate PCP concentrations in ambient air resulting from evaporation ponds, volatilization from treated wood, evaporation from cooling towers, and open burning of PCP-treated wood. The maximum level expected from these sources totals 140 ug/m³ and, assuming a breathing rate of 20 m³/day, total exposure to the general population via inhalation is between 2 and 3 ug PCP per day. Certain subpopulations may be exposed to higher local levels of PCP (1 km) downwind from cooling towers (maximum 2 mg/day)

and from waste evaporation ponds (2 ug/day). Inhalation of airborne PCP from freshly treated wood indoors and during application may also result in high exposures (OWRS, 1980f).

4.2 Water Exposure

PCP has been found in drinking water in the United States at low concentrations. In 1976, PCP was found in 86 out of 108 samples with a median of less than 0.01 ug/L and a maximum of 0.7 ug/L. In a more recent survey, PCP was detected (in concentrations ranging from 1.3 to 12 ug/L) in only 8 out of 135 systems sampled. Assuming an intake of 2 liters a day, exposure to the general population would be less than 0.02 ug/day, while the maximum would be 24 ug/day (OWRS, 1980e).

The only other monitoring information available on chlorophenols in finished drinking water is for 2,4-DCP. This compound was detected in 56 out of 108 samples at a mean level of 0.18 ug/L (for positive values). Assuming a 2 liter daily consumption of drinking water, a daily exposure of about 0.4 ug of 2,4-DCP can be estimated (OWRS, 1980e).

According to the limited ambient water data for several chlorophenols (2-CP, 2,4-DCP, and 2,4,6-TCP), concentrations are usually less than 50 ug/L. Therefore, daily exposure through drinking water has been estimated to be 60 to 100 ug/day as a maximum value. Such an estimate is an upper limit which assumes consumption of untreated water and is probably not applicable to the general population. The exposure level of 0.4 ug/day for 2,4-DCP is probably more indicative of normal exposure levels (OWRS, 1980e).

A characteristic which would tend to decrease the likelihood of human exposure to chlorophenols in general is the low odor thresholds of the compounds in water. The EPA Water Quality Criteria proposed for various chlorophenols reflect this property (OWRS, 1980a). Chlorination of water containing phenol, a common water impurity, is reported to result in the formation of chlorophenols. However, the monitoring data needed to address this potential source have not been collected (OWRS, 1980e).

4.3 Other Exposure Routes

Food

In the case of PCP, recent FDA surveys reported PCP in 13 out of 240 composite samples. PCP residues were found in the following commodities (average values, ug/kg): dairy products (0.5), grains and cereals (1.0), root vegetables (1.0), and sugars and adjuncts (6.0). Based on FDA data, EPA estimated an average PCP intake of 1.5 ug/day and a maximum of 18 ug/day (43 FR 48446). High levels of PCP have also been reported in some samples of other foods, especially fish (1-5 mg/kg) and peanut butter; however, the significance of these measurements is not clear (OWRS, 1980f).

While the source of PCP in most foods is not known, the presence of PCP in grain and sugar products has been attributed to storage of these products in PCP-treated wooden containers (ORNL, 1979). PCP in peanut butter may be due to the breakdown of pentachloronitrobenzene which was also found in peanut butter (OWRS, 1980f).

As part of its compliance program, FDA collected milk samples for analysis in 1979. Of 198 samples analyzed, 39 contained PCP at or above 5 ppb (231 ppb maximum). Liver samples have also been collected by USDA from beef, swine, and poultry throughout the United States. This survey showed that in all instances the percentage of positive findings of PCP residues exceeded 85% (OPP, 1981). Based on the past two years of surveys, USDA has concluded that PCP is virtually ubiquitous in U.S. meat and poultry supplies. The highest levels of PCP were found in swine and turkeys. In 12% of the swine samples PCP levels exceeded 0.5 ppb; nearly 1% of cattle sampled showed levels of 250 to 500 ppb. This nationwide survey showed that levels of PCP in chickens were below 50 ppb.

Recent FDA analysis has also revealed PCP, heptachlorodioxin, and octachlorodioxin residues in eggs and poultry in Texas. Maximum levels of PCP in eggs were about 300 ppb; the levels of dioxins were much lower (up to 0.19 ppb). The source of contamination appears to have been the use of PCP in curing hides. Flesh scraped from PCP-treated hides was used by rendering plants in Texas to produce poultry feed products. FDA has also reported that PCP residues in eggs may arise from the use of PCP-treated wood chips for litter in hatcheries.

A possible source of exposure to 2,4-DCP and 2,4,5-TCP may result from the metabolism of ingested herbicides (2,4-D and 2,4,5-T) by grazing animals. Conversion of herbicides to 2,4-DCP and 2,4,5-TCP occurs in animals such as cows and sheep. Consumption of contaminated liver from cattle fed 2,4-D-treated fodder may lead to significant ingestion of 2,4-DCP. However, dairy cattle dosed with high levels of 2,4-DCP did not accumulate the compound in their milk (OWRS, 1980e).

Based on theoretical bioconcentration factors for chlorophenols in fish, EPA has estimated levels expected to be found in fish. Assuming ambient water levels of 10 ug/L of the chlorophenol, fish residues were predicted for 2-CP (4 mg/kg), 2,4-DCP (1.2 mg/kg), and 2,4,6-TCP (4.5 mg/kg). Actual residues of these compounds in fish are limited, and the theoretical bioconcentration factors (derived from octanol/water partition coefficients) provide an upper limit for uptake. Furthermore, metabolic data indicate that fish rapidly metabolize and excrete these chlorophenols so that significant bioaccumulation probably does not occur (OWRS, 1980e).

Occupational

The greatest occupational exposure to PCP occurs in wood treatment plants. Air level data for pressure treatment plants indicate that inhalation exposure can be significant for general operations (up to 240 ug/day) and even higher exposures are likely for some

operations. Occupational end-users (carpenters, construction workers) are also likely to incur inhalation exposure to PCP from the use of PCP treated lumber (OPP, 1981).

5. DATA BASES

5.1 Chemical in Commerce Information System (CICIS)

The inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available in the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Geri Nowack at FTS 382-3568 or Robin Heisler at FTS 382-3557.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. (EPACASR is scheduled to be added to CIS in 1984.) For further information, contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information, contact Dr. Steve Heller at FTS 382-2424.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Doug Sellers at FTS 382-2320.

5.5 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is a sophisticated switching network based on heterogeneous distributed data base management and networking concepts. CSIN offers efficient access to on-line information resources containing data and information relevant to chemical substances, as well as information covering other scientific disciplines and subject matters. The purposes of CSIN are two-fold: first to meet the growing chemical data and information requirements of industry, academe, government (Federal and State), public interest groups, and others; and secondly to reduce the burden on the private and public sector communities when responding to complex Federal legislation oriented to chemical substances.

CSIN is not another data base. CSIN links many independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems." Users may converse with any or all systems interfaced by CSIN without prior knowledge of or training on these independent systems, regardless of the hardware, software, data formats, or protocols of these information resources.

Information accessible through CSIN includes data on chemical nomenclature, composition, structure, properties, toxicity, production uses, health and environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, seven independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), Chemical Information System (CIS), CAS-On-Line, SDC's ORBIT, Lockheeds's DIALOG, Bibliographic Retrieval Service (BRS), and the US Coast Guard's Hazard Assessment Chemical System (HACS). For further information contact Dr. Sid Siegel at 202-395-7285.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 500 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. The clearinghouse listed a total of 453 citations for the chlorophenols. For further information, contact Irvin Weiss at FTS 382-5918.

6. REGULATORY STATUS (Current as of 1/83)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- o Sections 301, 304, 306, and 307 - Chlorinated phenols are listed as toxic pollutants (40 CFR 401.15) and are subject to effluent limitations. However, no effluent guidelines specifically limit the release of chlorinated phenols at this time.
- o Section 311 - Pentachlorophenol and trichlorophenols are classified as hazardous substances (40 CFR 116.4) and discharges are subject to reporting requirements (40 CFR 117.3).
- o Sections 318, 402, and 405 - National Pollution Discharge Elimination System (NPDES) permit testing requirements; the following are listed as organic toxic pollutants based on gas chromatographic and mass spectroscopic analyses and are part of the consolidated permit program (40 CFR 122, App. D):
 - o 2-Chlorophenol
 - o 2,4-Dichlorophenol
 - o 2,4,6-Trichlorophenol
 - o Pentachlorophenol

Resource Conservation and Recovery Act (RCRA)

- o Section 3001 - The following chlorinated phenols have been identified as toxic hazardous wastes if and when they are discarded as commercial products or off-specification species (40 CFR 261.33):
 - o 2-Chlorophenol (U048)
 - o 2,4-Dichlorophenol (U081)
 - o 2,4,5-Trichlorophenol (U230)
 - o 2,4,6-Trichlorophenol (U231)
 - o 2,3,4,6-Tetrachlorophenol (U212)
 - o Pentachlorophenol (U242)

Chlorinated phenols are listed as hazardous constituents (40 CFR 261, App. VIII).

- o Sections 3002 to 3006 - Hazardous wastes are subject to further controls concerning generators, transporters, and treatment, storage and disposal facilities (40 CFR 262 to 265). Permit procedures are also included in consolidated permit regulations (40 CFR 122 to 124).

Federal Food, Drug, and Cosmetic Act (Administered by EPA)

- o Establishment of tolerance levels of 2 ppm and 0.05 ppm for 4-chlorophenol on mung bean sprouts and tomatoes, respectively (40 CFR 180.202).
- o Establishment of tolerance levels for residues of 2,4-dichlorophenol in food products of various animals (40 CFR 180.142).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- o General industry standards for workplace exposure to air contaminants (29 CFR 1910.1000):
 - o Pentachlorophenol

FDA - Federal Food, Drug, and Cosmetic Act

- o Use of pentachlorophenol (and/or its potassium or sodium salt) in numerous food contact situations is regulated (21 CFR 175.105; 176.200; 176.210; 176.300; 177.1210; 177.2600; 178.3120; 178.3800; 178.3900; 181.30). The uses of potassium salts of trichlorophenol are also permitted in some cases (21 CFR 176.200; 181.30).

DOT - Hazardous Materials Transportation Act

- o The following chlorophenols are listed as hazardous materials (49 CFR 172.101) and have general packaging requirements (49 CFR 173.510):
 - o Pentachlorophenol
 - o Sodium Pentachlorophenate

6.2 Proposed Regulations

6.2.1 EPA Programs

TSCA

- o Section 8 - Proposed requirement that chemical manufacturers report production and other data to EPA for 2-chlorophenol, 4-chlorophenol, 2,4,5-trichlorophenol, pentachlorophenol (44 FR 77477, 12/31/79), and 2,4-dichlorophenol (45 FR 13646, 2/29/80).

Comprehensive Environmental Response, Compensation and Liability Act
(CERCLA or Superfund)

- o CERCLA provides for the liability, compensation, cleanup, and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites (42 USC 96-01; PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities (RQ), claims procedures, and the confidentiality of business records (46 FR 54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47 FR 10972).
- o Seven chlorophenols are hazardous substances under CERCLA and will be subject to regulations developed under Superfund. EPA has proposed adjustments to many of the RQs established under CERCLA and the CWA for chlorophenols (48 FR 23552).

6.3 Other Actions

EPA - Federal Insecticide, Fungicide, and Rodenticide Act

- o A Rebuttable Presumption Against Registration (RPAR) was issued against the use of pentachlorophenol as a wood preservative (43 FR 48154). A risk/benefit analysis was issued (46 FR 13020) and regulations were proposed concerning the use of PCP to reduce risks. The Agency has modified some proposals (48 FR 13257).

NIOSH - Occupational Safety and Health Act

- o Request for information for the preparation of information profiles on industrial chemicals. The information will be used in the evaluation of exposure and potential safety or health hazards in the workplace (47 FR 55736):
 - o 2,4,5-Trichlorophenol
 - o Pentachlorophenol

PHS - National Toxicology Program

Toxicological testing is scheduled or underway for several chlorophenols; 2,4-DCP and PCP are in the chronic phase of carcinogenicity bioassays.

FDA

FDA is examining nationwide samples of animal feed for PCP; these results, coupled with studies of PCP residues in cattle, poultry, and swine, may lead to FDA limits for PCP.

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- o OSHA standard for workplace exposure (29 CFR 1910.1000):

Pentachlorophenol (skin) 0.5 mg/m³ (8-hr. TWA)

- o American Conference of Government Industrial Hygienists (ACGIH) threshold limit values (TLV):

Pentachlorophenol (skin) 0.5 mg/m³ (8-hr. TWA)
1.5 mg/m³ (short term exposure limit)

7.2 Water

- o PCP and trichlorophenols are designated as hazardous substances under Section 311 of the CWA and require notification of discharge equal to or greater than a reportable quantity of 10 lbs. (40 CFR 117.3). Reportable quantities proposed under CERCLA are: 100 lbs. for 2-CP and 2,4-DCP; 10 lbs. for 2,3,4,6-TCP; and 1 lb. for PCP (48 FR 23552).

- o Water Quality Criteria (45 FR 79318)

Freshwater aquatic life (in ug/L; acute except where indicated):

2-Chlorophenol	4,380
2,4-Dichlorophenol	2,020
	365 (chronic)
2,4,6-Trichlorophenol	970 (chronic)
Pentachlorophenol	55
	3.2 (chronic)

Saltwater aquatic life (in ug/L; acute except where indicated):

4-Chlorophenol	29,700
Pentachlorophenol	53
	34 (chronic)

Human health

Since chlorophenols can cause taste and odor problems, criteria have been calculated based on organoleptic effects. Criteria based on organoleptic effects as well as toxic effects were calculated because: (1) sufficient toxicological data were not available for some chlorophenols; and (2) where toxicity-based

*See Appendix A for a discussion of the derivation, use, and limitations of these Criteria and Standards.

criteria could be calculated, the criteria based on organoleptic effects are lower. (Note that organoleptic problems have no demonstrated relationship to adverse human health effects):

	Organoleptic Criteria (ug/L)	Toxicological Criteria (ug/L)
2-Chlorophenol	0.1	None
4-Chlorophenol	0.1	None
2,4-Dichlorophenol	0.3	3.09
2,4,5-Trichlorophenol	1.0	2600
2,4,6-Trichlorophenol	2.0	12 (10 ⁻⁵ Cancer risk)*
2,3,4,6-Tetrachlorophenol	1.0	None
Pentachlorophenol	30	1010

7.3 Other

- o FDA permits the limited use of chlorophenols in food contact situations. See Section 6.1.2 of this document for CFR citations.

*Increased lifetime risk calculated from NCI bioassays (See Health Effects Section).

8. SPILL OR OTHER INCIDENT CLEANUP/DISPOSAL

8.1 Hazards and Safety Precautions

The toxic effects of chlorophenols are described in detail in Section 2 of this document. Most chlorophenols are readily absorbed via inhalation or through the skin. All are irritating to both the skin and the eyes, and dusts are irritating to the respiratory tract. Most chlorophenols are moderately toxic, and the presence of highly toxic impurities in many commercial samples is also of concern.

Only the lower chlorophenols (2-CP, 4-CP, and 2,4-DCP) are moderately or slightly flammable. However, all chlorophenols will emit toxic fumes (hydrochloric acid) at high temperatures.

8.2 First Aid

Move victim to fresh air; give oxygen if breathing is difficult. In case of contact, flush skin or eyes with running water for at least 15 minutes; remove contaminated clothing and shoes. Effects of contact or inhalation may be delayed.

8.3 Emergency Action

Spill or Leak - Keep upwind, isolate hazard area, and wear self-contained breathing apparatus and protective clothing. No flares or smoking in hazard area. In the case of small spills of monochlorophenols, flush area with water; large spills of monochlorophenols can be diluted with water and diked for later disposal. Small spills of other chlorophenols may be taken up with sand, earth, or other noncombustible absorbents; large spills may be diked for later disposal.

Fire - For small fires involving chlorophenols dry chemical or CO₂ extinguishers may be used. For large fires use foam or water. Stay away from ends of tanks and cool containers with water.

8.4 Notification and Technical Assistance

Section 103(a) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) requires notification of the National Response Center (NRC) at 800-424-8802 (or 426-2675 in the Washington, D.C. area) if releases of chlorophenols exceed reportable quantities (RQs). At present, the RQs for PCP, 2,4,5-TCP, and 2,4,6-TCP are all 10 lbs., as established under section 311 of the CWA. Regulations listing RQs under CERCLA have not been finalized, and until that time, a statutory RQ of 1 lb. is applicable for other chlorophenols (2-CP; 2,4-DCP; and 2,3,4,6-TCP).

For emergency assistance call:

CHEM TREC: 800-424-9300.

For further information call EPA Environmental Response Team (24-hour number: 201-321-6660) or the Division of Oil and Special Materials (1-202-245-3045). Confirm any treatment procedures with a responsible environmental engineer and regulatory officials.

8.5 Disposal

A generator of 1000 kg or more of hazardous waste is subject to the RCRA hazardous waste regulations concerning treatment, storage, and disposal. A number of chlorophenols (2-CP; 2,4-DCP; 2,4,5-TCP; 2,4,6-TCP; 2,3,4,6-TCP; and PCP) have been identified as toxic hazardous wastes when discarded as commercial product or off-specification species.

The following specific waste streams, which contain one or more chlorophenols, are also subject to hazardous waste regulations under RCRA. Hazardous wastes below are listed by industry and hazardous waste number; the specific chlorophenols contained in each waste stream are also noted in parenthesis:

Wood Preservation

K001 -- Bottom sediment sludge from treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol (2-CP, trichlorophenols, tetrachlorophenols, and PCP).

Pesticides

K043 - 2,6-Dichlorophenol waste from the production of 2,4-D (2,4-DCP and 2,4,6-TCP).

K099 - Untreated wastewater from 2,4-D production (2,4-DCP and 2,4,6-TCP).

Organic Chemicals

K105 - Separated aqueous stream from the reactor product washing step in the production of chlorobenzenes (2,4,6-TCP).

9. SAMPLING AND ACCEPTABLE ANALYTICAL TECHNIQUES

9.1 Air

The chlorophenols are not regulated air pollutants; therefore, no Agency-approved procedure for air analysis is available. However, sampling and analysis procedures have been issued by NIOSH for monitoring around production and user facilities (NIOSH Manual of Analytical Methods, Volume 4, NIOSH Pub. No. 78-175 and Volume 7, NIOSH Pub. No. 82-100). The published procedures specifically designed for the analysis of 4-CP and PCP are described below; however, these procedures can easily be adapted to collect and monitor for other chlorophenols.

In the NIOSH analytical method for 4-CP (Method 337, Volume 7), a known volume of air is drawn through a silica gel tube to absorb 4-CP vapor present; the chlorophenol is desorbed with acetonitrile and a sample is analyzed by high performance liquid chromatography (hplc). The hplc analysis employs a reverse phase column (C18-silica) and a UV detector. For a 3 liter air sample the working analytical range was 0.91-23 mg/m³, and the lowest level quantifiable for this method was 2.5 ug 4-CP per sorbent sample. For the overall sampling and analytical method in this range, the pooled relative standard deviation (RSD) for replicate measurements was 6.1%. For a 150 mg bed of silical gel, the maximum allowable sampling volume was about 40 L; this would permit analysis in the range of 0.064-1.6 mg/m³. Samples of 4-CP on silica gel were stable at 25° for seven days and 29 days at 0°. In addition to separating 4-CP, the chromatographic conditions specified in this method (gradient elution) will permit the separation of: 2-CP; all the dichlorophenol isomers; 2,4,5-TCP; PCP; and various other phenols.

A method specifically for PCP analysis in air (Method S297, Volume 4) has also been issued by NIOSH. A known volume of air is drawn through a filter connected in sequence to a bubbler with 15 mL of ethylene glycol. The filter is added to the glycol solution and, just before analysis, 10 mL of methanol is added. Hplc analysis of the sample uses a reverse phase column (C18-silica) and a UV detector. The procedure is validated over the range 0.265 to 1.13 mg/m³ using 180 L samples. The Coefficient of Variation for the combined sampling and analytical methods was 0.0721 in this range.

9.2 Water

A number of chlorophenols are listed as priority pollutants under Section 304 of the Clean Water Act. The suggested analytical method (Method 604 in "Guidelines Establishing Test Procedures for the Analysis of Pollutants," Fed. Regist. 44, 69484; 1979) may be used to determine levels of a variety of phenolic compounds, including: 2-CP; 2,4-DCP; 2,4,6-TCP; and PCP. The method given below is applicable to municipal and industrial discharge samples.

A 1 liter sample of wastewater is acidified (to pH 2 with H₂SO₄) and may be preserved with sodium thiosulfate (35 mg per ppm of free chlorine per liter) to retard subsequent chlorination. Samples should be extracted

within 7 days and analysis completed within 30 days of collection. The water sample is extracted (CH_2Cl_2) and the concentrated organic extract may be analyzed directly by gas chromatography (GC) using flame-ionization detection (FID). The method also provides for the preparation of pentafluorobenzylbromide (PFB) derivatives for GC analysis using electron-capture detection (ECD). An extraction procedure for cleanup which takes advantage of the acidic nature of phenols is also given. Assuming a 10 mL volume of extract from a 1 liter water sample and injection of 5 μL of the extract, the GC analysis using FID yields detection limits of 2-10 μg of chlorophenol per liter of water sample.

Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of sampling, and laboratory replicates should be analyzed to validate the accuracy of analysis. If doubt exists over the identification of a peak on the GC, confirmatory techniques such as mass spectroscopy (MS) should be used.

Similar procedures designed for the analysis of phenolic compounds have also been published. Method 510 in Standard Methods for the Examination of Water and Wastewater, 15th Edition (American Public Health Association, 1981) and Method D 2580-80 in the 1982 Annual Book of ASTM Standards, Part 31 (ASTM, 1982) both describe the GC analysis using FID of various phenolic compounds including mono- and dichlorophenols. A supplement (1981) to the 15th edition of Standard Methods also includes a technique for PCP which involves the formation of the methyl ether derivative (via diazomethane) and analysis by GC with ECD.

Colorimetric procedures for total recoverable phenolic compounds are also available (e.g., Methods 510B and 510C in Standard Methods). However, these techniques do not allow the different phenols to be differentiated, and they are of limited utility in the analysis of chlorophenols.

9.3 Solid Waste

Chlorophenols in waste materials may be determined by two methods described in detail in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (Office of Solid Waste and Emergency Response, July 1982, SW-846, Second Edition). Method 8.04 may be used to separate 2-CP; 2,4-DCP; trichlorophenols; tetrachlorophenols; and PCP, as well as numerous other phenolic compounds. Water samples are acidified ($\text{pH} \leq 2$) and extracted with CH_2Cl_2 . Solid samples are also acidified and extracted with CH_2Cl_2 , using soxhlet extraction or sonication procedures. Extracts are analyzed by GC using FID. This method also provides for preparation of PFB derivatives and cleanup procedures. Therefore, after extraction this method is similar to the GC method 604 for water described above.

Method 8.25 utilizes an extensive extraction procedure which permits the analysis of complex samples; the chlorophenols are concentrated in the extract from the acidified sample. GC analysis using MS separates and identifies the chlorophenols present. The detection limit for Method

8.25 for individual compounds is about 1 ug/g (wet weight) in waste samples. This technique is listed as being applicable to nearly all types of samples (water, sludges, acidic and basic liquors, oily wastes, tars, soils, sediments, etc.).

9.4 Other Samples

Bibliographic reviews of methods used to determine chlorophenol levels in a variety of matrices are available (ORNL, 1979; IARC, 1979). While extraction/cleanup procedures vary widely, nearly all methods use GC for separation and FID, ECD, or MS for detection. For example, a NIOSH procedure (Method 230 in the NIOSH Manual of Analytical Methods, Vol.1; NIOSH Pub. No. 77-157A) for the analysis of PCP in urine involves acidification, extraction, and analysis via GC equipped with a ⁶³Ni ECD. An important point to stress, however, is that such analytical methods for use with samples of biological origin may not measure the conjugated forms of the chlorophenols (e.g., glucuronide salts).

REFERENCES

The major references used in preparation of this document are listed below. EPA references are listed by EPA office of origin and year of publication. For further information refer to the contacts given throughout this document or contact the relevant EPA offices listed at the end of this section.

- (ECT, 1979) Encyclopedia of Chemical Technology, 3rd Ed., Kirk-Othmer, "Chlorophenols", pp. 864-872; Wiley (1979).
- (Hansch, 1979) Substituent Constants for Correlation Analysis in Chemistry and Biology, C. Hansch and A. Leo, Wiley (1979).
- (OPP, 1981) Creosote, Inorganic Arsenicals, and Pentachlorophenol. Position Document No. 2/3, EPA-540/9-82-004, Office of Pesticide Programs (1981).
- (ORNL, 1979) Reviews of the Environmental Effects of Pollutants. XI Chlorophenols, EPA-600/1-79-012, Oak Ridge National Laboratory (1979).
- (OTS, 1980) Materials Balance for Chlorophenols, Level I, EPA-560/13-80-004, Office of Toxic Substances (1980).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, EPA-440/4-79-029b, Office of Water Regulations and Standards (1979).
- (OWRS, 1980a) Ambient Water Quality Criteria for Chlorinated Phenols, EPA-440/5-80-032, Office of Water Regulations and Standards (1980).
- (OWRS, 1980b) Ambient Water Quality Criteria for 2-Chlorophenol, EPA-440/5-80-034, Office of Water Regulations and Standards (1980).
- (OWRS, 1980c) Ambient Water Quality Criteria for 2,4-Dichlorophenol, EPA-440/5-80-042, Office of Water Regulations and Standards (1980).
- (OWRS, 1980d) Ambient Water Quality Criteria for Pentachlorophenol, EPA-440/5-80-065, Office of Water Regulations and Standards (1980).
- (OWRS, 1980e) An Exposure and Risk Assessment for Chlorinated Phenols, EPA-Final Draft Report, Office of Water Regulations and Standards (1980).
- (OWRS, 1980f) An Exposure and Risk Assessment for Pentachlorophenol, EPA-Final Draft Report, Office of Water Regulations and Standards (1980).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-4173 (919-541-4173)

Carcinogen Assessment Group	382-7341
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	382-7571
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality and Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	382-7051
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
------------------------------	----------

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Information Management Division 382-3749

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division
Research Triangle Park, NC 629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division 382-7575

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division 755-0100

Effluent Guidelines Division 382-7120

Office of Solid Waste (OSW)

Permits and State Programs Division 382-4746

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division 382-2182
Hazardous Site Control 382-2443

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II 340-6635 (201-321-6635)

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis
Research Triangle Park, NC 629-2454 (919-541-2454)

Water Analysis
Cincinnati, OH 684-7311 (513-684-7311)

Waste Analysis
Las Vegas, NV

545-2137 (702-798-2137)

Office of Monitoring Systems
and Quality Assurance

382-5767

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Chemical Coordination Staff

Chemical Information
and Analysis

382-3375

1,4-Dichlorobenzene

1,4-DICHLOROBENZENE

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-2
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-1
Land Releases	3-1
<u>Exposure</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
Other Exposure Routes	4-1
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2
Other Actions	6-2

<u>Spill or Other Incident Clean-up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-1
 <u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
Hazardous Waste	9-4
 <u>References and Office Contacts</u>	 R-1

1,4-DICHLOROBENZENE

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

This document will focus on 1,4-dichlorobenzene; however, since Agency assessments and regulations often consider the 1,2- and the 1,3-isomer together with 1,4-dichlorobenzene, and because of the similar chemistry of the isomers, some information on all three will be presented.

Isomers: (synonyms) 1,2-dichlorobenzene (1,2-DCB, o-dichlorobenzene, ortho-dichlorobenzene), 1,3-dichlorobenzene (1,3-DCB, m-dichlorobenzene, meta-dichlorobenzene), 1,4-dichlorobenzene (1,4-DCB, p-dichlorobenzene, para-dichlorobenzene, PDB).

Chemical Abstract Service (CAS) Numbers:

1,2-DCB:	95-50-1
1,3-DCB:	541-73-1
1,4-DCB:	106-46-7
Mixed Isomers:	25321-22-6

1.1 Properties

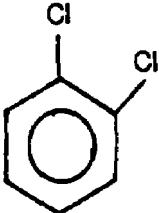
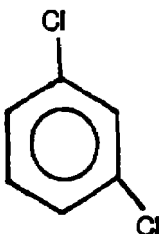
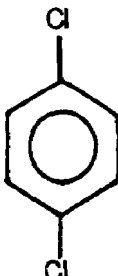
1,2-DCB and 1,3-DCB are colorless liquids at room temperature. 1,4-DCB is a white crystalline solid. All three isomers have a strong aromatic odor. DCBs are not naturally occurring compounds. 1,4-DCB and 1,2-DCB have varied and widespread uses and are produced in approximately equal amounts. 1,3-DCB has no commercial uses at present. The kinetics of current synthetic pathways favor overwhelmingly the formation of the 1,2- and 1,4-isomers (although 1,3-DCB is favored thermodynamically). Relevant physical/chemical properties are listed in Table 1.

1.2 Chemistry and Environmental Fate/Transport

Because of the lack of environmentally significant information, it is not possible to determine the predominant transport and aquatic fate of DCB. DCB has a high affinity for lipophilic materials, a relatively low aqueous solubility, and a low vapor pressure at ambient temperatures. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing transport processes. The rate at which these competing processes occur will determine which fate is predominant in the aquatic environment (OWRS, 1979).

Ninety-six percent of the DCBs, not converted to other products, are released to the air (OWRS, 1981b). Once in the atmosphere DCB is reported to be reactive toward hydroxyl radicals in air with a half life of approximately three days. The 1,2- and 1,4-isomer were also reported to be resistant to autooxidation by ozone in air (OWRS, 1979).

TABLE 1: PHYSICAL/CHEMICAL PROPERTIES

	<u>1,2-DCB</u>	<u>1,3-DCB</u>	<u>1,4-DCB</u>
CAS number:	95-50-1	541-73-1	106-46-7
Molecular formula:	$C_6H_4Cl_2$	$C_6H_4Cl_2$	$C_6H_4Cl_2$
Structure:			
Molecular weight:	147.01	147.01	147.01
Melting point, °C:	-17.0	-24.7	53.1
Boiling point, °C:	180.5	173.	174.
Flashpoint, °C:	66.1	---	65.6
Density (20) (4):	1.31	1.29	1.25
Vapor pressure at 25°C, torr:	1.5	2.28	1.18
Solubility at 25°C, mg/l:	145.0	123.0	79.0
Log octanol/water partition coefficient:	3.38	3.38	3.39

Because of their high lipid/low water solubility, DCBs can cross barrier membranes and be widely distributed to various tissues. (Blood, blood chemistry, neuromuscular function, liver and kidney structure and function have been shown to be affected in man and animal.) DCBs are detoxified in the liver by microsomal enzymes: DCBs are oxidized to isomers of dichlorophenols, (the major metabolites) depending on the DCB isomer, and excreted as conjugates of glucuronic and sulfuric acids. Excretion of all three isomers through the urine is slow, requiring about six days. (Presence of dichlorophenol levels in the urine can be used in assessing exposure.)(OWRS, 1980).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACT: Jerry Stara, FTS 684-7531; Penny Fenner-Crisp, FTS 472-4944)

2.1.1 Acute Toxicity

Acute dermal exposure of human subjects to 1,2-DCB resulted in burning sensation within 15 minutes. The response intensified with continued exposure and abated when the liquid was removed from the skin. However, hyperemia and blisters developed afterward at the site of application and were followed by a brown pigmentation that persisted at least three months. Inhalation of the vapor (>300 mg/m³) may result in eye and nose irritation (OWRS, 1980).

Acute dermal exposure to solid 1,4-DCB produces a burning sensation when held in contact with the skin, but the resulting irritation is slight. However, warm fumes or strong solutions may irritate the skin slightly on prolonged or repeated contact. Inhalation of solid particles of 1,4-DCB or heavy vapors or fumes (such as when heated and volatilized in poorly ventilated spaces) are painful to the eyes and nose. The painful effect of vapor is evident to most people at 300 to 480 mg/m³ (OWRS, 1980).

2.1.2 Chronic Toxicity

Most reported cases of human poisoning by DCBs have resulted primarily from long-term exposure by inhalation of vapors, but some have also resulted from oral or skin exposure. Most episodes were occupational; however, several involved the use of DCBs in the home (in toilet deodorant blocks, moth balls and cleaning products) (OWRS, 1980).

The principle target system or tissues are one or more of the following: liver, blood, CNS, respiratory tract, and integument. Clinical findings of chronic exposure to DCB include weakness, fatigue, dizziness, malaise, nausea, vomiting, headache; profuse rhinitis and periorbital swelling; upper respiratory tract irritation such as chronic progressive cough and dyspnea with mucoid sputum, wheezing, diminished breath sounds and rales resulting from pulmonary granulomatosis; esophageal verices; decreased appetite; weight loss and exhaustion. Hepatocellular derangement such as hepatomegaly, proteinuria, and bilirubinuria are common. Often DCB exposures result in severe acute hemolytic anemia, peripheral lymphadenopathy, leukocytosis, polynucleosis, and splenomegaly. Several cases of chronic lymphoid leukemia and acute myeloblastic leukemia have resulted after chronic exposure to 1,4-DCB (OWRS, 1980).

Evidence as to the mutagenicity of DCBs is inconclusive. The teratogenicity of any of the DCBs has not been studied and reported. Published studies of tests for carcinogenicity fall very short of establishing a cause-effect relationship and do not permit a quantitative risk assessment applicable to the general population. Although strong direct evidence of carcinogenicity for DCB is not available, there seems to be a sufficient collection of varied data

to suggest a prudent regard of the DCBs as suspected carcinogens, pending the availability of better data (OWRS, 1980). NTP is currently conducting large-scale carcinogenicity bioassays on both the 1,2- and 1,4-DCB isomers. These results are expected in 1982.

- 2.2 Environmental Effects (CONTACT: Charles E. Stephan FTS 783-9510;
John Gentile, FTS 838-4843;
Virginia M. Snarski, FTS 783-9584)

2.2.1 Aquatic Effects (OWRS, 1980)

DCBs in water result from anthropogenic sources: i.e., industrial and consumer discharges and water chlorination. There appears to be little difference (and no consistent difference) in aquatic toxic effects among the three DCB isomers.

Freshwater - The 48-hour EC_{50} values for Daphnia magna and a midge for 1,2-, 1,3-, and 1,4-dichlorobenzene ranged from 2,440 to 28,100 ug/l with no consistent difference due to location of the chlorine atoms or sensitivity of the two species. The range of LC_{50} values for three fish species and the same dichlorobenzenes was 1,120 to 27,000 ug/l, and the rainbow trout appears to be a little more sensitive than the two warmwater fish species.

Embryo-larval tests with the fathead minnow and 1,2-, 1,3-, and 1,4-dichlorobenzene have been conducted; the chronic values ranged from 763 to 2,000 ug/l. The acute-chronic ratio for both 1,3- and 1,4-dichlorobenzene was 5.2.

The freshwater alga, Selenastrum capricornutum, is less sensitive to the dichlorobenzenes with EC_{50} values that range from 91,600 to 179,000 ug/l.

Saltwater - The saltwater mysid shrimp has been exposed to 1,2-, 1,3-, and 1,4-dichlorobenzene and the 96-hour LC_{50} values were 1,970, 2,850, and 1,990 ug/l, respectively. For the sheepshead minnow and the same chemicals, the 96-hour LC_{50} values were in the range of 7,400 to 9,660 ug/l. No chronic toxicity data are available for any saltwater species.

The 96-hour EC_{50} for a saltwater alga and 1,2-, 1,3-, and 1,4-dichlorobenzene ranged from 44,100 to 59,100 ug/l.

2.2.2 Other Effects (OWRS, 1980)

The measured steady state bioconcentration factors for the three DCBs are in the range of 60 to 89 for the bluegill.

3. ENVIRONMENTAL RELEASE

Several Agency program offices have evaluated and ranked sources of DCB release. Even though the reported quantities emitted to the environment differ, there is general agreement as to the major sources of DCB releases. Table 2 lists both the use of DCB isomers and their release to the environment by media. The release data are only crude estimates and have not been verified by sampling and analyses.

3.1 Air Releases, 1,4-DCB (CONTACT: Dave Patrick, FTS 629-5645)

Significant Source:

- Manufacturing and processing, occupational exposure

Other Sources:

- Spills
- Domestic use (indoor air)
- Land disposal
- Vapor release from contaminated surface waters
- Ambient air in vicinity of solvent use and chemical intermediate plant

3.2 Water Releases, 1,4-DCB (CONTACT: Michael Slimak, FTS 426-2503)

Significant Source:

- Contamination of surface and groundwater from unconfined landfills

Other Sources:

- Water washdown of spills
- POTW effluents

3.3 Land Releases, 1,4-DCB (CONTACT: Ken Schuster, FTS 382-4654)

Significant Source:

- Release from unconfined landfills

TABLE 2: ENVIRONMENTAL RELEASES, 1978 (kg/yr)

Isomer	Category	Amount Used/Produced	Air	Water	Land
1,2-DCB	Production	27,000	96	230	6
	3,4-Dichloroaniline production	17,000	24	---	---
	Toluene diiso- cyanate manufacture	3,600	3,600	---	neg.
	Misc. solvents	1,900	1,900	10	20
	Dye synthesis	960	neg.	---	---
	Other ⁺	720	70	---	---
	Exports	3,200	---	---	---
1,4-DCB	Production	33,000	240	290	8
	Space deodorant	15,000	14,000	500	500
	Moth control	9,500	9,500	1	1
	Other ⁺⁺	2,700	5	---	---
	Exports	6,300	---	---	---
1,3-DCB	Negligible	---	---	---	---

⁺ Including: odor control in sewage, pesticide manufacturing, laboratory supply.

⁺⁺ Primarily pesticide manufacturing, abrasives, and textiles.

Source: OWRS (1981a).

4. EXPOSURE

DCB primarily enters the body through ingestion or inhalation. Respiratory absorption is rapid after inhalation; however, there are no data on the percentages absorbed. Absorption through ingestion is rapid, and under at least some circumstances can be complete (OWRS, 1980).

4.1 Air Exposure (CONTACT: Karen Blanchard, FTS 629-5519)

The seven DCB production facilities are a source of occupational and surrounding residential low-level chronic exposure. The frequent use of end products containing DCBs, especially moth balls, diaper pail deodorizers and toilet bowl deodorizers, can provide a low-level exposure route.

4.2 Water Exposure (CONTACT: Michael Slimak, FTS 426-2503;
Bill Coniglio, FTS 382-3035)

Accidental spills into drinking water supplies or contamination of groundwater from land disposal could result in high-level short-term or low-level long-term exposure, respectively.

4.3 Other Exposure Routes (CONTACT: Ken Schuster, FTS 382-4654)

Land disposal could result in exposure through either groundwater contamination or elevated ambient air levels near disposal sites.

TABLE 3: DCB EXPOSURE ESTIMATES

	<u>1,2-DCB</u>		<u>1,3-DCB</u>		<u>1,4-DCB</u>	
	Concentration (ug/l)	Exposure (mg/day)	Concentration (ug/l)	Exposure (mg/day)	Concentration (ug/l)	Exposure (mg/day)
<u>Drinking Water</u>						
Maximum observed	9.1	.018	--	--	2.0	4×10^{-3}
Mean observed	1.5	3×10^{-3}	.01	2×10^{-4}	.07	10^{-4}
Medium concentration	<.005	$<10^{-5}$	<.005	$<10^{-5}$	<.005	$<10^{-5}$
	<u>(ug/m³)</u>	<u>(mg/day)</u>	<u>(ug/m³)</u>	<u>(mg/day)</u>	<u>(ug/m³)</u>	<u>(mg/day)</u>
<u>Ambient Air (24 hrs.)</u>						
Range (11 sites)	0-.106	0-.002	0-.382	0-.009	0-.062	0-.001
Urban	--	--	.1	.02	2.7-4.2	.06-.09
Rural	--	--	<1	<.02	1.5-2.4	.03-.05
<u>Air at Industrial Sites</u>	.002-1.3	--	.001-1.2	--	.001-1.2	--
<u>Air at Disposal Sites</u>	<.03-12	--	<.03-34	--	<.01-7	--
<u>Occupational (1 site)</u>						
Maximum observed	--	--	--	--	4.21×10^5	4,042 mg/8 hr.
<u>Residential (space deoderizer or moth repellant)</u>						
in Bedroom	--	--	--	--	105	.6 mg/10 hr.
in Closet	--	--	--	--	315	.2 mg/.5 hr.
in Wardrobe	--	--	--	--	1700	.2 mg/.1 hr.

Source: OWRS (1981a).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA, which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), and production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available on the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purpose of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. For further information contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information contact Delores Evans at FTS 382-3546 or Irv Weiss at FTS 382-3524.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base that is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses source material at the Federal level only, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Delores Evans at FTS 382-3546 or Ingrid Meyer at FTS 382-3773.

5.5 Chemical Substances Information Network (CSIN)

The prototype CSIN, operational since November 1981, has been developed by merging the technologies of computer networking and distributed data base management. CSIN is not another data base, but a library of systems. Through the CSIN front-end intermediary management computer, the user may access and use independent and autonomous information resources that are geographically scattered, disparate for data and information content, and employ a variety of types of computer hardware, software, and protocols. Users may converse in and among multiple systems through a single connection point, without knowledge of or training on these independent systems.

Currently, six independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), CIS, EPA-CICIS, CAS-On-Line, SDC-orbit, and two files of Dialog: CRGS and TSCA Inventory. The CSIN management computer allows the user to create, retrieve, store, and manipulate data and queries. This eliminates the need for reentering long lists of chemical identifiers or other information elements that are part of the original query or that have been identified and acquired from one or more of the CSIN resources. For further information contact Sid Siegal at FTS 382-2256.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 475 individual data bases and models that contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained by offices within EPA. For further information, contact Charlene Sayers at FTS 755-9112.

The following data bases contain information on 1,4-DCB:

BAT Review Study for the Timber Products Processing, Gum and Wood, Chemicals, and the Printing and Publishing Industries
Best Management Practices, Timber Industry Effluent Guidelines -
Runoff

Best Management Practices, Timber Industry Effluent Guidelines -
Sludge

Chemicals in Commerce Information System

Compliance Sampling Toxicant Surveys

Consolidated Permits Program-Application Form 1,2b,2c

Data Collection Portfolio for Industrial Waste Discharges

Distribution Register Organic Pollutants in Water

Drinking Water

Effluent Guidelines GC/MS Screening Analysis Data Base

Energy and Mining Point Source Category Data Base

Federal Facilities Information System

Fine Particle Emissions Information System

Food Industry Group

Fugitive Emissions Information System

Gaseous Emissions Data System

Hazardous Waste Data Management System

Hazardous Waste Site Tracking System
 Hemlock, Michigan Environmental Samples
 Humacao Ambient Data Base
 IFB Organics Data Base
 Indicatory Fate Study
 Industrial Process Evaluations
 Infrared Spectra of Pollutants
 Innovative Technology, Timber Industry Effluent Guidelines
 Inorganic Chemicals Industry Regulation Record
 LiPari Landfill
 Liquid Effluents Data System
 Listing of Organic Compounds Identified in Region IV
 Love Canal Data Handling System
 Method Validation Studies of Priority Pollutants
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Permit Compliance
 Nationwide Urban Runoff Program
 Needs Survey
 New York Bight Ocean Monitoring Program
 Organic Chemicals/Plastics Industry
 Organic Transport thru Soil
 Paint and Ink Analytical Data
 Permit Compliance System
 Pesticide Incident Monitoring System
 Pharmaceutical Screening/Verification Data Base
 Precision and Accuracy for Screening Protocols
 Priority Pollutants-Region I
 Priority Pollutants-Region III
 Publicly Owned Treatment Works (POTW) Analytical Data
 Publicly Owned Treatment Works (POTW) Quality Control
 Puerto Rico Reservoirs
 Regional Toxics Monitoring Program
 Resource Conservation and Recovery Act (RCRA)-Hazardous Waste Site
 Inspections
 Screening Sampling Program
 Select Hazardous Chemicals-Ambient
 Sources of Toxic Pollutants Found in Influent to Sewage Treatment
 Plants
 Spill Prevention Control and Countermeasure
 System for Consolidated Permitting and Enforcement Data Base
 Textile Industry BAT Study-Toxic Sampling Data
 Toxics Monitoring
 U.S. Virgin Islands-St. Thomas, St. Croix
 Verification Data Base
 Verification Sampling Program
 Waste Characterization Data Base
 Water Enforcement Regional System
 Water Quality Information System

6. REGULATORY STATUS (current as of 4/23/82)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- Sections 301, 304, 306, and 307 - All isomers of DCB are listed as priority pollutants (toxic pollutants, 40CFR401.15). No standards specific for DCBs have been issued.
- Section 311 - DCB is designated as a hazardous substance (40CFR116.4) and is subject to reporting requirements (40CFR117.3).

Resource Conservation and Recovery Act (RCRA)

- Section 3001 - All three isomers of DCB have been designated as toxic hazardous wastes (T) if and when they are discarded as a commercial product or an off-specification species: U070 (1,2-DCB), U071 (1,3-DCB), and U072 (1,4-DCB). Contaminated and spill residues are also considered hazardous wastes (40CFR261.33).

The following wastestreams are designated as toxic hazardous wastes (T), due in part to the presence of DCB (40CFR261.31, 40CFR261.32).

-F002- The following spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, ortho-dichlorobenzene, and trichlorofluoromethane; and the still bottoms from the recovery of these solvents.

-K042- Heavy ends or distillation residues from the distillation of tetrachlorobenzene in the production of 2,4,5-T.

-K085- Distillation or fractionation column bottoms from the production of chlorobenzenes.

-K105- Separated aqueous stream from the reactor product washing step in the production of chlorobenzenes.

- Sections 3002 to 3006 - Regulations for generators and transporters of hazardous waste and standards for treatment, storage, and disposal facilities are applicable for the above hazardous wastes (40CFR262 to 265). Permitting procedures are included in the Consolidated Permit Regulations (40CFR122 to 124).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- Employee exposure to 1,2-DCB is limited by an acceptable ceiling concentration. Employee exposure to 1,4-DCB is limited by an 8-hour time weighted average (TWA) (29CFR1910.1000).

DOT - Hazardous Materials Transportation Act

- Regulations concern the listing, labeling, and shipping of hazardous materials including 1,2-DCB and 1,4-DCB (40CFR171 and 172.101).

FDA - Federal Food, Drug, and Cosmetic Act

- Regulations setting maximum levels in food-contacting material (21CFR121.614).

6.2 Proposed Regulations

6.2.1 EPA Programs

TSCA

- Section 4 - Proposed health effects test rule for chlorobenzenes; specific structural teratogenicity, reproductive effects, and subchronic/chronic effects testing (45FR48524, 7/18/80; 45FR68411, 10/15/80).

CAA

- New Stationary Source Performance Standards proposed which would limit VOC from fugitive emission sources in the synthetic organic chemical manufacturing industry. All three DCB isomers are among a number of VOC included in the proposal (46FR1136, 1/5/81).

6.3 Other Actions

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund)

- CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites (42USC9601; PL 96-510).
- EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46FR54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47FR10972).

- Hazardous substances as defined by Section 101(14) of CERCLA include: hazardous wastes designated under Section 3001 of the RCRA; hazardous air pollutants regulated under Section 112 of the CAA; water pollutants listed under Sections 307 and 311 of the CWA (and also any substances regulated in the future under Section 7 of TSCA and Section 102 of CERCLA). Therefore, DCBs are hazardous substances under CERCLA and will be subject to regulations issued under Superfund.

Safe Drinking Water Act (SDWA) - DCBs are among a number of substances discussed in an Advance Notice of Proposed Rulemaking (ANPR) for possible inclusion in revised National Primary Drinking Water Regulations for volatile synthetic organic chemicals (47FR9350, 3/4/82).

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- Current OSHA standard for 1,2-DCB (29CFR1910.1000): 300 mg/m³ (ceiling)
- Current OSHA standard for 1,4-DCB (29CFR1910.1000): 450 mg/m³ (8-hr TWA)

7.2 Water (CONTACT: Penny Fenner-Crisp, FTS 472-4944)

- The Agency expects to develop Health Advisories (HA) for both 1,2-DCB and 1,4-DCB in 1982.
- Water Quality Criteria (for DCB):

Human health	400 ug/l (ingestion of both water and contaminated organisms)
Freshwater aquatic life (acute)	1,120 ug/l
(chronic)	763 ug/l
Saltwater aquatic life (acute)	1,970 ug/l
- Hazardous spill rules require notification of discharges equal to or greater than 100 lb (40CFR117.3).

7.3 Other

- FDA food contact maximum level .8 mg/kg in polyphenylene sulfide resins (21CFR121.614).

* See Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL
(CONTACT: National Response Center, 800-424-8802, in Washington, D.C., 426-2675)

8.1 Hazards and Safety Precautions

DCBs readily volatilize to a moderately toxic vapor that may irritate the eyes and upper respiratory tract. DCB can be absorbed through the skin and is a skin irritant.

DCBs are combustible and when handled at elevated temperatures the isomers present a flammable hazard in the presence of an ignition source (sparks or flames). Fire produces extremely toxic combustion products.

8.2 First Aid

Move victim to fresh air, and call medical help. Give artificial respiration if victim is not breathing, or oxygen if breathing is difficult. In case of contact, immediately flush skin with running water, followed by washing with soap and water. Remove contaminated clothing. In case of contact with eyes, flush eyes with flowing water for 15 minutes. If taken internally, vomiting should be induced. An emetic such as soapy water should be taken followed by drinking as much water as possible. Call a physician.

8.3 Emergency Action

Spill or Leak - Stay upwind, isolate hazardous area, and wear self-contained breathing apparatus and full protective clothing (including eye protection such as full-face mask). Remove ignition sources and use carbon or peat on soluble portion. Pump or vacuum from bottom. For dissolved portions, use carbon or peat.

Fire - For small fires use dry chemical, CO₂, water spray, or foam. For large fires, use water spray or foam. Move containers from fire area if possible; cool containers exposed to fire with water until well after fire is out. Isolate for one-half mile in all directions if tank or tankcar is involved in a fire.

8.4 Notification and Technical Assistance

Section 103 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or "Superfund" requires notification of the National Response Center (NRC, 800-424-8802 or in the Washington, D.C. area, 426-2675) if releases exceed reportable quantities (100 lbs. in the case of DCB). For emergency assistance call CHEMTREC: 800-424-9300. For information call the Division of Oil and Special Materials at 1-202-245-3045.

8.5 Disposal

Generators of more than 1,000 kg/month of commercial product (or residues from spill cleanup) are subject to RCRA regulations.

The following specific wastestream is subject to Subpart D regulations:

- dichlorobenzene solvents or solvent-recovery still bottoms.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air (CONTACT: Joseph F. Walling, FTS 629-7954)

1,4-dichlorobenzene is not a criteria pollutant; therefore, no Agency or reference procedures exist. Although measurements of this pollutant have been made and reported, there are no well-documented method descriptions available for quantitative measurements in ambient air. Therefore, monitoring for this pollutant must be approached with great caution.

A procedure using Tenax adsorbent for sampling and gas chromatography/mass spectrometry (GC/MS) for analysis has been used (EPA Method #601, 40CFR136) but little is known about the precision and accuracy of the procedure. GC/MS requires special expertise and expensive, sophisticated equipment. For these reasons, monitoring for one compound alone using the Tenax GC/MS procedure is rarely cost effective and the approach is most suitable when monitoring for an array of volatile compounds is desired.

The preparation of Tenax suitable for sampling is demanding. Tenax background is a problem that must be addressed (e.g., by using a blank). Precautions about permissible maximum air volumes, sampling rates, and ambient temperatures during sampling must be observed and these, in turn, govern allowable sampling times.

Detection limits and accuracy are not known; reproducibility is estimated to be 50-100 percent. Quality assurance materials composed of blank Tenax sampling cartridges spiked with known amounts of 1,4-dichlorobenzene can be prepared and must be used in any monitoring program.

NIOSH - NIOSH certifies detector tubes calibrated for direct-reading of 1,2-DCB and 1,4-DCB. These are listed under 42CFR84. Also, analytical methods for 1,2-DCB and 1,4-DCB are available in the NIOSH Manual of Analytical Methods, Volumes 2 and 3, respectively, 1977 (GPO Nos. 017-033-00260-6 and 017-033-00261-4, respectively).

9.2 Water (CONTACT: Thomas Bellar, FTS 684-7311 or
James Lichtenberg, FTS 684-7308)

There are several approved and proposed gas chromatographic procedures for the analyses of 1,2-DCB and 1,4-DCB in natural, waste, and drinking waters. The primary difference between the methods is the extraction procedure and the means of injecting the extracts into the gas chromatograph. Mass spectrometry and halogen specific detectors are normally used to improve qualitative accuracy.

Direct Aqueous Injection EPA # Method 8 (1)
ASTM # D 2908-74 (2)

Major Equipment Required: Gas chromatograph

One to 5 ul of the neat sample is injected directly into the gas chromatograph. The method detection limit is approximately 1 mg/l when mass spectrometry, flame ionization, or halogen specific detectors are used. For nickel-63 electron capture detectors the method detection limit is approximately 1 ug/l.

Liquid-Liquid Extraction EPA # 612(3) 625 (4)

Major Equipment Required: Gas chromatograph

A measured volume of sample, approximately 1 liter, is solvent extracted with methylene chloride using separatory funnel techniques. The methylene chloride is dried and solvent exchanged to hexane during concentration to a volume of 10 ml or less. One to five ul of the extract is then injected into a gas chromatograph equipped with an electron capture detector. The method detection limit is approximately 1.0 ug/l (4.4 ug/l for 625 Base/Neutral Extractions).

Purge and Trap EPA # 601,(4) 624,(4) 502.1,(5) 503.1 (7)
ASTM # D-3871-79(6)
Standard Methods - To be included in the 15th Edition

Major Equipment: Gas chromatograph and purge and trap apparatus

Five ml of the aqueous sample is placed into a purging device. 1,4-dichlorobenzene and other volatile water insoluble organic compounds are transferred from the aqueous phase to the gas phase. The volatilized compounds are swept from the purging device by the purge gas and are trapped in a short column containing a suitable sorbent. After a predetermined period of time the trapped compounds are thermally desorbed and backflushed into a gas chromatograph equipped with a mass spectrometer, flame ionization, or a halogen specific detector.

The method detection limit for the mass spectrometer (full scan) and the flame ionization detector is approximately 1 ug/l. For a carefully optimized halogen specific detector method, detection limits as low as 20 ng/l have been achieved.

Samples are collected in narrow-mouth screen-cap bottles with TFE fluorocarbon seals. Samples are stored head-space free at 4°C in the dark. Sodium thiosulfate is normally used to remove free residue chlorine. Spiked river water samples have been stored for up to 7 days under these conditions with no apparent losses.

Single laboratory test data on simple spiked matrices have been collected by EPA. Intralaboratory accuracy and precision and method detection limit data are currently being collected (see Table 4). Quality control and performance evaluation samples (methanolic concentrates containing the isomer to be spiked into water) are available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, USEPA, Cincinnati, Ohio 45268.

References for Water Analysis

1. "A Method for Organochlorine Solvents in Industrial Effluents," National Pollutant Discharge Elimination System Appendix A, Federal Register 38, No. 7S Pt. II.
2. "Standard Test Method for Measuring Volatile Organic Matter in Water by Aqueous - Injection Gas Chromatography," Annual Book of ASTM Standards, 1980, Part 31, Water, ASTM D-2908-74.
3. Federal Register, Thursday, November 29, 1979, Volume 44. No. 231, 40CFR, Appendix C - Parts I and II.
4. Federal Register, Monday, December 3, 1979, Volume 44, No. 233, 40CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants.
5. "The Determination of Halogenated Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method," Method 502.1, September 1980, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
6. "Standard Test Method for Measuring Purgeable Organic Compounds in Water Using Headspace Sampling," ASTM D-3871-79, Part 31, Water, Annual Book of ASTM Standards, 1980.
7. "The Analysis of Aromatic Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method," Method 503.1, May 1980, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

TABLE 4: LIST OF WATER PROCEDURES FOR 1,4-DICHLOROBENZENE

Method	Type	MDL	Recovery* (%)	Standard Deviation (%)	Status
EPA 625	LLE	4.4 ug/l	67	22	Proposed
EPA 624	P&T	ND	ND	ND	Proposed
EPA 601	P&T	.24 ug/l	ND	ND	Proposed
EPA 502.1	P&T	<0.1 ug/l	90	7	Proposed
EPA 503.1	P&T	<0.1 ug/l	106	9	Untested
EPA 8	DAI	1 mg/l	ND	ND	Official+
Standard Methods	P&T	ND	ND	ND	Untested
ASTM D-2098-74	DAI	ND	ND	ND	Untested
ASTM D-3871-79	P&T	ND	ND	ND	Untested
EPA 612	LLE	1.34 ug/l	89	20	Proposed

P&T = Purge and Trap

LLE = Liquid/Liquid Extraction

DAI = Direct Aqueous Injection

Status - As of March 1981.

* Single laboratory recovery from spiked reagent water or spiked wastewater.

+ Official for the analysis of organohalides in wastewater.

9.3 Hazardous Waste (CONTACT: Donald F. Gurka, FTS 545-2113 or Werner F. Beckert, FTS 545-2137)

The RCRA regulations, Part 261, Appendix III, refer to tests 8.25, 8.01, 8.02, and 8.12 in "Test Methods for Evaluating Solid Waste," SW-846 as suitable for the analyses of dichlorobenzenes.

REFERENCES

The major references used in preparation of this document are listed below. EPA documents are referenced by EPA Office of origin and the year of publication. For further information refer to contacts given throughout this document or contact the relevant EPA Program Offices listed in the next section.

- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, Vol. II, EPA-440/4-79-029b, Office of Water Regulations and Standards (1979).
- (OWRS, 1980) Ambient Water Quality Criteria for Dichlorobenzenes, EPA 440/5-80-039, Office of Water Regulations and Standards (1980).
- (OWRS, 1981a) An Exposure and Risk Assessment for Dichlorobenzenes, Office of Water Regulations and Standards (1981).
- (OWRS, 1981b) Strategy for Controlling Environmental Exposure to 1,2-DCB, 1,3-DCB, and 1,4-DCB, Office of Water Regulations and Standards (1981).

OFFICE CONTACTS

The EPA Offices and Divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
---------------------------------	----------

Effluent Guidelines Division	426-2571
------------------------------	----------

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergenices call the National Response Center at 1-800-424-8802 (1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ, Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information and Analysis Program

382-2249

1,2-DICHLOROETHANE

Table of Contents

	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-2
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-1
<u>Exposure</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2
Other Actions	6-3

<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
 <u>Spill or Other Incident Clean-up/Disposal</u>	 8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-2
 <u>Sampling, Acceptable Analytical Techniques and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
 <u>References and Office Contacts</u>	 R-1

1,2-DICHLOROETHANE

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

1,2-Dichloroethane (also known as ethylene dichloride or EDC) is a short-chain chlorinated aliphatic hydrocarbon. It is the largest volume chlorinated organic chemical currently produced in the United States. EDC is consumed almost exclusively as a chemical feedstock in the production of vinyl chloride and other chlorinated organic chemicals. Only a very small percentage (0.1%) has been used in solvent applications. Unlike most chlorinated solvents, EDC is flammable. It is also slightly soluble in water. Relevant physical/chemical properties are listed in Table 1.

1.2 Chemistry and Environmental Fate/Transport

EDC is released to the environment largely through its manufacture and the manufacture of its end products. Greater than 95% is released directly to the atmosphere. Once in the troposphere, EDC is attacked by hydroxyl radicals to yield chloroacetyl chloride as the initial product. The half-life for this photooxidation reaction is reported to be approximately 0.3 months. Less than 1% will be transported to the stratosphere where it will either undergo photodissociation by high energy ultraviolet light or be carried back to earth during the precipitation process (OWRS, 1979).

Volatilization is the major transport process for the removal of EDC from surface water. The evaporative half-life is approximately 30 minutes. Other processes such as hydrolysis, oxidation, or microbial degradation do not appear to be significant (OWRS, 1979).

EDC released to land would be expected to volatilize and percolate down through the soil column. There does not appear to be any efficient mechanism to remove EDC from ground water (OWRS, 1981).

Like most chlorinated hydrocarbons, EDC is not readily biodegraded. Living matter finds it difficult to metabolize carbon-chlorine bonds; however, some manufacturers do employ aerobic oxidation (with acclimated sludge) to treat some EDC wastes (OSW, 1980).

EDC has been detected in urban air, near industrial vinyl chloride monomer (VCM) production sites, in industrial water and waste water samples in finished and raw drinking waters, and in (expired) human air (IARC, 1979).

TABLE 1: PHYSICAL/CHEMICAL PROPERTIES OF 1, 2-DICHLOROETHANE

Synonyms:	Ethylene dichloride, EDC
CAS number:	107-06-2
Molecular formula:	$C_2H_4Cl_2$



Molecular weight:	98.96
Melting point:	-35°C
Boiling point:	83°C
Flashpoint:	15°C
Density:	1.2 (20°C)
Vapor pressure:	61 torr (20°C)
Solubility:	8,690 mg/l (20°C)
Log octanol/water partition coefficient:	1.48

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACTS: William Lappenbusch, FTS 472-6820 or Bob McGaughy, FTS 755-3968)

2.1.1 Acute Toxicity

Ingestion of 1 or 2 ounces, about 400 to 800 mg/kg body weight, of EDC by an adult male is fatal. Clinical symptoms of acute 1,2-dichloroethane poisoning by ingestion usually appear within 2 hours after exposure. Typically, they include headache, dizziness, general weakness, nausea, vomiting of blood and bile, dilated pupils, heart pains and constriction, pain in the epigastric region, diarrhea, and unconsciousness. Pulmonary edema and increasing cyanosis are often observed. Deaths are usually attributed to circulatory or respiratory failure (ODW, 1980).

Exposure to 4,000 ppm of EDC vapor for 1 hour produces serious illness in humans. The effects of acute exposure by inhalation are similar to those described for ingestion, but the primary target appears to be the central nervous system. Neural depression increases with the amount of 1,2-dichloroethane absorbed. Damage to the liver, kidneys, and lungs also occurs, and reports of leukocytosis and elevated serum bilirubin are common (ODW, 1980).

The absorption of 1,2-dichloroethane through skin produces effects similar to those reported for inhalation, but large doses are required to cause serious systemic poisoning. Brief contact of 1,2-dichloroethane with skin seldom causes serious difficulties; however, repeated or prolonged contact results in extraction of normal skin oils and can cause cracking. Although pain, irritation and lacrimation normally occur when 1,2-dichloroethane contacts eye tissue, significant damage usually occurs only if the compound is not promptly removed by washing (ODW, 1980).

2.1.2. Chronic Toxicity

Chronic exposures in humans to EDC by inhalation or absorption usually result in progressive effects that closely resemble the symptoms described for acute exposure, especially neurological changes, loss of appetite, gastrointestinal problems, irritation of the mucous membranes, and liver and kidney impairment. The literature indicates chronic symptoms may appear after 8-hour exposures to 10 to 100 ppm for durations of a few weeks to a few months. Odor is not a dependable guide for avoiding dangerous chronic exposures to EDC. The odor may be thought pleasant until well above 180 ppm, and may be missed completely below 100 ppm (ODW, 1980).

Animal ingestion tests (mouse and rat) indicate that EDC is a carcinogen when ingested. Animal inhalation tests have been negative (ingestion tests used technical grade EDC while inhalation tests used pure EDC. Different strains of the test animals were used for each) (OHEA, 1978; ODW, 1980).

IARC (1979) states that in the absence of adequate data in humans, it is reasonable, for practical purposes, to regard EDC as if it presented a carcinogenic risk to humans.

EDC is mutagenic in Salmonella typhimurium (Ames test), Drosophila melanogaster, Hordeum vulgare and E. Coli. (IARC, 1979).

2.2 Environmental Effects (CONTACTS: John Eaton, FTS 783-9557 or
John Gentile, FTS 838-4843)

2.2.1 Aquatic Effects (OWRS, 1980).

Freshwater - Freshwater acute toxicity for bluegill ranged from 431,000 to 550,000 ug/l (96 hr. LC₅₀). The 48-hour LC₅₀ for Daphnia magna is 218,000 ug/l.

The available freshwater data for EDC indicate that acute toxicity occurs at concentrations as low as 118,000 ug/l and chronic toxicity occurs at concentrations as low as 20,000 ug/l.

Saltwater - The measured LC₅₀ (96-hour) for mysid shrimp is 113,000 ug/l. Acute toxicity to fish and invertebrate species occurs at concentrations as low as 113,000 ug/l.

2.2.2 Other Effects (OWRS, 1980).

The steady state bioconcentration factor (BCF) for bluegill is 2 (14 days).

3. ENVIRONMENTAL RELEASE (CONTACTS: Michael Slimak, FTS 426-2503 or
Bill Coniglio, FTS 382-3035)

U.S. production of EDC is almost 6,000,000 kkg/yr. Excluding a small quantity exported, almost 99% of production is consumed as a feedstock in the production of vinyl chloride and other chemicals. About 1 percent is used as a leaded gasoline additive, nearly all of which is destroyed during combustion. A remaining 0.1% (4,700 kkg/yr) is dissipated to the environment following various solvent related uses. Overall, of the 29,000 kkg/yr environmental release, 96% is estimated to go to air, 3% to land, and less than 1% to water, as shown in Table 2 (OWRS, 1981).

3.1 Air Releases (CONTACT: Karen Blanchard, FTS 629-5519)

Significant Sources

- Chemical industries producing EDC or using it as feedstock (SIC 2869) are the sources contributing the greatest emissions to the ambient air. EDC is one of the highest volume chemicals used in the U.S. In 1977 about 80% of production was used for the synthesis of vinyl chloride monomer, a hazardous chemical. Domestic production emission sources are located in Louisiana, Texas, Kentucky, California and Puerto Rico.

Other Sources

- EDC is used as a leaded gasoline additive. It has been estimated that 30 million people are exposed to an EDC concentration of 1.5 ppb for 2.2 hr/yr while refueling their automobiles (OAQPS, 1979). Exposures to EDC may occur through its dispersive uses, including grain fumigants, paints, coatings, adhesives, cleaning, and the preparation of polysulfide. However, these uses represent only 1/10 of 1% of production.

3.2 Water Releases (CONTACT: Michael Slimak, FTS 426-2503)

Based on the above production and use considerations, most releases of EDC would be expected to occur at centralized production facilities rather than at widely dispersed solvent-using facilities, in sharp contrast to other chlorinated solvents. Although Effluent Guidelines Division detected dichloroethanes less frequently and in fewer industrial categories than the widely used solvents, EDC was still found in over 10% of the samples in the Mechanical Products, Pharmaceuticals, Pesticides, Organics and Plastics, Photographic, and Auto and Other Laundries industries (OWRS, 1981).

TABLE 2: EDC PRODUCTION, USE, AND DISPOSAL (kkg/yr)

Category	Production	Use	Air	Release to Water	Land
Production					
Balanced process	5,400,000		20,000	1	83
Direct Chlorination	380,000		1,100	1	95
Oxy chlorination	110,000		1,300	1	280
Use					
Vinyl chloride monomer		4,800,000	included in balanced process		
1,1,1-trichloroethane		200,000	1	Neg	Neg
Ethylene amines		230,000	360	1	20
Trichloroethene		110,000	63	29	Neg
Tetrachloroethene		110,000	75	35	Neg
Vinylidene chloride		100,000	Neg	Neg	Neg
Dispersive Uses					
Lead scavenger		72,000	800	Neg	Neg
Paints coating adhesives		1,300	1,300	Neg	Neg
Extraction solvent		1,300	1,300	Neg	Neg
Cleaning solvent		1,000	600	100	300
Polysulfide rubber		15	Neg	Neg	Neg
Grain fumigant		500	500	Neg	Neg
Diluent for pesticides		400	200	Neg	200
Film manufacture		150	8	Neg	Neg
Exports		310,000			
Total:			27,607 (96%)	169 (<1%)	978 (3%)

Source: Recommendations for Control of Dichloroethanes, Draft Report, OWRS, Oct. 81.

Neg. = Negligible

4. EXPOSURE (CONTACTS: Michael Slimak, FTS 426-2503 or
Bill Coniglio, FTS 382-3035)

The general population may be exposed to EDC through drinking water, urban air, and food products which have been treated with EDC.

The level of human exposure to EDC is difficult to identify with certainty due to sparse and conflicting measurements. Ambient air concentrations of both dichloroethane isomers are elevated by emissions from dichloroethane producers and to a lesser extent by EDC feedstock users. Concentrations are also somewhat elevated in all urban areas due to emissions as a leaded gasoline additive or solvent (OWRS, 1981).

Annual inhalation exposure to EDC in areas where it is produced may attain 800 ug/day (40 ug/m^3). Because EDC is seldom detected in drinking water, the estimate for average exposure via this route is also broad, 0.03 - 3 ug/day, depending on the concentration assumed for undetectables in either the National Organics Monitoring Survey (NOMS) or Stanford Research Institute (SRI) nationwide surveys. The highest waterborne exposure yet observed is 800 ug/day, via contaminated groundwater. Exposure to EDC via food cannot be estimated, due to lack of data; however, it is known that dichloroethanes are so weakly bioconcentrated that exposure via contaminated fish should be minor (OWRS, 1981).

Overall, it can be concluded that:

- Despite the massive combined production volume of dichloroethanes, very little is released to the environment. Troublesome ambient levels appear to be associated with production and feedstock consumption facilities.
- Dichloroethanes are primarily air pollutants. Population aggregated exposure is substantially greater via air than via surface or groundwater. Highest individual exposures appear to result from air or groundwater contamination.
- Ambient levels of EDC may contribute very slightly to cancer risks.

4.1 Air Exposure (CONTACT: Karen Blanchard, FTS 629-5519)

- In addition to exposure in the workplace, the human population near certain chemical manufacturing facilities may be exposed to EDC in the ambient air. It has been estimated that as many as 14 million people were exposed to concentrations of EDC ranging from .01-10 ppb (OAQPS, 1979).

4.2 Water Exposure

High level exposures may result via severely contaminated groundwater.

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available on the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purpose of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. For further information contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information contact Delores Evans at FTS 382-3546 or Irv Weiss at FTS 382-3524.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and International levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Delores Evans at FTS 382-3546 or Ingrid Meyer at FTS 382-3773.

5.5 Chemical Substances Information Network (CSIN)

The prototype CSIN, operational since November 1981, has been developed by merging the technologies of computer networking and distributed data base management. CSIN is not another data base, but a library of systems. Through the CSIN front-end intermediary management computer, the user may access and use independent and autonomous information resources which are geographically scattered, disparate for data and information content, and employ a variety of types of computer hardware, software, and protocols. Users may converse in and among multiple systems through a single connection point, without knowledge of or training on these independent systems.

Presently, six independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), CIS, EPA-CICIS, CAS-On-Line, SDC-orbit, and two files of Dialog: CRGS and TSCA Inventory. The CSIN management computer allows the user to create, retrieve, store, or manipulate data and queries. This eliminates the need for re-entering long lists of chemical identifiers or other information elements which are part of the original query or which have been identified and acquired from one or more of the CSIN resources. For further information contact Dr. Sid Siegal at FTS 382-2256.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 475 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained by offices within EPA. For further information, contact Charlene Sayers at FTS 755-9112.

The following data bases contain information on EDC compounds.

BAT Review Study for the Timber Products Processing, Gum and Wood, Chemicals, and the Printing and Publishing Industries
Best Management Practices, Timber Industry Effluent Guidelines -
Runoff
Chemicals in Commerce Information System
Compliance Sampling Toxicant Surveys
Consolidated Permits Program-Application Form 1,2b,2c
Data Collection Portfolio for Industrial Waste Discharges
Distribution Register of Organic Pollutants in Drinking Water
Effluent Guidelines GC/MS Screening Analysis Data Base
Energy and Mining Point Source Category Data Base
Federal Facilities Information System
Federal Reporting Data System
Fine Particle Emissions Information System
Food Industry Group
Fugitive Emissions Information System
Gaseous Emissions Data System
Hazardous Waste Data Management System
Hazardous Waste Site Tracking System
Hemlock, Michigan Environmental Samples

Humacao Ambient Data Base
 IFB Organics Data Base
 Indicatory Fate Study
 Industrial Process Evaluations
 Infrared Spectra of Pollutants
 Innovative Technology, Timber Industry Effluent Guidelines
 Inorganic Chemicals Industry Regulation Record
 LiParí Landfill
 Liquid Effluents Data System
 Listing of Organic Compounds Identified in Region IV
 Love Canal Data Handling System
 Method Validation Studies of Priority Pollutants
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Monitoring Reports
 Nationwide Urban Runoff Program
 Needs Survey
 New York Bight Ocean Monitoring Program
 Organic Chemicals/Plastics Industry
 Organic Transport thru Soil
 Paint and Ink Analytical Data
 Permit Compliance System
 Pesticide Incident Monitoring System
 Pharmaceutical Screening/Verification Data Base
 Precision and Accuracy for Screening Protocols
 Priority Pollutants-Region I
 Priority Pollutants-Region III
 Publicly Owned Treatment Works (POTW) Analytical Data
 Publicly Owned Treatment Works (POTW) Quality Control
 Puerto Rico Reservoirs
 Regional Toxics Monitoring Program
 Resource Conservation and Recovery Act (RCRA)-Hazardous Waste Site
 Inspections
 Screening Sampling Program
 Select Hazardous Chemicals-Ambient
 Sources of Toxic Pollutants Found in Influent to Sewage Treatment
 Plants
 Spill Prevention Control and Countermeasure
 System for Consolidated Permitting and Enforcement Data Base
 Textile Industry BAT Study-Toxic Sampling Data
 Toxics Monitoring
 U.S. Virgin Islands-St. Thomas, St. Croix
 Verification Data Base
 Verification Sampling Program
 Waste Characterization Data Base
 Water Enforcement Regional System
 Water Quality Information System

6. REGULATORY STATUS (Current as of 4/16/82)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- Sections 301, 304, 306, 307 - 1,2-Dichloroethane is classified as a toxic pollutant (40CFR401.15). As such, it is subject to effluent limitations reflecting "the best available technology economically achievable (BAT)." No standards specific for 1,2-dichloroethane have been issued.

Resource Conservation and Recovery Act (RCRA)

- Section 3001 - 1,2-Dichloroethane (U077) has been identified as a toxic hazardous waste (T) if and when it is discarded as a commercial product or an off-specification species. Contaminated soil and spill residues are also considered hazardous wastes. (40CFR261.33)

The following wastestreams are designated as toxic hazardous (T) wastes, due in part to the presence of EDC (40CFR261.32):

- K018 - Heavy ends from the fractionation column in ethyl chloride production.
- K019 - Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production.
- K020 - Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production.
- K029 - Wastes from the product steam stripper in the production of 1,1,1-trichloroethane.
- K030 - Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene.
- K096 - Heavy ends from the heavy ends column from the production of 1,1,1-trichloroethane.
- Sections 3002-3006 - Regulations for generators, and transporters of hazardous waste and standards for treatment, storage and disposal facilities are applicable (40CFR262 to 265). Permitting procedures are included in the consolidated permit regulations (40CFR122 to 124).

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- Tolerance exemptions for 1,2-dichloroethane residues (40CFR180).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- An employee's exposure to 1,2-dichloroethane is limited in any eight-hour shift of a 40-hour work week by eight-hour time-weighted averages (TWA) and acceptable ceiling concentrations (29CFR1910.1000).
- Safety and health regulations for construction under Federal service contracts (29CFR1925).

DOT

- EDC is listed as a flammable liquid and must comply with the appropriate labeling and transportation regulations (49CFR172.-101).

6.2 Proposed Regulations

6.2.1 EPA Programs

TSCA - Toxic Substances Control Act

- Section 8(a) - Proposed requirements requesting records, reports and other data possessed by manufacturers and processors of 1,2-dichloroethane.

CAA - Clean Air Act

- New Stationary Source Performance Standards proposed for Organic Solvent Cleaners. EDC covered under the volatile organic compounds (VOC) category (45FR39766, 6/11/80).
- New Stationary Source Performance Standards proposed which would limit VOC from fugitive emission sources in the Synthetic Organic Chemicals Manufacturing Industry. EDC is one of a number of VOC included in this proposal (46FR1136, 1/5/81).

6.2.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- Regulation of 1,2-dichloroethane as a mutagen under OSHA's general policy for the identification and regulation of physical and chemical substances posing potential carcinogenic risks to humans (29CFR1990).

DOT

- Coast Guard lists appropriate measures to prevent storage of EDC with incompatible materials during transport by boat (45FR48058).

6.3 Other Actions

- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) - CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites. (42USC9601; PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46FR54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47FR10972). Hazardous substances as defined by Section 101(14) of CERCLA include: hazardous wastes designated under Section 3001 of the RCRA; hazardous air pollutants regulated under Section 112 of the CAA; water pollutants listed under Sections 307 and 311 of the CWA (and also any substances regulated in the future under Section 7 of TSCA and Section 102 of CERCLA). Therefore, EDC is a hazardous substance under CERCLA and will be subject to regulations developed under Superfund.

Safe Drinking Water Act (SDWA)

- One of a number of substances discussed in an Advance Notice of Proposed Rulemaking (ANPR) for possible inclusion in revised National Primary Drinking Water Regulations for volatile synthetic organic chemicals (47FR9350, 3/4/82).

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- OSHA standard for workplace exposure (29CFR1910.1000).

TWA 50 ppm (8-hr. work day)

7.2 Water

- Hazardous spill rules require notification of discharge equal to or greater than 5,000 lb (40CFR116, 117).
- Water Quality Criteria (44FR60641)

Freshwater Aquatic Life	3,900 ug/l (24-hr. avg.)
	8,800 ug/l (maximum)

Saltwater Aquatic Life	880 ug/l (24-hr. avg.)
	2,000 ug/l (maximum)

Human Health	To protect human health zero risk at zero concen- tration. One additional case of cancer per 100,000 population (10^{-5}) at 9.4 ug/l.
--------------	---

* See Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL
(CONTACT: National Response Center, 800-424-8802, in Washington, 426-2675)

8.1 Hazards and Safety Precautions

EDC may be fatal if inhaled, swallowed or absorbed through the skin. Contact may cause burns to skin and eyes. Runoff from fire control or dilution water may cause pollution.

EDC will burn and may be ignited by heat, sparks and flames. Flammable vapor may spread away from spill. Container may explode in heat of fire.

Protect against physical damage. Outside or detached storage is preferable. Inside storage should be in a standard flammable liquids storage room or cabinet.

8.2 First Aid

Move victim to fresh air; call emergency medical care. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Remove and isolate contaminated clothing and shoes. In case of contact with material, immediately flush skin or eyes with running water for at least 15 minutes.

8.3 Emergency Action

Keep unnecessary people away; isolate hazard area and deny entry. Stay upwind; keep out of low areas. Wear positive pressure breathing apparatus and special protective clothing. Isolate for 1/2 mile in all directions if tank or tank car is involved in fire.

In case of spill or leak, no flares, smoking or flames in hazard area. Do not touch spilled material. Stop leak if you can do it without risk. Use water spray to reduce vapors. Small spills: take up with sand, or other noncombustible absorbent material, then flush area with water. Large spills: dike far ahead of spill.

In case of small fire use dry chemical, CO₂, water spray or foam. And in case of large fire use water spray, fog or foam. (Note: water may be ineffective on fire.) Wear goggles, self-contained breathing apparatus, and rubber overclothing (including gloves). Move container from fire area if you can do so without risk. Stay away from ends of tanks. Cool containers that are exposed to flames with water from the side until well after fire is out. Withdraw immediately in case of rising sound from venting safety device or discoloration of tank.

8.4 Notification and Technical Assistance

Section 103(a) and (b) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 requires persons who release hazardous substances in reportable quantities determined pursuant to

Section 102 of the Act to notify the National Response Center (NRC): 800-424-8802 (Washington, D.C., 426-2675).

EDC is designated as a hazardous substance under CWA Section 311. Its reportable quantity is 5,000 pounds.

For technical assistance call CHEMTREC (800-424-9300). Also, in case of water pollution, call local authorities. Other sources of technical information are (1) EPA's Oil and Hazardous Material Technical Assistance Data System (OHM-TADS) contained in the NIH/EPA Chemical Information System (CIS), which provides information pertinent to emergency spill response efforts, and (2) the CHRIS System which provides information on first aid, physical/chemical properties, hazard assessments, and response methods. Both systems can be accessed through NRC.

8.5 Disposal

Disposal of greater than 1,000 kg/month of commercial product is subject to subpart D regulations under RCRA.

The following specific wastestreams, which contain EDC, are subject to subpart D regulations:

- (1) Heavy ends from the fractionation column in ethyl chloride production.
- (2) Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production.
- (3) Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production.
- (4) Waste from the product steam stripper in the production of 1,1,1-trichloroethane.
- (5) Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene.
- (6) Heavy ends from the heavy ends column from the production of 1,1,1-trichloroethane.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air (CONTACT: Robert H. Jungers, FTS 629-2331)

EDC is not a criteria air pollutant; therefore, no Agency or reference procedures have been promulgated. A sampling and analysis procedure using charcoal for sampling, gas chromatography for component separation and mass spectrometry for analysis has been used for monitoring around production and user facilities. ("Monitoring of Ambient Levels of Ethylene Dichloride (EDC) in the Vicinity of EDC Production and User Facilities," EPA-600/4-79-029, April 1979). However, mass spectrometry requires sophisticated and expensive equipment and special expertise.

The method was evaluated over an EDC range of 2.5 to 348 ug/m³ (0.6 to 86 ppb), at temperatures of 25° and 30°C and relative humidities of 64% and 99%. The sampling rate is 65 cm³/min for 24 hours. Sampling at rates greater than 65 cm³/min and for times greater than 24 hours must be avoided, because higher sampling rates and larger total air volumes can lower collection efficiency substantially.

The precision, as measured by the relative standard deviation from replicate sampling and analysis by one laboratory, is reported to be 6%. Accuracy of the method is estimated to be between 72% and 97%.

Quality assurance materials composed of blank charcoal sampling cartridges spiked with known amounts of EDC can be prepared and must be used in any monitoring program.

9.2 Water (CONTACTS: Thomas Bellar, FTS 684-7311 or
James Lichtenberg, FTS 684-7308)

1,2-Dichloroethane is a proposed parameter under Section 304(h) of the Clean Water Act. It is listed as one of the priority pollutants.

There are several approved and proposed gas chromatographic procedures for the analysis of 1,2-dichloroethane in natural, waste and drinking waters. The primary difference between the methods is the extraction procedure and the means of injecting the extracts into the gas chromatograph. Mass spectrometry and halogen specific detectors are normally used to improve qualitative accuracy.

In one method, the Direct Aqueous Injection (EPA Method #8) 1 to 5 ul of the neat sample is injected directly into the gas chromatograph. The method detection limit is approximately 1 mg/l when mass spectrometry, flame ionization or halogen specific detectors are used.

A second method is the Liquid-Liquid Extraction (EPA Method #501.2) in which a small volume of sample is extracted with a low boiling water insoluble solvent such as pentane. Sample/solvent ratios of 5:1 are commonly used. One to 5 ul of the extract is then injected into a gas chromatograph equipped with an electron capture detector. The method detection limit is approximately 20 ug/l.

In the third method--Purge and Trap--(EPA Method #601) 5 ml of the aqueous sample is placed into a purging device. 1,2-Dichloroethane and other volatile water insoluble organic compounds are transferred from the aqueous phase to the gas phase. The volatilized compounds are swept from the purging device by the purge gas and are trapped in a short column containing a suitable sorbent. After a predetermined period of time the trapped compounds are thermally desorbed and back-flushed into a gas chromatograph equipped with a mass spectrometer, flame ionization or a halogen specific detector.

The method detection limit for the mass spectrometer (full scan) and the flame ionization detector is approximately 1 ug/l. For a carefully optimized halogen specific detector method detection limits as low as 20 ng/l have been achieved.

Samples are collected in narrow-mouth screen-cap bottles with TFE fluorocarbon seals. Samples are stored head-space free at 4°C in the dark. Sodium thiosulfate is normally used to remove free residue chlorine. Spiked river water samples have been stored for up to 27 days under these conditions with no apparent losses.

Single laboratory test data on simple spiked matrices have been collected by EPA. Intralaboratory accuracy and precision and method detection limit data are currently being collected. Quality control and performance evaluation samples (methanolic concentrates containing 1,2-dichloroethane to be spiked into water) are available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, USEPA, Cincinnati, Ohio, 45268.

The following table is a summary of methods with appropriate references:

ANALYTIC PROCEDURES FOR 1,2-DICHLOROETHANE

Method	Type	MDL	Recovery ^a (%)	Standard Deviation (%)	Status
EPA 624	P&T	2.8 ug/l	102-103	12-27	Proposed
EPA 601	P&T	.03 ug/l	106	8.4	Proposed
EPA 502.1	P&T	ND	110	7	Proposed
EPA 501.2	LLE	ND	ND	ND	Untested
EPA 8	DAI	1 mg/l	ND	ND	Official ^b
Standard Methods	P&T	ND	ND	ND	Untested
ASTM D-2098-74	DAI	ND	ND	ND	Untested
ASTM D-3871-79	P&T	ND	ND	ND	Untested

^a Single laboratory recovery from spiked reagent water or wastewater.

^b Official for the analysis of organohalides in wastewater.

P&T - Purge and Trap

LLE - Liquid/Liquid Extraction

DAI - Direct Aqueous Injection

Status - As of March 1981.

References for Sampling and Analysis

1. "A Method for Organochlorine Solvents in Industrial Effluents." National Pollutant Discharge Elimination System Appendix A, Federal Register 38, No. 7S Pt. II.
2. "Standard Test Method for Measuring Volatile Organic Matter in Water by Aqueous - Injection Gas Chromatography," Annual Book of ASTM Standards, 1980, Part 31, Water, ASTM D-3908-74.
3. Federal Register, Thursday, November 29, 1979, Volume 44. No. 231, 40 CFR, Appendix C - Parts I and II.
4. Federal Register, Monday, December 3, 1979, Volume 44. No. 233, 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants.
5. "The Determination of Halogenated Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method," Method 502.1, September 1980, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
6. "Standard Test Method for Measuring Purgeable Organic Compounds in Water Using Headspace Sampling," ASTM D-3871-79, Part 31, Water, Annual Book of ASTM Standards, 1980.

REFERENCES

The major references used in preparation of this document are listed below. EPA documents are referenced by the EPA office of origin and the year of publication. For further information refer to the contacts given throughout this document or contact the EPA Program Offices listed in the next section.

- (IARC, 1979) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 20, International Agency for Research on Cancer, World Health Organization (1979).
- (OAQPS, 1979) Assessment of Human Exposure to Atmospheric Ethylene Dichloride, EPA Contract 68-02-2835, Office of Air Quality Planning and Standards (1979).
- (ODW, 1980) Criteria Document for 1,2-Dichloroethane, Draft Report, Office of Drinking Water (1980).
- (ODW, 1981) Draft SNARL Review - 1,2-Dichloroethane, Office of Drinking Water (1981).
- (OHEA, 1978) The Carcinogen Assessment Group's (CAG) Preliminary Report on Ethylene Dichloride, Office of Health and Environmental Assessment (1978).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, Vol. II, EPA-440/4-79-029b, Office of Water Regulations and Standards (1979).
- (OWRS, 1980) Ambient Water Quality Criteria for Chlorinated Ethanes, EPA 440/5-80-029, Office of Water Regulations and Standards (1980).
- (OWRS, 1981) Recommendations for Control of Dichloroethanes, Draft Report, Office of Water Regulations and Standards (1981).
- (OSW, 1980) Wastes Resulting from Chlorinated Hydrocarbon Manufacture, Preliminary Draft Report, Office of Solid Waste (1980).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
Effluent Guidelines Division	426-2571

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergenices call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ, Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information and Analysis Program

382-2249

FORMALDEHYDE

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-3
<u>Environmental Release</u>	3-1
<u>Exposure Routes</u>	4-1
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2
Other Actions	6-3
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
<u>Spill Clean-Up or Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-2

<u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	9-1
Air	9-1
Water	9-1
Solid Waste	9-2
Other Procedures	9-2
<u>References and Office Contacts</u>	R-1

FORMALDEHYDE

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Formaldehyde is a flammable gas having a pungent odor and an irritating effect on mucous membranes. Because formaldehyde polymerizes readily, it is only available in stabilized aqueous solutions or polymeric forms. Aqueous solutions range from 37 to 56 percent formaldehyde. Polymeric forms include a cyclic trimer (trioxane) and paraformaldehyde, a linear polymer of varying composition. Table 1 summarizes properties of formaldehyde in the form of gaseous monomer, solid trimer and aqueous solution (OTS, 1976).

United States commercial production of aqueous formaldehyde (37 percent by weight) in 1980 was about 2,520 metric tons, down slightly from record levels in 1978. Formaldehyde is produced by the catalytic vapor phase oxidation of methanol or by a combination oxidation-dehydration process. The largest end uses for formaldehyde are in the production of synthetic resins, particularly phenol-formaldehyde and urea-formaldehyde resins. These resins are used as adhesives in wood products, principally for particleboard, fiberboard, plywood, and in making foam insulation. Formaldehyde also has many diverse uses as a chemical intermediate and preservative (OTS, 1982).

1.2 Chemistry

Formaldehyde is extremely reactive and will combine chemically with many classes of organic compounds. On reduction, formaldehyde yields methanol, while oxidation gives formic acid or carbon dioxide and water. The major reactions of formaldehyde with other compounds (X-H) involve formation of hydroxymethyl derivatives (X-CH₂-OH). Many of these reactions, such as hydration, are reversible and free formaldehyde may be regenerated under proper conditions. Formaldehyde is useful in the production of resins due to its dual reactivity. For example, formaldehyde initially reacts with phenol, urea, or melamine to form the hydroxymethyl derivative. Further reaction involves the loss of water to yield thermoset resins which are highly cross-linked by methylene groups (-X-CH₂-X-) (OTS, 1976; NRC, 1981).

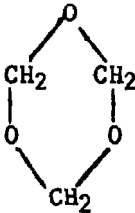
The major sources of formaldehyde contamination in the environment are combustion processes, especially automobile emissions. Formaldehyde vapors are released due to the incomplete combustion of hydrocarbons. In addition, hydrocarbons from automobile exhaust are oxidized to formaldehyde through photochemical processes in the atmosphere. Formaldehyde is a recognized component of smog and can react photochemically in the atmosphere to form radicals which undergo a wide variety of reactions. The half-life of formaldehyde in the atmosphere is estimated to be less than a few hours in sunlight.

Although formaldehyde itself is probably not transported far in the atmosphere due to its reactivity, hydrocarbons which are precursors for formaldehyde may be widely dispersed (NRC, 1981).

Biological degradation is the primary destruction process for formaldehyde and its hydrates in water. Formaldehyde, per se, does not persist in water, but is rapidly converted to glycols which are biodegradable. Thus, only very low concentrations of formaldehyde would be expected in ambient waters, except in extreme cases such as spills of concentrated solutions (OTS, 1982; NRC, 1981).

Due to the highly reactive nature of formaldehyde, this compound is expected to be immobilized in clay soil by adsorption. The persistence of adsorbed formaldehyde, however, is uncertain, especially in wet soils. Formaldehyde is a natural metabolic product and does not bioconcentrate (OTS, 1976; OTS, 1982).

TABLE 1: PROPERTIES OF FORMALDEHYDE AND COMMERCIALY AVAILABLE FORMS^a

	Formaldehyde	Trioxane	Formalin ^b
<u>State:</u>	Monomer; gas	Trimer; solid	Aqueous solution 37% by wt.
<u>Synonym:</u>	Methanal, oxymethane	S-trioxane	Formol
<u>CAS No.:</u>	50-00-00	110-88-3	--
<u>Molecular Formula:</u>	CH ₂ O	C ₃ H ₆ O ₃	CH ₄ O ₂ (hydrate)
<u>Structure:</u>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$		$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{H} \text{ (hydrate)}^c \\ \\ \text{OH} \end{array}$
<u>Melting Point (°C):</u>	-92	64	--
<u>Boiling Point (°C):</u>	-20	115	99
<u>Flash Point (°C):</u>	--	45	85
<u>Density:</u>	1.07 (vapor)	1.17 (65°C)	1.11 g/ml (18°)
<u>Water Solubility (25°C):</u>	55%	210 g/l	--

^aSource: The Merck Index, 9th edition (1976), unless otherwise noted.

^bSee Chemical and Process Technology Encyclopedia, p. 517; D.M. Considine, ed., McGraw Hill (1974). Commercial formalin contains varying amounts of methanol as a stabilizer; constants cited are for formalin containing 1% methanol.

^cPolymeric forms dominate at high formaldehyde concentrations.

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACTS: Bob McGaughy, FTS 755-3968; Yogi Patel, FTS 472-4944)

2.1.1 Acute Toxicity

Ingestion of aqueous formaldehyde solutions causes immediate and severe abdominal pain, collapse, loss of consciousness and anuria. Vomiting and diarrhea may also occur and death can result from circulatory failure. Ingestion may also lead to necrosis and shrinkage of mucous membranes, and degenerative effects on the liver, kidneys, heart, and brain. A fatal human dose of formalin (37 percent aqueous solution of CH_2O by weight) is estimated to be 30-90 ml (1 to 3 oz.); the oral LD_{50} for rats is about 800 mg/kg (OTS, 1976).

Formaldehyde vapor can be quite irritating at low concentrations. The level of irritation and resulting symptoms is a function of the formaldehyde concentration and the sensitivity of individuals. The variability of individual responses to gaseous formaldehyde is well established. In general, the irritation threshold is about 1 ppm (1200 ug/m^3) which is also reported to be the odor threshold. However, odor thresholds as low as 0.06 ppm (70 ug/m^3) have been reported in sensitive individuals. While most people can tolerate 2-3 ppm (2400 to 3600 ug/m^3) without any apparent discomfort, above this level discomfort becomes pronounced. Symptoms include coughing, sneezing, lacrimation, headache, and feelings of suffocation. Exposure to high concentrations (above 5 ppm) can cause damage to the respiratory tract; bronchitis and laryngitis may result. Exposure to levels in the range of 50-100 ppm can cause pulmonary edema, lung inflammation, and death (OTS, 1976).

Edema and hemorrhages of the lung and damage to the liver and kidneys of rats have been reported after exposure by inhalation or subcutaneous injection. The LC_{50} for rats exposed for 30 minutes to formaldehyde vapor is 800 ppm (1 g/m^3) (OTS, 1976).

2.1.2 Chronic Toxicity

Dermatitis from exposure to formaldehyde is a common problem in workers and others who contact the chemical regularly. Formaldehyde is known to be an allergen in sensitive individuals. Reported symptoms experienced by residents in some homes insulated with urea formaldehyde insulation include: nose and eye irritation, asthmatic attack, headaches, coughing and respiratory irritation, dry and sore throat, nausea, vomiting, skin irritation, and anaphylatic shock (allergic reaction). Some individuals are reported to become hypersensitive to formaldehyde resulting in allergic reactions seen as asthma (OTS, 1976).

Carcinogenicity, Mutagenicity, and Teratogenicity--The experimental data available indicates formaldehyde is carcinogenic in animals. A recent chronic inhalation study by the Chemical Industry Institute of Technology (CIIT) exposed rats and mice (120 animals of each sex and

species per exposure group) to 0, 2, 6, and 15 ppm formaldehyde for up to 24 months (6 hours a day, 5 days a week). A high incidence of nasal tumors (squamous cell carcinomas) were observed in rats (51 males and 52 females) from the 15 ppm group. The mice tested showed a much lower incidence of nasal tumors (2 male mice in the 15 ppm group). This type of tumor is quite rare in unexposed animals and none were observed in the unexposed control groups. Inhalation of formaldehyde was also associated with an exposure-related increase in frequency, severity and distribution of nasal lesions (squamous metaplasia) in rats from all exposure groups. In contrast to the rat, marked irritant-induced effects in mice were observed only at the highest exposure level (15 ppm) (CIIT, 1981).

Several groups (NIOSH, IARC, IRLG, EPA) regard the animal evidence adequate to implicate formaldehyde as a potential carcinogen in humans. However, there are no epidemiological studies to date which indicate that formaldehyde is carcinogenic in humans (CAG, 1979; NTP, 1980; NIOSH, 1981).

There is an extensive data base showing that formaldehyde is mutagenic in several species, including mice, Drosophila, plants, yeast (S. cerevisiae) and several strains of bacteria (S. typhimurium, E. coli). Formaldehyde also produced unscheduled DNA synthesis in a human cell line (HeLa) and sister chromatid exchanges in Chinese hamster ovary (CHO) cell line and in cultured human lymphocytes (CAG, 1979; OSW, 1980).

The available evidence does not indicate that formaldehyde is teratogenic. Formaldehyde has been found negative in teratogenicity assays in beagle dogs, rats, and mice (ODW, 1981).

2.1.3 Absorption, Distribution and Metabolism

Under normal conditions formaldehyde can enter the body through dermal and eye contact, inhalation, and ingestion. On dermal contact, formaldehyde reacts with proteins of the skin resulting in cross-linking and precipitation of the proteins. Inhalation of formaldehyde vapors produces irritation and inflammation of the bronchi and lungs; once in the lungs, formaldehyde can be absorbed into the blood. Ingestion of formaldehyde is followed immediately by inflammation of the mucosa of the mouth, throat, and gastrointestinal tract. Absorption appears to occur in the intestines (OTS, 1976).

Following absorption into the blood stream, formaldehyde disappears rapidly due to condensation reactions with tissue components and oxidation to formic acid (which exists in the form of the formate anion at physiological pH). The main metabolic pathway for formaldehyde appears to involve initial oxidation to formic acid, followed by further oxidation to CO₂ and H₂O. Liver and red blood cells appear to be the major sites for the oxidation of formaldehyde to formic acid. Some of the formic acid metabolite is excreted in the urine as the sodium salt; most, however, is oxidized to CO₂ and eliminated via the lungs (OTS, 1976).

2.2 Environmental Effects

2.2.1 Aquatic Effects

The use of formalin (aqueous formaldehyde) as a chemotherapeutant for control of fungus on fish eggs and ectoparasites on fish is a widely accepted and successful technique. However, unless certain criteria are met, formalin may cause acute toxic effects in fish. Analysis of toxicity levels indicates that a wide range of tolerances exists for different species; striped bass appear to be the most sensitive with an LC₅₀ of 5.6 to 13 ppm of formaldehyde. The LC₅₀ of formaldehyde for invertebrates (Daphnia magna) is reported to range between 100 to 1,000 ppm. The 48-hour median threshold limit (TLM) for Daphnia was about 2 ppm. No effects were observed in crayfish (Procambarus blandingi) exposed to 100 ul/l of formalin for 12 to 72 hours (OTS, 1976; OSW, 1980).

3. ENVIRONMENTAL RELEASE* (CONTACT: Nancy Pate, FTS 629-5502)

The sources of formaldehyde can be grouped into two major categories: direct (or commercial) production and indirect production. The chemical is not imported in any appreciable quantities.

Commercially, formaldehyde is produced from the catalytic oxidation of methanol, using either silver oxide or a mixed-metal oxide as the catalyst. Processes accounting for the indirect production of formaldehyde include the photochemical oxidation of airborne hydrocarbons from vehicular exhausts, the incomplete combustion of hydrocarbons in fossil fuels and refuse, and other natural processes.

Formaldehyde serves as a feedstock for many products and processes. The chemical may enter into and leave these products and processes essentially unaltered (non-consumptive use), altered in an irreversible manner (consumptive use) or altered in a manner that may be reversed under certain conditions (pseudo-consumptive use). The type of use plays a significant role in determining the release levels of formaldehyde that are associated with secondary and subsequent applications of the primary products.

The available data on the production, uses, and release levels (with pollution control devices) of formaldehyde indicate the following (all data are expressed as 100 percent formaldehyde for the year 1978):

- (1) Approximately 1,580,000 kkg of formaldehyde were produced in 1978: 1,070,000 kkg (68 percent) from direct production and 510,000 kkg (32 percent) from indirect production.
- (2) All of the formaldehyde indirectly produced (510,000 kkg) was released to the atmosphere; these releases accounted for 97 percent of the total airborne emissions of formaldehyde in 1978 (525,000 kkg).
- (3) Of the releases from indirect production (510,000 kkg), 330,000 kkg (63 percent) were generated from the combustion of fossil fuels and refuse, and 180,000 kkg (34 percent) were generated from the photochemical oxidation of airborne hydrocarbons from vehicular exhaust.
- (4) Most (94 percent; approximately 1,000,000 kkg) of the formaldehyde directly produced was consumed in subsequent chemical reactions (consumptive and pseudo-consumptive uses).

*The data for this section was taken from the recent technical document prepared by the Office of Toxic Substances (OTS, 1982).

- (5) Approximately 588,000 kkg (55 percent) of the commercially produced formaldehyde were consumed in the manufacture of two products: urea-formaldehyde and phenol-formaldehyde resins. The urea resins (pseudo-consumptive use) consumed 300,000 kkg (28 percent), and the phenol resins (consumptive use) consumed 288,000 kkg (27 percent).
- (6) No more than 55,000 kkg (5 percent) of the direct production levels were used in non-consumptive applications.
- (7) No solid waste or waterborne releases of formaldehyde could be quantified.

For a better perspective on the significance of the sources of release, the release levels are ranked in order of decreasing quantity in Table 2.

In general, the emissions from indirect production are concentrated in urban and industrial areas. Most of the facilities involved in the manufacture and processing of formaldehyde and products containing formaldehyde are located in the Northeastern United States, along the Gulf Coast, and in the Pacific Northwest. The plants range in size from large, fully integrated plants that produce the raw materials, resins, and end-use products to small, specialized facilities that may produce only one product line of a particular consumer good.

Formaldehyde is potentially released from many sources that could not be quantitatively addressed. These sources include derivative chemicals containing residual levels of formaldehyde (e.g., 1,4-butanediol), products containing unreacted formaldehyde (e.g., embalming fluids and deodorizing agents), and derivatives containing labile formaldehyde bonds (e.g., urea-formaldehyde resins). Releases from these sources may occur during their production, processing, use by consumers, or disposal and may be emitted to air, land, or water throughout the United States.

Note: Recent estimates from OAQPS for formaldehyde emissions from stationary and mobile sources and from photochemical oxidation are included in a footnote to Table 2. The value for photochemical production differs considerably from that estimated by OPTS. Attempts are underway to develop agreed-upon air emission estimates for the indirect production of formaldehyde (CONTACT: Jack McGinnity, FTS 629-5504).

TABLE 2: SUMMARY OF AIRBORNE FORMALDEHYDE RELEASES, 1978^a

Source	Formaldehyde Releases	
	Quantity (10 ³ kkg)	Percent of total
Formaldehyde indirect production: ^b		
Combustion of fossil fuels and refuse	330.0	63.0
Photo-oxidation of vehicular exhaust	180.0	34.0
Urea-formaldehyde resin production	3.7	0.7
Phenol-formaldehyde resin production	3.5	0.7
Miscellaneous chemical production	2.7	0.5
Pentaerythritol production	1.5	0.3
Formaldehyde production, direct	1.1	0.2
Acetal resins production	1.0	0.2
Melamine-formaldehyde resin production	0.6	0.1
1,4-Butanediol production	0.6	0.1
Hexamethylenetetramine production	0.2	<0.1
Trimethylolpropane production	<u>0.01</u>	<u><0.1</u>
Total	525	100%

^aSource: (OTS, 1982)

^bRecent data submitted by OAQPS for indirect production as follows (10³ kkg): mobile sources, 208; combustion of fuel oil, gas, and coal, 63; incineration of refuse, 34; oil refineries, 42; photochemical oxidation in the atmosphere, 1390 (Contact: Jack McGinnity, FTS 629-5504).

4. EXPOSURE ROUTES* (CONTACT: Nancy Pate, FTS 629-5502)

Over 97 percent of the formaldehyde releases are airborne and are associated with the incomplete combustion of fossil fuels and trash, and the photochemical oxidation of hydrocarbons from vehicular exhaust. These processes occur primarily in urban and industrial areas. Much lower levels of inadvertent release are expected to occur in rural areas.

Because of the scarcity of data concerning exposure via routes other than inhalation, only the inhalation route will be discussed in detail. Table 3 is a summary of the available inhalation exposure data. The table shows that three situations have the potential for significant exposure: residences using particleboard and/or urea-formaldehyde foam insulation; biology laboratories; and autopsy rooms. Two other situations, mushroom farming and particleboard veneering, also show potential for significant exposures based on monitoring data, but these data may not be representative of general levels for those occupations. Exposure for most other occupations related to formaldehyde is in an order-of-magnitude range below the high exposure situations mentioned above. Typical ambient exposures (0.001 to 0.03 ppm) are rather low in comparison to almost all occupational exposures. The highest levels of atmospheric formaldehyde have been recorded in urban areas. Typical urban levels are on the order of 0.005 ppm while in non-urban areas levels can be assumed to be between the background level of 0.0004 ppm and the typical urban level of 0.005 ppm.

The reader is cautioned that most of the data used for this exposure assessment, while useful for obtaining rough estimates of exposure, probably are not statistically representative of the categories for which they were used. Assessing risk based on these exposure values should therefore be done with care.

The most significant limitations in the exposure data are that many of the data probably are not statistically representative and that some of the data represent levels that probably could not be tolerated by a person for more than a brief period of time. The lack of statistical representativeness has been confirmed for some of the data. Because, in general, sampling sites were selected purposefully from among those locations where a formaldehyde problem was suspected and because time periods for air sampling appeared to be selected arbitrarily, the data probably are not representative of the average exposures for the studied populations. In many cases, the data are of marginal analytical quality, generally because of insufficient information on sampling, analytical, and quality assurance procedures. Although these limitations are recognized, there are at present no hard data on which to make more representative and more realistic estimates of exposure. The procedures used to arrive at these exposure estimates and their limitations are described in detail in the source document (OTS, 1982).

* The information in this section is taken from a recent document prepared by the Office of Toxic Substances (OTS, 1982).

Almost half the formaldehyde produced is consumed to make resins for adhesives. These adhesives are used by the construction industry for manufacturing particleboard, plywood, and urea-formaldehyde foam insulation. Release of formaldehyde from these products may be a major source of exposure in the home. While many formaldehyde-derived plastics release little formaldehyde during normal use, urea-formaldehyde resins may decompose and release formaldehyde at a faster rate.

Formaldehyde is very water soluble and may be discharged to aquatic environments. However, there is essentially no data which would permit water releases to be estimated. The amount of formaldehyde present in wastes and subsequent releases associated with incineration or leachate from landfills also cannot be estimated.

Formaldehyde contamination of foods from anthropogenic sources (such as the use of formaldehyde in packaging materials) is not apparent from the available monitoring data. Formaldehyde has been detected in some foods, but the sources are frequently non-anthropogenic. For example, in some fish species, reduction of trimethylamine oxide yields formaldehyde. Studies indicate that formaldehyde levels in fish and shrimp increase with storage time.

TABLE 3: SUMMARY OF INHALATION EXPOSURE ESTIMATES

Subpopulation	Estimated number of people exposed	Exposure level (ppm)	Duration (hr/wk)	Individual exposure (ppm-hr/yr)*	Estimated yrs exposed
<u>I. Occupational exposures</u>					
Direct producers of formaldehyde	420	1.1-1.6 a	40	2,300-3,300 a	40 x 10 a
Users of formaldehyde:					
Resin producers	2,000-6,200	0.1-1.7 a	40	200-3,500 a	40 x 10 a
Plywood/particle- board manufacturing	21,000-30,000	1-2.5 r	40	2,000-5,200 r	40 x 10 a
Furniture production (veneering)	unknown	0.008-6.4 r	40	17-13,000 r	40 x
		0.4-2.8 a	40	800-5,800 a	10 x
Office trailer occupants	unknown	0.02-0.10 r	40	42-200 r	15 x
		0.06 a	40	120 a	5 a
Workers in U-F foam insulated buildings	unknown	<0.5-3.1 r	40	<1,000-6,400 r	40 x 10 a
U-F foam producers/ distributors	30-80	0.06-5.4 r	40	125-11,000 r	40 x
		0.19-1.5 a	40	395-3,100 a	10 a
U-F foam installers/ dealers	2,000-15,000	<0.02-1.3 r	40	<42-2,700 r	40 x 10 a
Molded products producers	unknown	0.01-4 r	40	<20-8,300 r	40 x
		0.09-0.53 a	40	190-1,100 a	10 a
Textile producers	360-6,000	<0.1-1.4 r	40	<200-2,900 r	40 x
		0.25-0.7 a	40	520-1,600 a	10 a

TABLE 3. SUMMARY OF INHALATION EXPOSURE ESTIMATES (Continued)

Subpopulation	Estimated number of people exposed	Exposure level (ppm)	Duration (hr/wk)	Individual exposure (ppm-hr/yr)*	Estimated yrs exposed
Paper and paper products producers	7,200-45,000	0.01-0.28 r 0.05-0.08 a	40 40	20-580 r 100-170 a	40 x 10 a
Fertilizer producers, appliers	500-900	0.2-1.9 r 0.9 a	30 30	310-3,000 r 1,400 a	40 x 10 a
Users of formaldehyde as a disinfectant or preservative:					
Embalmers/funeral services	70,000	0.20-4.0 r 0.52-2.1 a	20 20	200-4,200 r 540-2,200 a	40 x 10 a
Pathologists	12,000	0.06-7.9 r 4.8 a	30 30	12,000 x 7,500 a	40 x 10 a
Agricultural production (mushroom farms)	unknown	<0.5->10 r 2.68 a	40 40	<1,000->20,000 x 5,600 a	40 x 10 a
Biology instructors (college/univ.)	13,000	2.75-14.8 r 8.3 a	20	2,000-11,000 r 6,000 a	40 x 10 a
Biology instructors (high school)	22,000	2.75-14.8 r 8.3 a	5	500-2,700 a 1,500 a	40 x 10 a
College students	1,200,000	2.75-14.8 r 8.3 a	10	990-5,300 r 3,000 a	8 x 4 a
High school students	unknown	2.75-14.8 r 8.3 a	1	99-530 r 300 a	2 x 1 a

TABLE 3. SUMMARY OF INHALATION EXPOSURE ESTIMATES (Continued)

Subpopulation	Estimated number of people exposed	Exposure level (ppm)	Duration (hr/wk)	Individual exposure (ppm-hr/yr)*	Estimated yrs exposed
Producers of rubber and misc. plastics (rubber hose production)	6,100-28,000	0.02-0.04 r 0.04 a	40 40	<42-83 r 83 a	40 x 10 a
Glue producers	unknown	0.09-0.17 r	40	193-350 r	40 x 10 a
Producers of paving and roofing materials	unknown	0.03-0.07 r 0.05 a	40 40	60-150 x 100 a	40 x 10 a
Primary metal industries (includes iron and steel foundries)	540-15,000	<0.02-18.3 r 0.43	30 30	<30-29,000 r 670 a	40 x 10 a
Locomotive mechanics	unknown	0.015-0.07 r	40	31-150 r	40 x 10 a
II. Consumer use exposures					
Residents, from plywood/particleboard					
Mobile homes	2,200,000	<0.03-2.54 r 0.4 a	100-150	<156-20,000 r 2,000-3,100 a	15 x 5 a
Conventional homes	unknown	0.04-1.8 r 0.5 a	100-150	200-14,000 r 2,600-3,900 a	15 x 5 a
Residents, from U-F foam	1,330,000-1,560,000	0.05-3.4 r 0.72 a	100-150	260-27,000 r 3,700-5,600 a	15 x 5 a

TABLE 3. SUMMARY OF INHALATION EXPOSURE ESTIMATES (Continued)

Subpopulation	Estimated number of people exposed	Exposure level (ppm)	Duration (hr/wk)	Individual exposure (ppm-hr/yr)*	Estimated yrs exposed
Residents from foam/particleboard (unspecified or both)	unknown	0.1-2.92 r 0.22-0.99 a	100-150	520-23,000 r 1,100-7,700 a	5 a
III. Ambient exposures					
Air (U.S. ambient)	220,000,000	<0.001-0.03 r	168	<9-262 r	70 a
Water	220,000,000	negligible			.

x = maximum data observed or "worst case"

r = range

a = average, median, or "typical" value

* Yearly exposures for occupations where weekly exposures are 40 hrs per week were estimated using a 2,080-hr work year. Occupations where exposures are less than 40 hours per week were estimated as a fraction of the 2,080-hr work year (e.g., for embalmers, weekly exposure is 20 hrs/wk, and yearly exposure is based on 20/40 x 2,080, or 1,040 hrs/yr). Items which relate to school settings were calculated using a 36-week year times the weekly exposure duration. Non-occupational exposure, such as residential exposures or ambient exposures, were based on a 52-week year times the weekly exposure duration.

Source: (OTS, 1982); categories for which no exposure level could be estimated have been deleted. See the OTS document for other potential occupational exposure sections.

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available in the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568 or Robin Heisler at FTS 382-3557.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. (EPACASR is scheduled to be added to CIS in early 1984.) For further information, contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information, contact Dr. Steve Heller at FTS 382-2424.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Doug Sellers at FTS 382-2320.

5.5 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is a sophisticated switching network based on heterogeneous distributed data base management and networking concepts. CSIN offers efficient access to on-line information resources containing data and information relevant to chemical substances, as well as information covering other scientific disciplines and subject matters. The purposes of CSIN are two-fold: first to meet the growing chemical data and information requirements of industry, academe, government (Federal and State), public interest groups, and others; and secondly to reduce the burden on the private and public sector communities when responding to complex Federal legislation oriented to chemical substances.

CSIN is not another data base. CSIN links many independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems". Users may converse with any or all systems interfaced by CSIN without prior knowledge of or training on these independent systems, regardless of the hardware, software, data, formats, or protocols of these information resources.

Information accessible through CSIN provides data on chemical nomenclature, composition, structure, properties, toxicity, production uses, health and environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, seven independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), Chemical Information System (CIS), CAS-On-Line, SDC's ORBIT, Lockheeds's DIALOG, Bibliographic Retrieval Service (BRS), and the US Coast Guard's Hazard Assessment Chemical System (HACS). For further information contact Dr. Sid Siegel at 202-395-7285.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 500 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. The clearinghouse listed 38 citations for formaldehyde. For further information, contact Irvin Weiss at FTS 382-5918.

6. REGULATORY STATUS (Current as of 9/83)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- o Section 311 - Formaldehyde is classified as a hazardous substance (40CFR116) and discharges are subject to reporting requirements (40CFR117.3).

Resource Conservation and Recovery Act (RCRA)

- o Section 3001 - Formaldehyde is listed as a toxic waste (40CFR261.33) and as a hazardous waste constituent (40CFR261.32) in wastes generated in the production of acetaldehyde (Waste streams Nos. K009 and K010) and in the production of the pesticide phorate (Nos. K038 and K040).
- o Section 3002 to 3006 - Standards concerning the generation, transportation, treatment, storage and disposal of hazardous wastes as defined above (40CFR262 to 265).

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- o As an inert ingredient, formaldehyde is exempt from any tolerance when used at less than 1 percent of pesticide ingredients (40CFR180.1001(d)).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- o Specifies permissible exposure limit for formaldehyde (3 ppm) as an 8-hour TWA, with ceiling level (5 ppm) and peak level (10 ppm) for 30 minutes (29CFR1910.1000). Construction industry standards under the Contract Work Hours and Safety Standards Act are the same (29CFR1926.55).

DOT - Hazardous Materials Transportation Act

- o Regulations for transporting hazardous materials; identification and listing of hazardous materials, including formaldehyde (49CFR171 to 177).
- o Port and Tanker Safety Act - Regulations governing shipping vessels carrying hazardous liquids (46CFR150, 151, 153, and 154a).

FDA - Federal Food, Drug, and Cosmetic Act

- o Regulations concern permissible components of the color additive FD & C Blue No.2 (21CFR74.102); defoaming agents used in processed foods (21CFR173.340); adhesives used in food packaging

(21CFR175.105..300); food contacting paper and paperboard (21CFR176.170 .180, .200, .210, .177). Also permissible use in food additives (21CFR178, 181). These regulations apply to formaldehyde or formaldehyde copolymers.

6.2 Proposed Regulations

6.2.1 EPA Programs

Clean Air Act

- o New Source Performance Standards (NSPS) have been proposed for the Synthetic Organic Chemicals Manufacturing industry. The standards would limit the emissions of volatile organic chemicals (VOC), including formaldehyde (46FR1136).

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund)

- o CERCLA provides for the liability, compensation, cleanup, and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites (42USC9601; PL-96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46FR54032).
- o Revisions to the National Contingency Plan (NCP) required by CERCLA have been issued in a proposed rule (47FR10972). Adjustments to the statutory reportable quantities have been proposed; however, the RQ for formaldehyde is still under assessment, and the statutory RQ based on Section 311 of the CWA is still in effect (48FR23552).

6.2.2 Other Programs

DOT - Port and Tanker Safety Act

- o Proposed revision of regulations for vessels carrying hazardous liquids (45FR48058).

DHUD

- o The Department of Housing and Urban Development has proposed formaldehyde standards to control indoor air quality in manufactured (mobile) homes. Product standards would limit formaldehyde emissions from plywood and particle board materials (48FR37136).

6.3 Other Actions

- o EPA (Office of Drinking Water) has issued an informal guidance level for formaldehyde (see Section 7.2).
- o A rule issued by the Consumer Product Safety Commission (CPSC) banning the use of urea-formaldehyde foam (UFF) insulation in households and schools (47FR14366) has been vacated by the United States Fifth Circuit Court of Appeals. CPSC voted to establish a Chronic Hazard Advisory Panel (CHAP) on formaldehyde and to initiate a new program to address hazards associated with formaldehyde in insulation and other consumer products.
- o FDA's National Center for Toxicological Research (NCTR), under the sponsorship of EPA, will convene a Consensus Workshop on Formaldehyde to examine existing scientific data and to identify future research needs (48FR36201; CONTACT: William McCallum, FTS 542-4513).

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- o OSHA limits (40FR1910.1000)
 - 8-hour TWA 3 ppm
 - Ceiling 5 ppm
 - Peak 10 ppm
- o NIOSH recommended ceiling: as low as practically possible
- o American Conference of 2 ppm
 Governmental Hygienists
 (ACGIH) threshold limit
 value (TLV)
- o The Department of Housing 0.4 ppm
 and Urban Development
 (DHUD) has proposed product
 standards to regulate
 formaldehyde levels in
 mobile homes. DHUD estimated
 that this level provides
 reasonable protection
 (48FR37136).

7.2 Water

- o Hazardous spill rules require 1000 lbs
 notification of spills equal
 to or greater than the
 reportable quantity
 (40FR117.3)
- o A Health Advisory suggesting 30 ug/l
 an acute exposure guidance
 level for short term exposure
 to formaldehyde in drinking
 water has been issued by the
 Office of Drinking Water (ODW).

* See Appendix A for a discussion of the derivation, use, and limitations of these criteria and standards.

8. SPILL OR OTHER INCIDENT CLEAN UP/DISPOSAL (CONTACT: National Response Center 800-424-8802; in Washington, 426-2675)

8.1 Hazards and Safety Precautions

Formaldehyde solutions emit toxic formaldehyde fumes, producing irritation of eyes, nose, throat and skin. Formaldehyde is a suspected human carcinogen and should be handled with caution.

Formaldehyde will burn and may be ignited by heat, sparks and flame. Flammable vapor may spread from spill. Vapor is an explosion hazard indoors, outdoors, or in sewers. Fire produces poisonous gases.

8.2 First Aid

Move victim to fresh air. If not breathing give artificial respiration; if breathing is difficult, give oxygen. In case of contact, flush eyes or skin with running water. If ingested, dilute, inactivate, or absorb formaldehyde by giving milk, activated charcoal, or water. Do not use gastric lavage or emetics. Treat for shock.

8.3 Emergency Action

Spill or Leak

Do not touch spilled material; use water spray to reduce vapors. Stay upwind and wear protective clothing and breathing apparatus. Remove all ignition sources.

Fire

For small fires, use dry chemical, CO₂, water spray, or foam. For large fires, use water spray, fog, or foam. Move containers from fire area if possible, stay away from ends of tanks, and cool containers with water from the side until well after fire is out.

Isolate for one-half mile in all directions if tank or tank car is involved in fire.

8.4 Notification and Technical Assistance

Section 103(a) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or "Superfund") requires notification of the National Response Center (NRC; 800-424-8802; in Washington, 426-2675) if releases exceed reportable quantities (1,000 lbs in the case of formaldehyde).

For emergency assistance call CHEMTREC: 800-424-9300. Within EPA, information may be obtained from the Division of Oil and Special Materials (1-202-245-3045).

8.5 Disposal

Generators of more than 1,000 kg (2,200 lbs) of hazardous waste (or residues from spill cleanup) per month are subject to RCRA regulations. The following specific waste streams which contain formaldehyde are subject to RCRA regulations:

- Distillation bottoms (K009) and side cuts (K010) from the production of acetaldehyde from ethylene.
- Wastewater from washing and stripping (K038) and treatment sludge (K040) from the production of the pesticide phorate.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air (CONTACTS: Michael E. Beard, FTS 629-2623)

Formaldehyde (CH_2O) is not a regulated air pollutant,* therefore, no Agency-approved procedure is available. However, measurements of atmospheric CH_2O using a chromotropic acid procedure have been reported in the literature and a tentative method has been published by the Intersociety Committee (Methods of Air Sampling and Analysis, 2nd Edition, American Public Health Association Intersociety Committee, 1015 Eighteenth St., NW, Washington, D.C. 20036).

Formaldehyde is sampled by bubbling ambient air through an absorber containing distilled water. A sampling rate of one liter per minute for 24 hours is recommended, but shorter sampling times may be used where concentrations are sufficiently high. The effect of storage on the sample is unknown.

Formaldehyde in the solution is determined by adding chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulfonic acid disodium salt) and sulfuric acid to form a purple solution. The absorbance of the solution at 580 nm is proportional to the formaldehyde concentration. A range of 0.1 ug/ml to 2.0 ug/ml of formaldehyde can be measured in the solution using this procedure. A concentration of 0.1 ppm CH_2O can be determined from a 25-liter air sample. Analyses of samples containing 1 to 20 ug CH_2O by three laboratories gave a precision of ± 5 percent. There are no significant positive interferences, including other aldehydes, but several negative interferences are reported. An 8:1 excess of phenols over CH_2O results in a negative interference of 10 to 20 percent. A 10:1 ethylene and propylene excess over CH_2O results in a negative interference of 5 to 10 percent. A 15:1 excess of 2-methyl-1,3-butadiene showed a 15 percent negative interference. Aromatic hydrocarbons and cyclohexanone also produce negative interferences.

No quality assurance reference materials are currently available for formaldehyde.

9.2 Water

Formaldehyde is not a priority pollutant and there are no Agency procedures at this time for the analysis of formaldehyde in water. However, methods used for analysis of formaldehyde air samples may presumably be applied to water samples because formaldehyde is usually analyzed in water solutions in these procedures (see Sections 9.1 and 9.4).

* Formaldehyde is indirectly regulated as a "volatile organic compound" but no procedure is required for the specific analysis of formaldehyde.

9.3

Method 8.01 in Test Methods for Evaluating Solid Waste - Physical/Chemical Methods (US EPA/SW-846/1980) is approved for analyses of formaldehyde in solid wastes.

Three possible sample preparation techniques that could be applicable to the formaldehyde determination by GC/MS are solvent extraction, modified purge and trap, and vacuum extraction. However, no recovery and precision data are available for any of the above methods when applied to the quantitation of formaldehyde--most methods have problems.

The solvent extraction technique is recommended only for concentrations exceeding 1 ppm, while purge and trap methods may give low recoveries because of the relatively high solubility of formaldehyde in water.

With the vacuum extraction technique, the volatiles are extracted from the sample using a vacuum. The extracted volatiles are collected in a liquid nitrogen-cooled trap. After extraction, 5 ml of water are added to the extract and the sample is analyzed as a 5-ml water sample using Method 624 (44FR69532, gas chromatography/mass spectroscopy).

In a recent Japanese publication (referenced in Chem. Abstracts 94:141037v) a method is described for the determination of formaldehyde at the ppb level in clothes. The compound is extracted into water, derivatized, the derivative extracted into hexane and determined by GC/EC.

Standards can be obtained from Radian Corporation or EMSL-Las Vegas (see Contact above). Supleco supplies diluted standards but the concentrations are not verified. Standard solutions may also be prepared in the laboratory from reagent-grade formaldehyde (40 percent) to the appropriate dilution using methanol.

9.4

The NIOSH Manual of Analytical Methods, 2nd Edition, contains procedures for the collection and analysis of formaldehyde vapors. Methods 125 and 235 (Vol. 1) employ chromotropic acid to form a colored derivative which is detected spectrophotometrically. Collection by drawing the air through alumina followed by desorption with 1 percent methanol in water (method 235) allows measurement in the 0.4 to 52 mg/m³ range (0.3 to .43 ppm).

In Method S327 (Vol. 4) air is drawn through a solution of Girad's T reagent which traps formaldehyde in an ionic water soluble form. The derivative is then analyzed by polarography. The working range is reported to be 1.4 to 20 ppm.

The most recent NIOSH procedure (318, Vol. 6) involves adsorption of formaldehyde on impregnated charcoal, desorption with H_2O_2 to yield formic acid ($HCOOH$), and isolation and quantification by ion exchange chromatography. Recoveries are excellent, precision is 9.7 percent (16 to 320 ug/sample), and the working range is 0.03 to 2 mg/ m^3 for a 9.6 liter air sample (3 to 200 ug/sample).

Monitoring and analysis methods for formaldehyde have recently been summarized in a document prepared by the Office of Toxic Substances (OTS, 1982).

REFERENCES

The major references used in the preparation of this document are listed below. EPA references are listed by the EPA office of origin and the year of publication. For further information refer to the contacts given throughout this document or contact the relevant EPA offices given at the end of this section.

- (CAG, 1979) Preliminary Risk Assessment on Formaldehyde-Type I-Air Program, Carcinogen Assessment Group, Office of Health and Environmental Assessment (1979).
- (CIIT, 1981) Final Report on a Chronic Inhalation Toxicology Study in Rats and Mice Exposed to Formaldehyde, by Battelle Labs for the Chemical Industry Institute of Toxicology (1981). [For a summary, see CIIT Activities, Vol. 2, No. 3; March, 1982].
- (NIOSH, 1981) Current Intelligence Bulletin 34: Formaldehyde-Evidence of Carcinogenicity, National Institute of Occupational Safety and Health, April 15, (1981).
- (NRC, 1981) Formaldehyde and Other Aldehydes, National Research Council, NTIS No. PB82-128075 (1981).
- (NTP, 1980) Report of the Federal Panel on Formaldehyde, National Toxicology Program, RTP, November (1980).
- (ODW, 1981) Informal Guidance Level for Formaldehyde, EPA Draft, Office of Drinking Water, August (1981).
- (OPTS, 1980) Level I Materials Balance: Formaldehyde, EPA Draft, Contract No. 68-01-5793, Office of Pesticides and Toxic Substances (1980).
- (OSW, 1980) Background Document-RCRA Subtitle C, Appendix A: Health and Environmental Effects Profile, P. 104, Office of Solid Waste (1980).
- (OTS, 1976) Investigation of Selected Potential Environmental Contaminants: Formaldehyde, EPA-560/2-76-009, Office of Toxic Substances (1976).
- (OTS, 1982) Technical Document: Formaldehyde EPA-Draft Document, Office of Toxic Substances, March (1982).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
Effluent Guidelines Division	426-2571

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergenices call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information and Analysis Program

382-2249

Lead

LEAD

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-4
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-1
<u>Exposure</u>	4-1
Air Exposure	4-4
Water Exposure	4-4
Other Exposure Routes	4-5
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-3
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Hazardous Waste	7-1
Other	7-1

<u>Spill or Other Incident Clean-Up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-2
Disposal	8-2
 <u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
Solid Waste	9-4
Other Samples	9-4
Quality Assurance	9-4
 <u>References and Office Contacts</u>	 R-1

LEAD

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Lead has by far the largest use in the United States of any heavy metal due to its utility and abundance. Although widely used in metallic form (Pb), there also are over 70 lead compounds produced in the United States. Table 1 lists the physical/chemical properties of some lead compounds of commercial or environmental significance. Automotive uses dominate the market for lead in the form of lead oxides for storage batteries and as alkyl lead fuel additives (IERL, 1979).

Some properties of metallic lead that enhance its utility are softness, malleability, high density, low melting point, and corrosion resistance. Inorganic lead compounds are generally ionic, nonvolatile, and moderately or highly insoluble in water. In contrast, organolead compounds are usually nonionic, volatile, and lipid soluble. The only widely used organolead derivatives are tetraethyl lead (TEL) and tetramethyl lead (TML) (HERL, 1978).

1.2 Chemistry and Environmental Transport

Although lead can exist in two oxidized states (+2,+4), the divalent species (Pb^{+2}) dominates the inorganic chemistry of lead. Divalent lead has a strong affinity for inorganic ions containing oxygen (e.g., carbonate) or sulfur (sulfide). Furthermore, lead can complex with electron-rich ligands in many organic compounds such as amino acids, proteins, and humic acid. In organolead compounds the lead is tetravalent, (e.g., TEL) and the covalent Pb-carbon bond can dissociate thermally or photolytically to yield free radicals (HERL, 1978; OTS, 1979).

The atmosphere is the primary medium for transport of lead (in the form of inorganic particulates). The combustion products of fuels containing antiknock lead compounds (TEL or TML) are the largest source of atmospheric lead pollution. The organometallic TEL and TML decompose during combustion and the lead is scavenged from the engine by halogenated fuel additives. Lead is emitted in the exhaust as particulate matter primarily in the form of lead halides (e.g., $PbBrCl$). Although much of this particulate lead settles very closely to roadways, smaller particles are widely dispersed so that the average residence time of lead in the atmosphere is about 10 days. Complex chemical and photochemical reactions in the atmosphere transform lead halides to relatively insoluble salts (i.e., $PbCO_3$, PbO , $PbSO_4$). Atmospheric lead particles are removed by sedimentation, dry deposition, and precipitation (HERL, 1978; ORD, 1977).

TABLE 1: PROPERTIES OF LEAD COMPOUNDS^a

Chemical Name and Formula	CAS Number and Synonyms	Melting Point (°C)	Boiling Point (°C)	Water Solubility (per liter)	Specific Properties and Uses
Lead	7439-92-1	328	1,740	0.3 mg	High density (11.3 g/cm ³). Often used in alloy form with tin and/or antimony
Lead acetate, trihydrate Pb(OOCCH ₃) ₂ ·(H ₂ O) ₃	6080-56-4 Acetic acid, lead (2+) salt, trihydrate; sugar of lead	75	200 (dec)	456g (15°C)	Sweet tasting. Used in paints and textile dyeing
Lead carbonate PbCO ₃	598-63-0 Carbonic acid, lead (2+) salt (1:1); white lead	315 (dec)	---	1.1 mg (20°C)	Used commercially in paints and ceramics in the form of basic lead carbonate
Lead chloride PbCl ₂	7758-95-4 Lead (2+) chloride	501	950	9.9 g (20°C)	Automotive combustion product. Used in paints and manufacturing lead compounds
Lead nitrate Pb(NO ₃) ₂	10099-74-8 Nitric acid, lead (2+) salt	470 (dec)	---	376 g (0°C)	Used in manufacturing lead compounds, and the match industry
Lead oxide PbO	1317-36-8 Lead monoxide; litharge	886	1,472	17 mg (20°C)	Used as oxidized powder in batteries

TABLE 1: PROPERTIES OF LEAD COMPOUNDS (cont.)

Chemical Name and Formula	CAS Number and Synonyms	Melting Point (°C)	Boiling Point (°C)	Water Solubility (per liter)	Specific Properties and Uses
Lead sulfide ^b PbS	1314-87-0 Lead monosulfide; galena	1,114	---	0.86 mg (20°C)	Major mineral source for lead production
Lead sulfate ^b PbSO ₄	7446-14-2 Sulfuric acid, lead (2+) salt (1:1)	1,170	---	42 mg (25°C)	Used in pigments and batteries
Tetraethyl lead ^b Pb(C ₂ H ₅) ₄	78-00-2 Plumbane, tetraethyl	-137	200 (dec) Flash point 85°	0.2 mg (20°C) [soluble in organic solvents]	Density, 1.65 Degraded photochemically Antiknock agent
Tetramethyl lead ^b Pb(CH ₃) ₄	75-74-1 Plumbane, tetramethyl	-28	110 Flash point 38°	20 mg (20°C) [soluble in organic solvents]	Density, 2.0 Degraded photochemically Antiknock agent

^a From data summarized in (IARC, 1980) unless otherwise noted.

^b (Weast, 1979).

Lead has a low solubility in natural waters due to the limited dissolution of the carbonate, sulfide, and sulfate salts. In hard water, the carbonate concentration is sufficient to keep lead concentrations low (30 ppb). However, a drop in pH in soft water can result in alarming increases in lead solubility. Lead introduced into surface waters is readily adsorbed onto sediments with organolead complexes (e.g., with humic acid) facilitating sorption by clays or metal hydroxides. Due to the relative immobility of lead in water it tends to accumulate wherever delivered. However, anaerobic sediment microbes can methylate several lead derivatives to form a volatile organolead compound (TML). Furthermore, any changes in water characteristics caused by acid rain, urban runoff, industrial effluents or dredging may release lead from sediments. The effectiveness of these biological, chemical, and physical mechanisms in remobilizing lead is unknown (OWRS, 1979; OWRS, 1980b).

Soils represent the major sink for pollutant lead. The adsorption or precipitation of lead in soils is promoted by the presence of organic matter, carbonates, and phosphate minerals. Lead usually accumulates in topsoil due to complexation with organic matter and the transformation of soluble lead compounds to relatively insoluble sulfate or phosphate derivatives. The efficient fixation of lead by most soils greatly limits the transfer of lead to aquatic systems and also inhibits absorption of lead by plants. However, leaching of lead can be relatively rapid from some soils, especially at highly contaminated sites or landfills (HERL, 1978; OTS, 1979).

2. EFFECTS INFORMATION

- 2.1 Health Effects (CONTACTS: Jerry Stara, FTS 684-7531;
Les Grant, FTS 629-2266; Bob McGaughy,
FTS 755-3968; Bill Marcus, 382-3037)

Lead (Pb) poisoning, often referred to as "plumbism", can result from its inhalation, ingestion, and in some cases, absorption through skin. The effects of lead in humans are well documented and levels once considered acceptable have been lowered due to increasing evidence of subtle effects. The principal target organs affected by lead are the erythroid cells of bone marrow, the kidney, and the central and peripheral nervous system. The extent of lead toxicity varies with different lead compounds and their physical/chemical properties (e.g., soluble lead salts are considered more toxic than insoluble lead salts and organic lead compounds, in general, are more toxic than inorganic lead compounds) (HERL, 1978).

Many toxic effects of inorganic lead can be attributed to the affinity of lead for thiol groups (-SH) and other organic ligands in proteins. Low concentrations of Pb^{+2} inhibit a select group of enzymes including thiol-dependent enzymes involved in heme synthesis and mitochondrial energetics. The toxicologic effects of lead may result from the ability of Pb^{+2} to uncouple oxidative phosphorylation and modify mitochondrial ion transport (especially for calcium, Ca^{+2}). The volatile, lipid soluble organoleads, TEL and TML, are rapidly absorbed either by inhalation or percutaneously. The extreme toxicity of tetraalkyl lead compounds is apparently due to their rapid metabolism to unstable and highly toxic trialkyl and dialkyl lead derivatives (HERL, 1978).

2.1.1 Acute Toxicity

The following symptoms may occur after acute lead exposure: anorexia, vomiting, malaise, and convulsions due to increased intracranial pressure. Severe acute exposure may lead to acute lead encephalopathy. These symptoms are most common in young children with a history of pica. Colic has also been demonstrated in cases of acute poisoning (HERL, 1978). The mechanism for this occurrence is not understood. Short-term exposure to high lead levels ($>100PbB^*$) can produce severe renal (kidney) effects (e.g., aminoaciduria) due to reversible tubular damage (WHO, 1977).

Anemia is an early symptom of both acute and chronic lead poisoning. Anemia due to lead poisoning is thought to result from a decrease in red blood cell production and increased destruction due to lead interference (HERL, 1978). Because this form of anemia has many morphologic features in common with iron deficiency anemia and thalassemia, it is often not easily distinguished as lead poisoning (NAS, 1972).

* PbB 's are expressed as micrograms of lead per 100 ml of blood, ug/dl.

2.1.2 Chronic Toxicity

The effects of lead on the hematopoietic system are particularly important since current knowledge suggests that this system is the "critical organ." The disruption of hemoglobin synthesis is generally considered the first observable adverse effect of lead exposure. Lead inhibits d-aminolevulinic acid dehydrase (ALAD) and heme-synthetase (enzymes involved in hemoglobin synthesis) both in vitro and in vivo at relatively low levels of chronic lead exposure. Elevation of the concentrations of the substrates for these two enzymes in plasma and urine (ALA) and in erythrocytes (PROTO) increase as blood lead levels (PbBs) increase. Rises in PROTO and ALA occur at PbBs somewhat below those associated with a decrement of hemoglobin. A decrement in hemoglobin first appears at PbB = 50 in adults and at PbB = 40 in children, whereas a distinct elevation in ALA in the urine (ALAU) first appears at PbB = 40 in men and children and somewhat lower in women. Rises in PROTO first appear at PbB = 15 to 20 in women and children and at PbB = 25 in men (OWRS, 1980a).

Exposures to high concentrations of lead, resulting in PbBs ranging from 80-120 ug/dl of blood can give rise to lead encephalopathy. The major features are dullness, irritability, ataxia, headaches, loss of memory and restlessness. These symptoms often progress to delirium, mania, coma, convulsions, and even death. In addition to central nervous system damage, peripheral neuropathy (paralysis) has been reported at somewhat lower PbBs. The same general effects are also described in infants and young children. Encephalopathy due to lead is probably more frequently fatal in children than adults because lead exposure is usually not suspected and because children do not communicate signs and symptoms as readily as adults. The mortality rate among children has been variously reported as being from 5 to 40 percent (OWRS, 1980a).

Subtle neurobehavioral effects occur in children chronically exposed to lead at levels which do not result in clinical encephalopathy. The minimal level of lead exposure, the duration of exposure required, and the period of greatest sensitivity cannot be specified with any degree of certainty. The blood lead levels associated with neurobehavioral deficits (minimal brain dysfunction) in asymptomatic children appear to be in excess of 50 to 60 ug/dl. Future research may reveal that this cut-off point is actually lower (OWRS, 1980a; WHO, 1977).

Chronic toxicity resulting from exposure to organic lead compounds is manifested in elevated blood-lead levels. Inhalation of organic lead compounds first results in toxicity to the central nervous system, but in order to be absorbed into the bloodstream, it must be retained in the lower portions of the lung long enough to be solubilized. The effects of organic lead on the hematopoietic system are not as well documented as those of inorganic lead. Organic lead compounds have a greater affinity for lipid tissues--the brain, body fat, and the liver--than the bone marrow (HERL, 1978).

No conclusive statement can be made as to whether lead is carcinogenic in humans. Although rodents are susceptible to a variety of lead-induced cancers, epidemiological evidence to date indicates no carcinogenic effect on humans. The teratogenic and mutagenic effects of lead in humans also need clarification. Animal studies show that parental exposure to lead increases reproductive problems and teratogenic effects of lead in animals are manifested by congenital skeletal malformations. In humans, however, embryotoxicity apparently precedes tetratogenicity (HERL, 1978).

Lead Poisoning in Children

Children between the ages of 1-5 are most susceptible to acute and chronic lead poisoning. Lead is prevalent in big cities, especially where deteriorated housing exists; paint peelings from this source can contain up to 40 percent lead by weight. (See Section 4 for complete discussion of exposure routes). The majority of lead-poisoning cases in children are due to ingestion of the paint chips containing lead. This can be attributed in part to the sweet taste of leaded chips and to the tendency of children to put foreign objects into their mouths ("pica" - the repetitive ingestion of non-food materials). A higher percentage of ingested lead is absorbed by children than adults (HERL, 1978).

According to a 1976 National Academy of Science (NAS) report, childhood lead poisoning occurs primarily in three stages:

- (1) Asymptomatic lead poisoning in which no clinical symptoms are apparent, but in which measurable metabolic changes occur.
- (2) Symptomatic poisoning in which clinical symptoms such as anorexia, vomiting, apathy, atoxia, drowsiness, or irritability occur.
- (3) Lead encephalopathy with cerebral edema, in which coma or convulsions occur.

Other manifestations of lead poisoning are learning disabilities and hyperkinesis (OTS, 1979).

Because young children are more susceptible to lead-induced neurologic damage (the brain is still growing in a child's early years) and because of their tendency toward pica, children are less resistant to lower levels of lead than adults. Diet (e.g., malnutrition, and calcium and iron deficiencies) has been implicated as a possible cause for elevated intestinal absorption rates for lead and high calcium or phosphate levels have been effective in decreasing lead absorption (OTS, 1979; HERL, 1978).

The fetus is highly sensitive to the neurological effects of lead (due to lack of a blood brain barrier, efficient absorption, and rapid brain growth rate). Lead has been shown to enter the placenta in laboratory animals as well as in humans; lead has been detected

in 12-week-old fetuses and has been shown to increase throughout gestation. Newborns have shown a correlation between their urinary ALA levels with blood-lead levels indicating that heme damage must have occurred "in utero" (OTS, 1979).

2.2 Environmental Effects (OWRS, 1980a)
(CONTACTS: Duane Benoit, FTS 783-9507; John Gentile, FTS 838-4843)

2.2.1 Aquatic Effects

In addition to the acute toxicity of lead towards aquatic life, chronic exposure to lead can delay embryonic development, suppress reproduction, and inhibit the growth rate of fish, crab, polychaetes, ciliate protozoans, and plankton, and reduce photosynthesis and respiration in algae and diatoms.

Freshwater - Three invertebrate freshwater species demonstrate a wide range of susceptibility to lead. LC₅₀ values ranged from 124 ug/l for a scud to 40,800 ug/l for a rotifer. In exposures up to 28 days the scud has been shown to be more sensitive to lead than a snail, cladoceran, and immature stages of the chironomid, mayfly, stonefly, and caddisfly. Edible fish (rainbow trout, brook trout, bluegill) appear to be less sensitive to lead than invertebrate species.

Acute toxicity values ranged from 1,170 ug/l to 8,000 ug/l for rainbow trout and 4,100 ug/l for brook trout in flow-through studies. In static tests, rainbow trout and bluegill species demonstrated acute toxicities of 471,000 ug/l and 442,000 ug/l, respectively, in water of similar hardness. The acute toxicity of lead to other freshwater fish species ranged from 2,400 ug/l to 7,330 ug/l for fathead minnows, 31,500 ug/l for goldfish and 20,600 ug/l for guppies in static tests conducted in water of similar hardness. Acute toxicity decreases as water hardness increases.

The relative acute sensitivities of various freshwater organisms indicate that benthic insects are the least sensitive to lead.

The chronic toxicity of lead has been determined for only two freshwater invertebrate species, Daphnia magna and a snail Lymnea palustris. The acute-chronic ratio of 8.2 was obtained for Daphnia. A lifecycle test with snails demonstrated that lead at a concentration of 25 ug/l significantly decreased survival but not growth or reproduction. This value is lower than the chronic value, 119 ug/l, reported for daphnids.

Chronic tests, in hard and soft water, have been conducted with six species of freshwater fish. These experiments were not lifecycle studies but determined that lead induced spinal deformities in rainbow trout fry at concentrations of 850 ug/l in hard water and as low as 31 ug/l in soft water. This demonstrates that lead is more chronically toxic in soft water than in hard water. Spinal deformities have also been caused by lead in lifecycle tests with brook trout and in early life stage tests with rainbow trout, northern pike, and

walleye. Spinal deformities have not been determined in similar tests with lake trout, channel catfish, white sucker, and bluegill.

Based on static short exposure tests with algae and diatoms, adverse effect concentrations of lead ranged from 500 to 28,000 ug/l. It is assumed that any adverse effects on aquatic plants are unlikely at concentrations below those at which chronic effects on freshwater animals occur.

Saltwater - No standard lead acute toxicity values for saltwater fish species are available. The most sensitive invertebrate species is a copepod Acartia clausi with an LC₅₀ of 668 ug/l. The least sensitive is the soft shell clam Mya arenaria with an LC₅₀ of 27,000 ug/l. The LC₅₀ value of 2,450 ug/l was obtained with oyster larvae Corassostrea virginica and a value of 2,960 ug/l was obtained for mysid shrimp Mysidopsis bahia.

The mysid shrimp Mysidopsis bahia is the only saltwater species for which a chronic test has been conducted on lead. The most sensitive observed adverse effect was reduced spawning at a lead concentration of 25 ug/l. The acute-chronic ratio is 11.9.

No saltwater plant species have been experimentally exposed to inorganic lead. One saltwater algal species has been exposed to two organolead compounds (tetramethyl and tetraethyl). Tetraethyl lead was at least 10 times more toxic. However, no data are available comparing the relative toxicities of inorganic and organic lead compounds.

2.2.2 Other Effects

The bioconcentration factors for four freshwater invertebrate species exposed to lead ranged from 499 to 1,700. Fish do not appear to accumulate lead as readily as the invertebrate species they may eat, as indicated by bioconcentration factors of 42 and 45 for brook trout and bluegills, respectively.

Of concern may be the relatively high bioaccumulation by saltwater species used for human food. The bioconcentration factors for mussels and oysters were 2,570 and 1,400, respectively. Hard clams had a relatively low factor of 17.5.

3. ENVIRONMENTAL RELEASE (CONTACT: Michael Slimak, FTS 426-2503)

Lead is a naturally occurring element in the earth's crust; however, natural sources of emissions are insignificant when compared to anthropogenic releases. Lead enters the environment primarily from auto emissions, ore mining and smelting, and ammunition production. However, the amount of lead released to the environment from auto emissions has been decreasing since 1973. Fifty-six percent of the lead emitted to the environment is released to the atmosphere. Although some lead remains in the atmosphere, a large proportion rapidly settles out in the vicinity of the source. Forty-two percent of lead emissions goes to the land, 1 percent is discharged to the water, and less than 1 percent is indirectly discharged from POTW's. Based on Best Practical Technology (BPT), the Iron and Steel Industry accounts for 87 percent of the industrial point source discharge to the aquatic environment (OWRS, 1980b).

Table 2 lists both the uses of lead and its releases to the environment by media. The release data are only crude estimates and have not been verified by sampling and analysis. Note that lead batteries constitute a non-dissipative use of lead so that 80 percent (Bureau of Mines estimate) of the lead used in storage batteries is recycled (OWRS, 1980b).

3.1 Air Releases (CONTACT: John Copeland, FTS 629-5595)

Significant Sources

- Mobile source: automotive combustion of leaded gasoline
- Primary and secondary lead smelters (SIC 3332 and SIC 3313-3316)
- Battery production plant
- Lead gasoline additive plants
- Primary copper smelters (SIC 3331)

Other Source

- Primary zinc smelters (SIC 3333)

3.2 Water Releases (CONTACT: Michael Slimak, FTS 426-2503)

Significant Source

- Iron and Steel Industry

Other Sources

- Non-ferrous metal
- Pulp and paper
- Inorganic chemicals

TABLE 2: CONSUMPTION OF LEAD AND SOURCES TO THE ENVIRONMENT
FOR 1976 (kkg/yr and %)

I. USES OF LEAD

	<u>kkg/yr</u>	<u>% of Total Uses</u>
A. Lead batteries	764,000	64.5
B. Gasoline antiknock additives	217,500	18.4
C. Red and white lead paint pigments	77,500	6.6
D. Ammunition	66,500	5.6
E. Solder	57,500	4.9

II. RELEASES TO ENVIRONMENT

	<u>kkg/yr</u>	<u>% of Discharges to Land</u>	<u>% of Total Releases</u>
A. Land Discharges			41.9
1. Domestic ore (mining, milling, smelting, refining)	55,989	40.9	17.1
2. Ammunition	50,000	36.6	15.3
3. Weights and ballasts	10,143	7.4	3.1
4. Bearing metals	9,478	6.9	2.9
5. Solders	5,734	4.2	1.8
6. Iron and steel production	5,400	3.9	1.7

	<u>kkg/yr</u>	<u>% of Emissions to Air</u>	<u>% of Total Releases</u>
B. Airborne Emissions			56.2
1. Gasoline additives ^a	175,584	95.5	53.7
2. Combustion of oil	2,630	1.4	0.8
3. Copper and zinc smelting	1,800	1.0	0.6
4. Domestic ore (mining, milling, smelting, refining)	1,403	0.8	0.4
5. Iron and steel production	1,243	0.7	0.4
6. Ammunition	1,147	0.6	0.4

TABLE 2: CONSUMPTION OF LEAD AND SOURCES TO THE ENVIRONMENT
(kkg/yr and %) (cont.)

	<u>kkg/yr</u>	<u>% of Industrial Discharge to Water</u>	<u>% of Total Releases</u>
C. Aquatic Discharges			1.9
1. Industrial discharges			
a. Iron and steel manufacture ^b	1,309	87.2	0.4
b. Inorganic chemical manufacture ^b	83	5.5	
c. Nonferrous metals	53	3.5	
d. Paper and pulp	36	2.4	
e. Pigments	15	1.0	
f. Textiles	6	0.4	
2. POTW's	1,375		0.4
3. Urban Runoff	3,700		1.1

Source: Strategy for Controlling the Environmental Exposure to Lead, Draft Report, OWRS (1980). Most values were adopted from a draft report entitled Exposure and Risk Associated With Lead, OWRS, July 1981, revised March 1982.

^a This value is decreasing because of decrease of use of leaded gasoline.

^b Updated 1980 value, OWRS.

EXPOSURE

The pathways of human exposure to lead are numerous and complex. Humans are exposed to environmental lead through inhalation, ingestion (food and water), and in the case of organolead compounds, through cutaneous absorption. Under normal conditions, the concentration of organic lead present in the environment is so low that cutaneous absorption of organic lead can be ignored, except in cases of accidental or occupational exposure. Inhalation is the major contributor to body burden among those occupationally exposed to lead. For the general population, dietary lead is probably the most significant pathway of exposure, constituting 54-90 percent of all lead intake in adults. However, relative to dietary lead, inhalation may provide an equal or more important route of exposure for persons living in the immediate vicinity of major stationary sources or heavily traveled automobile freeways (OTS, 1979; OWRS, 1980b).

Food packaged in lead-soldered cans contributes 45 percent of lead intake. Remaining lead exposure to food occurs from consumption of leafy crops grown near sources of lead emissions (e.g., highways and smelters). Total individual intake of lead via food ingestion is estimated to be 200 ug/day in urban and rural areas and 1,000 ug/day for those living in the vicinity of smelters (OWRS, 1980b).

Inhalation of lead from the atmosphere is negligible except in localities in which there are ore mining and smelting operations, where estimates of individual lead inhalation are 200 ug/day. Drinking water generally contributes little to daily lead intake, approximately 20 ug/day (OWRS, 1980b).

Consumption of paint, dirt, and dust containing lead represents the largest exposure route for children. Higher exposure occurs in urban areas than in rural areas. Preliminary results of a recently completed four-year study* suggests that between 1976 and 1980, there was a 36.7 percent reduction in the overall mean blood-level in the U.S. population. Decreases were found in all races, ages, and both sexes. The reduction in mean blood levels parallels the reduction in the amount of lead used in the production of gasoline. The amount of lead added to the environment from gasoline dropped from 190,000 kkg in 1976 to 90,000 kkg in 1980 under restrictions imposed on the use of lead as an antiknock additive for gasoline. This means that the high-risk young children living in environments with high doses of lead (i.e., leaded paint, lead already deposited in dust and soil, etc.) will have a greater margin of safety.

Exposure is probably greater in urban areas, since contact with contaminated dirt and dust may result. Infants depending entirely on canned formulas are exposed to significantly greater amounts of lead

*Second National Health and Nutrition Examination (NHANES II), National Center for Health Statistics, reported in the Centers for Disease Control Morbidity and Mortality Weekly Report, Friday, March 19, 1982.

TABLE 3: LEAD EXPOSURE/ABSORBANCE LEVELS

Population Effected	Pathway	Subpopulation	Exposure Conc. (ug/day)	Absorbed Dose (ug/day)	Exposure Criteria (ug/day)	Exceed Criteria
Adults	food	Rural	200	20	----	----
		Urban	200	20	----	----
		Smelting	1,000	100	----	----
	drinking water	Rural	<20	<2	100 ^a	No
		Urban	<20	<2	100	No
		Smelting	<20	<2	100	No
		Leadpipes	100-200	10-20	100	Yes
	air	Rural	2-15	1-5	30 ^b	No
		Urban	15-62	5-21	30	Yes
		Smelting	200	60	30	Yes
Children	food	Rural	100-140	50-70	----	----
		Urban	100-140	50-70	----	----
		Smelting	500	250	----	----
	drinking water	Rural	<10	<5	50 ^c	No
		Urban	<10	<5	50	No
		Smelting	<10	<5	50	No
		Leadpipes	50-100	25-50	50	Yes
	air	Rural	.3-3.4	.1-1.0	6 ^d	No
		Urban	3-13	1-4	6	Yes
		Smelting	40	13	6	Yes

TABLE 3: LEAD EXPOSURE/ABSORBANCE LEVELS (cont.)

Population Effectuated	Pathway	Subpopulation	Exposure Conc. (ug/day)	Absorbed Dose (ug/day)	Exposure Criteria (ug/day)	Exceed Criteria
Children with Pica	paint	wherever avail.	1,000 ^f	500	300 ^e	Yes
	dirt & dust	Urban	1,000	500	300	Yes
		Smelting	1,000	500	300	Yes
	paint, dust & dirt	Urban	2,000	1,000	300	Yes
		Smelting	2,000	1,000	300	Yes

Source: Strategy for Controlling the Environmental Exposure to Lead, Draft Report, OWRS (1980).

a EPA Water Quality Criteria of 50 ug/l; assuming adult consumption of 2 liters/day.

b EPA Air Quality Criteria of 1.5 ug/m³; assuming adult inhalation of 20 m³/day.

c EPA Water Quality Criteria of 50 ug/l; assuming child consumption of 1 liter/day.

d EPA Air Quality Criteria of 1.5 ug/m³; assuming child inhalation of 4 m³/day.

e Calculated from 0.3 mg maximum daily permissible child intake levels (King, 1971).

f Estimates vary widely - figures, however, are representative of consumption due to pica.

than breast-fed infants. Table 3 provides a detailed lead exposure summary (OWRS, 1980b).

4.1 Air Exposure (CONTACT: John Copeland, FTS 629-5595)

Inhalation of particulate lead, usually in the form of elemental lead or lead oxide, can arise near lead and non-ferrous smelters, heavily traveled urban roads, sand blasting (for removal of leaded paints), and roof vents from indoor firing ranges.*

4.2 Water Exposure

In areas where water supplies are stored in lead-lined tanks or transported to the tap by lead pipes, lead concentrations may reach in excess of 1,000 ug/l. The concentration of lead in water transported through lead pipes is dependent upon standing time, pH, and the concentration of dissolved salts. At acidic pH values and low salt concentrations, the solubility of lead in the water is increased. Plastic pipes may release lead stearate (OWRS, 1980a).

The extent of excessive lead in tap water is not known. Special attention should be given to soft water supplies, since they are low in dissolved salts and frequently have pH values at or below pH 6.5 (OWRS, 1980a).

A survey taken of 100 major U.S. cities in 1964 found that 95 percent contained lead at concentrations less than 10 ug/l. A similar study conducted 6 years later of 969 public water supply systems in the United States showed that only 37 sites exceeded the current National Interim Primary Drinking Water Standard of 50 ug lead/liter. This indicates that drinking water as a major source of lead exposure poses a relatively small hazard except in circumstances where lead pipe or lead service connections are in contact with corrosive water. In these cases substantial lead extraction and high drinking water levels occur (OWRS, 1980a).

Hazardous substances from industrial waste land disposal sites are capable of migrating into ground water. Records of hazardous waste incidents include high lead contamination of local ground water. Sludges from POTW may also contain high lead levels and hazards may result from disposal of municipal sludges.**

An analysis of STORET data for the U.S. reveals concentrations of lead at the 50th percentile of 300 ug/l in fish tissue, 25,000 ug/l in sediments, and 14 ug/l in ambient waters. STORET data also show that the criterion for protection of human health (50 ug/l) is exceeded in only 8.4 percent of the water samples (OWRS, 1980b).

* Supplied by OAQPS.

** Supplied by OSW.

4.3 Other Exposure Routes

Food constitutes the major source of lead ingestion by the general population. The nature of food processing may either lower or raise the concentration of lead in the raw product. Washing lowers the lead content but packing in metal cans with lead solder seams tends to increase it. Most of the lead intake from food is attributed to lead introduced during the canning process. The lead is thought to be in the form of microscopic pellets of metallic lead which are not as readily absorbed as are lead salts (OWRS, 1980a).

The content of lead in milk may be another major route of exposure, especially for children who normally consume it in large quantities. Whole raw cow's milk averages about 9 ug/l whereas retail milk contains about 40 ug/l. Evaporated milk averages vary but values of 110 to 870 ug/l have been reported. The higher source of lead in evaporated milk is attributed to lead solder seams and lead particles in the metal containers (OWRS, 1980a).

There is no evidence of lead biomagnification in the food chain, from aquatic vegetation to the edible portions of fish and shellfish. Therefore, fish are not a highly significant source of lead in man's diet. However, of concern may be the relatively high bioaccumulation by some saltwater species used for human food (e.g., mussels and oysters) (OWRS, 1980a).

Adults may acquire clinically significant proportions of lead from "moonshine," or storage of acidic beverages in improperly glazed earthenware (OWRS, 1980a).

Occupational exposure to lead may be excessive. Storage battery plants, primary lead smelters, welding and cutting lead-painted metal structures, automobile radiator repair, and production of lead-base paints may lead to excessive lead exposure. Inhalation and hand-to-mouth transfer are the principal hazards (OWRS, 1980a).

Large numbers of children are exposed to lead from miscellaneous sources. The major source is lead-base paints in the interior of the home and in the soil surrounding the homes. Street dust and associated soil also contain relatively high levels of lead. High levels of lead in soil near roads can be attributed to the combustion of gasoline with lead additives. A study conducted in 1972 of lead content in industrial, agricultural, and residential soils found that there was approximately 2.7 times as much lead in industrial soil as in residential soil. Residential soils were found to contain a slightly higher lead content than agricultural soils. Soil located alongside heavily traveled highways contain the highest concentrations of lead. A sample of soil taken near an expressway in Chicago yielded up to 7,600 ppm at distances up to 13.7 meters from the expressway and 900 ppm up to 45.7 meters (OTS, 1979). These sources could double the daily blood levels of lead in a young child. Also children with pica can acquire high levels of lead in the blood (OWRS, 1980a).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available in the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568 or Robin Heisler at FTS 382-3557.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. (EPACASR is scheduled to be added to CIS in early 1984.) For further information, contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information, contact Dr. Steve Heller at FTS 382-2424.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Doug Sellers at FTS 382-2320.

5.5 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is a sophisticated switching network based on heterogeneous distributed data base management and networking concepts. CSIN offers efficient access to on-line information resources containing data and information relevant to chemical substances, as well as information covering other scientific disciplines and subject matters. The purposes of CSIN are two-fold: first to meet the growing chemical data and information requirements of industry, academe, government (Federal and State), public interest groups, and others; and secondly to reduce the burden on the private and public sector communities when responding to complex Federal legislation oriented to chemical substances.

CSIN is not another data base. CSIN links many independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems". Users may converse with any or all systems interfaced by CSIN without prior knowledge of or training on these independent systems, regardless of the hardware, software, data, formats, or protocols of these information resources.

Information accessible through CSIN provides data on chemical nomenclature, composition, structure, properties, toxicity, production uses, health and environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, seven independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), Chemical Information System (CIS), CAS-On-Line, SDC's ORBIT, Lockheeds's DIALOG, Bibliographic Retrieval Service (BRS), and the US Coast Guard's Hazard Assessment Chemical System (HACS). For further information contact Dr. Siegel at 202-395-7285.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 500 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. The clearinghouse listed 146 citations for lead. For further information, contact Irvin Weiss at FTS 382-5918.

6. REGULATORY STATUS (Current as of 9/83)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Air Act (CAA)

- o Section 211 - EPA regulates the amount of lead permitted in leaded gasoline (40CFR80.20). Revised regulations have been issued which remove the temporary exemption for small refineries effective July 1, 1983 (47FR49322; 48FR5724; 48FR13428); all must meet a standard of 1.10 grams of lead per gallon of leaded gasoline. A maximum level for lead in unleaded gasoline is also in effect (40CFR79.31).
- o Section 109 - A National Ambient Air Quality Standard (NAAQS) has been issued for lead and its compounds (40CFR50.12).

State implementation plans (SIP) have been adopted (40CFR51, parts).

- o Section 111 - New Stationary Source Performance Standards (NSPS) have been issued covering particulate emissions from primary lead smelters (40CFR60.180-.181) and secondary lead smelters (40CFR60.120-.123). Although lead emissions are not directly controlled, particulate lead is indirectly limited by these and other NSPS. NSPS for lead-acid battery manufacture include explicit limits for lead emissions (40CFR60, Subpart KK).

Clean Water Act (CWA)

- o Section 311 - Twelve lead compounds designated as hazardous substances (40CFR116.4) are subject to reporting requirements (reportable quantities, 40CFR117.3) in case of discharge.
- o Sections 301, 304, 306, and 307 - Lead and its compounds are listed as Toxic Pollutants, also known as priority pollutants (40CFR401.15), and are subject to effluent limitations reflecting "best available technology economically achievable" (BAT). Effluent guidelines for lead, including New Source Performance Standards (NSPS) and/or Pretreatment Standards (PS), have been issued for all or parts of the following industrial point source categories:

Inorganic Chemicals (40CFR415)
Iron and Steel Manufacturing (40CFR420)
Glass Manufacturing (40CFR426)
Rubber Processing (40CFR428)
Electroplating (40CFR413)
Nonferrous Metals Manufacturing (40CFR421)
Ore Mining and Dressing (40CFR440)

Porcelain Enameling (40CFR466)
Metal Finishing (40CFR430)
Copper Forming (40CFR468)

- o Sections 402 and 404 - Discharged toxic pollutants such as lead are controlled by requiring permits under the National Pollutant Discharge Elimination System (NPDES). The Army Corps of Engineers issue permits for discharge of dredged or fill materials (40CFR122 to 125)

Safe Drinking Water Act (SDWA)

- o Section 1412 - Establishes interim primary drinking water standards, including a maximum contaminant level (MCL) for lead (40CFR141.11).
- o Sections 1421 to 1424 - Establishes an underground injection control (UIC) program to protect underground sources of drinking water (40CFR146). Requirements and criteria to be used by states incorporate all hazardous wastes as defined by RCRA (40CFR261), including lead and its compounds.

Resource Conservation and Recovery Act (RCRA)

- o Section 3001 - This section identifies specific hazardous wastes, waste sources, and criteria for listing waste as hazardous (40CFR261). Lead and its compounds are designated as toxic wastes (261.33) and/or hazardous constituents (261, App VIII); total extractable lead may also characterize waste as hazardous (EP toxicity, 261.24). The only nonspecific source of hazardous waste which contains lead is industrial painting activities (261.31, App VII). Waste streams containing lead from the following industries are listed as specific sources of hazardous waste: pigment production, petroleum refineries, tanning, explosives, paint manufacturing, ink formulation, and production of iron, steel, copper, zinc, lead and ferroalloys (261.32, App VII). [See also "Disposal," Section 8.5 of this document.]
- o Sections 3002 to 3006 - Hazardous wastes containing lead are subject to further control under RCRA. Regulations cover generators (40CFR262) and transporters (40CFR263) of such waste; and treatment, storage, and disposal facilities are also subject to standards (40CFR264 and 265).

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- o Residue tolerances are set for lead arsenate on fruits and vegetables (40CFR180.194).
- o Requirements are given for disposal of lead-based pesticide residues and containers (40CFR165.7 to .9).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- o Section 6 - A permissible exposure limit (PEL) of 50 micrograms per cubic meter for lead has been established (29CFR1910.1025). The standard must be achieved through some combination of engineering controls, work practice plans, and respiratory protection. Lead exposure in mines is controlled under the limits adopted by the Mine Safety and Health Administration (29CFR1910.1000).

CPSC - Consumer Product Safety Act (CPSA)

- o Lead-based paint and surfaces covered with lead paint are regulated under CPSA. Lead-based paint exceeding 0.06 percent lead and most surfaces coated with same are banned (16CFR1145, 1303, 1500).

HUD - Lead-based Paint Poisoning Prevention Act

- o In HUD-associated housing, this Act requires the elimination of lead-based paint hazards, prohibits use of lead-based paints, and requires notification of tenants or purchasers of the hazards of lead-based paints (24CFR35).

DOT - Hazardous Materials Transportation Act

- o Regulations concerning the packaging, labeling, and shipping of hazardous materials, including lead compounds (49CFR171-177, parts). Amendments incorporate hazardous substances and wastes regulated by EPA, including lead and its compounds (40CFR116 and 261).

FDA - Federal Food, Drug and Cosmetic Act

- o Quality standards for bottled water include a maximum lead concentration (21CFR103.5).
- o Lead is a regulated impurity in a variety of color additives: D&C Orange Nos. 5, 10, and 11; D&C Green Nos. 3, 5 and 6; D&C Red Nos. 21, 22, 27, 28, and 30; D&C Blue No. 2; D&C Yellow No. 10 (21CFR73, 74, 81, and 82).
- o Lead is regulated as a food additive in Natamycin (21CFR172.155) and sucrose fatty acid esters (21CFR172.859).

6.2 Proposed Regulations

6.2.1 EPA Programs

CAA

- o New Source performance Standards (NSPS) have been proposed which limit particulate matter release. Lead is known to be present in particulates released from steel plants, electric arc furnaces, and argon-oxygen decarburization vessels (40FR37338), as well as from plants that extract or process lead (40FR36859).

CWA

- o Effluent guidelines, including NSPS and PS, or revisions to existing guidelines concerning lead, have been proposed for various industry point source categories.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund)

- o CERCLA provides for the liability, compensation, cleanup, and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites. (42USC9601); PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46FR54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47FR10972).
- o Lead compounds are hazardous substances under CERCLA and are subject to regulations developed under Superfund. Although adjustments to many of the reportable quantities (RQs) have been proposed, the RQs for lead compounds are still under assessment and statutory values derived from CWA Section 311 or CERCLA itself (1 lb.) apply (48FR23552).

6.2.2 Programs of Other Agencies

FDA

- o In an Advance Notice of Proposed Rulemaking (ANPR), FDA announced a program to reduce lead levels in canned food. Significantly, FDA intends to regulate lead as a food additive under section 409 of FCDA and set action levels on lead levels in food (44CFR51233). A proposed tolerance level for lead in evaporated milk (39FR42740) is due to be withdrawn and replaced with action levels.
- o Proposal to affirm as Generally Recognized as Safe (GRAS) in corn sugar, syrup, invert sugar, and sucrose (48FR15270).
- o Proposal to regulate lead as an impurity in a color additive for contact lenses (48FR34946).

Department of Interior

- o Under the National Environmental Policy Act, a rule has been proposed describing areas requiring non-toxic shot for waterfowl hunting (46FR31030).

6.3 Other Actions

- o EPA has designated another equivalent method for the determination of lead in particulate matter collected from ambient air. The new method uses Inductively Coupled Argon Plasma Optical Emission Spectrometry (48FR14748).
- o EPA has published a draft of the Revised Air Quality Criteria Document for Lead (EPA-600/8-83-028A).

7.1 Air

- ## 7.2 Water

- o Effluent limitations (various industries, 40CFR413 to 440). see Section 6.1 of this document

7.4 Other

- | | |
|-----------------------------|-------|
| citrus fruits | 1 ppm |
| other fruits and vegetables | 7 ppm |

October, 1983

- o FDA maximum concentration level of total lead in bottled water (21CFR103.35). 0.05 mg/l
- o CPSC maximum lead content in consumer paint (16CFR1303). 0.06% by weight
- o HUD definition of lead-based paint (24CFR35). 0.5% by weight
- o OSHA Permissible Exposure Limit (29CFR1910.1025). 0.05 mg/m³ (8-hr TWA)

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL (CONTACT: National Response Center: 800-424-8802; in the Washington area: 426-2675)

General information pertaining to lead compounds will be presented first, followed by specific information applicable to the individual chemicals for which information was available. The term "lead" will refer to all lead compounds.

8.1 Hazards and Safety Precautions

Lead is a poisonous material which may be fatal if inhaled or ingested. Contact with some lead compounds may cause burns to skin or eyes. Fire may produce irritating or poisonous gases. Runoff from fire control or dilution water may cause pollution.

Tetramethyl lead and tetraethyl lead are flammable liquids which may be ignited by sparks and flames.

Lead nitrate and lead perchlorate are strong oxidizing agents and should be kept away from oxidizable materials.

Store in tightly closed containers in well-ventilated areas away from food products.

Lead nitrate and lead perchlorate should be protected against physical damage. Store in cool dry place; avoid storage on wood floors. Separate from combustible, organic or other readily oxidizable material. Immediately remove and dispose of any spilled material.

8.2 First Aid

Move victim to fresh air; call emergency medical care. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Remove and isolate contaminated clothing and shoes. In case of contact with material, immediately flush skin or eyes with running water for at least 15 minutes.

8.3 Emergency Action

Avoid contact and inhalation of the spilled cargo. Stay upwind; notify local fire, air, and water authorities of the accident. Evacuate all people to a distance of 200 feet upwind and 1,000 feet downwind of the spill. Dam stream to prevent additional movement. Wear full protective clothing including NIOSH-approved rubber gloves and boots, safety goggles or face mask, hooded suit, and either a respirator whose cannister is specifically approved for this material, or a self-contained breathing apparatus. Care must be exercised to decontaminate fully or dispose of all equipment after use.

The "Hazardous Materials 1980 Emergency Guidebook" recommends the following general procedures for containment and clean-up for lead spills. Small spills, take up with sand, or other noncombustible absorbent material, then flush area with water. For small dry

spills, shovel into dry containers and cover, move containers, then flush area with water. Large spills, dike far ahead of spill for later disposal.

OEM-TADS recommends the following actions: reduce dissipation by water movement with a physical barrier. Due to low solubility of material, dredging or bottom vacuum may be effective. Under controlled conditions, chemical treatment is as follows: pump water into suitable container. Add calcium hydroxide to a pH of 8.5 to precipitate lead. Filter. Use carbon as a polishing step. For more details see Envirex Manual EPA 600/2-77-227.

Fire can be extinguished with water in flooding quantities as fog, foam, dry chemical, or carbon dioxide. If water or foam is used, contain flow to prevent spread of pollution, keep from drains and sewers. Remove container from fire area if you can do it without risk.

In case of tetramethyl lead or tetraethyl lead fire, cool containers that are exposed to flames with water from side until well after the fire is out. For massive fire in cargo area, use unmanned hose holder or monitor nozzles. If this is impossible, withdraw from area and let fire burn.

8.4 Notification and Technical Assistance

Section 103(a) and (b) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 requires persons who release hazardous substances into the environment in reportable quantities determined pursuant to Section 102 of the Act to notify the National Response Center (NRC): 800-424-8802 (Washington, D.C. 426-2675).

A variety of lead compounds are designated as hazardous under the CWA Section 311; all have reportable quantities of 5,000 lbs with the exception of lead flouride and tetraethyl lead which have reportable quantities of over 1,000 and 100 lbs respectively: lead acetate, lead arsenate, lead chloride, lead flouroborate, lead flouride, lead iodide, lead nitrate, lead stearate, lead sulfate, lead sulfide, and lead thiocyanate.

For technical assistance, call CHEMTREX (Chemical Transportation Emergency Center): 800-424-9300. Other sources of technical information are (1) the EPA's Oil and Hazardous Materials - Technical Assistance Data System (OEM-TADS) contained in the NIH-EPA Chemical Information System (CIS) which provides information pertinent to emergency spill response efforts, and (2) the CHRIS System which provides information on first aid, physical/chemical properties, hazard assessments, and response methods. Both systems can be accessed through NRC.

8.5 Disposal

Persons generating more than 1,000 kg of hazardous waste per month, or spill clean-up residue or debris resulting from the clean-up are

subject to regulation under RCRA. Such wastes include waste lead as well as wastes that fail the EP toxicity test, 40CFR261.24, (concentration is greater than 5.0 mg/l).

The following specific waste streams are subject to Subpart D regulations.

- (1) Wastewater treatment sludges from the manufacturing formulation and loading of lead-based initiating compounds.
- (2) Dissolved air flotation (DAF) float from the petroleum refining industry.
- (3) Slop oil emulsion solids from the petroleum refining industry.
- (4) API separator sludge from the petroleum refining industry.
- (5) Tank bottoms (leaded) from the petroleum refining industry.
- (6) Emission control dust/sludge from the primary production of steel in electric furnaces.
- (7) Spent pickle liquor from steel finishing operations.
- (8) Acid plant blowdown slurry/sludge resulting from the thickening of blowdown slurry from primary copper production.
- (9) Surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities.
- (10) Sludge from treatment of process wastewater and/or acid plant blowdown from primary zinc production.
- (11) Electrolytic anode slimes/sludges from primary zinc production.
- (12) Cadmium plant leachate residue (iron oxide) from primary zinc production.
- (13) Emission control dust/sludge from secondary lead smelting.
- (14) Solvent washes and sludges, caustic washes and sludges, or water washes and sludges from cleaning tubs and equipment used in the formulation of ink from pigments, driers, soaps, and stabilizers containing chromium and lead.
- (15) Waste leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air (CONTACT: Lary Purdue, FTS 629-2665)

A national ambient air quality standard for lead and a reference method for the determination of lead in suspended particulate matter collected from ambient air have been promulgated by EPA (40CFR Part 50.12, Appendix G). The standard of 1.5 ug Pb/m³ is an arithmetic mean averaged over a calendar quarter.

Sampling is accomplished by collecting airborne particulate matter on a glass-fiber filter for 24-hours using a high-volume sampler. Lead in the particulate matter is solubilized by extraction with nitric acid facilitated by heat or by a mixture of nitric and hydrochloric acid facilitated by ultrasonication.

The lead content of the sample extract is analyzed by atomic absorption spectrometry using an air-acetylene flame and the 283.3 or 217.0 nm lead absorption line. The method has a typical range of 0.07 to 7.5 ug Pb/m³, assuming an upper linear range of analysis of 15 mg Pb/l and an air volume of 2,400 m³. Only minor chemical interferences are reported and no corrections are recommended. Interferences due to light scattering are overcome instrumentally or by a chelation-extraction technique. The high-volume sampling procedure used to collect airborne particulate has an interlaboratory relative standard deviation of 3.7 percent over the range 80 to 125 ug/m³. The combined extraction-analysis procedure has an average interlaboratory relative standard deviation of 7 to 9 percent over the range 1.5 to 15 mg/l.

9.2 Water (CONTACTS: Theodore D. Martin, FTS 684-7312; or
Gerald D. McKee, FTS 684-7372)

Lead is a Clean Water Act 304(h) parameter and is listed as an inorganic priority pollutant. It is also a drinking water parameter with a maximum contaminant level of total lead set at 0.05 mg/l. The term "total lead" is defined as the sum of the concentrations of lead in both the dissolved and suspended fractions of the sample. Samples collected for the analyses of total lead are not filtered and must be preserved with nitric acid to pH <2 as soon as possible, preferably at the time of collection. When a sample contains suspended material and is to be analyzed for total lead, a sample digestion step is required. Dissolved lead is that portion of an unacidified sample that will pass through a 0.45 um membrane filter. Samples to be analyzed for dissolved lead are preserved with nitric acid to pH <2 after filtration. When a colorimetric, stripping voltammetry, or chelation/extraction method is to be used for the analysis of dissolved or total lead, a sample digestion step is also required to ensure that the lead is in the proper chemical state and available for reaction.

There are a variety of approved methods for lead analysis. The most commonly used method is atomic absorption spectroscopy (AA). AA analysis may be conducted by direct aspiration of the sample into an

air/acetylene flame. For this method the optimum concentration range for the 283.3 nm absorption is 1 to 20 mg/l with an estimated detection limit of 0.1 mg/l. Chelation/extraction is used to concentrate and/or separate lead from an interfering matrix and can extend the working range for direct aspiration downward to less than 0.05 mg/l. Interlaboratory standard deviations for analysis of lead samples by flame AA varied from 4.2 to 13.8 percent as the lead concentrations decreased from 1.57 to 0.026 mg/l; recoveries ranged from 98 to 104 percent. A more sensitive atomic absorption method is the graphite furnace technique which is often used for analysis of trace amounts of lead. For every matrix analyzed, verification is necessary to determine that the method of standard addition is not required. Hydrochloric acid must be avoided to prevent volatilization of the lead before atomization. The optimum range for graphite furnace methods (for 20 ul injection) is 0.005 to 0.100 mg/l with an estimated detection limit of 0.001 mg/l. Interlaboratory analysis of samples containing 0.026 and 0.046 mg Pb/l by the AA-graphite furnace method yielded standard deviations of 7.7 percent and 13 percent respectively with recoveries of 102 percent and 103 percent.

In the colorimetric method, lead reacts with dithizone in chloroform to form lead dithizonate. The lead is extracted at a high pH (10 to 11.5) and the absorbance of the cherry-red dithizonate complex is measured spectrophotometrically at 510 nm. The analytical range for this method is 1.0 to 30.0 ug Pb in the sample aliquot used for extraction. In a single laboratory using a surface water matrix spiked at concentrations of 0.01 mg Pb/l and 0.026 mg Pb/l, the relative standard deviations were ± 6.8 percent and ± 4.8 percent, respectively. The recovery at these levels were 98.6 percent and 115 percent, respectively.

In the differential pulse anodic stripping voltammetry method (DPAS-voltammetry) the sample is digested with nitric acid. After deposition onto a mercury electrode at constant potential, the lead is stripped back into solution using differential pulse scanning. The current is measured and the lead concentration determined using the standard addition technique. The limit of detection is 0.001 mg/l and the method is applicable up to 0.1 mg/l of lead. Samples containing 0.02 to 0.08 mg Pb/l were analyzed by DPAS-voltammetry in an interlaboratory study. The standard deviations varied from 20 percent to 12 percent and recoveries ranged from 96 percent to 108 percent.

In response to the improved state-of-the-art of multi-element analysis, a water/wastewater related method which includes lead has been promulgated by EPA (FEDERAL REGISTER, 44, p. 69559, December 3, 1979). The revised method (200.7) uses inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The atomic-line emission spectra is processed by computer to subtract background and to correct for any spectral interference. While the estimated instrument detection limit is 0.04 mg/l (at 220.3 nm), the optimum working range for lead by the ICP technique is considered to be from 0.1 mg/l to near 1 g/l. In an interlaboratory study, samples containing 0.08,

and 0.25 mg Pb/l were analyzed by ICP-AES. The relative standard deviations were +14 percent, and +16 percent, respectively and recoveries at these levels were 100 percent, and 94 percent.

The following table summarizes the approved method with appropriate references:

LIST OF APPROVED TEST PROCEDURES FOR TOTAL LEAD

	Reference Method No.			
	<u>EPA</u> ¹	<u>Standard Methods</u> ²	<u>ASTM</u> ³	<u>USGS</u> ⁴
Digestion ⁵ followed by	239.1	303A or	D3559-78	I-3399-78 or
AA-direct aspiration		303B	(A or B)	I-3400-78
AA-graphite furnace	239.2	304	---	---
ICP-AES ⁶	200.7	---	---	---
DPAS-Voltammetry	---	---	D3559-78C	---
Colorimetric (Dithizone)	---	316B	---	---

1. "Methods for Chemical Analysis of Water and Wastes, 1979," EPA-600/4-79-020.
2. "Standard Methods for the Examination of Water and Wastewater," 15th Edition.
3. "Annual Book of Standards," Amer. Society for Testing and Materials, Part 31, Water.
4. "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments," U.S. Department of the Interior, Geological Survey, Open-file Report 78-679.
5. Sample digestion of the filtrate for dissolved metals, or digestion of the original sample solution for total metals may be omitted for AA (direct aspiration or graphite furnace) or ICP analyses provided the sample has a low COD and meets the following criteria: a) visibly transparent, b) no odor, c) free of particulate matter following acidification.

Note: If the sample digestion procedure included in one of the other approved references is different than an EPA procedure, the EPA procedure must be used.

6. Inductively Coupled Plasma Optical Emission Spectrometric Method (ICP) for Trace Element Analysis of Water Wastes; Method 200.7 published by U.S. EPA, EMSL-Cincinnati.

9.3 Solid Wastes

Approved methods for lead analysis in solid wastes are given in "Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods," (USEPA/SW-846/May 1980), Method No. 8.56. The sample is digested with HNO_3 and analyzed by the flame atomic absorption or graphite furnace method. Both procedures are similar to the AA methods approved for lead determination in water.

9.4 Other Samples

A procedure is given for the determination of lead in sediments and other solids in "Chemistry Laboratory Manual for Bottom Sediments and Elutriate Testing," (Region V, USEPA, CRL, Chicago; EPA-905/4-79-014). The dry sediment is digested ($\text{HNO}_3/\text{H}_2\text{O}_2$) and analyzed by either ICP-AES or AA.

Typical methods for lead analysis in a variety of biological and environmental matrices are summarized in an IARC monograph (IARC, 1980). A review of the various analytical methods used for lead is available (see HERL, 1978).

9.5 Quality Assurance (CONTACT: John Winter, FTS 684-7325)

ORD has a full range of Quality Assurance support available which includes the following items:

- Unknown performance evaluation samples
- Known quality control check samples

These are available to the regions through the Quality Assurance Branch of EMSL--Cincinnati.

Quality control samples for analysis of airborne lead consisting of lead deposited on glass-fiber filter strips are available from the Performance Evaluation Branch, Quality Assurance Division (MD-77), EMSL/USEPA, Research Triangle Park, North Carolina 27711 (Telephone: FTS: 629-2188). Specific guidance for a Quality Control Program for the TSP Reference Method and the Lead Reference Method can be found in the Quality Assurance Handbook for Air Pollution Measurement System, Volume II, Section 2.09, EPA-600/4-77-027a, May 1977.

REFERENCES

The major references used in preparation of this document are listed below. EPA references are listed by EPA Office of origin and the year of publication. For further information refer to contacts given throughout this document or contact the relevant EPA offices listed at the end of this section.

- (HERL, 1978) Reviews of the Environmental Effects of Pollutants: VII Lead, EPA-600/1-78-0029, Health Effects Research Lab, Cincinnati, OH (1978).
- (IARC, 1980) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 23, International Agency for Research on Cancer, Lyon (1980).
- (IERL, 1979) Status Assessment of Toxic Chemicals: Lead, EPA-660/2-79-210h, Industrial Environmental Research Lab, Cincinnati, OH (1979).
- (NAS, 1972) Lead: Airborne Lead in Perspective, National Academy of Sciences, Washington, DC (1972).
- (ORD, 1977) Air Quality Criteria for Lead, EPA-600/3-77-017, Office of Research and Development (1977).
- (OTS, 1979) Health and Environmental Impacts of Lead - An Assessment of a Need for Limitations, EPA-560/2-79-001, Office of Toxic Substances (1979).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, EPA-440/4-79-029a, Office of Water Regulations and Standards (1979).
- (OWRS, 1980a) Ambient Water Quality Criteria for Lead, EPA 440/5-80-057, Office of Water Regulations and Standards (1980).
- (OWRS, 1980b) Strategy for Controlling the Environmental Exposure to Lead, EPA-Draft, Office of Water Regulations and Standards (1980).
- (Weast, 1979) Handbook of Chemistry and Physics, 59th edition, The Chemical Rubber Co., R.C. Weast, ed. (1979).
- (WHO, 1977) Environmental Health Criteria 3: Lead, World Health Organization, Geneva (1977).

OFFICE CONTACTS

The EPA Offices and Divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, Minn., Region V	783-9550 (218-727-6692)
-------------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division 382-3546

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division
Research Triangle Park, NC 629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division 472-5016

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division 755-0100

Effluent Guidelines Division 426-2571

Office of Solid Waste (OSW)

State Programs and Resources 755-9107
Recovery Division

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division 245-3045

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II 340-6634 (201-321-6634)

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division 755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis Research Triangle Park, NC	629-2454 (919-541-2454)
Water Analysis Cincinnati, OH	684-7311 (513-684-7311)
Waste Analysis Las Vegas, NV	545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Office of Toxic Integration

Chemical Information and Analysis Program	382-2249
---	----------

Mercury

MERCURY

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-2
Other Effects	2-3
<u>Environmental Release</u>	3-1
<u>Exposure</u>	4-1
Air Exposure	4-2
Water Exposure	4-2
Other Exposure Routes	4-3
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-3
Other Actions	6-3

July, 1982

<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Hazardous Waste	7-1
Other	7-1
<u>Spill or Other Incident Clean-up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-2
<u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	9-1
Air	9-1
Water	9-1
Solid Wastes	9-2
Other Samples	9-2
Quality Assurance	9-3
<u>References and Office Contacts</u>	R-1

MERCURY

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Mercury is used in many industrial processes and commercial products because of its unique physical/chemical properties. Elemental mercury is a dense, silver liquid at room temperature with excellent electrical conductivity, chemical stability, and alloying ability. Mercury and many of its organic derivatives are relatively volatile and most inorganic mercury compounds decompose upon heating to yield mercury vapor. Some mercury compounds will also degrade to elemental mercury due to the action of sunlight. Biological transformations of mercury, coupled with its volatility, enhance both the toxicity and environmental mobility of mercury (IERL, 1979; WHO, 1976).

Most mercury is used in metallic form in various electrical products (e.g., alkaline batteries and fluorescent bulbs) and in the electrolytic production of chlorine and sodium hydroxide (chlor-alkali industry). The cytotoxic properties of organomercurials also led to their use as preservatives in pharmaceuticals, paints, and other products, although less so in recent years. The high toxicity of mercury and its organic and inorganic derivatives has resulted in stringent regulations to control contamination. While most metallic mercury used is imported, a variety of mercury compounds are produced domestically; Table 1 lists the properties and uses of various mercury derivatives (IERL, 1979).

1.2 Chemistry and Environmental Fate/Transport

Mercury (Hg) can exist in three oxidation states: elemental, mercurous (Hg^{+1}), and mercuric (Hg^{+2}). Most common inorganic mercurials and essentially all organic mercury compounds contain divalent mercury. Organomercurials may contain one or two covalent carbon-mercury bonds (e.g., $\text{CH}_3\text{-Hg-Cl}$ or $\text{CH}_3\text{-Hg-CH}_3$). An important species of environmental significance owing to its toxicity and tendency to bioaccumulate is the methylmercury ion (CH_3Hg^+). Mercury compounds are highly reactive and can form stable complexes with various organic ligands found in proteins (e.g., sulfhydryl groups) and nucleic acids. The old name "mercaptan" (mercury seizing) for sulfhydryl compounds ($-\text{SH}$) stems from their great affinity for mercury (WHO, 1976; OWRS, 1979).

The atmosphere plays a dominant role in the transport of mercury, usually in the form of mercury vapor. Although natural degassing is the primary source of mercury air emissions, the use and disposal of mercury products and fossil fuel combustion are also significant sources. Mercury is removed from the atmosphere primarily by particulate fallout or precipitation (OWRS, 1980). According to various estimates, the residence time for mercury in the atmosphere varies from 6 to 90 days; a value of 11 days is currently accepted as most authoritative (NAS, 1978).

TABLE 1: PROPERTIES OF MERCURY COMPOUNDS

Chemical Name and Formula	CAS Number and Synonyms	Mp (°C)	Bp (°C)	Water Solubility (per liter)	Properties and Uses
Mercury Hg	7439976 Quicksilver	-39	356 v.p. 0.002mm (25°)	0.08 mg (30°C) (airfree water) Lipid soluble	Dense (d_{25} 13.5 g/cm ³) silver liquid. Used in chlor-alkali in- dustry and in elec- trical apparatus.
Mercurous chloride HgCl	7546307 Mercury (I) chloride; calomel	400 sub.	--	2 mg (25°C)	Disproportionates readily to Hg and HgCl ₂ . Used in standard electrodes.
Mercuric acetate Hg(CH ₃ COO) ₂	1600277 Acetic acid, mercury (2+) salt	178 dec.	--	250 g (10°C)	Used in manufacture of mercurials, catalyst.
Mercuric chloride HgCl ₂	7487947 Mercury (II) chloride; corrosive sublimate	276	302	69 g (20°C) Also sol. in org. solv.	Yields slightly acid solution upon dis- solution; used as fungicide and insect- icide.
Mercuric oxide, red HgO	1344452 Red precip- itate	500 dec.	--	53 mg (25°C)	Also exists in yellow form. Decomposes thermally or photo- chemically to Hg +O ₂ .
Mercuric sulfide, red HgS	1344485 vermillion	584 sub.	--	0.010 mg (18°C)	Also exists as black metastable form. Mineral form of HgS (cinnabar) is the major mineral source. Used in pigments.

TABLE 1: PROPERTIES OF MERCURY COMPOUNDS (cont.)

Chemical Name and Formula	CAS Number and Synonyms	Mp (°C)	Bp (°C)	Water Solubility (per liter)	Properties and Uses
Dimethylmercury (CH ₃) ₂ Hg	593748 Mercury, dimethyl	--	96 v.p. 20mm (20°)	2.5 g (20°) Also sol. in org. solv.	Flammable, volatile, and toxic. Environ- mental contaminant produced together with monomethyl mercury in bottom sediments.
Ethylmercuric chloride C ₂ H ₅ HgCl	107277 Mercury, chloroethyl-	193	sublimes at 40°	1 mg (18°) Also sol. in org. solv.	Highly toxic; absorbed through skin. Fung- icide.
Phenylmercuric acetate C ₆ H ₅ HgCH ₃ COO	62384 Mercury (acetato) phenyl-; PMA	149	--	2 g (20°) Also sol. in org. solv.	Preservative, herb- icide, and fungicide. Available in a var- iety of other organic salts.

Source: (Stokinger, 1962)

The adsorption of mercury by sediments and subsequent biotransformation are the two most important processes determining the fate of mercury in water. While the elemental metal is essentially insoluble in water, the presence of oxygen and organic substances facilitates oxidation to more soluble mercuric salts. The mild reducing conditions in anaerobic sediments can cause mercury to precipitate as the sparingly soluble sulfide (HgS). Mercury compounds are released from sediments through methylation by bacteria to form methylmercury and, to a lesser extent, dimethylmercury. This methylation process could enhance the evaporative loss of mercury as dimethylmercury from aquatic systems. More importantly, the lipophilic nature of methylmercurials permits them to rapidly cross body membranes. Consequently, even low concentrations of methylmercury produce dangerous accumulations in fish and other aquatic biota (OWRS, 1980a).

Although most of the mercury released due to human activity goes to landfills, little is known about the fate of mercury lost to land areas. Mercuric compounds bind strongly to humic substances and the affinity of mercury for organic matter retards leaching. However, mercuric compounds may be biotransformed to different, more mobile forms of mercury. Thus, methylation by soil microorganisms can produce methylmercurials, and certain bacteria in soil can convert Hg^{+2} to elemental mercury by a bioreductive process. The reduction of ionic mercury in soils (by either chemical or microbiological processes) may be a major mechanism for natural degassing of mercury vapor to the atmosphere (NAS, 1978; WHO, 1976).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACT: Jerry Stara, FTS 684-7531)

2.1.1 Acute Toxicity

Acute mercury intoxication following oral intake of inorganic mercury salts is characterized by paresthesia, metallic taste, abdominal pain, nausea and vomiting, diarrhea, salivation, and upper gastrointestinal tract edema (Dreisbach, 1977). Large doses result in kidney damage and may lead to death. The lethal oral dose in man for mercuric chloride (HgCl_2) is estimated to be 1 to 4 grams (OWRS, 1980a).

Organic mercury compounds, particularly alkyl derivatives such as methylmercury salts, are highly toxic and can produce ataxia, dysarthria, constricted visual fields, and altered plantar reflexes. Dermatitis can also result from dermal contact with or ingestion of alkyl mercurials (OWRS, 1980a).

Acute mercurial pneumonitis results from exposure to high concentrations of mercury vapor (above 1 mg/m^3). The condition is characterized by symptoms similar to those observed for ingestion of inorganic mercury. Death from lung edema is also possible (OWRS, 1980a).

2.1.2 Chronic Toxicity

Neurotoxicity--The critical organ system in chronic exposure appears to be the central nervous system (CNS), although kidney damage is also observed. The onset of chronic poisoning may be slow; the early symptoms are usually a progressive numbness of the extremities, lips, or tongue, and tremors. With increasing exposure, symptoms progress to malaise, muscular weakness, ataxic gait, clumsiness, slurred speech, deafness, and impaired vision, as well as numerous psychological effects. Generally, severe neurological symptoms are not reversible. The onset of CNS effects are noted at 200 ug Hg/day for a 70 kg human (OWRS, 1980a).

Carcinogenicity--Little information has been published on animals and none on humans that indicates any significant carcinogenic potential for mercury compounds (OWRS, 1980a).

Mutagenicity--No assessment of mutagenicity in systems such as the Ames salmonella assay has yet been made and data concerning genetic and reproductive effects of mercury compounds are meager. Methylmercury is a weak mutagen in Drosophila and can interfere with chromosome segregation in plants and animals. The significance of these and other results for human health remains unclear, and the effects of methylmercury on human reproduction and chromosomes should be investigated further. No evidence has been published concerning the mutagenicity of inorganic mercury salts in humans (OWRS, 1980a).

Teratogenicity--Psychomotor retardation due to fetal exposure to methylmercury is well documented. Although brain damage due to pre-natal exposure occurs, no anatomical defects have been reported in

humans. In animals prenatal exposure to methylmercury has resulted in cleft-palates and reduced birth weights, as well as brain damage. Teratological effects of inorganic and metallic mercury have been reported in animals, but little is known about prenatal effects of these mercury forms in humans (OWRS, 1980a).

2.1.3 Absorption, Distribution, and Metabolism

The absorption and toxicity of mercury and its compounds varies with the chemical species involved and the exposure route. Toxicity by ingestion in humans increases in accordance with the extent of absorption through the gastrointestinal tract, i.e., metallic mercury < inorganic salts < methylmercurials. Metallic mercury vapor and alkylmercury compounds are absorbed in the human lung with approximately 80% efficiency. Absorption of mercurials through the skin is reported to occur but is not usually a significant exposure route (OWRS, 1980a).

Methylmercury (i.e., $\text{CH}_3\text{-Hg}^+$) is of special concern because it is readily absorbed, crosses the blood-brain barrier, and is eliminated from the human body more slowly than other mercurials. The metabolism of elemental mercury is complex and is thought to proceed as follows. After inhalation of mercury vapor and absorption into the bloodstream, the mercury is oxidized (to Hg^{+2}). However, despite this rapid oxidation, some elemental mercury reaches the blood-brain barrier and rapidly crosses into brain tissue. Subsequent oxidation in the tissue then traps the mercury in toxic form (Hg^{+2}) and leads to cumulative neurological damage (WHO, 1976).

Due to their lipid solubility, both methylmercury and elemental mercury are readily transferred from mother to fetus across the placenta. Thus, these forms of mercury pose special hazards to developing embryos and fetuses (WHO, 1976).

The presence of selenium is reported to reduce the toxic effects of methylmercury. The mechanism of the protective effect of selenium is unclear; selenium appears to immobilize methylmercury, but does not speed elimination. Vitamin E is also reported to provide some protection from methylmercury toxicity (NAS, 1978).

2.2 Environmental Effects (CONTACT: Howard McCormick, FTS 783-9548 John Gentile, FTS 838-4843)

2.2.1 Aquatic Effects (OWRS, 1980a)

Virtually any mercury compound entering water can become a bioaccumulation hazard due to conversion to methylmercury. Aquatic organisms absorb and magnify methylmercury at each trophic level of the food chain. Therefore, mercury pollution in water can be a serious hazard to humans through ingestion of fish or shellfish containing methylmercury. Among the factors which affect aquatic toxicity are: temperature, salinity, pH, water hardness, and interactions with other chemicals.

Acute Toxicity--In fresh water the reported 96-hour LC₅₀ values for inorganic mercury vary from 0.02 ug/l to 2,000 ug/l among aquatic species. For rainbow trout, the most acutely sensitive fish tested, methylmercury is 10-fold more toxic than inorganic mercury. In general, however, data for methylmercurials are limited.

Salt water animals appear to be much less sensitive to mercury, with LC₅₀ values for inorganic mercury varying from 3.5 ug/l to 1680 ug/l. Molluscs and crustaceans are more sensitive than fishes to the acute toxic effects of mercury.

Chronic Toxicity--Available chronic data indicate that methylmercury is the most chronically toxic mercury compound tested. Chronic values for Daphania magna and brook trout are 1.0 and 0.52 ug/l respectively. The acute/chronic ratios for sensitive species in freshwater and saltwater are both approximately 3.0 for inorganic mercury.

Cold-blooded species, such as fish, retain mercury for long periods; i.e., elimination half-times for methylmercury for fish and crustaceans are 1 to 3 years. Mercury and its compounds elicit a variety of sublethal responses in aquatic organisms, including loss of appetite, abnormal development, reduced growth and reproduction, blindness or "pop-eyes," loss of nervous control, and tissue damage. Numerous studies claim a degree of acclimation to low levels of mercury by various species.

Aquatic Plants--Freshwater plant toxicity values of methylmercury vary widely; effects are observed at concentrations as low as 4.8 ug/l. In general, freshwater plants are relatively insensitive to inorganic mercury, and more sensitive to methylmercurials.

Reductions in saltwater algae growth were reported to occur at mercury (HgCl₂) levels ranging from 10 to 160 ug/l. The toxicity of organomercurials to saltwater plant life has not been studied adequately.

Water Quality Criteria*--The criteria to protect freshwater aquatic life are 0.20 ug/l as a 24-hour average, with a maximum limit at any time of 4.1 ug/l. The corresponding criteria for saltwater species are 0.10 ug/l for the 24-hour average and a maximum level of 3.7 ug/l.

2.2.2 Other Effects (OWRS, 1980a)

The mercury burdens in terrestrial mammals usually are directly related to diets and are low compared to marine mammals. Herbivores have the lowest mercury levels, while carnivores that prey on aquatic organisms have the highest body burdens**. Non-fish-eating animals

* 46FR40919 (correction to 45FR79318)

** It should be recognized that carnivores other than those that prey upon aquatic organisms may be contaminated if they consume carnivores that feed directly on fish or other aquatic organisms.

and birds usually concentrate less than 0.02 parts per million (ppm) of mercury. Levels of methylmercury in plants are usually extremely low, with the exception of plants grown on contaminated soil or from mercury-treated seed stock.

Bioconcentration--Due to the concern over dangers to human health from eating mercury-containing fish, mercury bioaccumulation has been well studied in aquatic environments. Methylmercury is readily absorbed by fish both from food and through the water. Due to the difficulty fish have in eliminating methylmercury, bioconcentration factors (BCF) for mercury can become extremely high.

Equilibrium BCF values vary from 12,000 to 63,000 for methylmercury in freshwater fish. A BCF value of 40,000 has been reported for methylmercury in oysters.

3. ENVIRONMENTAL RELEASE (OWRS, 1980b, 1980c)
(CONTACT: Michael Slimak, FTS 426-2503)

Approximately 1660 kkg of mercury were used in the U.S. in 1978, down from the 1976 level of 2230 kkg. Table 2 lists both the uses of mercury and its releases to the environment by media. The year 1976 was selected for the use/release analyses because it was the most recent year for which a complete set of data was available. The release data are only crude estimates and have not been verified by sampling and analysis.

Electrical products such as dry-cell batteries, fluorescent light bulbs, switches, and other control equipment account for 50% of mercury used. Mercury is also used in substantial quantities in electrolytic preparation of chlorine and caustic soda (chlor-alkali industry, mercury cell process; 25%), paint manufacture (12%), and dental preparations (3%). Lesser quantities are used in industrial catalyst manufacture (2%), pesticides manufacture (1%), general laboratory use (1%), and pharmaceuticals (0.1%).

Consumer use and disposal of products containing mercury eventually release more mercury to the overall environment than do manufacturing processes. Only 2% of the mercury released due to human activities goes directly to surface waters. A large proportion (72%) of that which is discharged goes to landfills and most of the remainder goes to air. Only 1% goes to or through POTWs.

While over 60% of the mercury consumed in the U.S. in 1978 has been or will be disposed of to landfills, relatively little is known about the movement of mercury in landfills. There is general recognition that mercury originating in other media is quite mobile in the environment due to a cycle of deposition in sediments or soil, followed by chemical interactions and/or revaporization.

Natural releases of mercury to the U.S. environment are substantial although there is considerable disagreement on the reliability of current estimates and the relative importance of natural contributions. Air emissions due to outgassing of soils and rock strata are estimated to total approximately 1020 metric tons per year (150% of man-made air emissions). Direct aquatic discharges due to mercury in groundwater and non-urban runoff are estimated to total approximately 190 metric tons per year (250% of the comparable man-made contribution).

3.1 Air Releases (CONTACT: Dave Patrick, FTS 629-5645)

Significant Sources--The following stationary sources have been found to contribute significant amounts of mercury emissions to the ambient air.

- Mercury-cell chlor-alkali plants (SIC 2812)
- Primary mercury smelting (SIC 3339)
- Sewage sludge incineration (SIC 4953)

TABLE 2: CONSUMPTION OF MERCURY AND ANTHROPOGENIC SOURCES TO THE ENVIRONMENT

(kkg/yr and %)				
I. <u>Uses of Mercury</u>		<u>kkg/yr</u>	<u>% of Total Uses</u>	
A. Electrical products		1120	50	
B. Chlor-alkali plants		550	25	
C. Paints		270	12	
D. Dental preparations		70	3	
E. Industrial catalysts		40	2	
F. Pesticides		20	1	
G. General laboratory		20	1	
H. Other		140	6	
II. <u>Releases to Environment</u>		<u>kkg/yr</u>	<u>% of Discharges to Land</u>	<u>% of Total Releases</u>
A. Land Discharges		1836		72
1. Electrical products	880	48	34	
2. Chlor-alkali plants	530	29	21	
3. Fertilizer	190	10	7	
4. From POTW	50	3	2	
5. Paint applications	50	3	2	
6. Industrial catalysts	40	2	2	
7. Pesticides	20	1	1	
8. Dental preparations*	50	3	2	
9. Fossil fuel combustion	10	0.5	<1	
10. Cu, Zn, and Pb smelting	5	<0.5	<1	
11. General laboratory	1	<0.5	<1	
12. Other	10	0.5	<1	
		<u>kkg/yr</u>	<u>% of Emissions to Air</u>	<u>% of Total Releases</u>
B. Airborne Emissions		650		25
1. Paint applications	200	31	8	
2. Fossil fuel combustion	180	28	7	
3. Electrical products	150	23	6	
4. Cu, Zn, and Pb smelting	50	8	2	
5. From POTW	40	6	1	
6. Chlor-alkali plants	20	3	1	
7. Other	10	2	<1	

* This value may range from 20-50 kkg, depending on amount of recycle for trapped amalgams from dental offices.

TABLE 2: CONSUMPTION OF MERCURY AND ANTHROPOGENIC SOURCES TO THE ENVIRONMENT
(cont.)

II. <u>Releases to Environment</u> (continued)		% of Industrial Discharge to Water	% of Total Releases
C. Aquatic Discharges	<u>kg/yr</u> 75		3
1. Industrial Discharges	55		2
a. Paint applications	20	36	
b. Electrical products	20	36	
c. Dental preparations**	<5	9	
d. Fossil fuel combustion	5	9	
e. Cu, Zn, and Pb smelting	5	9	
2. POTWs**	20	--	1

** Although approximately two-thirds of the nation is served by POTWs, this calculation assumes a tendency toward urban location of dental offices. Therefore, a much higher level of treatment (>90%) is a more appropriate assumption. Dental preparations then account for 15 kg/yr discharged to POTWs.

Source: Environmental Material Balance for Mercury, draft report, OWRS (1980) with revision of dental preparations value by OWRS.

EXPOSURE ROUTES

Mercury occurs naturally in many rock strata and soils at trace levels (less than 1 ppm). Because mercury is very volatile, a large amount of mercury vapor enters the atmosphere from outgassing of soils or rock, from fossil fuel combustion, and from various industries. A significant percent of this vapor is quickly adsorbed to very fine particulates which later wash out or fall out onto soils, pavements, or surface waters. As a consequence, virtually all surface and ground water contain very low levels of mercury (less than 1 ppb average) except in cases of improper management of landfills (See 4.2) (OWRS, 1980b).

Consistent with this is the pattern of increased levels of mercury in the vicinity of large stationary emission sources which gradually diminish to background within 10-15 kilometers. However, calculations indicate that nowhere near all of the emitted mercury has been deposited within a 15 kilometer radius. No good estimates of the exact percentage sorbed on particulates in air have been reported. The average life-times reported for mercury vapor in air have ranged from 5 to 90 days but the most authoritative recent figure appeared to be 11 days. Concentrations of mercury in air in rural areas are usually 1-5 ng/m³ while urban concentrations average from 12-13 ng/m³ (OWRS, 1980b).

Many mercury-containing consumer products end in landfills (along with large amounts of chlor-alkali sludge). Since many landfills are not well designed (e.g., acid environment, location over porous or non-clay deposits), some further movement of mercury to the aquatic environment may occur (OWRS, 1980b).

At present, mercury contamination of ambient air, drinking water, and soil presents little risk to the general U.S. population. The primary route of human exposure to mercury appears to be through eating fish or shellfish. The World Health Organization (WHO) has recommended that weekly intake be limited to less than 200 ug of methylmercury and less than 300 ug total mercury based on dietary intake. Human intake of total mercury from food in the U.S. typically ranges from 35 to 100 ug/week, and inhalation exposure in general ranges from 10 to 20 ug/week. Average ingestion of total mercury from drinking water is less than 7 ug/week, for a total of 50 to 130 ug/week. Highest exposure is very likely attained by dentists (300-3000 ug/week, by inhalation) and a small subpopulation who derives most of its diet from fish (more than 700 ug/week). Several other occupational groups are also at somewhat higher risk than the general population as are pregnant women and developing embryos. (The WHO permissible levels were based on clinical observations and should not be equated with threshold levels. Other, more subtle effects such as behavioral or intellectual deficits might not have been detectable by the procedures used.) (WHO, 1976).

4.1 Air Exposure* (CONTACT: Dave Patrick, FTS 629-5645)

Elemental mercury may be inhaled as a vapor. This vapor may be the result of evaporation of elemental mercury or as part of an industrial process.

Major sources of exposure are:

- Mercury-cell chlor-alkali plants:
hydrogen and end box ventilation
gas streams; cell room floor
- Processing mercury ores: from
rotary kilns and the condenser
- Emissions from a sewage sludge
incinerator

4.2 Water Exposure

Analytical data obtained by the U.S. Geological Survey at its National Stream Quality Accounting Network (NASQAN) stations indicate that no significant changes have occurred in mercury concentrations in surface waters for the U.S. in general between 1974 and early 1980, although small variations in average concentrations have occurred from year to year. On the other hand, 1979 STORET data indicate that mercury levels in surface waters at a number of locations are above the threshold for deleterious, but sublethal, effects for "most sensitive" aquatic species. However, LC₅₀ values for "most sensitive" species are generally more than 10 times the average river basin concentrations. Fish-eating wildlife living near contaminated waters may be at significant risk due to bioaccumulation of mercury in fish (OWRS, 1980b).

Results of a nationwide reconnaissance of mercury in U.S. Waters (Department of Interior) show that with few exceptions the mercury content of groundwater samples was below the level of detection (0.1 ug/l). Hazardous waste incidents, however, have resulted in significantly higher levels in certain local situations. Major uses of mercury, which generate mercury-containing solid waste residuals, include use; as the cathode in the electrolytic preparation of chlorine and caustic soda, in electrical apparatus, in industrial and control instruments, in general laboratory applications, in dental amalgams, and in anti-fouling and mildew-proofing paints.**

* Supplied by the Office of Air Quality Planning and Standards.

** Supplied by the Office of Solid Waste.

4.3 Other Exposure Routes

The primary route of human exposure appears to be through the eating of fish or shellfish (WHO, 1976).

In foodstuff other than fish and fish products, the concentrations of mercury are so low as to be near or below the limit of detection by the analytical methods used. In the United States most foodstuffs have total mercury levels below 20 ng Hg/g. Due to the uncertainties in these numbers, it is impossible to calculate average daily intakes for non-fish food in the United States. These findings are consistent with the knowledge that non-fish-eaters have the lowest blood concentration of mercury (OWRS, 1980a).

The average concentration of mercury in most fish is less than 200 ng/g and nearly all the mercury in fish muscle is in the form of methylmercury compounds. Large carnivores like swordfish can exceed 1,000 ng/g. Canned tuna samples indicated an average total mercury concentration of about 250 ng/g. In heavily polluted areas concentrations ranging over 20,000 ng/g have been reported. Also, the older the fish the higher the mercury concentration. Fish that are carnivorous and at the end of a food chain have the highest concentrations. Therefore, freshwater fish like the northern pike and oceanic fish such as the shark and swordfish have elevated mercury levels compared to other fish. Marine mammals may obtain levels in the order of 340,000 ng/g in their livers (OWRS, 1980a).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The CICIS Inventory was compiled under the authority of Section 8 of TSCA, which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available on the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purpose of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. For further information contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information contact Delores Evans at FTS 382-3546 or Irv Weiss at FTS 382-3524.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base that is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses source material at the Federal level only, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Delores Evans at FTS 382-3546 or Ingrid Meyer at FTS 382-3773.

5.5 Chemical Substances Information Network (CSIN)

The prototype CSIN, operational since November 1981, has been developed by merging the technologies of computer networking and distributed data base management. CSIN is not another data base, but a library of systems. Through the CSIN front-end intermediary management computer, the user may access and use independent and autonomous information resources that are geographically scattered, disparate for data and information content, and employ a variety of types of computer hardware, software, and protocols. Users may converse in and among multiple systems through a single connection point, without knowledge of or training on these independent systems.

Currently, six independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), CIS, EPA-CICIS, CAS-On-Line, SDC-orbit, and two files of Dialog: CRGS and TSCA Inventory. The CSIN management computer allows the user to create, retrieve, store, and manipulate data and queries. This eliminates the need for reentering long lists of chemical identifiers or other information elements that are part of the original query or that have been identified and acquired from one or more of the CSIN resources. For further information contact Dr. Sid Siegal at FTS 382-2256.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 475 individual data bases and models that contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. For further information, contact Charlene Sayers at FTS 755-9112.

The following data bases contain information on mercury:

BACT/LAER Determinations

Baseline Survey of Public Water Supplies on Indian Lands

BAT Review Study for the Timber Products Processing, Gum and Wood, Chemicals, and the Printing and Publishing Industries

Best Management Practices, Timber Industry Effluent Guidelines -
Runoff

Best Management Practices, Timber Industry Effluent Guidelines -
Sludge

Boone County Field Site

Compatibility Studies to Determine Effectiveness of Treatment
Alternatives for Selected Industrial Wastewaters

Compliance Data System

Compliance Sampling Toxicant Surveys

Consolidated Permits Program-Application Form 1,2b,2c

Continuous Monitoring Subset

Contrary Creek Project-803801

Conventional Water Pollutants

Crete, Illinois Metals Environmental Samples

Data Collection Portfolio for Industrial Waste Discharges

Discharge Monitoring Report

Discharge Monitoring Report Files
 Dredging-Special Studies Metals
 Drinking Water
 Drinking Water Special Study
 Energy and Mining Point Source Category Data Base
 EPA, Region X, Point Source File
 Federal Facilities Information System
 Federal Reporting Data System
 Federal Reporting Data System-Regional
 Fine Particle Emissions Information System
 Fish Kills
 Food Industry Group
 Fugitive Emissions Information System
 Hazardous Waste Data Management System
 Hazardous Waste Site Tracking System
 Hemlock, Michigan Environmental Samples
 Hewlett-Packard
 Humacao Ambient Data Base
 IFB Organics Data Base
 Indicatory Fate Study
 Industrial Process Evaluations
 Inhalable Particulate Analysis Bank
 Inhalable Particulate Network
 Innovative Technology, Timber Industry Effluent Guidelines
 Inorganic Chemicals Industry Regulation Record
 Inventory (Regional National Pollutant Discharge Elimination System)
 LiPari Landfill
 Liquid Effluents Data System
 Love Canal Data Handling System
 Method Validation Studies of Priority Pollutants
 Model State Information System
 Multimedia Assessment of the Inorganic Chemicals Industry
 National Pollutant Discharge Elimination System (NPDES) Permit
 Compliance-Region III
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Monitoring Reports-Region VII
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Monitoring Reports-Region I
 National Water Quality Surveillance System
 Nationwide Urban Runoff Program
 Needs Survey
 New York Bight Ocean Monitoring Program
 New York Harbor Survey
 Ocean Dumping
 Organic Chemicals/Plastics Industry
 Paint and Ink Analytical Data
 Permit Compliance System
 Pharmaceutical Screening/Verification Data Base
 Priority Pollutants-Region I
 Priority Pollutants-Region III
 Publicly Owned Treatment Works (POTW) Analytical Data
 Publicly Owned Treatment Works (POTW) Quality Control
 Puerto Rico Reservoirs
 Regional Air Pollution Study-Ambient

Regional Air Pollution Study-Point and Area Source
 Regional Toxics Monitoring Program
 Resource Conservation and Recovery Act (RCRA)-Hazardous Waste Site
 Inspections
 Screening Sampling Program
 Sludge Distribution and Marketing Regulations-Community Impact Survey
 Soil, Water, Estuarine Monitoring System
 Solid Discharge Data System
 Source Test Data System
 Sources of Toxic Pollutants Found in Influent to Sewage Treatment
 Plants
 Storage and Retrieval of Aerometric Data
 System for Consolidated Permitting and Enforcement Data Base
 Textile Industry BAT Study-Toxic Sampling Data
 Toxic Metals
 Toxicant Control Fish Tissue Analyses
 Toxics Monitoring
 U.S. Virgin Islands-St. Thomas, St. Croix
 United Nuclear Corporation (UNC) Spill-Rio Puerco Monitoring
 UPGRADE
 Utility Simulation Model Data Base
 Verification Data Base
 Verification Sampling Program
 Waste Characterization Data Base
 Wasteload Allocation File
 Water Enforcement Regional System
 Water Quality Information System
 Wisconsin Power Plant Impact Study Data Center

6. REGULATORY STATUS (current as of 4/23/82)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Air Act (CAA)

- Section 112 - Mercury is listed as a hazardous air pollutant and EPA has issued national emissions standards (NESHAPs) for mercury smelters, chlor-alkali plants, and for sludge incineration or drying plants (40CFR61, Subpart E).

Clean Water Act (CWA)

- Section 311 - Five mercury compounds designated as hazardous substances (40CFR116.4) are subject to reporting requirements (40CFR117.3).
- Sections 301, 304, 306 and 307 - Mercury and its compounds are listed as toxic pollutants, also known as Priority Pollutants (40CFR401.15), and are subject to effluent guideline limitations which may include pretreatment standards and new source performance standards. Regulations have been issued for the chlor-alkali industry (40CFR415, Subpart F), and for certain subcategories of the ore mining and dressing industry (40CFR440, Subpart B and F) and the pesticide chemical industry (40CFR455).
- Sections 402 and 404 - Discharge toxic pollutants such as mercury are controlled by permits required under the National Pollutant Discharge Elimination System (NPDES). Permits for discharge of dredged or fill materials are issued by the Army Corps of Engineers (40CFR122 to 123).
- Section 403 - Restricts dumping of mercury in the ocean except as a "trace" contaminant (40CFR227.6).

Safe Drinking Water Act (SDWA)

- Section 1412 - EPA has issued a National Interim Primary Drinking Water Standard for mercury (40CFR141.11).
- Sections 1421 to 1424 - Establishes an underground injection control (UIC) program to protect underground sources of drinking water (40CFR146).

Resource Conservation and Recovery Act (RCRA)

- Section 3001 - Mercury and its compounds are designated as toxic wastes (40CFR261.33) and/or hazardous constituents (40CFR261, App VIII). Extractable mercury also characterizes waste as hazardous (40CFR261.24). Specific sources of hazardous waste that contain mercury are from the chlor-alkali industry (K071, K106) (40CFR261.32).

- Sections 3002 to 3006 - Regulations for generators and transporters of hazardous wastes and standards for treatment, storage, and disposal are applicable to wastes characterized as hazardous due to mercury levels (40CFR262 to 265).

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- All pesticide uses of mercury have been banned except for a limited number of approved uses as fungicides or preservatives (41FR 26742, 36068, and 164971).
- Procedures for disposal of organic mercury pesticides and containers (40CFR165.7 -.9).

6.1.2. Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- An industry standard for airborne mercury is in effect (29CFR1910.1000).

CPSC - Federal Hazardous Substances Act

- Among products subject to the Act are mercury switches and batteries. However, no regulatory action is expected in the near future.

DOT - Hazardous Materials Transportation Act

- A number of mercury compounds have been designated Class B poisons and must be handled according to DOT regulations. Air shipment of metallic mercury is prohibited (49CFR171-177).

FDA - Federal Food, Drug, and Cosmetic Act

- Standard for mercury content of bottled water (21CFR103.35[d][1]).
- Regulations governing use of mercury compounds in cosmetics (21CFR700.13) and hair coloring (21CFR73.2396).
- Administrative guideline sets action level for mercury in aquatic animals (44FR4012).
- Color additives containing mercury are subject to certification--D&C Orange #10 and #11 and D&C Green #6 (21CFR74, 81, 82).

Note: The Bureau of Biologics at FDA has a limited control program for mercury. Mercury levels are determined to check if the manufacture complies with the product license.

6.2 Proposed Regulations

6.2.1 EPA Programs

CAA

- State implementation plan requirements; emission rates that trigger need for controls (44FR51937).

CWA

- Effluent guidelines, including pretreatment standards and new source performance standards, concerning mercury have been proposed for subsections of the following industry point source category:

Inorganic chemical manufacturing 45FR49450 (7/24/80)

6.2.2 Programs of Other Agencies

Atomic Energy Act

- Standards for disposal of residual radioactive materials from uranium processing will limit resultant groundwater contamination by mercury (46FR2556).

6.3 Other Actions

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund)

- CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites. (42USC9601; PL 96-510).
- EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46FR54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47FR10972).
- Hazardous substances as defined by Section 101(14) of CERCLA include: hazardous wastes designated under Section 3001 of the RCRA; hazardous air pollutants regulated under Section 112 of the CAA; water pollutants listed under Sections 307 and 311 of the CWA (and also any substances regulated in the future under Section 7 of TSCA and Section 102 of CERCLA). Therefore, mercury and compounds are hazardous substances under CERCLA and will be subject to regulations issued under Superfund.

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- National Emission Standards (NESHAP) (40CFR61, Subpart E):

Mercury smelters and chlor-alkali plants 2.3 kg/day

Sludge incineration or drying plants 3.2 kg/day

7.2 Water

- Hazardous spill rules require notification of discharges equal to or greater than the following reportable quantities (40 CFR117.3):

Mercuric cyanide 1.0 lb

Mercuric nitrate; mercuric sulfate; mercuric thiocyanate; mercurous nitrate 10 lbs

- Maximum concentration level of total mercury for drinking water (40CFR141.11) 2 ug/l

- Water Quality Criteria (45FR79318)

Freshwater aquatic life 0.20 ug/l (24-hr avg)
4.1 ug/l (maximum)

Saltwater aquatic life 0.10 ug/l (24-hr avg)
3.7 ug/l (maximum)

Human health 0.144 ug/l (ambient)

7.3 Hazardous Waste

- Waste is designated hazardous if the concentration of mercury equals or exceeds this maximum for extractable mercury (EP toxicity, 40CFR261.24) 200 ug/l

7.4 Other

- FDA maximum concentration of mercury in bottled water (21CFR103.35[d][1]) 2 ug/l

* See Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

- FDA maximum for the level of mercury preservatives in cosmetics (21CFR700.13):

Eye area cosmetics 65 ppm

Other cosmetics 1.0 ppm

- FDA guideline action level for mercury in aquatic animals (44FR4012) 1.0 ppm

- OSHA standard for workplace exposure to mercury in air (29CFR1910.1000). (A NIOSH criteria document recommends a 50 ug/m³ limit.) 100 ug/m³ (8-hr avg)

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL (CONTACT: National Response Center, 800-424-8802, or 426-2675 if in Washington, D.C.)

General information pertaining to mercury compounds will be presented first, followed by specific information applicable to the individual chemicals for which information is available. The term "mercury" will refer to all mercury compounds.

8.1. Hazards and Safety Precautions

Mercury is a highly toxic material that may be fatal when inhaled or ingested. Fire will produce highly toxic mercury fumes. Runoff from fire control or dilution water may cause pollution. Some of these materials may burn but do not ignite readily.

Store mercury in tightly closed containers in well ventilated areas and protect from light.

8.2 First Aid

Move victim to fresh air; call emergency medical care. In case of contact with material, immediately flush skin or eyes with running water for 15 minutes.

8.3 Emergency Action

Avoid contact with and inhalation of the spilled cargo. Stay upwind; notify local fire, air, and water authorities of the accident. Keep unnecessary people away. Use full protective clothing including NIOSH-approved rubber gloves and boots, safety goggles or face mask, hooded suit, and either a respirator whose cannister is specifically approved for this material or a self-contained breathing apparatus. Care must be exercised to decontaminate fully or dispose of all equipment after use.

In case of spill or leak, OHM-TADS recommends the following action: dam the stream to reduce the flow and to retard dissipation by water movement. Dredging or bottom vacuum may be effective. Information on a specific mercury compound can be found in the OHM-TADS data base or the Envirex Manual (EPA 600/2-77-227).

Fire can be extinguished with water in flooding quantities as fog, foam, dry chemical, or carbon dioxide. If water or foam is used, contain flow to prevent spread of pollution; keep from drains and sewers. Remove container from fire area if you can do it without risk. Cool containers that are exposed to flames with water from side until well after the fire is out. For massive fire in cargo area, use unmanned hose holder or monitor nozzles. If this is impossible, withdraw from area and let fire burn.

8.4 Notification and Technical Assistance

Section 103(a) and (b) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 requires persons who release

hazardous substances into the environment in reportable quantities determined pursuant to Section 102 of the Act to notify the National Response Center (NRC): 800-424-8802 (Washington, D.C. 426-2675).

A variety of mercury compounds are designated as hazardous under the CWA Section 311. These compounds (and their reportable quantities) are: mercuric cyanide (1 lb), mercuric nitrate (10 lb), mercuric sulfate (10 lb), mercuric thiocyanate (10 lb), mercurous nitrate (10 lb), and phenylmercury acetate (100 lb).

For technical assistance, call CHEMTREX (Chemical Transportation Emergency Center): 800-424-9300. Other sources of technical information are (1) the EPA's Oil and Hazardous Materials - Technical Assistance Data System (OHM-TADS) contained in the NIH-EPA Chemical Information System (CIS), which provides information pertinent to emergency spill response efforts, and (2) the CHRIS System, which provides information on first aid, physical/chemical properties, hazard assessments, and response methods. Both systems can be accessed through NRC.

8.5 Disposal

Persons generating more than 1000 kg of hazardous waste per month, or spill clean-up residue or debris resulting from the clean-up, are subject to regulation under RCRA. Such wastes include waste mercury as well as wastes that fail the EP Toxicity test, 40 CFR 261.24, (extractable concentration is greater than 0.2 mg/l).

The following specific waste streams are subject to Subpart D regulations:

- (1) Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used.
- (2) Wastewater treatment sludge from the mercury cell process in chlorine production.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air (CONTACT: Sharon Harper, FTS 629-2443)

Mercury is a hazardous air pollutant; therefore reference procedures have been promulgated (40CFR61).

Test Method 101 is applicable for the determination of particulate and gaseous mercury emissions when the carrier gas stream is principally air. The method is for use in ducts or stacks at stationary sources. Test Method 102 is applicable for the determination of particulate and gaseous mercury emissions when the carrier gas stream is principally hydrogen. The method is for use in ducts or stacks at stationary sources.

In both methods, particulate and gaseous mercury emissions are isokinetically sampled from the source and collected in acidic iodine monochloride solution. The mercury collected (in the mercuric form) is reduced to elemental mercury in basic solution by hydroxylamine sulfate. Mercury is aerated from the solution and analyzed using spectrophotometry.

9.2 Water (CONTACT: Theodore D. Martin, FTS 684-7312 or
Gerald D. McKee, FTS 684-7372)

Mercury is a Clean Water Act 304(h) parameter and is listed as an inorganic priority pollutant. It is also a drinking water parameter with a maximum contaminant level of total mercury set at 2 ug/l. The term "total mercury" is defined as the sum of the concentrations of all forms of mercury in both the dissolved and suspended fractions of the sample. Samples collected for the analyses of total mercury are not filtered and must be preserved with nitric acid to pH < 2 as soon as possible, preferably at the time of collection.

The approved method for mercury analysis is a flameless cold vapor atomic absorption procedure based on the absorption of ultraviolet radiation at a wavelength of 253.7 nm by mercury vapor. For the analysis of total mercury, a sample digestion step is required to ensure the mercury is in the proper chemical state and available for reduction to elemental mercury. After reduction with stannous sulfate, the solution is aerated and the mercury is passed through an absorption cell positioned in the light path. The absorbance of the mercury is measured as a function of concentration. The analytical range of the manual cold vapor method is 0.2 to 10 ug Hg/l.

In an interlaboratory precision and accuracy study, where 11 laboratories participated and 3 acidified distilled water samples containing 0.52, 2.2, and 8.7 ug Hg/l were analyzed by the manual cold vapor method, the standard deviations were ± 0.052 , ± 0.28 , and ± 1.51 , respectively. Recoveries at these levels were 99%, 100%, and 94%, respectively. In a single laboratory with concentrations of 1.0, 3.0, and 4.0 ug Hg/l spiked in surface water, the standard deviations were ± 0.14 , ± 0.10 , and ± 0.08 with recoveries of 89%, 87%, and 87%, respectively.

The cold vapor method can also be automated using a Technicon Auto Analyzer and vapor-liquid separator. The analytical range of the automated method is 0.2 to 20.0 ug Hg/l. Precision in a single laboratory was determined using standards at concentrations of 0.5 to 10.0 ug Hg/l. The reported standard deviations varied from 8% to 4%. Recovery from surface water spiked with ten organic mercurials at 10 ug/l level ranged from 87% to 117%.

9.3 Solid Waste (CONTACTS: Thomas Hinnners, FTS 545-2140; and Werner Beckert, FTS 545-2137)

A waste is defined as hazardous if the extractable mercury equals or exceeds 0.2 ug/l. The extraction procedure is explained in detail in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (EPA Publication SW-846, 1980, Method 8.5.7). After extraction and conversion to the volatile elemental form, the extractable mercury is measured by a cold vapor atomic absorption procedure similar to method 245.1 for water.

At present there are no EPA approved methods available for determining total mercury content in waste. However, the procedure described for sediments (Section 9.4) has been applied to waste materials.

9.4 Other Samples

A procedure for the determination of total mercury in sediments, soils, and sludge materials is given in "Methods for Chemical Analysis of Water and Wastes," (1979, EPA-600/4-79-020; Method 245.5). This method uses cold vapor atomic absorption, and has a useful range of 0.2 to 5 ug/g. Samples are dried (60°C), digested (aqua regia), and oxidized (KMnO₄), before analysis.

Precision and accuracy studies gave the following standard deviations on replicate sediment samples at indicated mercury levels: 0.29 ug/g \pm 0.02; 0.82 ug/g \pm 0.03. Recoveries were 97% and 94% respectively.

Table 3 summarizes the approved method with appropriate references.

The "NIOSH Manual of Analytic Methods" (2nd ed., Vol. 1, 1977) contains flameless atomic absorption methods for mercury detection in several media: air (Method 175), blood (Method 167), and urine (Method 165). The analytical technique for air uses a three-stage collection tube which permits separate determinations of particulate, organic, and metallic mercury.

A procedure for methylmercury determination in biological media (e.g., fish) has been proposed by EPA (J. E. Longbottom, et al., J. Assoc. Offic. Anal. Chem., 56:1297 [1973]). Cupric sulfate is used to free methylmercury from inorganic and organic ligands. Addition of excess KBr forms CH_3HgBr which is separated by gas chromatography. Sensitivity is reported to be 10 ppb, with a precision of $\pm 10\%$ and recoveries of $>95\%$.

TABLE 3. LIST OF APPROVED TEST PROCEDURES FOR TOTAL MERCURY

	Reference Method No.			
	<u>EPA</u> ¹	<u>Standard Methods</u> ²	<u>ASTM</u> ³	<u>USGS</u> ⁴
Manual Cold Vapor	245.1	303F	D3223-79	I-3462-78
Automated Cold Vapor	245.2	--	--	--

1. "Methods for Chemical Analysis of Water and Wastes," 1979 EPA-600/4-79-020.
2. "Standard Methods for the Examination of Water and Wastewater," 15th Edition.
3. "Annual Book of Standards," Amer. Society for Testing and Materials, Part 31, Water.
4. "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments" U.S. Department of the Interior, Geological Survey, Open-file Report 78-679.

9.5 Quality Assurance (CONTACT: John Winter, FTS 684-7325)

ORD has a full range of Quality Assurance support available which includes the following items:

- unknown performance evaluation samples
- known quality control check samples

These are available to the regions through the Quality Assurance Branch of EMSL-Cincinnati.

Quality assurance materials and assistance are also available for air analysis (CONTACT: J. Puzak, FTS 629-2188).

Waste materials with certified levels of mercury are available from the Office of Standard Reference Materials, National Bureau of Standards (telephone: 301-921-2045).

REFERENCES

The major references used in preparation of this document are listed below. EPA documents are referenced by EPA Office of origin and the year of publication. For further information refer to contacts given throughout this document or contact the relevant EPA Program Offices listed in the next section.

- (Dreisbach, 1977) Handbook of Poisoning, Dreisbach, R.H., Lange Medical Publications (1977).
- (IERL, 1979) Status Assessment of Toxic Chemicals: Mercury, EPA-600/2-79-2101, IERL, Cincinnati (1979).
- (NAS, 1978) An Assessment of Mercury in the Environment, National Academy of Sciences, Washington, D.C. (1978).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, EPA-440/4-79-029a, Office of Water Regulations and Standards (1979).
- (OWRS, 1980a) Ambient Water Quality Criteria for Mercury, EPA-440/5-80-058, Office of Water Regulations and Standards (1980).
- (OWRS, 1980b) Strategy for Controlling Environmental Exposure to Mercury, draft report, Office of Water Regulations and Standards (1980).
- (OWRS, 1980c) Environmental Material Balance for Mercury, EPA Contract No. 68-01-3852, Office of Water Regulations and Standards (1980).
- (Stokinger, 1962) Industrial Hygiene and Toxicology, Ch. 27, Stokinger, H.E., Interscience, New York, N.Y. (1962).
- (WHO, 1976) Environmental Health Criteria 1 - Mercury, World Health Organization (1976).

OFFICE CONTACTS

The EPA Offices and Divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
---------------------------------	----------

Effluent Guidelines Division	426-2571
------------------------------	----------

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergenices call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ, Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS OR QUESTIONS

Office of Toxic Integration (OTI)

Chemical Information and Analysis Program

382-2249

Polychlorinated Biphenyls

POLYCHLORINATED BIPHENYLS (PCBs)

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-2
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-3
Other Effects	2-3
<u>Environmental Release</u>	3-1
<u>Exposure Routes</u>	4-1
Air Exposure	4-2
Water Exposure	4-2
Other Exposure	4-2
<u>Data Bases</u>	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical in Commerce Information System (CICIS)	5-2
Chemical Substances Information Network (CSIN)	5-2
Graphic Exposure Modeling System (GEMS)	5-3
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-5
Other Actions	6-6
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Food	7-1

<u>Spill or Other Incident Clean-Up/Disposal</u>	8-1
Hazards	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-2
 <u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
Solid Waste	9-3
Other Samples	9-4
Quality Assurance	9-5
 <u>References and Office Contacts</u>	 R-1

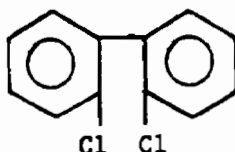
POLYCHLORINATED BIPHENYLS

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

The term polychlorinated biphenyls (PCBs) refers to a class of chlorinated aromatics which were commercially produced in this country as a series of complex mixtures known as Aroclors (Monsanto trademark). Individual Aroclors were identified by a set of four digits; usually the last two digits denote the approximate chlorine content by weight. For example, Aroclor 1242, had an average chlorine content of 42% and consists primarily of di-, tri-, and tetrachloro-biphenyls.

Of the total 209 compounds resulting from the partial or total chlorination of biphenyl, approximately 100 individual compounds have been detected in the various Aroclors. The structure of a typical PCB is shown below.



2,2'-dichloro-1,1'-biphenyl

Higher chlorine content results from increased chlorination and corresponds, in general, to greater persistence in the environment. Most PCBs marketed in the U.S. are still in service, primarily in electrical equipment. The remainder is believed to be primarily in landfills and dumps across the country. No PCBs have been intentionally produced in the United States since 1977, and the distribution and use of PCBs are severely limited by regulations (OTS, 1977).

While individual PCBs vary in their physical properties, all have very low water solubility, low vapor pressure, low flammability, low electrical conductivity, and a high degree of thermal and chemical stability. Because of these properties PCBs have been extensively used in "closed" or "semi-closed" systems such as electrical transformers and capacitors, heat transfer systems, and hydraulic systems. PCBs used in transformers are usually present as a mixture with trichlorobenzenes called Askarels.

Environmentally relevant physical properties of the Aroclors are given in Table 1. It must be emphasized that the Aroclors are mixtures of different PCBs and the physical properties cannot be properly defined as constants. An additional problem arises because two grades of PCB mixtures existed; for most Aroclors a darker, less pure grade was available. No compounds other than chlorobiphenyls were found in commercial PCBs at 0.01% or more of product weight. However, small amounts of chlorinated dibenzofurans and chlorinated naphthalenes were detected in some batches (NAS, 1979).

TABLE 1: PROPERTIES OF AROCLORS^a

	1016	1221	1232	1242	1248	1254	1260
CAS NO.	12674-11-2	11104-28-2	11141-16-5	53469-21-9	12672-29-6	11097-69-2	11096-82-5
Distillation Range (°C)	325-356	275-320	290-325	325-366	340-375	365-390	385-420
Water Solubility (mg/l)	0.42	[15]	[1.45]	0.24	0.054	0.012	0.0027
Log u/cP ^b	4.38	[2.8]	[3.2]	4.11	[5.75]	[6.03]	[7.14]
Vapor Pressure (torr, 25°C)	[4x10 ⁻⁴]	[6.7x10 ⁻³]	[4.1x10 ⁻³]	4.1x10 ⁻³	4.9x10 ⁻⁴	7.7x10 ⁻⁵	4.0x10 ⁻⁵
Density (g/cm ³ ; 25°C)	1.33	1.15	1.24	1.35	1.41	1.50	1.58

^a Bracketed data are estimated; the last two digits of the Aroclor identity number indicate the approximate chlorine percentage content by weight except for Aroclor 1016 which was a more recent mixture containing 41% chlorine.

^b Octanol/water partition coefficient.

Source: From data summarized in (OWRS, 1979)

1.2 Chemistry and Environmental Fate/Transport

PCBs are extremely stable compounds and nearly inert under normal environmental conditions. Chemical oxidation, reduction, isomerization, and hydrolysis only occur under extreme conditions. For example, thermal conversion of PCBs to chlorinated dibenzofurans occurs only upon heating to 500-600°C. PCBs are reported to undergo photolytic loss of chlorine (NAS, 1979; OWRS, 1979).

The ubiquitous distribution of PCBs is apparently due to volatilization and transport as an aerosol followed by fallout in dust or rain. PCBs may exist in vapor form and attached to atmospheric particles. Vapor pressure data suggest that the more volatile (less chlorinated) PCBs should preferentially accumulate in the atmosphere. Although laboratory results indicate that PCBs undergo photodegradation in the vapor state, no direct evidence exists concerning the environmental relevance of such a process (NAS, 1979).

PCBs have low water solubility, high octanol/water partition coefficients, and are readily adsorbed onto suspended solids, especially those high in organic carbon. In natural waters, adsorption to sediments is the major process for immobilizing PCBs. The persistence of these chemicals, however, allows resuspension of these sediments which may cause them to be released back into the water. The biota are another environmental compartment into which these compounds are concentrated; measured bioconcentration factors range from 10^4 to 10^6 . Biodegradation is most important for the less chlorinated compounds and is the only process known to degrade PCBs under environmental conditions. While evaporative half-lives of Aroclors from water are estimated to be about 10 hours, volatilization from natural waters is probably as much as 100-fold slower, perhaps due to absorption by suspended solids (OWRS, 1979).

PCBs are adsorbed most efficiently on soils with high clay or organic content. Transfer of PCB isomers from soil to water closely follows their physical properties; thus, the higher chlorinated compounds are not leached from soils, while those with lower chlorine content are leached with difficulty. Losses do occur by volatilization and biotransformation. Ambient air analysis over landfills indicates that evaporation may be the principal mode of PCB transport from land disposal sites (OTS, 1976; NAS, 1979).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACTS: Jerry Stara, FTS 684-7531; Penny Fenner-Crisp 472-4944)

2.1.1 Acute Toxicity

PCBs have low acute toxicity. Most instances of human toxicity have resulted from long-term exposure and accumulation in the body. In a well-known instance of acute poisoning by PCB-contaminated rice oil in Japan (Yusho disease), average total ingestion of 2 g PCB was associated initially with increased eye discharge and swelling of upper eyelids, acneform eruptions and follicular accentuation, and pigmentation of the skin. Other symptoms including dermatologic problems, swelling, jaundice, numbness of limbs, spasms, hearing and vision problems, and gastrointestinal disturbances were prominent among the complaints of patients seen within the first eight months after exposure. Other changes observed during this period included lowered blood counts, and skin, liver and eye abnormalities. Persistence of the compounds in the body resulted in long-term and reproductive effects. However, due to the high levels of chlorinated dibenzofurans also present in the rice oil, (average total intake was estimated to be 10 mg), the above effects cannot conclusively be attributed to PCB toxicity (IARC, 1978; NAS, 1979).

2.1.2 Chronic Toxicity

Occupational exposure to PCBs often results from inhalation and dermal contact. Worker complaints after months or years of PCB exposure include chloracne, other dermal effects, irritation of eye, nose, or throat, and gastrointestinal disturbance. Other effects include changes in fat metabolism and mild disturbances in liver function. PCB levels of 5.2-6.8 mg/m³ caused severe chloracne; a level of 0.1 mg/m³ caused mild chloracne. Lower levels not causing overt toxicity may affect liver function. Levels of 10 mg/m³ are reported to be unbearably irritating.

Other systemic effects of PCBs in mammals include porphyria, increased thyroxin metabolism, inhibition of ATPases, and interference in oxidative phosphorylation. Alterations in steroid hormone metabolism are produced by PCBs in rats; it has been suggested that effects on reproduction may be due to induction of steroid metabolizing enzymes. Aroclors appear to reduce liver vitamin A levels in several species and some authors suggest vitamin A may play a role in detoxification of PCBs. PCBs have also shown immunosuppressive effects in various species (WHO, 1976; OWRS, 1980).

Carcinogenicity, Mutagenicity and Teratogenicity

Several studies using rodents indicate that some PCB mixtures are carcinogenic; however, other studies, including a recent study by NCI, have been negative for some Aroclors. PCBs are classified as carcinogenic by the International Agency for Research on Cancer (IARC) and the EPA (IARC, 1978; OWRS, 1980).

The only firm data exists for female rats which were given a 100 ppm diet of Aroclor 1260 (4.3 to 11.6 mg/kg body weight per day) for 21 months. The incidence of hepatocellular carcinoma (liver cancer) was 26/184 (controls, 1/173); in addition, nonmalignant (neoplastic) nodules were observed in liver at high frequencies (170/184) in these PCB-treated animals. It should be noted that none of the studies on PCBs was a lifetime study; in all cases animals were treated, killed, and examined. Lifetime studies might help to elucidate the significance of nonmalignant tumors induced by PCBs, i.e., whether or not these nonmalignant tumors become malignant. Data on carcinogenicity of PCBs in humans are inconclusive at this time (OWRS, 1980).

PCBs have also been shown to have a significant effect on carcinogenic properties of other chemicals. The co-carcinogenic properties of PCBs apparently results from induction of mixed-function oxidases, particularly in the liver. PCBs can stimulate microsomal enzyme activity responsible for metabolizing many xenobiotic chemicals; this may increase the carcinogenicity of chemicals that must undergo microsomal activation, and decrease the activity of those chemicals which are detoxified by the microsomal enzymes (IARC, 1978).

The mutagenicity of PCB isomers has been tested in several systems. The only marked genetic effect observed at any level was with the single isomer 4-chlorobiphenyl, and attempts to reproduce this experiment have not been successful. Despite the apparent weak mutagenicity of PCBs in the systems examined to date, the fact that most animals probably metabolize PCBs through an arene oxide intermediate, (reactive compounds which could react with nucleic acids and cause genetic effects), indicates that the mutagenic potential of PCBs should not be casually dismissed (OWRS, 1980; IARC, 1978).

Evidence concerning teratogenic effects of PCBs is lacking. No fatal abnormalities were produced in rats by daily doses of Aroclors 1242, 1254, or 1260 at 10 and 30 ppm, or Aroclors 1254 at 100 ppm in the diet. Indications of structural malformations or genetic changes have been rare. However, controlled experiments using nonhuman primates have illustrated reproductive abnormalities due to low-level PCB exposure. In addition to alterations in menstrual cycles and births of small infants, nonhuman primates had more early abortions. The infants born to exposed mothers also showed some immunological and behavioral deficiencies (WHO, 1976; OWRS, 1980).

2.1.3 Absorption, Distribution, and Metabolism

Commercially prepared PCBs are a complex mixture of chlorinated biphenyls and may be contaminated with other toxicants, such as chlorinated naphthalenes and chlorinated dibenzofurans. The toxicological properties of these mixtures vary according to their composition. Exposure may occur through ingestion, inhalation, or dermal contact; absorption is efficient by all routes. Human exposure has resulted largely from consumption of contaminated food. PCBs accumulate in the fatty tissues and skin of man and other mammals. The amount stored depends on the susceptibility to metabolism and, therefore, on the degree of chlorination and availability of adjacent unsubstituted carbons in the aromatic rings (NAS, 1979).

Metabolism of PCBs occurs by formation of phenolic and dihydroxy metabolites with arene oxides as probable intermediates. The rate of metabolism and excretion slows dramatically as the number of chlorines on the biphenyl nucleus increases. PCBs may be transferred either transplacentally or in breast milk. Apparently, nonhuman primates retain PCBs more efficiently than rodents (NAS, 1979).

2.2 Environmental Effects (CONTACT: Gilman Veith, FTS 783-9534)

2.2.1 Aquatic Effects

The acute toxicity of several polychlorinated biphenyls (PCBs) to freshwater animals has been measured with three invertebrate and four fish species, and the species mean acute LC₅₀ values for the various compounds range from 2.0 to 283 ug/l. The data from flow-through tests with measured concentrations are similar for fish and invertebrate species, and probably accurately reflect the toxicity of the compounds. The data from static tests are more variable, and many may not reflect actual toxicity, due to volatility, solubility, bioconcentration, and adsorption characteristics of the various PCB compounds. Eleven life-cycle or partial life-cycle tests were completed with three invertebrate and two fish species; the chronic no-effect levels range from 0.2 to 15 ug/l. Species mean acute LC₅₀ values for PCBs and saltwater animals range from 10.5 to 20 ug/l in six tests on three invertebrate species. Two chronic tests have been conducted on the sheepshead minnow, providing chronic no-effect levels for this species of 7.14 and 0.098 ug/l (OWRS, 1980).

The freshwater residue data show that PCBs accumulate to relatively high levels in fish and invertebrate tissues, and that for most species PCBs are not rapidly eliminated when exposure is discontinued. Bioconcentration factors (BCF) for invertebrate species range from 2,700 to 108,000. Bioconcentration factors for PCB exposures of fish species range from 3,000 to 274,000. Bioconcentration data for PCBs in saltwater fish and invertebrate species show bioconcentration factors ranging from 800 to 230,000 for invertebrate species and from 14,400 to 670,000 for fish species (OWRS, 1980).

The Water Quality Criteria document lists criteria to protect aquatic life that are very low. For freshwater a 24-hour average of 0.014 ug/l is suggested and the value for saltwater is 0.03 ug/l. Drinking water has seldom been found to be contaminated with PCBs (OWRS, 1980).

2.3 Other Effects

Assessment of effects of PCBs on the environment is not clear-cut. Although many "hot spots" with high PCB levels exist, these compounds have not been detected in agricultural soil. Average PCB concentrations in vegetation are not known. Available data in birds deal with predators, and since levels depend on diet it is difficult to derive an average value for PCB concentration in wildlife (see Section 4).

While PCBs are found in many places the toxic effects are subtle and difficult to detect. Reduced reproductive capability and morphological and functional changes in the livers of test animals have been observed. PCBs accumulate in adipose tissues and severe effects may arise when the animal is under sufficient stress to mobilize the PCB-containing lipids (NAS, 1979).

3. ENVIRONMENTAL RELEASE

There is no substantial evidence suggesting that PCBs are produced in the environment, either from natural sources or from chemical transformation of the compounds. Therefore, all environmental contamination by PCBs is inferred to have resulted from the production and use of materials and equipment containing PCBs. Also, no significant degradation processes, either environmental or biological are operative for free PCBs which contain four or more chlorine atoms per molecule (NAS, 1979).

Overview of PCBs Industrial Usage in the United States

Over the four years from 1971-1975 the domestic production and use of polychlorinated biphenyls were approximately constant with averages of 40 million pounds per year for production and 33 million pounds per year for domestic sales. During this period Monsanto Industrial Chemicals Corp., the sole domestic producer, supplied approximately 99% of the domestic market. Monsanto sold several PCB mixtures under the generic trade name Aroclor, and purchase was limited to intended use in nominally closed electrical systems (transformers and capacitors) since 1971 under voluntary restrictions imposed by Monsanto. No PCBs have been produced in the U.S. since 1977 (OTS, 1977).

Of the domestic sales of PCBs, 65% to 70% were to manufacturers of capacitors, and the remainder to manufacturers of transformers. An average of 2,000 to 2,500 pounds of PCBs (in the form of a mixture with trichlorobenzenes) are used in PCB transformers. Approximately 5% of the transformers in service in this country were estimated to contain PCBs as of 1976 (most transformers contain mineral oil instead of PCBs). Capacitors containing PCBs are of two general types; small capacitors which are built into electrical appliances such as fluorescent lights, TV sets and small motors, and large capacitors which are used as separate units in electrical power distribution systems and with large industrial machinery such as electric motors and welding machines. Most small capacitors in use in radios and other electronic equipment are solid-state units and do not contain PCBs (OTS, 1977).

Cumulative PCBs Production and Usage in the United States

Estimates developed for total PCBs production and utilization in the U.S. since their introduction to industry in 1930 are presented in Table 2. These data define the estimated proportions of PCBs used in various applications, and an accounting, based on available data plus estimates, of the current distribution of this material (as of 1975). Of the roughly 1.25 billion pounds purchased by U.S. industry, it is estimated that only 55 million pounds, or 4.4% have been destroyed by incineration or by degradation in the environment. About 60% of the total domestic sales is still in service, almost all in capacitors and transformers. The remainder, about 440 million pounds, are in the environment; it is estimated that 290 million pounds are in landfills or dumps and 150 million pounds are "free" in the general environment (air, water, soil, sediments) and presumably

available to the biota. Some of the values in Table 2 are relatively well-established, while others are gross estimates resulting from a lack of data in the area. The estimated reliability for each value presented is shown in the table (OTS, 1977).

One of the more important conclusions from this work is the estimation that the amount of PCBs in landfills and dumps is nearly twice the amount of PCBs already "free" in the environment. The material in land disposal sites may be considered a threat to become widely dispersed over a long period of time through slow vaporization and leaching (OTS, 1976).

Routes of entry into the environment in the past which are no longer important are: releases from PCB production and industrial use and losses from open-end and nominally closed systems in service. Present and future routes of entry into the environment are (NAS, 1979):

- Land disposal of obsolete materials containing PCBs (e.g., capacitors).
- Leakage from electrical equipment and accidental releases due to fires or spills.
- Disposal of PCB-containing materials through incineration.
- PCB evaporation into air from landfills containing PCB waste.

TABLE 2: ESTIMATES OF CUMULATIVE PCBs PRODUCTION, USAGE, AND GROSS ENVIRONMENTAL DISTRIBUTION IN THE UNITED STATES OVER THE PERIOD 1930-1975 IN MILLIONS OF POUNDS

	Commercial Production	Industrial Purchases	PCBs Currently in Service	PCBs Currently in Environment	PCBs Destroyed	Estimated Reliability of Values
U.S. PCB Production	1,400					+ 5%, -20%
Total U.S. PCB Imports	3					+30%
Total U.S. PCB Exports		150				+20%
PCB by Use Category:						
Petroleum Additives		1				+50%
Heat Transfer		20				+10%
Misc. Industrial		27				+15%
Carbonless Copy Paper		45				+ 5%
Hydraulics and Lubricants		80				+10%
Other Plasticizer Uses		115				+15%
Capacitors		630	450			+20%
Transformers		335	300			+20%
Use Other Than Electrical			8			+60%
PCB Degraded or Incinerated:						
Environmentally Degraded					30	+70%
Incinerated					25	+10%
Landfills and PCBs in Dumps:						
Production Wastes				110		+20%
Obsolete Elect. Equipment				80		+40%
Other (paper, plastic, etc.)				100		+40%
Free PCBs in the Environment (soil, water, air, sediment)				150		+30%
TOTAL	1,403	1,253	758	440	55	----

Source: (OTS, 1976).

4. EXPOSURE ROUTES

Environmental Levels

Average PCB levels for possible exposure routes are given below (NAS, 1979):

<u>ROUTE</u>	<u>AVERAGE PCB LEVEL</u>
Food	(see Section 4.3)
Atmosphere	
Rural and Oceanic	0.05 ng/m ³
Urban and Suburban	5.0 ng/m ³
Major U.S. Rivers	0.1 to 3.0 ug/l*
Soil (1 cm)	2 x 10 ⁻⁵ ug/kg

The North Atlantic Ocean appears to be the dominant sink for PCBs, accounting for 50% to 80% of PCBs in the environment, and freshwater sediment is a major continental reservoir. Environmental load estimates for the United States and the Atlantic Ocean are presented for the following compartments (NAS, 1979):

	<u>Amounts (x 10⁶ kg)</u>
Atmosphere	0.018
Hydrosphere	
Freshwater	0.012 - 0.035
Freshwater sediment	1.400 - 7.100
Freshwater biota	0.030
Marine sediment	0.660 - 2.700
Marine water	6.000 - 66.00
Marine biota	0.300
Lithosphere	0.140 - 2.800

The estimated distribution and amount of PCBs in the lithosphere are summarized below. The uncertainty involved in attempting to estimate the distribution and amount of PCBs in the biota must be noted, particularly in the two largest compartments, soil and plants (NAS, 1979).

ESTIMATED PCB LEVELS IN THE LITHOSPHERE

Compartment	<u>PCB Concentration</u> (mg/kg)		<u>Amount of PCBs</u> (kg)	
	low	high	low	high
Soil (1 cm)	2 x 10 ⁻⁷	2 x 10 ⁻³	2.7 x 10 ¹	2.7 x 10 ⁵
Plants	2 x 10 ⁻³	4 x 10 ⁻²	1.3 x 10 ⁵	2.5 x 10 ⁶
Wildlife	2 x 10 ⁻²	4 x 10 ⁻¹	1.3 x 10 ¹	2.6 x 10 ²
Livestock	2 x 10 ⁻³	10 ⁻¹	1.3 x 10 ²	6.3 x 10 ³
Man	3.5 x 10 ⁻¹		4.9 x 10 ³	4.9 x 10 ³
		TOTAL	1.4 x 10 ⁵	2.8 x 10 ⁶

* These estimates appear to be too high, probably due to proximity to point sources. Low and high estimates for freshwater levels of PCBs are 1 and 3 ng/l for four geographic areas in the U.S. (NAS, 1979).

PCBs in Humans

Studies suggest that about half the American population has PCB levels of one part per million or more; levels of PCBs in human adipose tissue have been well documented, and the mean level in the U.S. population is 1.2 mg/kg. The concentration detected in adipose tissue can be converted into whole body levels, assuming that lipid constitutes 30% of body weight. Accordingly, a PCB concentration of 0.35 mg/kg body weight has been suggested. No adverse effects have been associated with PCBs at these concentrations found in adipose tissue or at levels measured in blood, or milk of individuals whose only exposures were from general environmental contamination (NAS, 1979).

4.1 Air Exposure (CONTACT: Dave Patrick, FTS 629-5645)

Presently there are no known sources of low-level long-term atmospheric emissions of PCBs. Potential for exposure exists for populations living near incinerators and landfills used for PCB disposal. Fires or explosions involving electrical equipment containing PCBs can result in short-term exposures. Daily intake from air is likely to be much less than 1 ug according to the World Health Organization (WHO, 1976).

4.2 Water Exposure

The highest concentration of PCBs reported in tap water is 100 ng/l (in Japan), but levels probably do not exceed about 1 ng/l. Therefore, daily intake from water consumption should also be much less than 1 ug (WHO, 1976).

4.3 Other Exposure Routes

Food

The primary exposure route for the general population is through food consumption. FDA and USDA monitoring programs in the past have shown that fish, cheese, eggs and by-products used in animal feed were the main commodities in the U.S. contaminated with PCBs. However, the PCB content of all food items has decreased between 1971 and 1975 except for fish; it was estimated that PCB intake from diet was about 15 ug/day in 1971 and 8.7 ug/day in 1975 (IARC, 1978).

The measures taken in the 1970's to limit releases of PCBs and to remove them from food processing environments has reduced direct contamination of food to a low level. The bioconcentration potential and persistence of PCBs in the aquatic environment have maintained fish as a dietary source however (OWRS, 1980).

5. DATA BASES

5.1 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. For further information, contact Jim Cottrell at FTS 382-3546.

CIS contains numeric, textual, and bibliographic information in the areas of toxicology, environment, regulations, and physical/chemical properties. Several of these data bases are described below.

5.1.1 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information.

EPACASR is now available on CIS for internal use by EPA personnel and is expected to be accessible from a public CIS account in the near future. The publication and computer tapes are also available through the National Technical Information Service (NTIS). For further information on EPACASR, contact Eleanor Merrick at FTS-382-3626.

5.1.2 Industry File Indexing System (IFIS)

IFIS is an on-line system which contains information relating to the regulation of chemicals by EPA through industry-specific legislation. IFIS enables the user to determine, for any particular industry, which chemicals are used and produced and how these chemicals are regulated. IFIS is currently available on CIS for internal use by some EPA personnel and is expected to be accessible from a public CIS account soon. For more information on IFIS, contact Daryl Kaufman at FTS 382-3626.

5.1.3 Scientific Parameters in Health and the Environment, Retrieval and Estimation (SPHERE)

SPHERE is being developed by the EPA Office of Toxic Substances as a system of integrated data bases, each representing a compilation of extracted scientific data. The system is being released to the public in stages as part of CIS, and the accessibility of component data bases should be confirmed with the contact given below. The

components currently available (either through public CIS accounts or the internal EPA system) include: DERMAL, which provides quantitative and qualitative health effects data on substances admitted to humans and test animals via the dermal route; AQUIRE, a component containing aquatic toxicity data for about 2,000 chemicals; GENETOX, a mutagenicity data base; ISHOW, and ENVIROFATE, both of which are compilations of physical/chemical parameters useful in assessing environmental fate and transport. For more information contact Paula Miles, FTS 382-3760.

5.1.4 Oil and Hazardous Materials Technical Assistance Data System (OHMTADS)

OHMTADS is a data base created by EPA to aid spill response teams in the retrieval of chemical-specific response information. The file currently contains data for approximately 1,200 chemicals including physical/chemical, biological, toxicological, and commercial information. The emphasis is on harmful effects to water quality. OHMTADS is available to the public through CIS.

5.1.5 Chemical Evaluation Search and Retrieval System (CESARS)

CESARS provides detailed information and evaluations on a group of chemicals of particular importance in the Great Lakes Basin. CESARS was developed by the State of Michigan with support from EPA's Region V. Presently, CESARS contains information on 180 chemicals including physical-chemical properties, toxicology, carcinogenicity, and some aspects of environmental fate. Information for most chemicals is extensive and consists of up to 185 data fields. CESARS is accessible through public CIS accounts.

5.2 Chemicals in Commerce Information System (CICIS)

CICIS is an on-line version of the inventory compiled under the authority of TSCA. This law required manufacturers of certain chemicals (excluding food products, drugs, pesticides, and several other categories) to report production and import data to EPA. CICIS contains production volume ranges and plant site locations (for 1977) for over 58,000 chemical substances. There is also a Confidential Inventory in which data for some chemicals are claimed confidential and are not available in the public inventory. A version of CICIS (TSCA Plant and Production, or TSCAPP) is now accessible through CIS. For more information contact Geri Nowak at FTS 382-3568.

5.3 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is not another data base, but rather a sophisticated switching network. CSIN links may independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems." Users may converse with any or all systems interfaced by CSIN without training on these independent systems, regardless of the hardware, software, data formats, or protocols of these information resources.

Information accessible through CSIN includes data on chemical nomenclature, composition, structure, properties, toxicity, production uses, environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, twelve independent information resources are accessible through CSIN, including: National Library of Medicine (NLM); Chemical Information System (CIS); CAS-On-Line; SDC's ORBIT; Lockheeds's DIALOG, and the Bibliographic Retrieval Service (BRS). For further information contact Dr. Sid Siegel at FTS 395-7285.

5.4 Graphical Exposure Modeling System (GEMS)

EPA has developed GEMS, an interactive computer system, to provide a simple interface to environmental modeling, physiochemical property estimation, statistical analysis, and graphical display capabilities. GEMS is being developed for use by the Office of Toxic Substances to support integrated exposure/risk analyses. The system provides environmental analysts who are unfamiliar with computer programming with a set of sophisticated tools to undertake exposure assessments. For information about the system and the current accessibility of GEMS, contact Bill Wood at FTS 382-3928.

6. REGULATORY STATUS (Current as of 6/10/84)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- o Section 311 (b)(2)(A) - Polychlorinated biphenyls (PCBs) are designated as hazardous substances (40 CFR 116.4). Accordingly, PCBs are subject to the general provisions, reporting quantities, and notification requirements established in CFR 117.
- o Sections 307, 308, and 501 - Effluent standards for the toxic pollutants, PCBs, are established for the following (40 CFR 129.105):
 - PCB manufacturers,
 - Electrical capacitor manufacturers,¹ and
 - Electrical transformer manufacturers.¹
- o Sections 301, 304, 306, 307, and 316 - PCBs are designated as toxic pollutants (40 CFR 401.15). Accordingly, effluent limitations, pretreatment standards, new source performance standards (NSPS), and performance standards for new (PSNS) and existing (PSES) sources have been promulgated for various sections of the following industries:
 - Electroplating (40 CFR 413),²
 - Steam electric power generating (40 CFR 423),
 - Metal finishing (40 CFR 433),² and
 - Aluminum forming (40 CFR 467).²
- o Sections 318, 402, and 405 - Under the National Pollutant Discharge Elimination System (NPDES) permit testing requirements, PCBs are listed as organic toxic pollutants on the basis of gas chromatographic and mass spectroscopic analyses (40 CFR 122, App. D, Table II). Other permitting requirements are covered in 40 CFR 123 to 124.

¹ Applies to those manufacturers of electrical capacitors and transformers which contain PCBs or PCB-containing compounds as part of the dielectric.

² PCBs are controlled by limiting the total toxic organics (TTOs) which are the summation of all quantifiable values greater than 0.01 mg/l.

Resource Conservation and Recovery Act (RCRA)

- o Sections 1008 and 4004 - When applied to land used for the production of animal feeds, including pasture crops for animals raised for milk, solid waste containing PCBs at concentrations equal to or greater than 10 mg/kg (10 ppm; dry weight) must be incorporated into the soil (40 CFR 257.3-5 (b)).

Section 3001 - PCBs are listed as hazardous waste constituents (40 CFR 261, App. VIII).

Toxic Substances Control Act (TSCA)

- o Section 12(b) - Requires notification to EPA of intent to import or export PCBs for any purpose other than disposal (40 CFR 707.60 (b)-(c)).
- o Section 6(e)(3)(B) - Allows manufacturers to apply for exemptions from the PCB manufacturing ban (40 CFR 750.10 - 750.21).
- o Section 6(e) - Prohibits the manufacture, processing, distribution in commerce, and use of PCBs or PCB items regardless of concentration, in any manner other than in a totally enclosed manner within the United States except those PCBs or PCB items resulting from certain excluded manufacturing processes or recycled PCBs (40 CFR 761.20). The excluded processes and items are those in which:
 - The concentration of inadvertently generated PCBs in products manufactured in or imported into the U.S. have an annual average of less than 25 ppm, with a 50 ppm maximum (49 FR 28189).
 - The concentration of inadvertently generated PCBs in the components of detergent bars manufactured in or imported into the U.S. is less than 5 ppm (49 FR 28190).
 - The release of inadvertently generated PCBs at the point at which emissions are vented to ambient air is less than 10 ppm; and, the amount of inadvertently generated PCBs added to water discharged from a manufacturing site is less than 100 g per resolvable gas chromatographic peak per liter of water discharge (49 FR 28190).
 - Recycled PCBs in paper products at concentrations less than 25 ppm with 50 ppm maximum or asphalt materials that have no detectable concentration and have emissions into the atmosphere of less than 10 ppm, with other requirements for exclusion. (40 CFR 761.3 as amended by 49 FR 28190, July 10, 1984).

Manufacturing Export Exemptions

- o Items containing PCBs in concentrations less than 50 ppm can be exported or imported for disposal.

Distribution in Commerce Exemptions

- o PCBs or PCB items at concentrations of 50 ppm or greater, sold before July 1, 1979, for purpose other than resale can be distributed in commerce only in a totally enclosed manner after that date.
- o PCBs or PCB items at concentrations of less than 50 ppm are allowed to be processed and distributed in commerce for the purpose of disposal, and
- o PCBs or PCB items at concentrations of 50 ppm or greater may be processed and distributed in commerce for the purpose of disposal in accordance with 40 CFR 761.
- o Section 6(e)(2)(B) - PCB use authorizations have been approved for the following non-totally enclosed uses:
 - o In transformers (except transformers for railroad locomotives and self-propelled railroad cars), including rebuilding and servicing (40 CFR 761.30(a)(1)(i) - (2)(vii)),
 - o Use and servicing of railroad transformers, and may be processed and distributed in commerce for the purposes of servicing these transformers (40 CFR 761.30(b)(1)(i) - (2)(vii)),
 - o Use and servicing of mining equipment (40 CFR 761.30(c)(1) - (5)),
 - o Intentionally manufactured PCBs in heat transfer systems at a concentration of less than 50 ppm (49 FR 28190, July 10, 1984),
 - o Intentionally manufactured PCBs produced after July 1, 1984, may be used in hydraulic systems at a concentration of less than 50 ppm (49 FR 28190, July 10, 1984),
 - o In carbonless copy paper (40 CFR 761.30(f)),
 - o In "Diarylide" and "Phthalocyanin" pigments containing 50 ppm PCBs or greater if exempted under TSCA (6)(e)(3)(B), (40 CFR 761.30(g)),
 - o Use and servicing of electromagnets, switches, and voltage regulators (40 CFR 761.30(h)(1) - (2)(vii)),

- o Indefinitely in the compressors and in the liquids of natural gas pipelines at a concentration level of less than 50 ppm (49 FR 28191, July 10, 1984),
- o In small quantities for research and development (49 FR 28202, July 10, 1984),
- o As a permanent microscopic mounting medium (49 FR 28202),
- o In capacitors (40 CFR 761.30(1)(1)(i) - (ii)),
- o Use and servicing of circuit breakers, reclosers, and cables (40 CFR 761.30(m)(1)(i) - (ii)),
- o As an immersion oil in fluorescence microscopy (49 FR 28202), and
- o Indefinitely as optical liquids (49 FR 28202, July 10, 1984).

On July 10, 1984, EPA granted, under Section 6(e)(3)(B) of TSCA, one year exemptions for the manufacturing, processing, and distribution in commerce of certain PCB items (49 FR 28171). Regulations under TSCA also cover marking (40 CFR 761.40); disposal (40 CFR 761.60); storage for disposal (40 CFR 761.65); incineration (40 CFR 761.70); chemical waste landfills (40 CFR 761.75); and decontamination (40 CFR 761.79).

6.1.2 Programs of Other Agencies

Federal Food, Drug, and Comestic Act (FFDCA) Administered by the FDA

- o Sections 306, 402, 406, 408, 409, and 701 - Establishes restrictions on the industrial uses of PCBs in establishments manufacturing food-packaging materials (21 CFR 109.15(a) - (c)).
- o Tolerances for PCBs in dairy products, poultry, eggs, finished animal feed, fish, infant foods, and paper packaging materials (21 CFR 109.30(a) - (b)). The tolerances and foods are presented in section 7.3; and, tolerances for unavoidable residues of PCBs in fish and shell-fish lowered from 5 ppm to 2 ppm (49 FR 21514, May 22, 1984. Effective date August 20, 1984.
- o Provisions providing for minimizing the accidental PCB contamination of animal feed in the production, handling, and storage of animal feed (21 CFR 500.45).
- o Provisions to preclude the accidental contamination of foods by PCBs (21 CFR 110.40(b)).

Hazardous Materials Transportation Act (DOT)

- o PCBs are classified within the other regulated materials (ORM-E) hazard class for the purposes of transportation (49 CFR 172.101 and 49 CFR 173.1300, Subpart O).
- o PCB packaging requirements (49 CFR 173.510).
- o Other transportation regulations that cover PCB hazardous materials (49 CFR 173-177).

Occupational Health and Safety Act

- o Standards for employees exposed to hazardous air contaminants limit occupational exposure to PCBs (29 CFR 1910.1000, Table 2-1).

6.2 Proposed Regulations

6.2.1 EPA Programs

TSCA

- o EPA withdrew the proposed rule (45 FR 30989) restricting the use of PCBs at agricultural pesticide and fertilizer facilities on March 19, 1984 (49 FR 10133).
- o EPA is proposing to incorporate into existing American Society for Testing and Materials (ASTM) test methods for PCBs (40 CFR 761), a revised ASTM method (centrifugation of water and sediment in crude oils and fuels) to meet particular PCB requirements (49 FR 22836, June 1, 1984).
- o In an advance notice of proposed rulemaking (ANPR) EPA announced its interest in collecting data specific to the risks posed by fires involving electrical transformers that contain PCBs; and to solicit data on methods for eliminating these risks for the purpose of determining the need for further control through regulation (49 FR 11070, March 23, 1984).

Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund).

- o Sections 102(b), 103(a)(b) - CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the clean-up of hazardous waste disposal sites (42 USC 9601; PL 96-501). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantity requirements (RQ's), claims procedures, and the confidentiality of business records (46 FR 54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued (47 FR 10972).

PCBs are hazardous substances under CERCLA and will be subject to regulations developed under Superfund. EPA has proposed adjustments to the RO's established under CERCLA and the CWA (48 FR 23552).

6.2.2 Other Programs

- o USDA

Proposed amendments to the meat and poultry products inspection regulations concerning compliance with performance standards for retaining laboratory accreditation; requires a minimum proficiency level for the identification and quantification of PCB residues of 0.5 ppm (45 FR 73949).

6.3 Other Actions

Public Health Service (PHS) National Toxicology Plan

- o PCBs are recognized as substances or groups of substances that may reasonably be anticipated to be carcinogens (Third Annual Report on Carcinogens, Summary, September 1983, page 111).

7. STANDARDS AND RECOMMENDED CRITERIA^a

7.1 Air

- o OSHA workplace exposures to toxic air contaminants, 8 hour TWA (29 CFR 1910.1000, Table Z-1).

Chlorodiphenyl (42 percent chlorine)	1 mg/m ³
Chlorodiphenyl (54 percent chlorine)	0.5 mg/m ³

- o NIOSH recommendation of weekly average 1 µg/m³
- o American Conference of Governmental and Industrial Hygienists (ACGIH) recommended in 1980 TWA's identical to those promulgated by OSHA.

7.2 Water

- o Water Quality Criteria (WQC); 45 FR 79318.

Freshwater aquatic life: 24 hour average	0.014 µg/l
Saltwater aquatic life: 24 hour average	0.03 µg/l

An estimated lifetime cancer risk for human health of 10⁻⁵ corresponds to a criterion concentration of 0.79 ng/L for the ingestion of contaminated water and contaminated aquatic organisms. The human health criteria are based on the consumption of fish/shellfish (6.5 grams/day) in addition to water (2 liters/day). Because PCB bioconcentration factors average around 30,000, nearly all (99%) of the estimated exposure results from consumption of aquatic organisms. Because of this, the concentration corresponding to the 10⁻⁵ cancer risk for the ingestion of contaminated aquatic organisms only is also 0.79 ng/L.

- o Designated as hazardous substances under Section 311 of the CWA, notification is required if discharges of PCBs exceed 10 pounds (4.54 kg). The RQ proposed under CERCLA is 1.0 pound (0.454 kg), 48 FR 23552.

7.3 Food

- o FDA temporary tolerances for unavoidable residues of PCBs in certain foods and animal grains (21 CFR 109.30)

- Milk and dairy products (fat basis)	1.5 ppm
- Poultry (fat basis)	3.0 ppm

^aSee Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

- Eggs 0.3 ppm
- Finished animal feed (except feed concentrates, feed supplements, and feed premixes) 0.2 ppm
- Animal feed (originating from animals) 2.0 ppm
- Fish and shellfish^b 2.0 ppm
- Infant and junior foods 0.2 ppm
- Paper food-packaging material (Except those with functional barriers that prevent PCB migration). 10 ppm

21 CFR 109.30(a)(1-9) and 509.30

o FDA action levels

- Red meat 3 ppm

^bTolerance of 2 ppm, effectively upheld (49 FR 21514).

8. SPILL OR OTHER INCIDENT CLEAN-UP/DISPOSAL (CONTACT: National Response Center, 800-424-8802, or 426-2675 in Washington, D.C.)

8.1 Hazards

PCBs are moderately combustible and may be carcinogenic. Fire hazards are slight, but irritating or highly toxic gases are generated when some of these materials burn. Although PCBs pose few immediate health hazards, contact may cause burns to the skin and eyes. Vapors can cause eye and lung injury and irritation of the throat.

PCB runoff from fire control or dilution water may cause pollution. PCBs are toxic to aquatic life in very low concentrations.

8.2 First Aid

In case of contact with PCBs, immediately flush affected areas with plenty of water for at least 15 minutes. If in eyes, hold eyelids open and flush with lots of water. Remove and isolate contaminated clothing and shoes.

8.3 Emergency Action

Spill or Leak

Isolate contaminated area and wear self-contained breathing apparatus and full protective clothing. Stop discharge if possible without risk. Avoid contact and isolate and remove discharged material. In the case of small spills, take up with sand or other noncombustible absorbent material, then flush area with water. For large spills, dike far ahead of spill for later disposal. If water is contaminated, contact local health and pollution control authorities.

Fire

For small fires use dry chemical, CO₂, water spray or foam. For large fires use water spray, fog or foam. Move container away from fire area if possible.

8.4 Notification and Technical Assistance

Section 103 of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) or "Superfund" requires notification of the National Response Center (NRC, 800-424-8802; 426-2675 in the Washington, D.C. area) if releases exceed reportable quantities (10 lbs. in the case of PCBs). For emergency assistance call CHEMTREC: 800-424-9300. For information call the Division of Oil and Special Materials at 1-202-245-3045.

Disposal

No wastestreams containing PCBs were listed under RCRA regulations. Disposal and marketing of PCBs are regulated under TSCA Section 6(e). See Tables 3 and 4 for summary of the disposal requirements for PCBs and related materials. EPA has concluded in general that PCBs at levels of 50 ppm or greater must be disposed of in accordance with the requirements of 40 CFR Part 761. Under TSCA, PCBs in concentrations below 50 ppm (excluding dilutions of higher level PCBs) are not required to be disposed of in any special manner. EPA has a list of commercial landfill sites approved for PCB disposal and the contaminated items each location can accept. (CONTACT: TSCA Assistance Office, 800-424-9065; 382-3790 in the Washington area).

TABLE 3: SUMMARY OF PERMANENT DISPOSAL REQUIREMENTS
PART A: Liquid PCBs and Contaminated Debris
TSCA Regulatory Disposal Provisions

<u>PCB or PCB Item</u>	<u>Incinerator^a</u>	<u>Chemical Waste Landfill^b</u>	<u>High Efficiency Boiler^c</u>	<u>EPA-Approved Alternative^d</u>	<u>Municipal Solid Waste</u>
1. PCB Chemical Substances (above 500 ppm PCBs)	x				
2. Mineral oil dielectric fluid from PCB-contami- nated electrical equip- ment (50-500 ppm PCBs)	x	x	x		
3. Liquids, other than mineral oil dielectric fluid (50-500 ppm PCBs)	x	x	x		
4. Non-liquid PCBs in the form of contaminated soil, rags, or other debris (PCBs above 50 ppm)	x	x			
5. Dredged materials and municipal sewage treatment sludges (PCBs above 50 ppm)	x	x		x	

a. 40 CFR 761.70

b. 40 CFR 761.75

c. 40 CFR 761.60 (a) (2) (iii) & 40 CFR 761.60 (a) (3) (iii)

d. 40 CFR 761.60 (a) (5) (iii) & 40 CFR 761.60 (c)

TABLE 4: SUMMARY OF PERMANENT DISPOSAL REQUIREMENTS
PART B: PCB ARTICLES
TSCA Regulatory Disposal Provisions

<u>PCB or PCB Item</u>	<u>Incinerator^a</u>	<u>Chemical Waste Landfill^b</u>	<u>High Efficiency Boiler^c</u>	<u>EPA-Approved Alternative^d</u>	<u>Municipal Solid Waste</u>
1. PCB Transformers (PCBs above 500 ppm)	x	x ^e			
2. PCB-Contaminated Transformers (50-500 ppm PCBs)	x				x ^e
3. PCB-Contaminated Capacitors (50-500 ppm PCBs)	x	x			
4. PCB Small Capacitors containing less than 1.36 kg. (3 lbs.) dielectric fluid, otherwise fluid must be drained first and the contents properly disposed of (applies to present and former manufacturers of PCB capacitors or equipment)	x	g			
5. PCB Small Capacitors (applies to anyone other than present or former manufacturers of PCB capacitors or equipment)					x
6. PCB Large Capacitor, high or low voltage	x	g			

TABLE 4: SUMMARY OF PERMANENT DISPOSAL REQUIREMENTS
PART B: PCB ARTICLES
TSCA Regulatory Disposal Provisions

<u>PCB or PCB Item</u>	<u>Incinerator^a</u>	<u>Chemical Waste Landfill^b</u>	<u>High Efficiency Boiler^c</u>	<u>EPA-Approved Alternative^d</u>	<u>Municipal Solid Waste</u>
7. PCB Hydraulic Machines					x ^f
8. Other PCB Articles	x	x ^f			
9. PCB Containers (PCBs above 50 ppm)	x	x ^f			
10. PCB Containers (PCB concentration of less than 500 ppm)					x ^f

a. 40 CFR 761.70

b. 40 CFR 761.75

c. 40 CFR 761.60 (a) (2) (iii) & 40 CFR 761.60 (a) (3) (iii)

d. 40 CFR 761.60 (a) (5) (iii) & 40 CFR 761.60 (e)

e. The transformer must be drained of all free flowing liquid, flushed with solvent for at least 18 hours, and the solvent and liquid disposed of properly.

f. May be disposed of only after they have been drained of all free-flowing PCB liquid, and the liquid is properly disposed of.

g. The EPA has not allowed disposal of these items in a chemical waste landfill since 3/1/81. However, these restrictions may be relaxed if deemed necessary for future disposal of these items.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES AND QUALITY ASSURANCE

9.1 Air (CONTACT: Dr. Robert G. Lewis, FTS 629-3065)

PCBs are not criteria pollutants and therefore a criteria analysis methodology has not been promulgated for them. Methodology has been developed and used by ORD for sampling and analysis of PCBs in air. Two EPA reports, EPA-600/4-79-022 (Sources of Emissions of Polychlorinated Biphenyls into the Ambient Atmosphere and Indoor Air) and EPA-600/2-80-180 (Protocol for Assessment of Human Exposure to Airborne Pesticides), describe sampling and analysis methodology which has been determined to be more than adequate.

The collection medium of preference is polyurethane foam (open-cell polyether type; density 0.02 g/cm³). Air is drawn through the cylindrical plugs of the foam for periods of 4 to 24 hours using either low- or high-volume pumps, depending on the particular application. After extraction from the plugs with appropriate solvents, the samples are analyzed by electron capture GC and confirmed if necessary by GC-MS.

The method has been used successfully in the range of 0.1 ng/m³ to 11 µg/m³ (30 ng to 3 mg actual PCBs collected). Replicate sampling gives a relative standard deviation of 17%. The collection efficiency of the method is greater than 95% for all Aroclor mixtures tested with the low volume method and between 75% and 100%, depending on percent chlorine, for the high-volume method.

The limits of detection depend on the background interference arising from the foam and on the particular instrumentation being used for the analysis. They commonly range from 15 ng for Aroclor 1242 to 500 ng for Aroclor 1260.

9.2 Water (CONTACTS: Thomas Bellar, FTS 684-7311 or
James Lichtenberg, FTS 684-7308)

PCB - 1016	CAS No. 12674-11-2
PCB - 1221	CAS No. 11104-28-2
PCB - 1232	CAS No. 11141-16-5
PCB - 1242	CAS No. 53469-21-9
PCB - 1248	CAS No. 12672-29-6
PCB - 1254	CAS No. 11097-69-2
PCB - 1260	CAS No. 11096-82-5

These Aroclors (PCBs) are proposed parameters under Section 304(h) of the Clean Water Act. They are listed as priority pollutants.

The existing and proposed procedures for analysis of PCBs in natural waste and drinking waters is liquid-liquid extraction followed by analysis of extracts by gas chromatography.

Liquid-Liquid Extraction Methods: EPA #608, 625
ASTM #3534
Method #3 EPA

Major Equipment Required: Gas Chromatograph

A measured volume of sample, approximately 1-liter, is solvent extracted with methylene chloride using separatory funnel techniques. The methylene chloride extract is dried and exchanged to hexane during concentration to a final volume of 10 ml or less. Identification is made from gas chromatographic patterns obtained from injection of 1 to 4 μ l of the extract through two or more unlike columns. Detection and measurement are accomplished using electron capture, microcoulometric, or electrolytic conductivity detectors. The method detection limit is approximately 0.1 μ g/l. If EPA #625 is followed, detection is accomplished through Mass Spectrometry with a detection limit of approximately 35 μ g/l.

Samples must be collected in glass bottles following conventional sampling practices except the bottle must not be prewashed with sample before collection. Samples must be iced or refrigerated at 4°C from the time of collection until extraction. If the sample will not be extracted within 72 hours of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide or sulfuric acid. Spiked river water samples have been stored for up to 7 days under these conditions with no apparent losses.

LIST OF PROCEDURES FOR PCBs^a

Method	Detection Limit (MDL)	Recovery ^b (%)	Standard Deviation (%)	Status (As of 3/81)
EPA-3	N.D.	N.D.	N.D.	Official
EPA-608	c	88-96	2-5	Proposed
EPA-625	d	N.D.	N.D.	Proposed
ASTM-3534	1.0 ug/1	99	6.9	Proposed

^aAll are liquid-liquid extraction methods; N.D. means not determined.

^bSingle laboratory recovery from spiked reagent water or spiked wastewater.

^cMDL for PCB-1242 is 0.065 ug/1; all other PCB MDLs are undetermined for this method.

^dMDL for PCB-1221 is 30 ug/1; for PCB-1254 MDL is 36 ug/1. All other MDLs are undetermined for this method.

References for Water Analysis

"Method for Polychlorinated Biphenyls (PCBs) in Industrial Effluents." National Pollutant Discharge Elimination System Appendix A, Federal Register, 38, No. 75, Part II. (1973); Method, EPA-3.

"Standard Test Method for Measuring Polychlorinated Biphenyls (PCBs) in Water," ASTM D-3534-76, Part 31, Water, Annual Book of ASTM Standards, 1980.

"Methods for Organic Chemical Analysis of Water and Wastes by GC, HPLC, and GC/MS." Method 625, Base/Neutrals and Acids. USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

"Methods for Organic Chemical Analysis of Water and Wastes by GC, HPLC, and GC/MS." Method 608, Pesticides and PCBs, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

9.3 Solid Waste (CONTACTS: Werner Beckert, FTS 545-2137 and Donald Gurka, FTS 545-2113)

Method 8.08 and a Method for Polychlorinated Biphenyls (PCBs) in Water and Wastewater, p. 43 are approved for analyses of PCBs in solid wastes (Test Methods for Evaluation Solid Wastes: Physical/-Chemical Methods, USEPA/SW.846, 1980).

There is no approved method for analysis of PCBs in hazardous waste matrices. However, methods 608 and 625 for water have been employed

in some cases. Analyses via electron capture GC or GC/MS are generally reliable for 5 to 500 mg/kg samples, with detection limits of 1 mg/kg; certain matrices (e.g., soils, sediments, phthalate esters) may interfere however.

Standard deviations on successive analyses typically are 1-26 percent; spike recoveries of 76-109 percent and relative standard deviations of 2.0-11.5 percent were reported for PCBs in a motor oil matrix.

References for Solid Waste Analysis

Criterion Document: Polychlorinated Biphenyls. Criteria and Standards Division, Office of Water Planning and Standards, U.S. EPA, PB 296803.

T.A. Bellar and J.J. Lichtenberg, The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils. EPA-EMSL-Cincinnati, September 17, 1980.

J.W. Eichelberger, L.E. Harris, and W.L. Budde, Anal. Chem. 46, 227 (1974).

9.4 Other Samples

A method for analysis of PCBs in soils and bottom sediments may be found in Chemistry Laboratory Manual for Bottom Sediments and Elutriate Testing, (USEPA/Region V, Central Regional Laboratory, Chicago, Ill., p.108).

The soil or sediment sample is dried, sieved, and extracted for 16 hours (Soxhlet) with acetone/hexane (1:1). The extract is concentrated and passed through Florisil or silica gel for elimination of interferences. Sulfur is a common interfering substance. Analysis is affected by GC and ED or EC detection. Detection limit is about 2 mg/kg.

The NIOSH Manual of Analytic Methods contains several methods for PCB analysis. Method 244 (Vol. 1) describes a procedure for analysis of PCBs in air; adsorption onto Florisil and desorption with hexane is followed by analysis by electron capture GC. The range of detection is 0.01 to 10 mg/m³. The sample may be reacted with antimony pentachloride to yield decachlorobiphenyl which is easier to selectively quantify (method 253).

A method (329, Vol. 6) is also listed for analysis of PCBs in blood serum. The blood serum is extracted with ether/hexane (1:1), and the extract chromatographed, concentrated, and analyzed for PCBs by electron capture GC. The detection limit is about 0.026 mg/l (based on 5 ml sample) with a working range up to 10 mg/l. Pesticides and their metabolites may interfere; precision is about 14% and total recovery exceeds 80%.

Methods of analysis for PCBs in a wide variety of environmental samples have been reviewed briefly by IARC (IARC, 1978). Hutzinger, et al. (The Chemistry of PCBs, Cleveland, Ohio, Chemical Rubber Co., pp. 41-70, 189-193; 1974) gives a more detailed review of analytical techniques for PCBs.

9.5 Quality Assurance

Single laboratory test data on simple spiked matrices have been collected by EPA. Interlaboratory accuracy and precision and method detection limit data are currently being collected. Quality control and performance evaluation samples (concentrates of PCBs in acetone to be spiked into water) are available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, USEPA, Cincinnati, Ohio 45268.

REFERENCES

The major references used in the preparation of this document are listed below. EPA references are listed by the EPA office of origin and the year of publication. For further information refer to the contacts given throughout this document or contact the relevant EPA offices given at the end of this section.

- (IARC, 1978) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 18, pp. 43-103, International Agency for Research on Cancer, World Health Organization (1978).
- (NAS, 1979) Polychlorinated Biphenyls, National Academy of Sciences, Washington, D.C. (1979).
- (OTS, 1976) PCBs in the United States. Industrial Use and Environmental Distribution, EPA-560/6-76-005, Office of Toxic Substances (1976).
- (OTS, 1977) A First Order Mass Balance Model for the Sources, Distribution, and Fate of PCBs in the Environment, EPA-560/6-77-006, Office of Toxic Substances (1977).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, Vol. 1, Chapter 36, EPA-440/4-79-029a, Office of Water Regulations and Standards (1979).
- (OWRS, 1980) Ambient Water Quality Criteria for PCBs, EPA-440/5-80-068, Office of Water Regulations and Standards (1980).
- (WHO, 1976) Polychlorinated Biphenyls and Terphenyls. Environmental Health Criteria 2, World Health Organization (1976).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-4173 (919-541-4173)

Carcinogen Assessment Group	382-7341
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	382-7571
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality and Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	382-7051
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
------------------------------	----------

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Information Management Division 382-3749

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division
Research Triangle Park, NC 629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division 382-7575

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division 755-0100

Effluent Guidelines Division 382-7120

Office of Solid Waste (OSW)

Permits and State Programs Division 382-4746

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division 382-2182
Hazardous Site Control 382-2443

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II 340-6635 (201-321-6635)

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis
Research Triangle Park, NC 629-2454 (919-541-2454)

Water Analysis
Cincinnati, OH 684-7311 (513-684-7311)

Waste Analysis
Las Vegas, NV

545-2137 (702-798-2137)

Office of Monitoring Systems
and Quality Assurance

382-5767

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Chemical Coordination Staff

Chemical Information
and Analysis

382-3375

PHTHALATE ESTERS

PHTHALATE ESTERS

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-7
<u>Environmental Release</u>	3-1
<u>Exposure Routes</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
Other Routes	4-2
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substances Information Network (CSIN)	5-2
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-4
Other Actions	6-4
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
<u>Spill or Other Incident Clean Up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-2

<u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	9-1
Air	9-1
Water	9-1
Solid Waste	9-2
Other Samples	9-2
<u>References and Office Contacts</u>	R-1

PHTHALATE ESTERS

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Phthalate esters are alkyl esters of 1,2-benzene dicarboxylic acid. Most are produced commercially by the esterification of phthalic anhydride with alcohols in the presence of catalyst; alkyl benzyl phthalates also require benzyl chloride as a precursor. In recent years, annual domestic production of all phthalate esters has exceeded one billion pounds (OWRS, 1980a; OTS, 1980).

In general, the alkyl phthalates can be described as colorless (or lightly colored), oily liquids with little, if any, odor. They have relatively high boiling points and low vapor pressures; their water solubilities range from sparingly soluble for the longer chain alkylesters to moderately soluble for the glycol ether esters; and they are stable to heat and light (OTS 1981; OWRS 1979). Phthalate esters, most notably di(2-ethylhexyl) phthalate (DEHP), have found widespread use as plasticizers because of their unique combination of physical/chemical properties such as low volatility, resistance to migration from polymers, low temperature flexibility, chemical stability, freedom from odor and taste, and compatibility with polar polymers and additives over a wide range of compositions.

Table 1 lists most of the phthalate esters discussed in this report. Table 2 summarizes their physical/chemical properties. This report will focus on DEHP because of its high production volume, persistence in the environment, and potential for human exposure. Information on the other phthalate esters will be included where available.

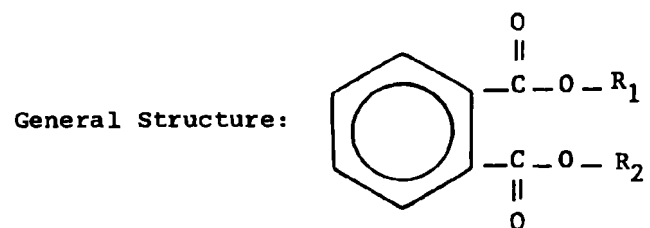
1.2 Chemistry and Environmental Fate/Transport

DEHP is the most studied of the phthalate esters. For several of the phthalate esters, very little specific data were available; therefore, the behavior of some of these compounds in the environment was inferred from data for the phthalate esters as a group.

Phthalate esters are widely distributed in the environment. They have been found in wells and drinking water, oil, soil, air, plants, fish, food, bacteria, fungi, worms, cattle pineal glands, bovine heart muscle, and humans. The fact that they are so commonly found suggests that some may be naturally-occurring. However, there is also a distinct possibility of sample contamination in collection and analyses. The extent of naturally-occurring phthalate esters, if any, is small when compared with anthropogenic sources (OWRS, 1979; OWRS, 1980a).

The two transport mechanisms that appear to be most important for the phthalates in the aquatic environment are adsorption onto suspended solids and particulate matter and complexation with natural organic

TABLE 1: STRUCTURE AND NOMENCLATURE OF THE PHTHALATE ESTERS



Side chain structures (R_1 and R_2) are given below for each phthalate.

NAME	ALTERNATE NAMES	CAS NO.	SIDE CHAIN (R_1 AND R_2)
Dimethyl phthalate	DMP; 1,2-Benzenedicarboxylic acid, dimethyl ester	131-11-3	$-\text{CH}_3$
Diethyl phthalate	DEP; 1,2-Benzenedicarboxylic acid, diethyl ester	84-66-2	$-\text{CH}_2\text{CH}_3$
Dibutyl phthalate	DBP; 1,2-Benzenedicarboxylic acid, dibutyl ester	84-74-2	$-(\text{CH}_2)_3\text{CH}_3$
Di-n-octyl phthalate ^a	DNOP; 1,2-Benzenedicarboxylic acid, dioctyl ester	117-84-0	$-(\text{CH}_2)_7\text{CH}_3$
Di(2-ethylhexyl) phthalate ^a	DEHP; 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester; bis(2-ethylhexyl) phthalate	117-81-7	$-\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$
Benzyl butyl phthalate	BBP; 1,2-Benzenedicarboxylic acid, butyl phenylmethyl ester	85-68-7	$-(\text{CH}_2)_3\text{CH}_3$ and $-\text{CH}_2\text{C}_6\text{H}_5$

^a DEHP and DNOP are sometimes mistakenly reported as each other in the literature.

TABLE 2: PROPERTIES OF PHTHALATE ESTERS^a

PROPERTY	DMP	DEP	DBP	DNOP	DEHP	BBP
Molecular weight	194	222	278	391	391	312 ^b
Melting point, °C	3	-41	-35	-25	-50	-35 ^b
Boiling point, °C	284	298	340	220(4 torr)	384	377 ^b
Vapor pressure, torr (°C)	1.0 (100)	0.05(70)	1.0(147)	<0.2(150)	1.21(200)	<0.01(25) ^b
Water solubility, mg/L (25°C)	4320 ^b	896 ^b	13 ^b	3	0.4	2.9 ^b
Log octanol/water partition coefficient	2.1	3.2	5.2	9.2	8.7	4.8-5.8 ^b
Specific gravity ^c	1.192	1.120	1.048	0.978 (20°/4°C)	0.985	1.115-1.123 ^d (25°/25°C)
Vapor density (air=1)	6.69	7.66	9.58	-	13.45	-
Flash point, open cup, °F	315	322	375	219	420	390 ^d

^a Source: (OTS,1981) unless otherwise noted.

^b Source: (OWRS, 1979).

^c The density at 20°C relative to water at 20° unless otherwise specified.

^d Source: Plasticizers and Resin Modifiers; Monsanto Co.; Technical Publication IC/PL-361.

substances, such as fulvic acid, to form water-soluble complexes or emulsions. Photolysis, oxidation, and hydrolysis are too slow to be environmentally significant. The second order rate constants from the alkaline hydrolysis of a group of phthalate esters were measured; the corresponding half-lives in neutral water ranged from 3.2 years for DMP to 2,000 years for DEHP. Volatilization is not considered to be a competitive transport process. The transport of the phthalate esters will be dependent upon the hydrogeologic conditions of the aquatic system (OWRS, 1979; OWRS, 1980a).

The fate of DEHP and DMP were evaluated in five simulated ecosystems using EXAMS (Exposure Analysis Modeling System). The simulation predicts that, for phthalates esterified with short-chain alkyl groups, biochemical transformations will compete with export in the ecosystems with long retention times (i.e., ponds or lakes). For phthalates esterified with larger alkyl groups such as DEHP, transformation processes are slow. Export will be the dominant process for all phthalate esters entering a river, regardless of chain length. Phthalate esters with alkyl chains of intermediate length exhibit intermediate behavior. The oceans may be considered the ultimate sink for phthalate esters introduced into unimpeded rivers (OWRS, 1979; OWRS, 1980a).

Phthalate esters have been identified in living matter, and data collected from field and laboratory studies indicate that they can be taken up and accumulated by a variety of organisms. The phthalates are degraded by microbiota and metabolized by fish and animals; they are not expected to biomagnify. The highest concentrations would be expected at intermediate levels of the food chain (e.g., invertebrates) rather than at the top as occurs with chemicals such as DDT. Thus, bioaccumulation, biotransformation, and biodegradation are important aquatic fate processes for phthalate esters (OWRS, 1979).

The fate of phthalate esters in air is expected to be controlled by hydroxyl radical attack. Adsorption onto particulates and rainout are expected to be less important fate processes (OWRS, 1980a).

Little information is available on the fate of phthalate esters in soil, even though the primary point of entry into the environment is the soil (via landfills). The migration of phthalate esters out of plastics is slow. The amount available for transport or degradation is expected to be low. However, the formation of soluble complexes may increase their mobility. The phthalate esters may also be subject to biodegradation; however, the degradation rates measured have been highly variable (OWRS, 1979).

2. EFFECTS INFORMATION

2.1 Health Effects

2.1.1 Acute Toxicity

While numerous reports document the toxic effects in animals due to short-term, high-level exposure to phthalate esters, the information for humans is severely limited. The meager toxicological data may be attributed to the long use of these esters with few cases of adverse effects noted in exposed populations. It has been suggested that patients receiving transfusions through PVC tubing and blood bags may have suffered "shocked-lung" syndrome due to the leaching of DEHP into the blood. While phthalates increase platelet adhesiveness and may be a factor in the formation of pulmonary emboli, evidence of in vivo toxicity in recipients of blood transfusions is lacking. Evidence has accumulated, however, to indicate that exposure to DEHP and other plasticizers is likely to occur from the use of PVC materials in transfusions (OWRS, 1980a; OTS, 1981).

The estimated lethal dose of DEP for humans is 0.5 g/kg and the lowest published toxic concentration in air for humans is 1.0 g/m³. A workman ingesting 10g DBP experienced nausea, vertigo, albuminuria, keratitis (cornea inflammation), and lachrymation a few hours after ingestion; these symptoms most likely resulted from the toxic effects of the hydrolysis products of DBP (butanol). In humans, ingestion of DMP is reported to cause irritation of the buccal mucosa (cheek), nausea, vertigo, vomiting, coma, and a drop in blood pressure. DMP is not irritating to the human skin, nor is dermal absorption efficient in humans (OWRS, 1980a).

A review of the acute toxicity of phthalate esters in experimental animals reveals that the phthalates exhibit relatively low acute toxicity. LD₅₀ values for various exposure routes and several mammalian species normally exceed 1 g/kg for all phthalates examined. Reported values range from 1 g/kg for DEP (oral LD₅₀ in rabbits) to 50 ml/kg for DEHP (i.p. LD₅₀ in rats) (OWRS, 1980b).

2.1.2 Chronic Toxicity

Chronic toxicity data in humans for the phthalate esters are limited. Industrial workers exposed to ambient levels of 10 to 66 mg/m³ of phthalate vapors or aerosols (a mixture of phthalates, primarily DBP) for 6 months to 19 years exhibited polyneuritis (nerve inflammation); the frequency and severity increased with length of exposure. The most frequent worker complaint was pain in the upper and lower extremities, often accompanied by numbness and spasms. This study, however, must be taken with some reservation because of the presence of other chemicals such as tricresyl phosphate, a substance known for inducing polyneuritis (OWRS, 1980b).

Symptoms of hepatitis have been observed in hemodialysis patients using new PVC dialysis tubing. Experiments revealed that phthalates were leached continuously from the tubing and that the symptoms disappeared shortly after a change to other hemodialysis tubing (OWRS, 1980a).

The chronic adverse effects for various phthalate esters in laboratory animals are shown in Table 3, and carcinogenic, mutagenic, and teratogenic/reproductive effects are also discussed below. The lowest effect levels (excluding the carcinogenicity of DEHP) shown are 0.4 g DEHP/kg for teratogenicity in mice (the no apparent effect level, NOEL, was 0.07 g/kg) and 0.6 to 0.7 g DEHP/kg for testicular atrophy in rats and mice. Most other reported effect levels for the phthalates exceed 1 g/kg (OWRS, 1980a).

DEHP has been shown to produce changes in liver function as indicated by increases in liver weight and morphological and biochemical alterations in rats, mice, and rhesus monkeys. DEHP also induces the proliferation of peroxisomes in liver cells (peroxisomes are organelles which are functionally involved in lipid metabolism, glyconeogenesis, and the detoxification of hydrogen peroxide). Sustained peroxisome proliferation in liver cells has been associated with increased appearance of liver cancer in rodents. A possible mechanism for DEHP induced carcinogenesis in rats may involve chronic proliferation of peroxisomes, however, supporting evidence is lacking (EHP, 1982). Recent testing under the direction of The Chemical Manufacturers Association (CMA) has confirmed that DEHP induces peroxisome proliferation in the liver.

Water Quality Criteria have been established for phthalate esters based on human health considerations. Allowable daily intakes (ADIs) for a 70 kg person were developed (using a NOEL and a safety factor of 100) for DMP (700 mg), DEP (438 mg), and DBP (12.6 mg). Note that these ADI values are not necessarily based on the data described below; also, the ADI for DEHP (42 mg) is no longer applicable due to the recently discovered carcinogenic potential (OWRS, 1980a; OWRS, 1980b).

Carcinogenicity - Adequate long term carcinogenicity testing has been conducted for DEHP. The evidence suggests that DEHP is a liver carcinogen in both rats and mice. DEHP was administered to rats of each sex at 0.0, 0.6, or 1.2% of the diet (equivalent to doses of about 300 mg/kg and 600 mg/kg per day for 300 g rats) and mice of each sex at 0.0, 0.3, or 0.6% of the diet (equivalent to doses of about 720 mg/kg and 1440 mg/kg per day for 25 g mice) for 103 weeks. DEHP was carcinogenic for rats and mice of either sex, inducing hepatocellular carcinomas or neoplastic nodules in rats and hepatocellular carcinomas or adenomas in mice. In rats, the neoplastic liver nodules were significantly elevated in all treatment groups compared with controls and the combined incidences of neoplastic nodules and hepatocellular carcinoma were significantly elevated in high dose male rats and in both high and low dose females. The incidence of hepatocellular carcinoma alone was statistically significant only for high dose female rats. Increased incidences of hepatocellular carcinoma were

observed in high dose male mice and in both low and high dose females. The combined incidences of hepatocellular carcinoma and hepatocellular adenoma were also elevated in these groups (OWRS, 1980a).

Other lifetime feeding studies have shown no increased incidence of neoplasms due to ingestion of DEHP, DBP, and DMP at levels of 200 to 1400 mg/kg/day. NTP test results for BBP are difficult to interpret. While no carcinogenic effects were noted for mice fed 0.6% and 1.2% BBP in their diet, female rats receiving 1.2% BBP showed an increased incidence of myelomonocytic leukemia. However, due to the variable and high background incidence of this lesion in similar groups of historical controls, the evidence for BBP was judged to be equivocal. In addition, excessive numbers of BBP-treated male rats died and no evaluation of tumorigenic response in male rats could be made. No data are available concerning the carcinogenicity of DEP and DNOP (OWRS, 1980a).

Mutagenicity - All of the phthalate esters under consideration in this document were examined in the Ames Salmonella test using metabolic activation under the National Toxicology Program protocol; all chemicals tested were judged to be nonmutagenic. However, other experiments indicate that some phthalates (DEP, DMP) are mutagenic in the Ames test in the absence of the activating S-9 enzymes. Conflicting results are also reported concerning the mutagenic potential of the phthalate monoesters formed in the presence of S-9 associated enzymes (EHP, 1982).

DEHP showed no increases in chromosomal aberrations in human fetal lung cells, human leukocytes, or Chinese hamster cells exposed in culture. While another study did report effects in Chinese hamster cells, the effects were weak. Chromosomal aberrations and sister-chromatid exchanges are also reported to show slight increases in Chinese hamster cells exposed to DBP; however, the increases were slight and no clear dosage effect was observed. Therefore, no definitive conclusions concerning the genetic risk from exposure to most phthalate esters can be drawn at this time (OWRS, 1980a).

As part of the negotiated testing program under section 4 of TSCA, CMA has submitted results of genotoxicity studies for DEHP, and mono-2-ethyl phthalate (MEHP). CMA reported no significant genotoxic effects were noted for these compounds. No mutagenic activity was found in Ames Salmonella tests (5 strains, with and without microsomal addition). Several other genotoxic tests also indicated no mutagenic or clastogenic activity for DEHP and MEHP (46 FR 53775). Other results of the CMA testing program suggest that DEHP does not bind to DNA in vivo (CPSC, 1983). EPA is evaluating this information for consideration of further testing.

TABLE 3: EFFECTS OF PHTHALATE ESTERS ON LABORATORY ANIMALS^a

Adverse Effects	Species	Lowest Reported Effect Levels		No Apparent Effect Levels
		g/kg	% Incidence	g/kg
DEHP				
Hepatocellular Carcinoma plus Neoplastic Nodules	Rat	0.6	26	-
Hepatocellular Carcinoma plus Adenoma	Mouse	0.36	52	-
Teratogenesis	Mouse	0.4	-	0.07
Testicular Atrophy	Mouse	0.72	14	0.36
	Rat	0.6	90	0.3
Embryotoxicity	Mouse	0.83	100	-
DMP				
Chronic Nephritis	Rat	4.0	-	2.0
Embryotoxicity	Chick/Embryo	0.005/egg	100	-
DEP				
Teratogenesis	Rat	1.9	81	-
DBP				
Teratogenesis	Mouse	2.1	-	0.8
Testicular injury	Rat	2.0	-	-
BBP				
Periportal Hepatitis	Mouse	0.5	-	-
Carcinogenicity	Mouse	-	-	1.4

^a Source: (OWRS, 1980a).

Teratogenicity and Reproductive Effects - Most phthalate esters are capable of producing teratogenic and reproductive effects at high doses by various routes. DEHP at high doses (> 5 ml/kg), induced gross abnormalities in both rats and mice. DMP (0.3 ml/kg), DBP (0.3 ml/kg), and DEP (0.5 ml/kg) have also produced skeletal malformations in rats. Injection of phthalate esters into developing chick eggs produced no teratogenic effects with DBP, BBP, or DMP; there was a single incidence with DEP. Increased embryo mortality was noted for DMP, DEP, DBP, DNOP, and BBP (OWRS, 1980a).

Feeding studies with pregnant mice yielded no-effect levels of about 70 mg/kg/day for DEHP and 370 mg/kg/day for DBP for the mouse fetuses. At dose levels of 410 mg/kg for DEHP and 2100 mg/kg for DBP increases in fetal resorption and external malformations were observed. The major malformations in this study were neural tube defects (exencephaly and spina bifida). These authors concluded that normal exposure to phthalate esters (< 1 mg/kg/day) should not pose an imminent threat to human fetal development (EHP, 1982).

With respect to reproductive changes, the administration of 200 mg DEHP/kg/day to the diet of rats for two years produced no adverse effects on reproductive functions. At high doses, DEHP produces dominant lethal and antifertility effects in mice after a single intraperitoneal injection (12.8 ml DEHP/kg). Damage to the testes has been reported to occur in rodents given high doses of DEHP and DBP. Administration of high doses (> 1 g/kg/day) of DMP, DEP, or DNOP to male rats had no effect on testicular tissues in short term experiments (OWRS, 1980a).

Phthalate-induced injury to rodent testes is accompanied by adverse effects on gonadal metabolism of zinc. Phthalates cause an increase in urinary excretion of zinc resulting in a depletion of this vital element in the testes. Experiments have confirmed that administration of zinc along with phthalates offered a measure of protection against testicular atrophy (EHP, 1982).

While there have been a number of studies in which DEHP concentrations were measured in tissues and blood of human patients exposed to DEHP during transfusions or hemodialysis, teratogenic or reproductive effects have not been documented. For example, hemodialysis of men who suffered from uremia resulted in restoration of spermatogenesis; conception and successful pregnancies in their spouses followed.

2.1.3. Absorption, Distribution, and Metabolism

The phthalate ester and/or derived metabolites are readily absorbed from the intestinal tract and the lungs; evidence concerning absorption through the skin is conflicting. The vehicle can play an important role in the absorption and distribution of the phthalates. From the present data, it appears that the diester phthalates can be hydrolyzed to the monoester in the gut and thus be absorbed primarily as the monoester; the efficiency of absorbance of the diester in the gut is not clear (OWRS, 1980b).

Based on current information, the phthalate esters appear to be rapidly distributed to various organs and tissues and are rapidly cleared from the body. Earlier studies, particularly those using the intravenous route, were complicated by poor solubility of the phthalates and artifacts later attributed to phthalate-solubilizer interactions. The bulk of DEHP and DBP administered by oral or parenteral routes is cleared from experimental animals within 24 hours and little is left 3 to 5 days after exposure. There is little evidence of tissue accumulation or prolonged retention. The major initial repositories for phthalate esters (or metabolites) are fat, gastrointestinal tract, liver, and kidney. Chronic administration of DEHP to rats showed progressive increases in the level of the phthalate (or metabolite) in the liver and abdominal fat. Rhesus monkeys infused (i.v.) repeatedly with small amounts of DEHP (total dose, 21 to 69 mg/kg) in blood showed some retention of DEHP in their livers for several months after infusion was halted (EHP, 1982).

Phthalate esters are metabolized to the monoesters by enzymes present in many tissues, but complete hydrolysis to phthalic acid apparently occurs only in the liver. Appreciable amounts of DMP are excreted as phthalic acid, but only small fractions of DEHP and other long-chain alkyl phthalates are completely hydrolyzed to phthalic acid. DMP and, to some extent, DBP are primarily excreted as the unchanged diester or as monoester metabolites. The phthalates with longer alkyl groups, such as DEHP, must undergo conversion to more polar metabolites for efficient excretion. Several animal species are known to form glucuronide conjugates with the monoesters of DBP and DEHP; however, rats seem unable to form glucuronide conjugates of the monoester (MEHP) formed from DEHP (EHP, 1982).

The inability of the rat to conjugate MEHP requires extensive oxidation of the remaining 2-ethylhexyl group to achieve sufficient water solubility for excretion. Studies of the metabolism of DEHP and MEHP in animals and humans indicate that the terminal or adjacent carbon atom in the ester side chain is successively oxidized to an alcohol, then to an aldehyde or ketone, and finally to a carboxylic acid; excretion via the urine occurs in the form of glucuronide conjugates of these oxidation products. Similar oxidation pathways have been documented for the metabolism of the monoester derivatives of other dialkyl phthalate esters. In light of the recent report that DEHP is a liver carcinogen in rats and mice, the elucidation of species differences in DEHP metabolism is crucial to understanding the applicability of these experiments to humans (EHP, 1982).

Results submitted by CMA under the negotiated testing program for phthalates are consistent with previous investigations on absorption and metabolism in rats; i.e., DEHP is rapidly absorbed from the GI tract, produces an enlarged liver, and induces peroxisome formation. The CMA reported results for marmosets which suggests that DEHP is poorly absorbed through the GI tract and that only a small degree of peroxisome proliferation is induced in monkeys. However, differences in the protocols used for the two species make it difficult to reach definitive conclusions from these studies (CPSC, 1983).

2.2 Environmental Effects

2.2.1 Aquatic Effects

Information regarding the toxicity of phthalate esters to aquatic organisms is sparse and inconsistent. No data are available on the toxic effects of DNOP, and only limited data exist on DEP, DMP, BBP, and DEHP. Most of the studies presented information on DBP. The available data focused more on aquatic invertebrates than on fish species and were taken from OWRS documents in most cases (OWRS, 1980a; OWRS, 1980b).

Some loss of phthalates from aqueous solution may occur in toxicity experiments as a result of volatilization and adsorption onto glass and plastic surfaces. Both static and flow-through systems may experience losses. When reviewing toxicity test results, rapid reduction in phthalate concentration should be considered.

Acute toxic effects on fish were reported at levels ranging from 0.7 mg/L to greater than 10 mg/L DBP and DEHP. DBP was the more toxic of the two compounds; however, the problems associated with testing DEHP prevent drawing conclusions about its relative toxicity. The only data available on the sublethal or chronic effects of phthalate esters pertained to ingested DEHP on the reproductive success in two species of fish. A level of 0.05 mg/kg in food reduced reproduction in zebra fish. It is difficult to compare these data with LC_{50} values (lethal concentration to 50% of the population) because different exposure routes were involved. The other phthalates had acute effects at levels greater than 29 mg/L in water.

Limited data exist that would support any conclusions regarding the greater sensitivity of coldwater fish species to phthalate esters. The only LC_{50} reported for a salmonid species, the rainbow trout, was higher than those reported for warmwater species. Levels of 0.014 mg/L DEHP significantly increased sac fry (young fish) mortality but had no effect on egg mortality or hatchability. No comparable studies on warmwater species were available.

Acute toxic effects have been measured for the bluegill and a number of phthalates. LC_{50} (96 hr.) values have been reported for DBP (10 mg/L), BBP (43.3 mg/L), DMP (49.5 mg/L), DEP (98.2 mg/L), and DEHP (100 mg/L).

The reported acute effects of phthalates on aquatic invertebrates had concentration ranges similar to those of vertebrates. Acute LC_{50} s ranged from 1.9 mg/L to 92.3 mg/L for all phthalates. Reproductive effects were reported at levels as low as 0.003 mg/L (DEHP) in *Daphnia*, while no significant effects were observed at 1.0 mg/L (DEHP, DMP, and DBP) in the mud crab and at 10 mg/L (DMP and DEP) in brine shrimp.

Data from chronic studies are conflicting, particularly regarding effects on *Daphnia* reproduction and early-life stage effects. In contrast to the 3ppb reproductive effect noted above, other studies

report that another fresh water invertebrate (midge) showed no effects (on midge emergence) when exposed to DEHP levels up to 0.24 mg/L. In addition, studies with BBP indicate that effects on *Daphnia* reproduction are not observed until the BBP level reaches 760 mg. Therefore, the reported effects at 0.003 mg/L should be confirmed, since this level is relatively low compared with other observed effects.

In every study where DBP was tested, it is reported as the most toxic phthalate. DBP's relationship to DEHP is uncertain, however, because of the difficulty in dissolving DEHP in water at levels greater than 1 mg/L (and possibly lower). DBP's effects, as well as those of other phthalates, were generally observed at levels greater than 1 mg/L. It is possible, therefore, that DEHP is toxic to some species at lower concentrations (less than DBP) than reported data indicate. An inverse correlation between solubility and toxicity has been suggested for some of the phthalates although not all phthalates under consideration in this assessment were represented.

Some evidence demonstrates that fish, like mammals, can rapidly metabolize certain phthalate esters. Low biomagnification factors in guppies (130 x) compared with those of aquatic invertebrates and plants (21,480-107,670 x) also indicate metabolization of DEHP. In fathead minnows, however, a lab study measured biomagnification factors as high as 1130. The order of magnitude difference may be attributed to species characteristics or varying experimental conditions.

3. ENVIRONMENTAL RELEASE

Phthalate esters are produced by reacting phthalic anhydride with appropriate alcohols in the presence of a catalyst (sulfuric acid, p-toluene sulfonic acid, or an amphoteric metal salt). The esters are high volume chemicals, the total U.S. production exceeding 500 metric tons (kkg) for the year 1981; 19 companies supplied the following amounts of individual esters:*

<u>Phthalate ester</u>	<u>Amount produced (10³ kkg)</u>
Di(2-ethylhexyl)	129.0
Diisodecyl	63.5
Ditridecyl	12.7
Dibutyl	9.0
Diethyl	9.0
Butyl octyl	5.0
Dimethyl	3.2
Other	276.0
Total	<u>507.4</u>

*Chemical Economics Handbook, SRI International, Feb. 1983.

The major phthalates in the "other" category are di(heptyl,nonyl, undecyl)phthalate (DHNUP), diisononyl phthalate (DINP), and BBP. DHNUP is a mixture of dialkyl phthalates containing C₇, C₉, and C₁₁ alkyl groups. A number of other dialkyl phthalates are produced as mixtures because they are prepared by reaction of phthalic anhydride with mixtures of isomeric or different alcohols (OTS, 1981).

Approximately 95% of the phthalate esters are used as plasticizers for various resins, primarily polyvinyl chloride (PVC). DEHP has the highest production figure because of its overall properties, i.e., compatibility, low vapor pressure, low solubility in water, long term stability, and low cost. Diisodecyl phthalate is used as a PVC plasticizer for wires and cables. Butyl benzyl phthalate is used primarily for vinyl flooring. DHNUP is widely used in automobile interiors and wire coatings. Both DHNUP and BBP have appreciable percentages of the total phthalate market (approximately 20% and 10% respectively). DEP and DMP are used in the manufacture of cellulosic resins; DMP is also used as an insect repellent. DBP is used as a plasticizer for epoxy and PVC resin (OWRS, 1980a).

Plasticizers are used to aid in processing or to impart desired characteristics to plastic (e.g., stain resistance in flooring, flexibility and temperature resistance in wire insulation, good adhesion in coatings and adhesives). Plasticized PVC formulations usually contain from 20 to 40% plasticizers (by weight) in the end product. The main uses of plasticizers in PVC applications are flooring, upholstery in automobiles and furniture, and wire coatings. Table 4 summarizes the recent end use pattern for the phthalate esters (OTS, 1981).

TABLE 4. PHTHALATE ESTER END-USE PATTERN FOR 1977

Flexible PVC	10 ⁶ kg	Percentage
Apparel		
Baby Pants	3.2	
Footwear	30.4	
Outerwear	<u>14.1</u>	
	47.7	8.7
Building Construction		
Flooring	108.1	
Swimming Pool Liners	6.8	
Weatherstripping	<u>7.3</u>	
	122.2	22.4
Electrical Wire and Cable Coatings	<u>87.6</u>	
	87.6	16.0
Home Furnishings		
Furniture	53.6	
Wall Coverings/Wood Surfacing Film	<u>19.2</u>	
	72.8	13.3
Housewares	<u>18.2</u>	
	18.2	3.3
Packaging Film	<u>7.0</u>	
	7.0	1.3
Recreation		
Sporting Goods	8.4	
Toys	<u>12.2</u>	
	20.6	3.8
Transportation		
Upholstery	53.6	
Other	<u>16.2</u>	
	69.8	12.8
Miscellaneous		
Garden Hose	5.0	
Medical Tubing	<u>5.5</u>	
	10.5	
Other PVC Uses	<u>21.6</u>	
	21.6	5.9
Subtotal for PVC Uses	477.6	87.5
Other Polymers and Resins	15.0	2.8
Non-Plasticizer	10.4	1.9
Export	<u>42.5</u>	7.6
Subtotal for non-PVC Uses	67.9	12.5
Total	545.8	100.0

SOURCE: (OTS, 1981)

The environmental release occurs with synthesis and continues through production, use and disposal. Table 5 shows the estimated amounts released at various stages of phthalate manufacturing and consumption. Losses of phthalates during production are small. During compounding with high temperatures, appreciable losses occur to air and water. Between 70 and 90% of the esters are disposed of in landfills.

The distribution of releases to the environmental compartments is shown in Table 6. The rate of release from the landfills is not known. It is speculated that the lipophilic phthalates partition into the soil which then becomes the interface for transport to lakes, rivers, and ocean via underground streams or rain runoff.

Phthalate-containing products may be grouped into four categories according to their 'ease' of release, based on the physical state, intermolecular forces, and surface area. In order of decreasing freedom of release, they are as follows (OTS, 1981):

Non-plasticizer uses

Cosmetics, lubricating oils, dielectric fluids, adhesives, etc., that do not physically bind or encase the phthalate. Nearly all of the phthalates from these mixtures are estimated to be released.

Plasticizer uses

- (a) Swimming pool liners, garden hoses, medical products (for transfusions, artificial kidney tubing). In these uses there is direct liquid contact with the phthalate-containing surface to facilitate release through partitioning.
- (b) Upholstery, flooring, food wrapping, seat covers, etc. These materials have high surface to volume ratios from which the phthalates can escape.
- (c) Household plastics, molded furniture, construction materials. These products are bulk materials of low surface area and, therefore, slow in releasing to the environment.

**TABLE 5. RELEASES OF PHTHALATES IN THE UNITED STATES AT VARIOUS
STAGES OF MANUFACTURING AND CONSUMPTION (10⁶ kg)^a**

	DEHP	DBP	DEP	DMP	OTHER	TOTAL	PERCENTAGE
Production	0.9	0.04	0.04	0.02	1.6	2.61	0.5%
Transportation	0.2	0.01	0.01	0.01	0.3	0.50	0.1%
Processing	14.9	0.50	0.5	0.2	22.3	38.99	7.7%
(Compounding)	(5.0)	(0.18)	(0.2)	(0.1)	(9.5)	(15.52)	(3.1%)
(Manufacturing)	(9.9)	(0.32)	(0.3)	(0.1)	(12.9)	(23.49)	(4.6%)
Product Use & Consumption	>3.4	>0.35	>0.30	>1.0	27.3	32.33	6.4%
Product Disposal (97% to Landfill)	<u>149.1</u>	<u>6.15</u>	<u>6.7</u>	<u>2.9</u>	<u>266.4</u>	<u>429.58</u>	<u>85.3%</u>
TOTAL	168.5	7.1	7.6	4.1	318.0	505.2	100%

^aSOURCE: (OTS, 1981); data for 1977.

**TABLE 6. DISTRIBUTION OF PHTHALATE RELEASES TO ENVIRONMENTAL COMPARTMENTS
IN THE UNITED STATES (10^6 kg)^a**

	DEHP	DBP	DEP	DMP	OTHER	TOTAL	PERCENTAGE
Released to air	4.3	0.3	0.2	0.5	13.6	18.9	3.7%
Released to water ^b	5.2	0.3	0.4	0.6	25.4	31.8	6.3%
Landfilled	154.1	6.3	6.8	2.9	270.6	440.7	87.3%
Incinerated	4.9	0.2	0.2	0.1	8.4	13.8	2.7%
TOTAL ^c	168.5	7.1	7.6	4.1	318.0	505.2	100.0%

^a Source: (OTS, 1981); data for 1977.

^b Includes process loss during manufacturing, estimated at 0.5% of production, all to water.

^c Includes U.S. supply plus process loss during manufacturing.

4. EXPOSURE ROUTES

In general, human exposure to phthalates is low; DEHP exposure is probably the most common. Food is the primary source of DEHP, with average food exposure levels of about 0.3 mg/day and maximum levels of about 2 mg/day. As described below, intake from drinking water, inhalation, and dermal absorption are comparatively low, although occupational exposures may be high. Certain subpopulations which may receive higher exposures include people receiving large quantities of blood, dialysis patients, and hemophiliacs. Possible exposure from PVC consumer products, especially children's products, are also of concern (OWRS, 1980a).

Monitoring data for phthalate esters in the environment are relatively scarce and interpretation of much of the information is complicated by possible phthalate contamination. Many monitoring studies reported in the literature, especially prior to 1975, do not give procedures for avoiding contamination during collection and analysis. The accuracy of the data on these substances may suffer from the ubiquitous nature of some of the phthalates (OTS, 1981).

4.1 Air Exposure

Based on the limited information available, exposure of the general population to airborne phthalates should be low. The meager monitoring data show mean levels of 0.011 to 0.07 ug/m³ of DEHP in urban areas and 0.001 to 0.018 ug/m³ in nonurban locales (OTS, 1982). Based on the mean concentrations of DEHP in urban air, inhalation of 20 m³ a day of air would result in exposures of only 0.2 to 1.4 ug DEHP per day. A single study reported higher levels of DEHP (0.3 ug/m³) and DBP (0.7 ug/m³) in the vicinity of an incinerator (OWRS, 1980a).

Plastics in flooring, furniture, and other materials may result in significant levels of phthalates indoors. DEHP has been detected in indoor air, but no levels were reported. While exposure to airborne phthalate esters in automobiles is likely due to the extensive use of vinyl materials, no quantitative measurements are available to estimate exposure. Although the use of DEHP plastics in car interiors has been discontinued in the U.S., other phthalates, such as diisodecyl phthalate and di(heptyl,nonyl,undecyl) phthalate, are still widely used (OTS, 1981; OWRS, 1980a).

4.2 Water Exposure

The most comprehensive study of finished drinking water for DEHP content was undertaken in EPA Region V. The 53 cities surveyed were selected on the basis of suspected high levels of organic pollutants. DEHP was detected in 20 out of 53 samples. The mean of detected values was 3 ug/L and the maximum level was 17 ug/L. In another drinking water study, the mean detected value of DEHP was 6 ug/L (maximum 53 ug/L); in this study, DEHP was detected in 10 out of 14 cities (OTS, 1982).

Other limited monitoring data suggest that several phthalate esters may be present in finished drinking water supplies. An EPA study of drinking water in ten cities reported DEHP, DEP, and DBP in water from several locations. Excluding the abnormally high levels reported for one city (Miami, Florida) the ranges reported were: DEHP, 0.04 to 0.8 ug/L; DBP, 0.01 to 5 ug/L; DEP, 0.01 to 0.05 ug/L (OWRS, 1980a).

A realistic upper limit of 10 ug/L has been suggested for DEHP in drinking water. Assuming a consumption of 2 liters of drinking water per day, intake from this source should not exceed 20 ug per day (OWRS, 1980a).

Although ambient water monitoring is also limited, results suggest that ambient levels of phthalate esters are generally less than 10 ug/L. Higher levels of these esters, primarily DEHP and DBP, are found in industrialized areas (OWRS, 1980a).

4.3 Other Routes

Food

Contamination of food can occur from surfaces of phthalate-containing PVC processing equipment and packaging film with which the food comes in contact. FDA regulates phthalate esters and approves uses that might result in migration of phthalates into foods under certain constraints. A variety of phthalates are approved providing conditions avoiding contamination are met. For example, DEHP, being hydrophobic, is only approved for use in packaging of foods with high water content (as opposed to fatty foods). Generally, regulations are based on the rate of migration and release that do not result in contamination. In a survey (1974) FDA found most samples contained DEHP levels of less than 1 mg/kg. This value in conjunction with dietary assumptions gives an estimated exposure of less than 2 mg/day/person. Information on other phthalate esters in food is incomplete. Butyl benzyl phthalate was found in margarine; and DBP in milk. The information is not sufficient to allow estimation of human exposure (OWRS, 1980a).

Consumer Products

In addition to inhalation and ingestion, a consumer is likely to be exposed dermally to phthalates used in nonplasticizer products, such as perfumes and cosmetics, and plasticized products, such as vinyl swimming pools, plasticized vinyl seats (on furniture and in cars), and clothing (jackets, raincoats, boots, etc.). For a skin surface area of 1080 cm² (midcalf to midhigh) in contact with plasticized vinyl fabric (i.e., boot) for 4 hours, 0.5 mg DEHP may transfer to the skin surface (OTS, 1982). There is also exposure from children's toys, mats, pacifiers, and teethingers made of phthalate plasticized PVC. CPSC has completed a risk/exposure assessment for DEHP in children's products. The total potential exposure of an infant to DEHP from both oral (mouthing) and dermal routes is estimated to be about 100 to 800 mg over the course of one to two years of use of DEHP-containing baby products (CPSC, 1983).

Occupational

Workers in plastics manufacture in which phthalate esters are used might have exposures of 20 to 800 ug/m³ in various areas of a DEHP production plant. Although it is known that DEHP is used in the fabrication of a variety of industrial products, few monitoring data are available on the producers or on the commercial users of such products. In every inspection, some of which monitored several different employees within a facility, the level was found to be below the established threshold value of 5 mg/m³ (OTS, 1982; IARC, 1982).

Intravenous

Humans may be exposed to phthalate esters through tubing and liquid storage bags used in transfusions. Blood stored in PVC bags has been shown to contain DEHP; an extraction rate of 0.25 mg DEHP/100 ml blood/day has been established over a 21-day period. The estimated exposure to patients who receive 4 to 63 units of blood is 14 to 600 mg DEHP, depending on the storage conditions (time and temperature) for each blood unit. Also, cryoprecipitate packs may contain 0.8 to 1.9 mg DEHP. Hemophiliacs may receive 400 bags of cryoprecipitates/year, representing a possible exposure of 2 mg DEHP/day (OTS, 1982).

Hemodialysis patients may also receive phthalate esters (primarily DEHP) from the dialysis apparatus. Assuming a 5 to 7 liter blood volume, a patient could receive 75-105 mg DEHP per treatment. Therefore, two-to-three treatments per week would lead to an exposure of 150 to 315 mg DEHP; this translates into a daily average dose of 21 to 45 mg DEHP/day (OWRS, 1980a). Monitoring data obtained from dialysis patients have confirmed the addition of DEHP to the blood; however, the amount of DEHP delivered varied widely (OTS, 1981).

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available in the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568 or Robin Heisler at FTS 382-3557.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information. Searches may be made by CAS Number or coded text. (EPACASR is scheduled to be added to CIS in 1984). For further information, contact Eleanor Merrick at FTS 382-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information, contact Dr. Steve Heller at FTS 382-2424.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base which is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Doug Sellers at FTS 382-2320.

5.5 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is a sophisticated switching network based on heterogeneous distributed data base management and networking concepts. CSIN offers efficient access to on-line information resources containing data and information relevant to chemical substances, as well as information covering other scientific disciplines and subject matters. The purposes of CSIN are two-fold: first to meet the growing chemical data and information requirements of industry, academe, government (Federal and State), public interest groups, and others, and secondly to reduce the burden on the private and public sector communities when responding to complex Federal legislation oriented to chemical substances.

CSIN is not another data base. CSIN links many independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems." Users may converse with any or all systems interfaced by CSIN without prior knowledge of or training on these independent systems, regardless of the hardware, software, data, formats, or protocols of these information resources.

Information accessible through CSIN provides data on chemical nomenclature, composition, structure, properties, toxicity, production uses, health and environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, seven independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), Chemical Information System (CIS), CAS-On-Line, SDC's ORBIT, Lockheed's DIALOG, Bibliographic Retrieval Service (BRS), and the US Coast Guard's Hazard Assessment Chemical System (HACS). For further information contact Dr. Sid Siegel at 202-395-7285.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 500 individual data bases and models which contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. The clearinghouse listed a total of 453 citations for the phthalate esters. For further information, contact Irvin Weiss at FTS 382-5918.

6. REGULATORY STATUS (Current as of 7/83)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- o Sections 301, 304, 306, and 307 - Phthalate esters are listed as toxic pollutants (40 CFR 401.15) and are subject to effluent limitations. However, no effluent guidelines specifically limit the release of phthalate esters at this time.
- o Sections 318, 402, and 405 - National Pollution Discharge Elimination System (NPDES) permit testing requirements; the following are listed as organic toxic pollutants based on gas chromatographic and mass spectroscopic analyses and are part of the consolidated permit program (40 CFR 122, App. D):
 - o Butyl benzyl phthalate
 - o Di(2-ethylhexyl) phthalate
 - o Dibutyl phthalate
 - o Diethyl phthalate
 - o Dimethyl phthalate
 - o Di-n-octyl phthalate

Resource Conservation and Recovery Act (RCRA)

- o Section 3001 - The following phthalate esters have been identified as toxic hazardous wastes if and when they are discarded as commercial products or off-specification species (40 CFR 261.33):
 - o Di(2-ethylhexyl) phthalate (U028)
 - o Dibutyl phthalate (U069)
 - o Diethyl phthalate (U088)
 - o Dimethyl phthalate (U102)
 - o Di-n-octyl phthalate (U107)

Also, phthalate esters are listed as hazardous constituents (40 CFR 261, App. VIII).

- o Sections 3002 to 3006 - Hazardous wastes are subject to further controls concerning generators, transporters, and treatment, storage, and disposal facilities (40 CFR 262 to 265). Permit procedures are also included in consolidated permit regulations (40 CFR 122 to 124).

Toxic Substances Control Act (TSCA)

- o Section 8(a) - Preliminary assessment reporting for the following (40 CFR 712):
 - o Dimethyl phthalate
 - o Diethyl phthalate

- o Dibutyl phthalate
- o Di(2-ethylhexyl) phthalate
- o Di-n-octyl phthalate
- o Butyl benzyl phthalate

Federal Food, Drug, and Cosmetic Act (administered by EPA)

- o Materials exempted from pesticide tolerance requirements under certain conditions (40 CFR 180.1001):
 - o Diethyl phthalate
 - o Butyl benzyl phthalate

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- o General industry standards for work place exposure to air contaminants (29 CFR 1910.1000):
 - o Dibutyl phthalate
 - o Dimethyl phthalate
 - o Di(2-ethylhexyl) phthalate

FDA - Food, Drug, and Cosmetic Act

- o Permissible components of adhesives used in food packaging, storage, and transport (21 CFR 175.105):

o Dibutyl phthalate	o Diisodecyl phthalate
o Diethyl phthalate	o Dicyclohexyl phthalate
o Di(2-ethylhexyl) phthalate	o Diphenyl phthalate
o Dimethyl phthalate	o Butyl phthalyl butyl glycolate
o Di-n-octyl phthalate	o Methyl phthalyl ethyl glycolate
o Butyl benzyl phthalate	
- o Permissible substances in paper and paperboard in contact with aqueous and fatty foods (21 CFR 176.170):

o Butyl benzyl phthalate	o Butyl phthalyl butyl glycolate
o Dibutyl phthalate	o Dicyclohexyl phthalate
- o Permissible components of paper or paperboard in contact with dry food (21 CFR 176.180):
 - o Dibutyl phthalate
 - o Butyl benzyl phthalate
 - o Dicyclohexyl phthalate
- o Permissible substances used as defoaming agents in manufacturing paper and paperboard used in food packaging (21 CFR 176.210):
 - o Butyl benzyl phthalate

- o Permissible substances for use in the preparation of slimicides used in the manufacture of paper or paperboard that contact food (21 CFR 176.300):
 - o Dibutyl phthalate
- o Limit on miscellaneous materials used in acrylic and modified acrylic plastics in contact with food (21 CFR 177.1010):
 - o Di(2-ethylhexyl) phthalate
 - o Dimethyl phthalate
- o Permissible component of cellophane used for packaging (21 CFR 177.1200):
 - o Di(2-ethylhexyl) phthalate
 - o Dibutyl phthalate
 - o Dicyclohexyl phthalate
- o Permissible components that facilitate or are added to cross-linked polyester resins used as articles intended for repeated contact with food (21 CFR 177.2420):
 - o Dibutyl phthalate
 - o Butyl benzyl phthalate
- o Permissible components used in the preparation of rubber articles intended for repeated use (21 CFR 177.2600):
 - o Dibutyl phthalate
 - o Di-n-octyl phthalate
 - o Diisodecyl phthalate
- o Permissible components used as plasticizers in polymeric substances used in the manufacture of articles intended for food contact (21 CFR 178.3740):
 - o Butyl benzyl phthalate
 - o Diphenyl phthalate
 - o Dicyclohexyl phthalate
- o Permissible substances used as surface lubricants in the manufacture of metallic articles that contact food (21 CFR 178.3910):
 - o Diethyl phthalate
 - o Di(2-ethylhexyl) phthalate

MSHA - Federal Mine Safety and Health Act

- o Performance requirements for respirators (30 CFR 11.183):
 - o Di-n-octyl phthalate

DOT

- o Regulations for bulk transportation (46 CFR 30.25):
 - o Butyl benzyl phthalate
 - o Dibutyl phthalate
 - o Di-n-octyl phthalate

Port and Tanker Safety Act/Dangerous Cargos Act

- o Regulations and standards for unmanned barges carrying certain bulk dangerous cargos (46 CFR 151.01; 46 CFR 154, Annex B):
 - o Butyl benzyl phthalate
 - o Dibutyl phthalate
 - o Di-n-octyl phthalate
 - o Diethyl phthalate
 - o Dimethyl phthalate
 - o Di (2-ethylhexyl) phthalate

6.2 Proposed Regulations

6.2.1 EPA Programs

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) (CERCLA or Superfund)

CERCLA provides for the liability, compensation, clean-up and emergency response for the release of hazardous substances into the environment. This Act also deals with the cleanup of hazardous waste disposal sites. (42 USC 9601; PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities (RQ), claims procedures, and the confidentiality of business records (46 FR 54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47 FR 10972).

Phthalate esters are hazardous substances under CERCLA and will be subject to regulations developed under Superfund. EPA has proposed adjustments to many of the RQ's established under CERCLA and the CWA (48 FR 23552).

6.3 Other Actions

Consumer Product Safety Commission (CPSC)

CPSC has decided to convene a Chronic Hazard Advisory Panel on DEHP to assist in determining whether regulatory action is needed. Of immediate concern is the potential exposure of children to DEHP from infant products. (CONTACT: Sandra Eberle, FTS 492-6957)

Public Health Service - National Toxicology Program (NTP)

- o Studies are in progress with selected phthalates including the investigation of the genotoxicity and carcinogenic mechanism of DEHP; in addition, the reproductive toxicity and carcinogenic potential of several other phthalates (diallyl-, diethyl-, and butyl benzyl phthalate) are under study. A variety of phthalates will also be analyzed for absorption, disposition, and clearance. The NTP studies are designed to complement other studies in progress, such as the CMA testing noted below (Contact: Dr. William Kluwe, FTS 629-4177).

EPA - TSCA

- o Under section 4(e) of TSCA, the ITC recommended the alkyl phthalates and BBP for testing (42 FR 55026; 45 FR 78432). EPA negotiated a comprehensive testing agreement with the Chemical Manufacturers Association (CMA) whereby the phthalate ester industry, through CMA, agreed to voluntarily test a variety of phthalate esters for environmental and health effects. Therefore, EPA decided not to propose, at that time, a section 4(a) rule to require testing. The Agency is free to pursue the issuance of a section 4(a) test rule in the future if more information is required (Contact: Larry Rosenstein, FTS 475-8163).

NTP/EPA Clearinghouse on Phthalates

- o The Phthalate Clearinghouse was set up by NTP and EPA to facilitate the collection and dissemination of information on phthalates. The clearinghouse attempts to provide up-to-date results of experimental work on phthalate esters (Contact: Joan Chase, FTS, 496-1152).

7. STANDARDS AND CRITERIA*

7.1 Air

- o OSHA standards for work place exposure to phthalates in air (29 CFR 1910.1000):

Dibutyl phthalate	5 mg/m ³ (8 hr. TWA)
Dimethyl phthalate	5 mg/m ³ (8 hr. TWA)
Di(2-ethylhexyl) phthalate	5 mg/m ³ (8 hr. TWA)

7.2 Water

- o Water Quality Criteria (45 FR 79318)

Freshwater aquatic life:

Phthalate esters	940 ug/L (acute)
	3 ug/L (chronic)

Saltwater aquatic life:

Phthalate esters	2,944 ug/L (acute)
------------------	--------------------

Human health criteria for the ingestion of water and contaminated aquatic organisms:

Dimethyl phthalate	313 mg/L
Diethyl phthalate	350 mg/L
Dibutyl phthalate	34 mg/L
Di(2-ethylhexyl) phthalate	15 mg/L

Human health criteria for the ingestion of contaminated aquatic organisms only:

Dimethyl phthalate	2,900 mg/L
Diethyl phthalate	1,800 mg/L
Dibutyl phthalate	154 mg/L
Di(2-ethylhexyl) phthalate	50 mg/L

- o Based on NTP animal bioassays for carcinogenicity, EPA has calculated water concentrations for DEHP which correspond to the 10⁻⁶ risk level. For ingestion of water and aquatic organisms the value would be 1.7 ug/L; for ingestion of aquatic organisms only, the criteria would be 5.8 ug/L.

* See Appendix A for a discussion of the derivation, use, and limitations of these criteria and standards.

8. SPILL OR OTHER INCIDENT CLEANUP/DISPOSAL

8.1 Hazards and Safety Precautions

Safety precautions when handling or cleaning up spills of phthalate esters are necessary because of their potential toxicity as described in Section 2. In general, phthalate esters are readily absorbed via inhalation or through the skin. Exposures to hot vapors or mists may cause irritation of the nasal passages, the mouth, and throat. Eye contact with the liquids causes pain. If swallowed, the esters may cause irritation of the stomach, dizziness, and unconsciousness. Most phthalates have slight or no odors. The various phthalates differ in their degree of toxicity. For example, dibutyl phthalate (DBP) if swallowed may cause light sensitivity, watering and redness of the eyes, in addition to the above general symptoms.

Chemically, the phthalate esters are relatively stable unless contact occurs with nitrates, strong oxidizers, strong alkalies, or strong acids which may cause fires and explosions. DMP has a flashpoint of 146°C (295°F; closed cup), and an auto ignition temperature of 556°C (1032°F). Flammability of the phthalate esters is generally low except for DMP.

8.2 First Aid

Move victim to fresh air; give artificial respiration if not breathing and oxygen if breathing is difficult. In case of eye or skin contact flush with running water; remove clothing as necessary to assure water flowing over the affected skin. Isolate contaminated clothing. There may be delayed effects after exposure. If swallowed, induce vomiting unless unconscious.

8.3 Emergency Action

Spill or Leak - Stay upwind, wear breathing apparatus, eye protection, and protective clothing and isolate area. Remove all ignition sources. Use water spray to control and reduce vapors.

Fire - For small fires use dry chemical, CO₂, water spray, or foam. For large fires use water spray or foam. Cool containers with water after fire is out.

8.4 Notification and Technical Assistance

Section 103 (a) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) requires notification of the National Response Center (NRC) in the event of a spill of a listed chemical; telephone: 800-424-8802 (in Washington D.C. area: 426-2675). The reportable quantity in effect for DBP is 100 lbs. Regulations listing RQs under CERCLA have not been finalized and a statutory RQ of 1 lb. is applicable for other phthalates.

For further information call EPA Environmental Response Team (24-hour number: 201-321-6660) or the Division of Oil and Special Materials (1-202-245-3045). Confirm any treatment procedures with a responsible environmental engineer and regulatory officials. For emergency assistance one may also call: CHEM TREC: 800-424-9300.

8.5 Disposal

General disposal procedures may be used for phthalates after confirming with a responsible environmental engineer and regulation officials. Thus, product residues and sorbent media may be packaged in epoxy-lined drums and disposed of at an approved EPA disposal site. Destruction by high temperature incineration or microwave plasma detoxification, if available, or encapsulation by organic polyester resin or silicate fixation may be also used.

A generator of 1000kg or more of hazardous waste is subject to RCRA regulations concerning treatment, storage, and disposal. A number of phthalate esters (BBP, DEHP, DBP, DEP, DMP, and DNOP) are listed as toxic hazardous wastes if discarded as commercial products or off-specification species.

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of the analysis. Of particular importance is the avoidance of plastics (e.g., tygon tubing) because phthalates are commonly used as plasticizers and are easily extractable. Phthalate residues have also been found in solvents and in chromatographic column packing materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced (OTS, 1981).

9.1 Air

The phthalate esters are not regulated air pollutants; no EPA approved procedure for air analysis has been adopted. Sampling and analysis procedures for DBP and DEHP have been issued by NIOSH for monitoring around production and user facilities (NIOSH Manual of Analytical Methods, Vol. 2, 1977, DHSS Pub. A77-157-B). A known volume of air is drawn through a cellulose membrane filter to adsorb the phthalate aerosol present. The filter is transferred into a disposable glass pipet and eluted with carbon disulfide. The eluted sample is analyzed by gas chromatography (GC) using flame ionization detection (FID). The method for DEHP was validated over the range of 2.03 to 10.9 mg/m³ for a 32-liter sample; the validation range for DBP is similar. For the conditions used with this sample size, the probable useful range of this method is 0.5 to 15 mg phthalate/m³. The limit of the method is dependent on the filtration efficiency of the cellulose membrane filter. The filtration efficiency for DBP and DEHP aerosol is greater than 95% when sampled for 30 minutes at 1 liter per minute from a test atmosphere containing 10 mg/m³. The variability corresponds to a standard deviation of 0.29 mg/m³ at the OSHA standard level (5 mg/m³). The average values obtained for the overall sampling and analytical method are 8% higher than the "true" values for DEHP and 8.6% lower for DBP.

Other procedures reported (IARC, 1982) for the analysis of airborne phthalates include: absorbance on Florisil or glass fiber filters followed by desorption and GC/FID analysis; and use of glass fiber filters plus foam plugs to trap the phthalate followed by extraction and GC/ECD analysis (detection limit given 0.1 ng/m³).

9.2 Water

A number of phthalate esters are listed as priority pollutants under section 304 of the Clean Water Act. The suggested analytical procedure (Method 606 in "Guidelines Establishing Test Procedures for the Analysis of Pollutants," 44 FR 69491; 1979) covers the determination of BBP, DEHP, DBP, DNOP, DEP, and DMP, and is applicable to the determination of these compounds in municipal and industrial discharges. This method is designed to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES).

If samples are not to be extracted within two days of collection, they should be adjusted to pH 6 to 8. All samples should be extracted within 7 days and analysis completed within 30 days. In the procedure a 1-liter sample of water is extracted with methylene chloride and the extract is dried and concentrated. Separation is carried out using gas chromatography (GC) and the phthalates are detected using electron capture (ECD) or flame ionization detectors (FID). For ECD detection limits range from 0.02 to 0.13 ug/L; for FID the limits are about two orders of magnitude higher. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms.

The Chemical Manufacturers Association (CMA) has submitted analytical characterization and interlaboratory recovery and measurement data for fourteen phthalate esters. These submissions are part of the negotiated testing program for phthalates accepted by EPA in lieu of a test rule under section 4 of TSCA. These studies are available in the public file on phthalates (47 FR 54161).

9.3 Solid Waste

Phthalate esters in waste solids may be determined as described by methods 806 and 825 in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (Office of Solid Waste and Emergency Response, July 1982, SW-846, Second Edition). Method 806 is used to determine the concentration of phthalate esters in groundwater, liquid, and solid sample matrices.

Specifically, Method 806 may be used to detect BBP, DEHP DBP, DNOP, DEP, and DMP. This method provides cleanup and GC conditions for the detection of ppb levels of phthalate esters. Water samples are extracted at a neutral pH with methylene chloride as a solvent and solid samples are extracted using either the Soxhlet apparatus or sonication procedures.

The extract is analyzed by gas chromatography using an electron capture detector (ECD) or a flame ionization detector (FID). The detection limits are lowest for the low molecular weight esters and highest for the high molecular weight compounds, i.e., 0.29 ug/L for DMP and 3.0 ug/L for DNOP using the ECD technique. In a single laboratory, the average recovery varied from 80-94% for the phthalates measured and the standard deviation ranged from 1.3 to 6.5%. Method 825 is a general procedure for analysis and separation of a wide variety of semivolatile organics by GC/MS.

9.4 Other Samples

A review of the methods used in the analyses of environmental samples for phthalates and possible sources of sample contamination has been completed for EPA. A summary of this review and the monitoring data is included in an EPA exposure assessment for DEHP (OTS, 1982). Other reference documents also review procedures for the sampling and analysis of phthalates in a variety of environmental matrices including: food; human serum and stored blood; PVC products; human and animal tissues and urine; and laboratory supplies (OTS, 1981; IARC, 1982).

REFERENCES

The major references used in the preparation of this document are listed below. EPA references are listed by EPA office of origin and the year of publication. For further information refer to contacts given throughout this document or contact the relevant EPA offices listed at the end of this section.

- (CPSC, 1983) Children's Chemical Hazards - Risk Assessment on Di(2-Ethylhexyl) Phthalate in Children's Products, Consumer Products Safety Commission, (1983).
- (EHP, 1982) Environmental Health Perspectives; Vol. 45, Nov. 1982.
- (IARC, 1982) IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans; Vol. 29, International Agency for Research on Cancer, World Health Organization (1982).
- (OTS, 1980) Priority Review Level I: Di(2-Ethylhexyl)Phthalate (DEHP); EPA Draft Report, Office of Pesticides and Toxic Substances (1980).
- (OTS, 1981) TSCA Section 4 Human Exposure Assessment-Alkyl Phthalates; EPA Final Report, Office of Toxic Substances (1981).
- (OTS, 1982) Exposure Assessment for DEHP; EPA Interim Draft Report, Office of Toxic Substances, November (1982).
- (OWRS, 1979) Water-related Environmental Fate of 129 Priority Pollutants; Vol. II, Chap. 94, EPA 440/4-79-029b, Office of Water Regulations and Standards (1979).
- (OWRS, 1980a) An Exposure and Risk Assessment for Phthalate Esters; EPA Final Draft Report, Office of Water Regulations and Standards (1980).
- (OWRS, 1980b) Ambient Water Quality Criteria for Phthalate Esters; EPA 440/5-80-067, Office of Water Regulations and Standards (1980).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-4173 (919-541-4173)

Carcinogen Assessment Group	382-7341
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	382-7571
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality and Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	382-7051
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
------------------------------	----------

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Information Management Division 382-3749

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division
Research Triangle Park, NC 629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division 382-7575

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division 755-0100

Effluent Guidelines Division 382-7120

Office of Solid Waste (OSW)

Permits and State Programs Division 382-4746

SPILL CLEAN-UP AND DISPOSAL (Section 8)

Note: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division 382-2182
Hazardous Site Control Division 382-2443

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II 340-6635 (201-321-6635)

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Labs (EMSL)

Air Analysis
Research Triangle Park, NC 629-2454 (919-541-2454)

Water Analysis
Cincinnati, OH 684-7311 (513-684-7311)

Waste Analysis
Las Vegas, NV 545-2137 (702-798-2137)

Office of Monitoring Systems
and Quality Assurance

382-5767

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Chemical Coordination Staff

Chemical Information
and Analysis Group

382-3375

2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (2,3,7,8-TCDD)

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-2
<u>Environmental Release</u>	3-1
<u>Exposure</u>	4-1
Air Exposure	4-1
Water Exposure	4-1
Other Exposure Routes	4-1
<u>Data Bases</u>	5-1
NIH/EPA Chemical Information System (CIS)	5-1
Chemicals in Commerce Information System (CICIS)	5-2
Chemical Substances Information Network (CSIN)	5-3
Graphic Exposure Modeling System (GEMS)	5-3
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-3
Other Actions	6-4
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1
Food	7-2

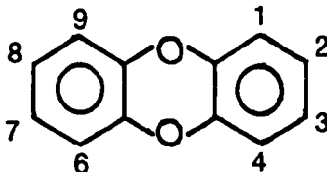
<u>Spill or Other Incident Clean-up/Disposal</u>	8-1
<u>Sampling, Acceptable Analytical Techniques and Quality Assurance</u>	9-1
Air	9-2
Water	9-2
Solid Waste	9-3
Other Samples	9-4
Quality Assurance	9-4
<u>References and Office Contacts</u>	R-1

2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN (2,3,7,8-TCDD)

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

There are a total of 73 different compounds classified as polychlorinated dibenzo-p-dioxins (PCDDs). PCDDs contain from two to eight chlorine atoms located in any of the eight positions on the two aromatic rings of the dibenzo-p-dioxin nucleus shown below. There are 22 isomers of tetrachlorodibenzo-p-dioxin (TCDDs), including 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). The Agency focus on 2,3,7,8-TCDD reflects both its presence in commercial formulations derived from 2,4,5-trichlorophenol and its high toxicity.



Some physical/chemical properties of 2,3,7,8-TCDD are presented in Table 1. The compound is lipophilic and has a very low solubility in water. It has a low vapor pressure and resists thermal decomposition (ASME, 1981).

1.2 Chemistry and Environmental Fate/Transport

PCDDs are formed as by-products during the synthesis of polychlorinated phenols and derived pesticides. Combustion of general municipal, commercial, and industrial wastes also may result in release of PCDDs. The PCDDs are chemically stable under most environmental conditions (OWRS, 1979).

2,3,7,8-TCDD has a uv absorption at 307 nm and may be susceptible to photochemical degradation in the atmosphere. Experiments carried out under environmental sunlight conditions indicate that the photolytic half-life of this compound in the gas phase is on the order of 5 to 24 days. Oxidation by hydroxyl radicals in the atmosphere may also be significant (ASME, 1981). Atmospheric transport of PCDDs occurs by way of airborne particulate matter which is released by combustion of wastes. Present estimates of potential TCDD emission from municipal waste combustors suggest that such releases do not present a public health hazard for residents living in the vicinity of the plants (EPA, 1981).

Data from microcosm experiments indicate that 2,3,7,8-TCDD reaching the aquatic environment is probably strongly adsorbed onto sediment.

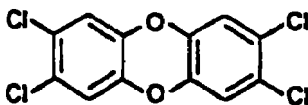
TABLE 1: PROPERTIES OF 2,3,7,8-TCDD^a

Chemical Name and Formula:	2,3,7,8-tetrachlorodibenzo-p-dioxin $C_{12}H_4Cl_4O_2$
-------------------------------	---

Chemical Abstract Service (CAS) Number and Synonyms:	1746-01-6 2,3,7,8-TCDD ^b
--	--

Molecular Weight:	322
-------------------	-----

Molecular Structure:



Melting Point:	305°C
----------------	-------

Decomposition Temperature:	>700°C
----------------------------	--------

Vapor Pressure (25°C)	10 ⁻⁶ to 10 ⁻⁷ torr (estimated)
-----------------------	---

Solubility:	Water	0.2 ug/l
	Benzene	0.57 g/l
	n-Octanol	0.048 g/l

Log octanol: water partition coefficient	7.14 (calculated)
---	-------------------

^a Source: (ASME, 1981).

^b Also popularly known as "TCDD" or "Dioxin".

Bioaccumulation of the compound is likely based on its lipophilic nature, and laboratory data on uptake by biota support this hypothesis. Photolysis of the chemical in water may be significant if reactive organic substrates (e.g., hydrogen atom donors) are available. While some reports suggest that volatilization and biodegradation may also be important processes for aquatic 2,3,7,8-TCDD, experimental verification is needed (OWRS, 1979; IERL, 1980).

The transport and fate of 2,3,7,8-TCDD in soil has been investigated to a limited extent. 2,3,7,8-TCDD is not leached from most soils due to its strong adsorption onto soil particle surfaces; mobility increases with decreasing amounts of organic matter in the soil. While 2,3,7,8-TCDD in soil is fairly immobile, transport with soil particles may occur and could result in surface water contamination. The evidence for biodegradation of 2,3,7,8-TCDD in soil is inconclusive; if biodegradation occurs, it is a slow loss mechanism from soil. Photodegradation of 2,3,7,8-TCDD on surface soil appears to be a possible loss mechanism. Uptake by plants does not appear to be an important fate for 2,3,7,8-TCDD (ASME, 1981).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACT: Jerry Stara, FTS 684-7531)

2.1.1 Acute Toxicity

On a molecular basis, 2,3,7,8-TCDD is one of the most toxic synthetic chemicals. An important consideration for understanding the potential significance of PCDD release is the widely differing toxicities of the individual PCDD compounds. The PCDDs with chlorine substituents on the 2,3,7, and 8 positions are recognized as having high acute toxicity; the toxicological information on 2,3,7,8-TCDD is by far the most extensive (ASME, 1981). The LD₅₀ values reported for 2,3,7,8-TCDD vary widely for different animal species. Representative LD₅₀ values for oral exposure are (ug/kg body weight): guinea pig, 0.6-2.1; rat, 22-45; mouse, 284 (IERL, 1980). Studies with experimental animals have shown that exposure to 2,3,7,8-TCDD leads to malfunction of liver, pancreas, CNS, and thymus; death is frequently delayed and may occur as long as 40 days after a single exposure (ASME, 1981).

Reports of human symptoms resulting from acute high-level exposure to 2,3,7,8-TCDD arise primarily from industrial accidents. Generally there is no quantitative measure of dose, and exposure to multiple chemicals often complicates interpretation. Immediate symptoms arise from the irritant nature of 2,3,7,8-TCDD which leads to irritation of the eyes, respiratory tract, and skin. As little as 20 ug of 2,3,7,8-TCDD on the skin is reported to lead to chloracne development. Other symptoms of exposure include: headache, dizziness, nausea, fatigue, insomnia, loss of libido, and arthralgias (pains in the joints). Other effects which may be delayed or immediate include porphyria (a disease associated with abnormal metabolism of porphyrins by the liver), liver dysfunction, hyperpigmentation, and hirsutism. A variety of metabolic, emotional, and neurological disorders also appear in some cases (IERL, 1980).

2.1.2 Chronic Toxicity

In humans, chronic exposure to dioxin can cause chloracne and another dermatologic disorder, porphyria cutanea tarda (PCT), a photosensitive dermatosis caused by altered porphyrin metabolism. Hepatic (liver) toxicity resulting from prolonged exposure to 2,3,7,8-TCDD (common in animal models) has been observed in human workers after industrial exposure (IERL, 1980).

In laboratory animals, dioxin has caused damage to renal (kidney) tubular epithelium and caused alteration in levels of serum gonadatrophin (pituitary hormones influencing reproductive organs). A profound deficit in cell-mediated immunity is produced in experimental animals exposed to 2,3,7,8-TCDD in the prenatal period. Along with thymic atrophy, exposure to 2,3,7,8-TCDD leads to depletion of cells in the spleen, lymph nodes and bone marrow (IERL, 1980; OWRS, 1981).

Carcinogenicity, Mutagenicity, and Teratogenicity - Bioassays have demonstrated that 2,3,7,8-TCDD is an animal carcinogen in rats and mice when ingested. Multiple studies which examined the effects of 2,3,7,8-TCDD administered in combination with other carcinogens indicate that 2,3,7,8-TCDD can also act as a potent cocarcinogen (OWRS, 1981).

The information with respect to human exposure is less conclusive. Epidemiological studies of cohorts of workers engaged in chlorophenol production and use, and their exposure to TCDDs in this country suggest that any overall carcinogenic effect on humans is small. A significant excess of stomach cancer, however, has been reported in a similar cohort of German workers. In addition, recent studies indicate that soft tissue sarcomas (a form of cancer) may be associated with long-term exposure to phenoxy herbicides which contain 2,3,7,8-TCDD. The human information available from the Seveso, Italy exposure in 1976 has not indicated that the local populations have developed any excess of cancer. However, it may be too early to evaluate the long-term effects from this exposure in view of the short period of time that has elapsed since the Seveso incident and the generally longer latency period for cancer development. More definitive work to address this question has been initiated by the National Institute of Occupational Safety and Health (NIOSH) and the National Cancer Institute (EPA, 1981; IERL, 1980).

2,3,7,8-TCDD displays an unusually high degree of reproductive toxicity in animals. It was found in numerous animal studies to cause teratogenic and fetotoxic effects and reduced fertility. In a three-generation reproductive study in rats, a reduction in fertility was observed after daily doses of 0.1 or 0.01 ug/kg/day. Equivocal effects were also seen at the lowest dose (0.001 ug/kg/day). Human epidemiological studies in this area are limited; those that have been conducted lack the statistical power to demonstrate clear exposure-related effects (EPA, 1981, OWRS, 1981). Related PCDDs were relatively nontoxic and are reported to have no observed teratogenic effects at the doses studied (IERL, 1980).

In genotoxicity tests, none of the Salmonella strains capable of detecting base-pair substitutions gave positive results when tested with 2,3, 7,8-TCDD. Some investigations have indicated that this chemical may be mutagenic in one Salmonella strain which detects frame shift mutations. A dominant lethal study with 2,3,7,8-TCDD was negative for male rats given daily oral doses of 4, 8, and 12 ug/kg for seven days before mating; there was no evidence of induction of dominant lethal mutations during postmeiotic phases of spermatogenesis (OWRS, 1981; IERL, 1980).

2.2 Environmental Effects (CONTACT: Douglas W. Kuehl, FTS 783-9559)

2.2.1 Aquatic Effects

No data are available concerning the acute toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin to freshwater fish. Delayed mortality has been observed following acute exposures of salmon to concentrations

as low as 0.056 ng/l. The salmon were exposed for 96 hours under static conditions and then transferred to control water; after 60 days there was 12% mortality compared to 2% among the control fish. Salmon exposed to a 100-fold higher concentration (0.0056 ug/l) showed a 55% delayed mortality (OWRS, 1981).

Although steady-state bioconcentration factors are not available, sufficient studies have been completed to indicate high bioconcentration factors as predicted by the high octanol; water partition coefficient. Data on the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin to freshwater aquatic life are few, but the high mammalian toxicity coupled with a high bioconcentration factor is strong evidence for a concern about residues produced by concentrations in water in the ug/l range or lower (OWRS, 1981).

No data are available concerning the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin to saltwater aquatic life.

2.2.2 Soil and Terrestrial Life

Several studies have examined the levels of 2,3,7,8-TCDD in animals living in contaminated areas. Available data indicate that 2,3,7,8-TCDD accumulates in environmentally exposed wildlife. Since the molecules are lipophilic they tend to accumulate in fatty tissue. Exposed wildlife tend to bioaccumulate TCDD at varying degrees, but biomagnification does not appear to be significant (IERL, 1980).

Few studies are available which determine whether PCDDs are incorporated into plants. Results available indicate that very small amounts of 2,3,7,8-TCDD can be accumulated in plants. 2,3,7,8-TCDD can be translocated from the soil and are usually found in newly forming organs of the plant. Below-ground portions of exposed plants tend to have higher concentrations than aerial portions. However, the fact that other studies have shown no uptake by plants emphasizes the need for further research (IERL, 1980).

3. ENVIRONMENTAL RELEASE

PCDDs are not manufactured commercially. However, they are formed inadvertently as impurities during the production of polychlorinated-phenols. Various PCDDs have been reported in commercial samples of 2,4,5-trichlorophenol (2,4,5-TCP), 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol. The 2,3,7,8-TCDD isomer is formed primarily in the production of 2,4,5-TCP. Because the major use of 2,4,5-TCP is in the manufacture of the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and Silvex, 2,3,7,8-TCDD is found as a trace impurity in these pesticides. 2,3,7,8-TCDD is also considered a possible trace contaminant in the bactericide hexachlorophene (ASME, 1981; IERL, 1980).

Parts-per-million quantities of TCDDs have been reported in 2,4,5-T manufactured in the past. However, 2,4,5-T with 2,3,7,8-TCDD isomer content of less than 0.1 ppm is now commercially available. Production and use of both Silvex and 2,4,5-T have declined in recent years due to severe restrictions on the use of these herbicides (IERL, 1980).

Detectable quantities of PCDDs have also been identified from various combustion sources. PCDDs have been found in collected fly ash samples (i.e., from electrostatic precipitators) from municipal waste incinerators in the U.S. and a number of other countries. PCDDs were also detected in industrial and hazardous waste incinerators. In general, levels of PCDDs from municipal incinerators appear to be lower than levels emitted from industrial incinerators. Levels of TCDDs detected in municipal incinerator fly ash vary widely (2-100 ppb), but are generally less than 10 ppb (10ng/g). Where isomer-specific data are available, the 2,3,7,8-TCDD isomer is not found to be a major component of the TCDDs collected (ASME, 1981; EPA, 1981).

PCDDs have also been detected in the flue gas from municipal and industrial incinerators. The PCDDs are probably adsorbed to the sub-micron particulates emitted, although it is possible that PCDDs exist partly in the vapor phase at stack temperatures (ASME, 1981). A recent study (OB, 1981), reported that PCDDs were detected only in stack gas and associated particulates from a municipal waste combustor and not in the fly ash as has been reported in other studies (ASME, 1981).

Because 2,3,7,8-TCDD is not commercially manufactured, limited data are available on its (inadvertent) production and release. However, based on its occurrence in commercial pesticide products, it was estimated that about 1 kg was produced annually (in 1976) as an impurity in 2,4,5-TCP and related herbicides. The decreased production and usage of Silvex in recent years coupled with lower levels of 2,3,7,8-TCDD in commercial products suggests that the current production volume could be significantly less than 1 kg/yr. The amount of 2,3,7,8-TCDD produced during combustion cannot be estimated at this time due to a lack of data (ASME, 1981; IERL, 1980).

A major route of entry of 2,3,7,8-TCDD into the environment appears to be release of compounds contaminated with 2,3,7,8-TCDD to the land through land application and land disposal of contaminated wastes. The principal route of entry into the aquatic environment is believed to be erosion and runoff from land. Current and past disposal of 2,3,7,8-TCDD-contaminated substances, through incineration and landfilling, represents an unknown and potentially significant source of entry of 2,3,7,8-TCDD into water. Probable sources of release of 2,3,7,8-TCDD to the air include contaminated particulates from incinerators, pesticide production and formulation areas, and undetermined quantities from combustion sources. 2,3,7,8-TCDD may also be released accidentally from spills during transportation or inadvertent release during the manufacture and formulation of 2,3,7,8-TCDD-contaminated pesticides.

The origin of PCDDs in particulates arising from combustion is not clear. PCDDs may form in most combustion processes (as claimed by Dow), or only in the presence of chlorinated phenol precursors. Another possibility is that the PCDDs may already be present as contaminants of the wastes being burned (ASME, 1981).

4. EXPOSURE ROUTES

2,3,7,8-TCDD may enter the body through dermal absorption, ingestion, and inhalation. However, many exposure determinations appear to be fraught with analytical difficulties because 2,3,7,8-TCDD is only one of many trace contaminants found in chlorinated industrial products. In essence, it is unclear in many cases what isomer was actually being measured (OWRS, 1981).

The most obvious groups at risk are those employed in the manufacture of chemicals in which 2,3,7,8-TCDD may occur as an unwanted by-product. The spraying of herbicides containing traces of 2,3,7,8-TCDD has become less of a problem because of restrictions on the use of such agents. Considering the reproductive toxicity of 2,3,7,8-TCDD, women of child-bearing age and especially the fetus may be at high risk from exposure to 2,3,7,8-TCDD (OWRS, 1981).

4.1 Air Exposure (CONTACTS: Jack McGinnity, FTS 629-5504 Warren Peters, FTS 629-5645)

No data pertaining to the inhalation exposure of 2,3,7,8-TCDD were found. It is clear that the spraying of 2,4,5-T could lead to a concomitant exposure to 2,3,7,8-TCDD, but it is not possible to estimate a typical exposure because of spray drift to nontarget sites, and because of the intermittent exposure during spraying. Potential airborne exposures to human populations living near chemical plants (e.g., 2,4,5-TCP, 2,4,5-T) may also occur. Human populations living in areas near incinerators could potentially be exposed to variable concentrations of PCDDs, dependent upon the materials consumed (OWRS, 1981).

A preliminary evaluation of the risks related to TCDDs emissions from municipal waste combustors has been made by EPA using mathematical dispersion models and data from five U.S. sites. This evaluation suggests that present emission levels of TCDDs from the incinerators do not present a health hazard for residents in the immediate vicinity. This was an interim report and EPA intends to monitor representative facilities for future TCDD emissions (EPA, 1981).

4.2 Water Exposure

Human exposure to 2,3,7,8-TCDD that can be directly attributed to drinking water alone appears to be low. No 2,3,7,8-TCDD has ever been detected in drinking water using methods with detection limits in the parts per trillion (ppt) range (OWRS, 1981).

4.3 Other Exposure Routes

Dermal exposure may be significant during the spraying of 2,4,5-T. However, accurate determinations of the amounts of 2,3,7,8TCDD absorbed during such operations appear to be lacking (OWRS, 1981).

The occurrence of 2,3,7,8-TCDD in food could result from (1) accidental spraying of plant crops with 2,3,7,8-TCDD-contaminated herbicides; (2) consumption by livestock of 2,3,7,8-TCDD-contaminated forage; or (3) magnification of residues through the food chain. Conceivably, 2,3,7,8-TCDD could also be deposited on food crops during the combustion of 2,4,5-T treated vegetation. Contaminated beef fat samples have been found to have concentrations varying between 3 to 6 ppt of 2,3,7,8-TCDD. 2,3,7,8-TCDD has also been reported in fish from the North Atlantic and the Great Lakes at concentrations ranging from below detection to 278 ppt. Because of the great analytical difficulties involved in all of these 2,3,7,8-TCDD analyses, these results must be viewed with caution (OWRS, 1981).

5. DATA BASES

5.1 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. For further information, contact Jim Cottrell at FTS 382-3546.

CIS contains numeric, textual, and bibliographic information in the areas of toxicology, environment, regulations, and physical/chemical properties. Several of these data bases are described below.

5.1.1 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purposes of the effort, and a source of additional information.

EPACASR is now available on CIS for internal use by EPA personnel and is expected to be accessible from a public CIS account in the near future. The publication and computer tapes are also available through the National Technical Information Service (NTIS). For further information on EPACASR, contact Eleanor Merrick at FTS-382-3626.

5.1.2 Industry File Indexing System (IFIS)

IFIS is an on-line system which contains information relating to the regulation of chemicals by EPA through industry-specific legislation. IFIS enables the user to determine, for any particular industry, which chemicals are used and produced and how these chemicals are regulated. IFIS is currently available on CIS for internal use by some EPA personnel and is expected to be accessible from a public CIS account soon. For more information on IFIS, contact Daryl Kaufman at FTS 382-3626.

5.1.3 Scientific Parameters in Health and the Environment,
Retrieval and Estimation (SPHERE)

SPHERE is being developed by the EPA Office of Toxic Substances as a system of integrated data bases, each representing a compilation of extracted scientific data. The system is being released to the public in stages as part of CIS, and the accessibility of component data bases should be confirmed with the contact given below. The components currently available (either through public CIS accounts or the internal EPA system) include: DERMAL, which provides quantitative and qualitative health effects data on substances admitted to humans and test animals via the dermal route; AQUIRE, a component containing aquatic toxicity data for about 2,000 chemicals; GENETOX, a mutagenicity data base; ISHOW, and ENVIROFATE, both of which are compilations of physical/chemical parameters useful in assessing environmental fate and transport. For more information contact Paula Miles, FTS 382-3760.

5.1.4 Oil and Hazardous Materials Technical Assistance Data System
(OHMTADS)

OHMTADS is a data base created by EPA to aid spill response teams in the retrieval of chemical-specific response information. The file currently contains data for approximately 1,200 chemicals including physical/chemical, biological, toxicological, and commercial information. The emphasis is on harmful effects to water quality. OHMTADS is available to the public through CIS.

5.1.5 Chemical Evaluation Search and Retrieval System (CESARS)

CESARS provides detailed information and evaluations on a group of chemicals of particular importance in the Great Lakes Basin. CESARS was developed by the State of Michigan with support from EPA's Region V. Presently, CESARS contains information on 180 chemicals including physical-chemical properties, toxicology, carcinogenicity, and some aspects of environmental fate. Information for most chemicals is extensive and consists of up to 185 data fields. CESARS is accessible through public CIS accounts.

5.2 Chemicals in Commerce Information System (CICIS)

CICIS is an on-line version of the inventory compiled under the authority of TSCA. This law required manufacturers of certain chemicals (excluding food products, drugs, pesticides, and several other categories) to report production and import data to EPA. CICIS contains production volume ranges and plant site locations (for 1977) for over 58,000 chemical substances. There is also a Confidential Inventory in which data for some chemicals are claimed confidential and are not available in the public inventory. A version of CICIS (TSCA Plant and Production, or TSCAPP) is now accessible through CIS. For more information contact Geri Nowak at FTS 382-3568.

5.3 Chemical Substances Information Network (CSIN)

The Chemical Substances Information Network (CSIN) is not another data base, but rather a sophisticated switching network. CSIN links many independent and autonomous data and bibliographic computer systems oriented to chemical substances, establishing a "library of systems." Users may converse with any or all systems interfaced by CSIN without training on these independent systems, regardless of the hardware, software, data formats, or protocols of these information resources.

Information accessible through CSIN includes data on chemical nomenclature, composition, structure, properties, toxicity, production uses, environmental effects, regulations, disposal, and other aspects of the life cycle of materials as they move through society. Currently, twelve independent information resources are accessible through CSIN, including: National Library of Medicine (NLM); Chemical Information System (CIS); CAS-On-Line; SDC's ORBIT; Lockheeds's DIALOG, and the Bibliographic Retrieval Service (BRS). For further information contact Dr. Sid Siegel at FTS 395-7285.

5.4 Graphical Exposure Modeling System (GEMS)

EPA has developed GEMS, an interactive computer system, to provide a simple interface to environmental modeling, physiochemical property estimation, statistical analysis, and graphical display capabilities. GEMS is being developed for use by the Office of Toxic Substances to support integrated exposure/risk analyses. The system provides environmental analysts who are unfamiliar with computer programming with a set of sophisticated tools to undertake exposure assessments. For information about the system and the current accessibility of GEMS, contact Bill Wood at FTS 382-3928.

6. REGULATORY STATUS¹ (Current as of 7/84)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- o Section 311 (b)(2)(A) - Three compounds potentially contaminated by 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) are 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2,4,5-trichlorophenoxy propionic acid (silvex), and 2,4,5-trichlorophenol (2,4,5-TCP). These three chemicals are designated as hazardous substances (40 CFR 116.4) and are subject to reporting requirements (reportable quantities, 40 CFR 117.3) in case of discharge.
- o Sections 301, 304, 306, 307 and 316 - 2,3,7,8-TCDD is listed as a toxic pollutant (40 CFR 401.15). Accordingly, effluent limitations, pretreatment standards, new source performance standards, and standards of performance for new and existing sources have been issued for sections of the following industries:
 - Electroplating² (40 CFR 413),
 - Steam electric power generating (40 CFR 423),
 - Pulp, paper, and paperboard³ (40 CFR 430),
 - Metal finishing² (40 CFR 433), and
 - Pesticide chemicals (40 CFR 455).

Resource Conservation and Recovery Act (RCRA)

- o Section 3001 - 2,3,7,8-TCDD is listed as a hazardous constituent (40 CFR 261, App. VIII). 2,3,7,8-TCDD is not listed as a hazardous waste under 40 CFR 261.33, however, several compounds which may contain TCDD as an impurity are listed, i.e., 2,4,5-TCP (Hazardous waste number (HWN) U230), 2,4,5-trichlorophenoxyacetic acid (HWN 232), and silvex (HWN 233). Extractable silvex (2,4,5-TP) also characterizes solid waste as hazardous under the EP toxicity test (40 CFR 261.24, Table 1).

¹While few regulations explicitly cover 2,3,7,8-TCDD, many regulations do cover compounds which may be contaminated with 2,3,7,8-TCDD. Therefore regulations concerning 2,4,5-TCP, 2,4,5-T and silvex will also be included in this Section.

²2,3,7,8-TCDD is controlled by limiting the total toxic organics (TTO), which is the summation of all quantifiable values greater than 0.010 milligrams per liter.

³Explicitly regulates trichlorophenol only.

Sections 3002-3006 - Regulations for generators and transporters of hazardous waste and standards for treatment, storage, and disposal facilities are applicable (40 CFR 262 to 265). Permitting procedures are included in the consolidated permit regulations (40 CFR 122 to 124).

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)

- o Section 12(b) - Establishes procedures for persons who export or intend to export 2,3,7,8-TCDD to submit notification to EPA (40 CFR 707).
- o Section 6 - Prohibits removal of TCDD-containing wastes at the Vertac Chemical Company facilities in Jacksonville, Arkansas. Also requires 60-day notice to EPA by any person disposing wastes containing TCDD (40 CFR 775).

Safe Drinking Water Act (SDWA)

- o Section 1412 - A National Primary Drinking Water Standard has been issued for silvex. 2,3,7,8-TCDD is a potential contaminant in silvex (40 CFR 141.11).
- o Section 1421 and 1424 - Establishes an underground injection control (UIC) program to protect underground sources of drinking water (40 CFR 146). Requirements and criteria to be used by States incorporate all hazardous wastes as defined by RCRA (40 CFR 261). Permitting procedures are given in the consolidated permit regulations (40 CFR 122 to 124).

Federal Food, Drug, and Cosmetic Act (FFDCA) Administered by EPA

- o Section 408 - Establishes tolerances for residues of silvex in or on pears resulting from post harvest application (40 CFR 180.340). 2,3,7,8-TCDD is a potential contaminant in silvex.

6.1.2 Programs or Other Agencies

Occupational Safety and Health Act (OSHA)

- o 2,4,5-T designated a toxic and hazardous air contaminant. Accordingly, OSHA has set a maximum allowable ambient air concentration in the workplace (29 CFR 1910.1000, Table Z-1). TCDD is a potential contaminant in 2,4,5-T.

Hazardous Materials Transportation Act (DOT)

- o 2,4,5-T, TCP, phenoxy-based, and benzoic-based pesticides are designated as hazardous materials for the purposes of transportation requirements (49 CFR 172.101). TCDD is a potential contaminant in these compounds.

6.2 Proposed Regulations

6.2.1 EPA Programs

CWA

- o EPA has proposed effluent guidelines, pretreatment standards, and new source performance standards for the pesticide chemicals manufacturing industry (40 CFR 455). The pollutants regulated are silvex isooctyl esters, silvex salts, silvex, and 2,4,5-T (47 FR 54011, November 30, 1982).

RCRA

- o EPA has proposed to list as acutely hazardous, those wastes containing certain chlorinated dioxins, and to specify certain management standards for these wastes. In addition, EPA has proposed to revoke regulations concerning the disposal of TCDD-contaminated wastes under TSCA at such a time as when the regulation becomes effective under RCRA. Parts of Title 40 affected by this proposal and the wastes involved are:
 - 40 CFR 261.31; HWNs F020, F021, F022, and F023,
 - 40 CFR 261.33; HWNs U212, U230, U231-U233, and U242,
 - 40 CFR 261, App. III; chlorinated dibenzo-p-dioxins,
 - 40 CFR 261, App. VII; tetra-, penta-, and hexa-chloro-dibenzo-p-dioxins,
 - 40 CFR 261, App. VIII; tetra-, penta-, and hexachloro-dibenzo-p-dioxins,
 - 40 CFR 261, App. IX; chlorinated dibenzo-p-dioxins
 - 40 CFR 264.231, .259, .283, and .317,
 - 40 CFR 265, and
 - 40 CFR 775 (removed when rule is finalized).(48 FR 14514, April 4, 1983).

Comprehensive Environmental Responses, Compensation, and Liability Act (CERCLA or Superfund)

- o CERCLA provides for the liability, compensation, clean-up, and emergency response for the release of hazardous substances into the environment. This Act also deals with the clean-up of hazardous waste disposal sites (42 USC 9601; PL 96-510). EPA is developing regulations concerning the designation of hazardous substances, the development of reportable quantities, claims procedures, and the confidentiality of business records (46 FR 54032). Revisions to the National Contingency Plan (NCP) as required by CERCLA have been issued in a proposed rule (47 FR 10972).

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD), 2,4,5-T and its acids, esters, amines, and salts, silvex, and 2,4,5-trichlorophenol (2,4,5-TCP) are hazardous substances under CERCLA and will be subject to regulations developed under Superfund. EPA has proposed adjustments to the RQ's established under CERCLA and the CWA (48 FR 23552).

6.3 Other Actions

- o FIFRA - EPA issues notice of intent to cancel the registrations of all products which contain as an active ingredient 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) or silvex (2,4,5-trichlorophenoxy propionic acid) or any salt, ester, amine, or derivative of 2,4,5-T or silvex, and revokes notice of intent to hold a hearing to determine if certain uses of 2,4,5-T or silvex should be cancelled (48 FR 48434). In an additional notice, EPA announced a policy statement concerning the legal ramifications of transferring, sales, distribution, or importation of any unregistered pesticide product containing 2,4,5-T or silvex (48 FR 48436, October 18, 1983).

In a February 29, 1984 notice EPA announced its intention to suspend the registrations of certain 2,4,5-T and silvex pesticide products because of failure to comply with an October 14, 1983 request for additional data in support of registration (49 FR 7443).

- o CWA - EPA announced on February 15, 1984 the availability of a final ambient water quality criteria (WQC) document for 2,3,7,8-TCDD and provided a summary of that WQC (49 FR 5831).
- o EPA announces the availability of the external review draft of the Health Assessment Document for polychlorinated dibenzo-p-dioxins (49 FR 19408, May 7, 1984).
- o The Office of Research and Development, EPA has completed a risk analysis of 2,3,7,8-TCDD contaminated soil. The Office of Solid Waste plans to use this analysis in support of regulations defining the level of TCDD which causes a soil to be hazardous. (Contact: John Schaum, FTS 382-7353)
- o The National Toxicology Program (NTP) published results of testing in the Third Annual Report on Carcinogens, September, 1983; TCDD is cited as being a substance that may reasonably be anticipated to be a carcinogen.
- o NIOSH has issued a Current Intelligence Bulletin (#40) on 2,3,7,8-TCDD which summarizes findings related to the human hazard potential (DHHS Publication No. 84-104).

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

- o OSHA workplace exposure to toxic air contaminants; 8-hour TWA, (29 CFR 1910.1000, Table Z-1).

2,4,5-T 10 mg/m³
(2,4,5-trichlorophenoxyacetic acid)

- o ACGIH suggested threshold limit values (1980).

2,4,5-T (8-hr TWA) 10 mg/m³
(15 minute STEL) 20 mg/m³

7.2 Water

- o Water Quality Criteria (WQC); 49 FR 5831

The estimated lifetime cancer risk of 10^{-5} from exposure to 2,3,7,8-TCDD from the consumption of contaminated water and aquatic organisms corresponds to a criterion of 1.3×10^{-7} µg/L. For ingestion of contaminated aquatic organisms only, the estimated lifetime cancer risk of 10^{-5} corresponds to a criterion concentration of 1.4×10^{-7} µg/L. If these estimates are made for the consumption of water only, the risk of 10^{-5} corresponds to criterion of 2.2×10^{-6} µg/L.

- o Section 311 of the CWA reportable quantities for discharge are:

- Silvex (2,4,5-TP acid)	100 pounds
- 2,4,5-T and	100 pounds
- 2,4,5-trichlorophenol	1.0 pounds

The RQs proposed under CERCLA are the same; in addition the following RQs have been proposed (48 FR 23552).

- 2,3,7,8-TCDD	1.0 pound
- Unlisted hazardous wastes that have characteristics of EP toxicity	1.0 pound
- Waste D017, (2,4,5-TP)	100 pounds

*See Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

Food

FDA has set a 50 parts per trillion (ppt) maximum level for 2,3,7,8-TCDD in food fish from the Great Lakes. (For information on the development of FDA action levels for 2,3,7,8-TCDD in food, contact Dick Schmitt, FDA, FTS 557-7324). The Canadian Ministry of Health and the New York State Department of Health have set maximum levels of 20 and 10 ppt respectively for food fish from the Great Lakes.

Agency policy on 2,3,7,8-TCDD is still evolving. There are no Agency criteria for any media except for a final Water Quality Criteria (49 FR 5831). Problems with PCDDs are being handled by the Chlorinated Dioxins Work Group (CDWG). Questions or requests for assistance can be referred to this Work Group by calling Donald Barnes, OPTS (202) 382-2897.

REFERENCES

The major references used in the preparation of this document are listed below. EPA documents are referenced by the EPA office of origin and the year of publication. For further information refer to contacts given throughout this document or contact the relevant EPA office listed in the next section.

- (ASME, 1981) Dioxin from Combustion Sources, American Society of Mechanical Engineers (1981).
- (EPA, 1981) Interim Evaluation of Health Risks Associated with Emissions of TCDDS from Municipal Waste Resource Recovery Facilities, EPA - Interim Report, November (1981).
- (IERL, 1980) Dioxins, EPA-600/2-80-197, Industrial Environmental Research Lab (1980).
- (NCI, 1980) National Cancer Institute Publications No. (NIH) 80-1757 and 80-1765.
- (OWRS, 1981) Ambient Water Quality Criteria for 2,3,7,8-Tetrachlorodibenzo-p-dioxin, EPA Draft 440/5-80-072, Office of Water Regulations and Standards (1981).
- (OWRS, 1979) Water-Related Environmental Fate of 129 Priority Pollutants, Vol. I, Chapter 34; EPA-440/4-79-029a, Office of Water Regulations and Standards (1979).
- (Reggiani, 1981) G. Reggiani, Regulatory Toxicology and Pharmacology, 1: 211-243 (1981).
- (OTS, 1981) Emissions of PCDDs and PCDFs from Combustion Sources, Office of Toxic Substances, October (1981).

OFFICE CONTACTS

The EPA offices and divisions that are listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters which are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-4173 (919-541-4173)

Carcinogen Assessment Group	382-7341
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	382-7571
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality and Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	382-7051
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
------------------------------	----------

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Information Management Division 382-3749

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division
Research Triangle Park, NC 629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division 382-7575

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division 755-0100

Effluent Guidelines Division 382-7120

Office of Solid Waste (OSW)

Permits and State Programs Division 382-4746

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division 382-2182
Hazardous Site Control 382-2443

Oil and Hazardous Materials Spills Branch

Edison, NJ; Region II 340-6635 (201-321-6635)

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis
Research Triangle Park, NC 629-2454 (919-541-2454)

Water Analysis
Cincinnati, OH 684-7311 (513-684-7311)

Waste Analysis
Las Vegas, NV

545-2137 (702-798-2137)

Office of Monitoring Systems
and Quality Assurance

382-5767

GENERAL IPP COMMENTS, CORRECTIONS, OR QUESTIONS

Chemical Coordination Staff

Chemical Information
and Analysis

382-3375

TOLUENE

<u>Table of Contents</u>	<u>Page</u>
<u>Physical/Chemical Properties and Chemistry</u>	1-1
Properties	1-1
Chemistry and Environmental Fate/Transport	1-1
<u>Effects Information</u>	2-1
Health Effects	2-1
Environmental Effects	2-3
Other Effects	2-3
<u>Environmental Release</u>	3-1
Air Releases	3-1
Water Releases	3-1
Land Releases	3-1
<u>Exposure Routes</u>	4-1
<u>Data Bases</u>	5-1
Chemicals in Commerce Information System (CICIS)	5-1
EPA Chemical Activities Status Report (EPACASR)	5-1
NIH/EPA Chemical Information System	5-1
Chemical Regulations and Guidelines System (CRGS)	5-1
Chemical Substance Information Network (CSIN)	5-1
EPA Information Clearinghouse	5-2
<u>Regulatory Status</u>	6-1
Promulgated Regulations	6-1
Proposed Regulations	6-2
Other Actions	6-2
<u>Standards and Recommended Criteria</u>	7-1
Air	7-1
Water	7-1

<u>Spill or Other Incident Clean-Up/Disposal</u>	8-1
Hazards and Safety Precautions	8-1
First Aid	8-1
Emergency Action	8-1
Notification and Technical Assistance	8-1
Disposal	8-1
 <u>Sampling, Acceptable Analytical Techniques, and Quality Assurance</u>	 9-1
Air	9-1
Water	9-1
Solid Wastes	9-3
Other Samples	9-3
Quality Assurance	9-4
 <u>References and Office Contacts</u>	 R-1

TOLUENE

1. PHYSICAL/CHEMICAL PROPERTIES AND CHEMISTRY

1.1 Properties

Of the toluene produced in the United States, only a small fraction (about 10%) is isolated as toluene. The remainder stays in gasoline as a benzene-toluene-xylene mixture (BTX). Even so, isolated toluene ranks fifteenth in the top 50 chemicals produced in the United States (5.1 million metric tons in 1980). Toluene is produced principally during the petroleum refining process by catalytic reformation. Isolated toluene is used in benzene production, as a gasoline additive, as a solvent, and in the synthesis of various aromatic compounds.

Some relevant physical and chemical properties of toluene are listed in Table 1. Toluene is a colorless liquid at ambient temperature. It is both volatile and flammable and has a benzene-like odor. The relatively high vapor pressure and low water solubility of toluene indicate that most toluene is likely to be found in the vapor phase mixed with air. Commercial toluene (isolated) may contain benzene as an impurity.

1.2 Chemistry and Environmental Transport

Toluene is a homolog of benzene in which one hydrogen atom is replaced by a methyl group. Although toluene is fairly stable, the methyl group increases the chemical reactivity of toluene over benzene. Toluene undergoes substitution reactions on both the methyl group ($-CH_3$) and on the benzene ring. The methyl group in toluene is susceptible to dealkylation and this process is used commercially to produce benzene. The methyl group also undergoes oxidation, both chemical and biochemical, to yield benzoic acid.

Due to its relative stability in the atmosphere, toluene undergoes short- and long-range transport away from urban emission sources. The primary mode of removal is probably through photochemical reactions in the troposphere. Washout from precipitation apparently is not a significant transfer mechanism. Toluene is susceptible to oxidation by photochemically generated hydroxyl radicals which may result in the formation of cresols, benzaldehyde, and nitrotoluenes as the major products. The half-life of toluene in the atmosphere is estimated to be on the order of two days; this value is based on laboratory data and is dependent on solar intensity, temperature, and pollutant concentrations. Photolysis of toluene in polluted atmospheres (containing NO_x) can also yield significant amounts of peroxy nitrates due to secondary reactions involving the initial oxidation products, cresol and benzaldehyde (NRC, 1980).

The volatility and low water solubility of toluene permit rapid transfer from water surfaces to the atmosphere; the evaporative

half-life in water is estimated to be on the order of five hours. Toluene does not undergo extensive chemical transformation in natural waters. However, toluene may form traces of chlorine-substituted products during chlorination procedures used for water purification. To date, experimental results from sediment analysis suggest that sorption onto sediments is not a significant pathway for removal of toluene from water. Toluene is readily biodegraded in aqueous media, both in surface water and during wastewater treatment (ECAO, 1981).

Although the fate of toluene in soil has not been thoroughly investigated, intermedia transfer to air is likely; the remaining toluene adsorbed to the soil is susceptible to biological degradation. Therefore, volatilization and biodegradation are probably the most important processes for toluene disposed of on land. Evaporative losses may be significantly lower from soils with high organic content (i.e., sludge), compared to sandy soils (ECAO, 1981).

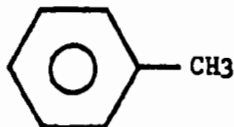
TABLE 1: PROPERTIES OF TOLUENE*

Synonyms: Methylbenzene, phenylmethane, toluol

CAS Number: 108-88-3

Molecular Formula: C₇H₈

Structure:



Physical Properties:

Melting point:	-95°C
Boiling point:	110.6°C
Vapor pressure (25°C):	28.7 torr
Flash point (close cup):	40°F (4.4°C)
Density (liquid, 20°C):	0.867 g/ml
Solubility in water (25°C):	0.53 g/l
Log octanol/water partition coefficient:	2.69
Concentration in Saturated Air (26°):	39,400 ppm (148 g/m ³)

*From data summarized in (ECAO, 1981).

2. EFFECTS INFORMATION

2.1 Health Effects (CONTACT: Robert McGaughy, FTS 755-3968; Penny Fenner-Crisp, FTS 472-4944)

2.1.1 Acute Toxicity

Acute exposures of humans to toluene have almost exclusively involved inhalation in experimental or occupational settings or during episodes of intentional abuse (i.e., "glue sniffing"). The health effect of primary concern is dysfunction of the central nervous system (CNS). Acute experimental and occupational exposures to toluene in the range of 200-1,500 ppm have elicited dose-related symptoms indicative of CNS depression, as well as impairments in reaction time and perceptual speed. Following initial CNS excitatory effects (e.g., exhilaration, lightheadedness), progressive development of narcosis has characterized acute exposures to excessive concentrations of toluene (i.e., levels approaching the air saturation concentration of approximately 30,000 ppm) (ECAO, 1981).

Single short-term exposures to moderate levels of toluene have, on occasion, been reported to cause transitory eye and respiratory tract irritation, but irritative effects have generally not been observed in workers exposed repetitively to toluene. Dermal contact with toluene may cause skin damage due to its degreasing action (OWRS, 1980).

The acute oral toxicity (LD₅₀) of toluene in rats is in the range of 6.0 to 7.5 g/kg, which indicates only slight toxicity in this species. An acute dermal toxicity (LD₅₀) was reported to be 12 g/kg in the rabbit. Inhalation studies have yielded values for LC₅₀ in the range of 5,300 to 6,900 ppm (6 to 7-hr. exposure) in mice and a value of 8,800 ppm (4-hr exposure) in rats (ECAO, 1981).

2.1.2 Chronic Toxicity

While a number of studies are available on the effects of chronic inhalation exposure to toluene, these studies have yielded conflicting results. Repeated occupational exposures to toluene vapors over a period of years at levels of 200-400 ppm have been reported to result in neurologic effects. However, a study of workers with at least 10 years exposure to atmospheres containing 200-400 ppm toluene concluded that these exposure levels do not cause adverse neurological effects. Prolonged abuse (i.e., "glue sniffing") of solvent mixtures containing toluene (at inhalation exposure levels of up to 30,000 ppm) has, on occasion, led to residual or permanent CNS effects. Chronic exposure to mixtures of organic solvent vapors containing predominantly toluene has reportedly caused impairments in visual accuracy and psychomotor performance of workers (ECAO, 1981).

Dysmenorrhea (painful menstruation) has been reported in Japanese women exposed for over 3 years to 60-100 ppm toluene and concomitantly to 20-50 ppm gasoline in a "few" working places. Distur-

bances of menstruation have also been reported in female workers exposed concurrently to toluene, benzene, and xylene, and to toluene and other unspecified solvents (ECAO, 1981).

There is little or no evidence that toluene is carcinogenic in animals or man. Inhalation exposure to toluene at concentrations of up to 300 ppm for 24 months did not produce an increased incidence of neoplastic, proliferative, inflammatory, or degenerative lesions in various organs of rats relative to unexposed controls. However, it should be noted that 300 ppm is not considered a maximum tolerated dose (MTD). Thus, it is unknown if higher exposure levels would produce the same responses. Other studies indicate that toluene is not carcinogenic when applied topically to the shaved skin of laboratory animals and that it does not promote the development of skin tumors following initiation with DMBA (ECAO, 1981).

Toluene has been shown to be non-mutagenic in a battery of microbial, mammalian cell, and whole organism test systems. The Russian literature reported chromosome aberrations in the bone marrow cells of rats exposed subcutaneously and via inhalation to toluene, but these findings have not been corroborated in other studies (ECAO, 1981).

Toluene has been reported to induce cleft palates in mice following oral exposure, but it was not teratogenic in mice or rats following inhalation exposure. Embryotoxic effects (increased incidence of skeletal anomalies and signs of retarded skeletal development, low fetal weights) and increased maternal toxicity were, however, noted in some of the rats and mice exposed via inhalation (OWRS, 1980; ECAO, 1981).

2.1.3 Absorption, Distribution, and Metabolism

Toluene is readily absorbed from the respiratory and gastrointestinal tracts. Studies in humans indicate approximately one-half of the amount inhaled is retained; ingestion leads to fairly complete absorption, based on experiments with animals. While liquid toluene may also be absorbed through the skin, this route does not appear to be significant for absorption of toluene vapor. Animals given toluene orally or by inhalation had high concentrations of toluene in their adipose tissue and bone marrow, and moderately high concentrations of toluene and its metabolites in their liver and kidney. These results are reasonable, based on tissue-blood partition coefficients and known routes of metabolism and excretion (ECAO, 1981).

The initial step in the metabolism of toluene is side-chain hydroxylation by the hepatic mixed-function oxidase system, followed by oxidation to benzoic acid. Benzoic acid is then conjugated with glycine to form hippuric acid and excreted in the urine. In both humans and animals, 60 to 75 percent of the absorbed toluene can be accounted for as hippuric acid in the urine, regardless of the dose or whether the chemical was administered orally or by inhalation.

The excretion of toluene and its metabolites is rapid; the major portion occurs within 12 hours of oral administration or the end of inhalation exposure (ECAO, 1981).

2.2 Environmental Effects (CONTACT: Teresa Norberg, FTS 783-9528)

2.2.1 Aquatic Effects

Lethal effects of toluene have been reported for numerous species of freshwater and marine fish and invertebrates. The acute LC₅₀ for 22 species of freshwater and marine organisms ranged between 3 and 1,180 ppm. Very little information, however, is available concerning the sublethal effects of toluene exposure on fish. Chronic toxicity data, for example, are only available for the sheepshead minnow. The lowest toluene concentration shown to cause sublethal effects was 2.5 ppm, in trout and in salmon. This value is lower than the lowest acute LC₅₀ value for any fish species, i.e., 3.08 ppm for coho salmon. In an embryo-larval test with sheepshead minnow, chronic effects occurred at a concentration 36 to 152 times lower than the acute LC₅₀ for this species. This suggests that chronic effects may occur at lower levels in more sensitive species (ECAO, 1981; OWRS, 1980).

Evaluation of the effects of toluene on aquatic organisms must take into account several factors. A primary consideration is the high volatility of toluene. The half-life for volatilization from a water column one meter deep has been reported to be between 30 minutes and 5 hours. Furthermore, the bioconcentration and biomagnification potential of toluene is low. Toluene is metabolized by fish and the rate of elimination is rapid (ECAO, 1981).

2.2.2 Other Effects

Except in cases of accidental spills, toluene is unlikely to be present at levels that would cause adverse effects on the ecosystem. Effects have been studied using aquatic organisms, bacteria, and higher plants. Toluene can both stimulate and inhibit the growth of algae, depending on the species and the toluene concentration. The no-effect level for most algal species is 10 mg/l. Several salt-water algal species and kelp have been tested and effects were observed between 8 and about 433 mg/l. In both microorganisms and higher plants toluene can disrupt cell membranes, thus causing toxic or lethal effects. Toluene does not accumulate in plants nor is it translocated. Ecosystem impacts of toluene spills or chronic low-level pollution are unknown. Adverse effects may occur but probably are limited by rapid rates of loss of toluene through evaporation and biodegradation (ECAO, 1981).

3. ENVIRONMENTAL RELEASE

As shown in Table 2 (based on 1978 estimates), toluene is released to the environment from production, usage, and inadvertent sources. It is evident from Table 2 that nearly all (99.9%) releases of toluene enter the atmosphere. The largest emitters of toluene are (1978 data): automobile exhaust, 640,000 kkg (58%); industrial use of toluene as a solvent, 375,000 kkg (34%); and evaporative loss of gasoline in marketing and automotive use, 37,000 kkg (3.4%). The relatively small amount of toluene released to surface water (<1,200 kkg) arises primarily from spills of gasoline, oil, and toluene. Land releases, which are also comparatively minor (278 kkg), are mainly due to transportation spills of gasoline (ECAO, 1981).

3.1 Air Releases

Significant Releases

- Automobile exhaust
- Industrial use as solvent

Other Releases

- Gasoline evaporation (in marketing and use)
- Catalytic reforming (toluene production)
- Ethylene-propylene rubber production
- Combustion processes

3.2 Water Releases

- Spills from transport of gasoline and toluene

3.3 Land Releases

- Spills from transport and storage of gasoline

TABLE 2. TOLUENE SUPPLY, CONSUMPTION, AND RELEASES PER YEAR^a
(1978 Data)

<u>Toluene Production</u>	<u>Supply (kkg)</u>	<u>Consumption (kkg)</u>	<u>Airborne Releases (kkg)</u>	<u>Aquatic Releases (kkg)</u>	<u>Discharge to POTWs (kkg)</u>	<u>Discharges to Land (kkg)</u>
Catalytic reforming						
Isolated	3,110,000	-	3,011	-		
Non-isolated (BTX) ^b	27,000,000	-				
Pyrolytic cracking						
Isolated	324,000	-	469	-		
Non-isolated (BTX)	197,000	-				
Styrene by-product	135,000	-	103	-		
Coke oven by-product						
Isolated	26,000	-	153	47	36	31
Non-isolated (BTX)	<u>96,000</u>	-	<u>28</u> from waste- water	<u>47</u>	<u>36</u>	<u>31</u>
Production totals	30,888,000		3,764	47	36	31
<u>Toluene Uses</u>						
Non-isolated (BTX)		27,293,000	c			
Isolated						
Benzene production		1,675,000	335			
Gasoline back-blending		1,465,000	c			
Solvent for paint and coatings		263,000	263,000	1		
Solvent for adhesives, inks, pharmaceuticals, and others		132,000	112,000	29		
Toluene diisocyanate		200,000	256			
Xylene production		98,000	20			
Benzoic acid		65,000	98			
Benzyl chloride		36,000	36			
Vinyl toluene		25,000	25			
Other uses		<u>39,000</u>	<u>39</u>			
Use totals		31,291,000	375,809	30	NA	NA

TABLE 2. TOLUENE SUPPLY, CONSUMPTION, AND RELEASES PER YEAR (Continued)
(1978 Data)

Miscellaneous Releases of Toluene	Supply (kkg)	Consumption (kkg)	Airborne Releases (kkg)	Aquatic Releases (kkg)	Discharge to POTWs (kkg)	Discharges to Land (kkg)
Gasoline marketing			19,000			
Auto gasoline evaporation			18,000			
Auto exhaust			640,000			
Transport spills:						
Oil				400		6
Gasoline				680		230
Toluene				3		11
Propylene oxide manufacture			36			
Polychloroprene manufacture			460			
Ethylene-propylene terpolymer and rubber production			4,290			
Wood preserving industry			-	6		
Acrylonitrile manufacture			59			
Combustion processes:						
Coal refuse piles			4,400			
Stationary fuel combustion			13,000			
Forest fires			7,000			
Agricultural burning			1,000			
Structural fires			<1,000			
Cigarette smoke			53			
Coke production (unrecovered)			10,560			
Others			8			
Miscellaneous subtotals			718,866	1,089		247
Combined totals ^d	30,888,000	31,291,000	1,098,439	1,166	36	278

^a Source: (ECAO, 1981).

^b BTX = Combined benzene, toluene, xylene gasoline product.

^c Listed under Miscellaneous Releases.

^d The discrepancy in production and consumption results from the fact that the former figure is reported by producers but the latter figure is a total of estimates only.

EXPOSURE ROUTES

The general population may be exposed to toluene through the following routes: (1) inhalation of air; (2) ingestion of water and foods; and (3) direct exposure through the skin. Certain segments of the population may be exposed to toluene through occupational exposure, cigarette smoking, and consumer products.

Air constitutes the most important exposure route for the general population although concentrations are many times lower than the vapor levels considered to be potentially harmful in occupational settings. Atmospheric toluene in urban areas arises primarily from automotive emissions with solvent losses as a secondary source. Dermal exposures of significance are primarily restricted to occupational uses.

Estimates of toluene exposure levels for various routes and population groups are given in Table 3. Inhalation exposure has been estimated for three areas: urban, rural/remote, and areas near manufacturing or user sites. The concentration of toluene in monitored urban areas in the United States ranged from less than 0.1 ug/m³ to about 200 ug/m³; average levels were in a range of approximately 4 to 40 ug/m³. Near manufacturing/user sites, measured toluene concentrations ranged from 0.1 to 600 ug/m³; atmospheric levels depend strongly on distance from release sites. In remote and rural areas, toluene levels averaged about 1 ug/m³ and ranged from a "trace" to 3.8 ug/m³. Intake estimates in Table 3 assume a daily breathing rate of 22.4 m³/day (157 m³/wk). It should be remembered that the amount of toluene inhaled is not the amount absorbed. Only about one-half of the amount inhaled is retained; also, much of the absorbed toluene is probably rapidly excreted (ECAO, 1981).

Population exposure through ingestion of food or drinking water is probably negligible compared to air exposure. Most (>80%) surface waters contain levels of toluene in the range of 0 to 10 ug/l. The range of concentrations found in drinking water was 0-19 ug/l. However, only one water supply examined had a concentration of 19 ug/l; most other levels of toluene detected were around 1 ug/l (ECAO, 1981).

TABLE 3. TOLUENE EXPOSURE ESTIMATES UNDER DIFFERENT EXPOSURE CONDITIONS a b

Exposure Route	Observed Range of Concentration	Frequency of Exposure	Total Volume Exposed or Amount Consumed	Inhalation or Ingestion Rate (mg/wk)
<u>General Population</u>				
Inhalation				
Urban areas	0.1-204 ug/m ³	168 hr/wk	157 m ³	0.02-32
Rural and remote areas	trace-3.8 ug/m ³	168 hr/wk	157 m ³	trace 0.6
Areas near manufacturing and user sites	0.1-600 ug/m ³	168 hr/wk	157 m ³	0.02-94
Ingestion				
Drinking water	0-19 ug/l	2 l/day	14 l	0-0.3
Food (fish)	0-1 mg/kg	6.5 g/day	45.5 g	0-0.45
<u>Occupational Group</u>				
Inhalation	380 mg/m ^{3b}	40 hr/wk	48 m ³	18,000 ^b
<u>Cigarette Smokers</u>				
Inhalation	0.1 mg/cigarette ^c	20 cigarettes/day	140 cigarettes	14

a Source: (ECAO, 1981).

b This value assumes 8-hr work day exposure to NIOSH recommended level of 100 ppm (8-hr average).

c From mainstream smoke only.

5. DATA BASES

5.1 Chemicals in Commerce Information System (CICIS)

The Inventory was compiled under the authority of Section 8 of TSCA which requires manufacturers to report to EPA the chemicals imported and manufactured during calendar year 1977. The Inventory lists the Chemical Abstract Service (CAS) preferred name for the chemicals, their respective CAS number (often used for identification purposes), production site, company name, and volume(s) of production and import. There is also a Confidential Inventory in which many of these characteristics are claimed confidential by the manufacturer. In these instances, the confidential information will not be available on the public inventory. CICIS can now be accessed through the NIH/EPA Chemical Information System (CIS - see 5.3). For further information, contact Gerri Nowack at FTS 382-3568.

5.2 EPA Chemical Activities Status Report (EPACASR)

EPACASR is an on-line system containing information on EPA's interest in chemicals. This system includes data on the Agency's regulations, research, and assessments directed toward specific chemicals. EPACASR is published annually and the data base is updated as information is received. A searchable subset itemizes NTP/NCI studies and results, as well as chemicals discussed in the IARC monograph series. (Other sources are added as appropriate.) Entries identify the statutory authority, the nature of the activity, its status, the reason for and/or purpose of the effort, and a source of additional information. Searches may be made by CAS Number or coded test. For further information contact Eleanor Merrick at FTS 381-3415.

5.3 NIH/EPA Chemical Information System (CIS)

This is a collection of various scientific data bases available through an interactive computer program. The linking system between these data files is the Structure and Nomenclature Search System (SANSS). CIS can also provide a list of non-CIS sources of information on a chemical of interest. However, these files have to be accessed individually by either separate on-line systems or in hard-copy. For further information contact Delores Evans at FTS 382-3546 or Irv Weiss at FTS 382-3524.

5.4 Chemical Regulations and Guidelines System (CRGS)

CRGS is an on-line data base that is being developed to provide information on chemical regulatory material found in statutes, regulations, and guidelines at the Federal, State, and international levels. Currently, only the first phase of CRGS, which encompasses only source material at the Federal level, is operational. Nationwide access to CRGS is available through Dialog. For further information, contact Delores Evans at FTS 382-3546 or Ingrid Meyer at FTS 382-3773.

5.5 Chemical Substances Information Network (CSIN)

The prototype CSIN, operational since November 1981, has been developed by merging the technologies of computer networking and distributed data base management. CSIN is not another data base, but a library of systems. Through the CSIN front-end intermediary management computer, the user may access and use independent and autonomous information resources that are geographically scattered, disparate for data and information content, and employ a variety of types of computer hardware, software, and protocols. Users may converse in and among multiple systems through a single connection point, without knowledge of or training on these independent systems.

Currently, six independent information resources are accessible through CSIN. They are: National Library of Medicine (NLM), CIS, EPA-CICIS, CAS-On-Line, SDC-orbit, and two files of Dialog: CRGS and TSCA Inventory. The CSIN management computer allows the user to create, retrieve, store, and manipulate data and queries. This eliminates the need for reentering long lists of chemical identifiers or other information elements that are part of the original query or that have been identified and acquired from one or more of the CSIN resources. For further information contact Dr. Sid Siegal at FTS 382-2256.

5.6 EPA Information Clearinghouse

The EPA Information Clearinghouse is a bibliographic data base composed of over 475 individual data bases and models that contain monitoring information and statistics on a variety of chemicals. The individual data bases are maintained for offices within EPA. For further information, contact Charlene Sayers at FTS 755-9112.

The following data bases contain information on toluene:

BAT Review Study for the Timber Products Processing, Gum and Wood, Chemicals, and the Printing and Publishing Industries
Best Management Practices, Timber Industry Effluent Guidelines -
Runoff
Best Management Practices, Timber Industry Effluent Guidelines -
Sludge
Chemicals in Commerce Information System
Compliance Sampling Toxicant Surveys
Consolidated Permits Program-Application Form 1,2b,2c
Data Collection Portfolio for Industrial Waste Discharges
Distribution Register Organic Pollutants in Water
Effluent Guidelines GC/MS Screening Analysis Data Base
Energy and Mining Point Source Category Data Base
Federal Facilities Information System
Fine Particle Emissions Information System
Fish Kills
Food Industry Group
Fugitive Emissions Information System
Gaseous Emissions Data System
Hazardous Waste Site Tracking System

Hazardous Waste Data Management System
 Hemlock, Michigan Environmental Samples
 Hewlett-Packard
 Houston Oxidant Modeling Study
 Humacao Ambient Data Base
 IFB Organics Data Base
 Indicatory Fate Study
 Industrial Process Evaluations
 Infrared Spectra of Pollutants
 Innovative Technology, Timber Industry Effluent Guidelines
 Inorganic Chemicals Industry Regulation Record
 LiPari Landfill
 Liquid Effluents Data System
 Listing of Organic Compounds Identified in Region IV
 Love Canal Data Handling System
 Method Validation Studies of Priority Pollutants
 National Pollutant Discharge Elimination System (NPDES) Discharge
 Monitoring Reports
 Nationwide Urban Runoff Program
 Needs Survey
 New York Bight Ocean Monitoring Program
 Northeastern Regional Oxidant Study
 Organic Chemicals/Plastics Industry
 Organic Transport thru Soil
 Ozone and its Precursors Data Base-Houston/Los Angeles
 Ozone and its Precursors Data Base-Midwest/Boston
 Ozone and its Precursors Data Base-Northeast
 Paint and Ink Analytical Data
 Permit Compliance System
 Pharmaceutical Screening/Verification Data Base
 Precision and Accuracy for Screening Protocols
 Priority Pollutants-Region I
 Priority Pollutants-Region III
 Publicly Owned Treatment Works (POTW) Analytical Data
 Publicly Owned Treatment Works (POTW) Quality Control
 Puerto Rico Reservoirs
 Regional Toxics Monitoring Program
 Resource Conservation and Recovery Act (RCRA)-Hazardous Waste Site
 Inspections
 Screening Sampling Program
 Select Hazardous Chemicals-Ambient
 Sources of Toxic Pollutants Found in Influent to Sewage Treatment
 Plants
 Spill Prevention Control and Countermeasure
 System for Consolidated Permitting and Enforcement Data Base
 Textile Industry BAT Study-Toxic Sampling Data
 Toxics Monitoring
 U.S. Virgin Islands-St. Thomas, St. Croix
 Verification Data Base
 Verification Sampling Program
 Waste Characterization Data Base
 Water Enforcement Regional System
 Water Quality Information System

6. REGULATORY STATUS (Current as of 4/16/82)

6.1 Promulgated Regulations

6.1.1 EPA Programs

Clean Water Act (CWA)

- Section 311 - Toluene is designated a hazardous substance (40-CFR116.4) and is subject to reportable quantity limitations (40CFR117.3).
- Section 307 - Toluene is listed as a toxic pollutant (40 CFR-401.15) as applied to effluents. However, no effluent guidelines specifically limit toluene release at this time.
- Sections 318, 402 and 405 - National Pollution Discharge Elimination System (NPDES) permit testing requirements; toluene is listed as a volatile organic pollutant based on gas chromatographic and mass spectroscopic analyses; it is part of the consolidated permit program (40CFR122 App. D).

Resource Conservation and Recovery Act (RCRA)

- Section 3001 - Toluene is identified as a toxic waste (U220) and listed as a hazardous waste constituent (40CFR261.33, App. VIII). Nonspecific sources of toluene-containing waste are solvent use (or recovery) activities (40CFR261.31). Waste streams from the following industries contain toluene and are listed as specific sources of hazardous waste: organic chemicals (benzylchloride production) and pesticides (disulfoton production) (40CFR261.32, App. VII).
- Sections 3002 to 3006 - Hazardous wastes are subject to further controls concerning generators, transporters, and treatment, storage and disposal facilities (40CFR262 to 265). Permit procedures are also included in consolidated permit regulations (40CFR122 to 124).

6.1.2 Programs of Other Agencies

OSHA - Occupational Safety and Health Act

- Sections 6(a) and 8(g) - general industry standards; specifies permissible exposure limit for toluene, including ceiling and peak levels (29CFR1910.1000).

CPSC - Federal Hazardous Substance Act

- Sections 2-3, 10 and 14 - Products requiring special labeling and exemptions (16CFR1500.14(a)(3) and (b)(3); - .83(a)(8); (a)(9), and (a)(13)).

DOT - Hazardous Materials Transportation Act

- Shipment of toluene is regulated due to its combustibility (49CFR172.101-102).

FDA - Food, Drug, and Cosmetic Act

- Sections 409 and 701 - Toluene is a permissible component in food packaging, i.e., an allowable indirect food additive (21CFR175 to 178).
- Section 512(i) - New animal drug dosage forms that are not subject to certification include toluene capsules (21CFR520.580).
- Section 408 - Toluene is exempt from tolerances for use as a solvent in pesticide formulations applied to growing crops (40CFR180.1001(d) and 180.1045).

DOE - Emergency Petroleum Allocation Act

- Regulations apply to toluene products produced in or imported into the United States (10CFR211.201, 212.31, 212.56, and 213.11).

6.2 Proposed Regulations

6.2.1 EPA Programs

Clean Air Act (CAA)

- New stationary source performance standards (NSPS) have been proposed for volatile organic chemicals from the synthetic organic chemicals manufacturing industry (46FR1136) and pressure-sensitive tape and label surface coating operations (45FR86278).

Toxic Substances Control Act (TSCA)

- Section 8(d) - Requires chemical manufacturers, processors, distributors, and others who possess health and safety studies on listed chemicals (including toluene) to submit the data to EPA (44FR77470).

6.3 Other Actions

EPA

- A Suggested No Adverse Response Level (SNARL) for toluene is being developed for drinking water (ODW).
- The National Ambient Air Quality Standard (NAAQS) for hydrocarbons indirectly regulates toluene. The hydrocarbon standard is for use as a guide in devising implementation plans to achieve photochemical oxidant (i.e., ozone) standards (40CFR50.10).

7. STANDARDS AND RECOMMENDED CRITERIA*

7.1 Air

● OSHA limits (29CFR1910.1000):

8-hour time-weighted average	200 ppm
Ceiling concentration	300 ppm
Maximum peak for 10 min.	500 ppm

● NIOSH recommended exposure limits:

8-hour time-weighted average	100 ppm
Ceiling concentration	200 ppm

7.2 Water

- Ambient water criterion level to protect human health (FR4579318). 14.3 mg/l
- Hazardous spill rules require notification of discharges equal to or greater than the reportable quantity (40CFR117.3). 1000 lb

*See Appendix A for a discussion of the derivation, uses, and limitations of these criteria and standards.

8. SPILL CLEAN-UP/DISPOSAL (CONTACT: National Response Center
800-424-8802; 426-2675 in
the Washington, D.C. area)

8.1 Hazards and Safety Precautions

Toluene readily volatilizes to a moderately toxic vapor that may cause dizziness, CNS depression, and reaction time impairments at levels of 200-1,500 ppm. Contact may irritate skin and eyes.

Toluene is extremely flammable and may be ignited by heat, sparks, or flames. Container may explode in heat of fire; vapor explosion hazard exists and runoff to sewers may create fire or explosion hazard. Fire produces toxic combustion products.

8.2 First Aid

Move victim to fresh air and call medical help. Give artificial respiration if not breathing or oxygen if breathing is difficult. In case of contact, immediately flush skin or eyes with running water. Remove contaminated clothing.

8.3 Emergency Action

Spill or leak

Stay upwind, isolate hazardous area, and wear self-contained breathing apparatus and full protective clothing. Remove ignition sources and use water spray to reduce vapors. Contain slick on waters; use oil skimming and sorbent foams. For dissolved portions, use carbon or peat.

Fire

For small fires use dry chemical, CO₂, water spray, or foam. For large fires, use water spray or foam. Move containers from fire area if possible; cool containers exposed to fire with water until well after fire is out. Isolate for one-half mile in all directions if tank or tankcar is involved in fire.

8.4 Notification and Technical Assistance

Section 103 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or "Superfund" requires notification of the National Response Center (NRC, 800-424-8802 or 426-2675 in the Washington, D.C. area) if releases exceed reportable quantities (1,000 lb in the case of toluene). For emergency assistance call CHEMTREC: 800-424-9300. For information call the Division of Oil and Special Materials at 1-202-245-3045.

8.5 Disposal

Toluene is classified as a toxic waste (U220) and generators of more than 1,000 kg of hazardous waste per month (or residues from spill

clean-up) are subject to RCRA regulations. The following waste streams are subject to Subpart D regulations:

- Still bottoms from the distillation of benzylchloride.
- Still bottoms from toluene reclamation distillation in the production of disulfoton.
- Wastewater treatment sludge from disulfoton production.
- Used solvents and wastes from recovery of solvents (generic wastestream).

9. SAMPLING, ACCEPTABLE ANALYTICAL TECHNIQUES, AND QUALITY ASSURANCE

9.1 Air (CONTACT: Joseph F. Walling, FTS 629-7954)

Toluene is not a criteria air pollutant*, therefore, no Agency or reference procedures exist. Although measurements of this pollutant have been made and reported, there are no well documented method descriptions available for quantitative measurements in ambient air. Therefore, monitoring for this pollutant must be approached with great caution.

A procedure using Tenax adsorbent for sampling and gas chromatography/mass spectrometry (GC/MS) for analysis has been used but little is known about the precision and accuracy of the procedure. GC/MS requires special expertise and expensive, sophisticated equipment. For these reasons, monitoring for one compound alone using the Tenax GC/MS procedures is rarely cost effective and the approach is most suitable when monitoring for an array of volatile compounds is desired.

The preparation of Tenax suitable for sampling is demanding. Tenax background is a problem that must be addressed. Precautions about permissible maximum air volumes, sampling rates, and ambient temperatures during sampling must be observed and these, in turn, govern allowable sampling times.

Detection limits and accuracy are not known; reproducibility is estimated to be 50-100 percent. The generation of artifacts during thermal elution with Tenax GC can be significantly reduced by proper clean-up and conditioning.**

9.2 Water (CONTACT: Thomas Bellar, FTS 684-7311;
James Lichtenberg, FTS 684-7308)

Toluene is a proposed parameter under Section 304(h) of the Clean Water Act. It is listed as one of the priority pollutants. There are three proposed procedures for the analysis of toluene in natural, waste, and drinking waters. All methods proposed use the purge and trap procedure. Two of the methods use gas chromatography for detection and quantification; the third calls for detection by a gas chromatograph/mass spectrometer.

* Toluene is indirectly regulated as a "volatile organic compound" (VOC), but no analytical procedure has been approved to analyze specifically for toluene.

** See G. Holzer, et.al., J. Chromatogr. 142, 755-64 (1977).

Purge and Trap Methods**

EPA Method #503.1

EPA Method #602

EPA Method #624

Major Equipment: Gas Chromatograph and Purge and Trap Apparatus.

Five ml of the aqueous sample is placed into a purging device. Toluene and other volatile water insoluble organic compounds are transferred from the aqueous phase to the gas phase. The volatilized compounds are swept from the purging device by the purged gas and are trapped in a short column containing a suitable sorbent. After a predetermined period of time the trapped compounds are thermally desorbed and backflushed into a gas chromatograph equipped with a mass spectrometer or photoionization detector. The method detection limit for the mass spectrometer is approximately 6.0 ug/l. For the photoionization detector method detection limits as low as 0.02 ug/l have been achieved.

Samples are collected in narrow-mouth screen-cap bottles with TFE fluorocarbon seals. Adjust the pH of the sample to about two by adding 50% HCl while stirring vigorously. If the sample contains free or combined chlorine, add sodium sulfite preservative. From time of collection to extraction the sample is stored head-space free at 4°C in the dark. Spiked river water samples have been stored for up to 14 days under these conditions with no apparent losses.

List of Procedures for Toluene

Method	Type ^a	MDL ^b	Recovery ^c %	Standard Deviation %	Status (March 1981)
EPA 624	P&T	6.0 ug/l	96	25	Proposed
EPA 602	P&T	0.2 ug/l	95	10.1	Proposed
EPA 503.1	P&T	0.02 ug/l	95	7.6	Proposed

a) Purge and Trap; b) MDL - Minimum Detectable Level; c) Single laboratory recovery from spiked reagent water or wastewater.

**References for Water Analysis

"The Analysis of Aromatic Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method" Method 503.1; May 1980, USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

"Methods for Organic Chemical Analysis of Water and Wastes by GC, HPLC, and GC/MS" Method 602; Purgeable Aromatics. USEPA, Environmental Monitoring Support Laboratory, Cincinnati, Ohio 45268. See also 44FR69474-78.

"Methods for Organic Chemical Analysis in Water and Wastes by GC, HPLC, and GC/MS" Method 624; Purgeables. USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. See also 44FR69532.

9.3 Solid Waste (CONTACT: Michael Hiatt, FTS 545-2118
Werner Beckert, FTS 545-2137)

Methods 8.02 and 8.24 in "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods" (USEPA/SW-846/1980) are approved for analyses of toluene in solid wastes.

In one modified purge and trap technique the volatile compounds are removed from the sample by heating the sample to 110°C while sweeping with helium carrier gas that is subsequently passed through 5 ml of water. The carrier gas then passes through a tenax-silica gel trap which absorbs the volatile organics. The volatiles are desorbed from the trap by heating and passed through a GC column. Sample preparation generally takes less than 30 minutes. Recoveries are reported to be 77% at 26 ppb with an 88% precision. This method has been tested for the ppb range. See:

David N. Speis, "Determination of Purgeable Organics in Sediment Using a Modified Purge and Trap Technique." Protocol, U.S. EPA, Region II, Edison, New Jersey, October 10, 1980.

In another modified purge and trap technique, which was used in the Love Canal Study, the sample is diluted with water and the resultant slurry is purged. A standard deviation of 24% has been reported for this method at the 20 ppb range. Recoveries are reported to be 35%. From: Quality Assurance Plan, Love Canal Study (unpublished).

With the vacuum extraction technique, the volatiles are extracted from the sample using a vacuum. The extracted volatiles are collected in a liquid-nitrogen-cooled trap. After extraction, 5 ml of water are added to the extract and the sample analyzed as a 5-ml water sample using Method 624. The precision at 25 ppb is 4% with a 102% recovery. The total sample preparation takes approximately 36 minutes. See:

Michael H. Hiatt, "Analysis of Fish and Sediment for Volatile Priority Pollutants." Accepted for publication in Analytical Chemistry.

9.4 Other Samples

A modification of the purge and trap method has been suggested by EPA, (1979, Chemistry Laboratory Manual for Bottom Sediments; NTIS PB294-596) for the analysis of soil and sediment samples. The modified purge and trap apparatus used for this purpose is described. The sample, contained in a specially designed glass vial, is heated at 80°C and purged with helium gas. The desorbed organics are trapped in a Tenax GC column. At the end of trapping, thermally desorbed organics from the column are analyzed by GC-FID as in the case of water and wastewater samples. The recovery of toluene was determined to vary between 32% and 44% when 0.1 ug to 3.0 ug of toluene was spiked onto a specially prepared soil matrix. Although the

recoveries were low, they were found to be linear and reproducible. Data on spiked environmental samples showed much higher recoveries (80-100%).

With the purge-trap system described, the minimum detection limit of 0.1 ppb can be attained. Thus, the method showed at least two orders of magnitude higher sensitivity than headspace analysis.

9.5 Quality Assurance

9.5.1 Water

Single laboratory test data on simple spiked matrices have been collected by EPA. Quality control and performance evaluation samples (methanolic concentrates containing toluene to be spiked into water) are available from the Environmental Monitoring and Support Laboratory, Quality Assurance Branch, USEPA, Cincinnati, Ohio 45268. (See Water Contact).

9.5.2 Solid Waste

Standards can be obtained from Radian Corporation or EMSL-Las Vegas (see Solid Waste Contact). Supelco supplies diluted standards but the concentrations are not verified. Standard solutions may also be prepared in the laboratory from reagent-grade toluene to the appropriate dilution using methanol.

Periodic performance evaluations with samples that include toluene are carried out by EMSL-CIN (Water Supply and Water Pollution Studies).

REFERENCES

The major references used in preparation of this document are listed below. EPA references are listed by the EPA office of origin and the year of publication. For further information refer to the contacts given throughout this document or contact the relevant EPA Program Offices given at the end of this section.

- (ECAO, 1981) Health Risk Assessment Document for Toluene, EPA-Contract No. 68-02-377, Environmental Criteria and Assessment Office (1981).
- (NRC, 1980) The Alkyl Benzenes, National Research Council, Washington, D.C. (1980).
- (OWRS, 1980) Ambient Water Quality Criteria for Toluene, EPA - 440/5-80-075; Office of Water Regulations and Standards (1980).

OFFICE CONTACTS

The EPA Offices and Divisions listed below may be contacted for more information relating to the indicated sections of this document. While these offices are, in many cases, the offices of origin for the data included in this paper, the personal contacts given throughout this document should be contacted first. Unless otherwise noted, the offices listed are situated in Headquarters, Washington, D.C., and the telephone numbers given are FTS (Federal Telecommunications System) numbers. For commercial telephone calls to Headquarters that are not placed on FTS, area code 202 must be used. Other commercial numbers are noted for the office contacts located outside Washington, D.C.

HEALTH AND ENVIRONMENTAL EFFECTS (Section 2)

Office of Health and Environmental Assessment (OHEA)

Environmental Criteria and Assessment Office:

Cincinnati, OH	684-7531 (513-684-7531)
Research Triangle Park, NC	629-2266 (919-541-2266)

Carcinogen Assessment Group	755-3968
-----------------------------	----------

Office of Drinking Water (ODW)

Health Effects Branch	472-6820
-----------------------	----------

Office of Toxic Substances (OTS)

Health and Environmental Review Division	382-4241
--	----------

Environmental Research Laboratory

Duluth, MN, Region V	783-9550 (218-727-6692)
----------------------	-------------------------

ENVIRONMENTAL RELEASES AND EXPOSURE (Sections 3 and 4)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Water Regulations and Standards (OWRS)

Monitoring and Data Support Division	426-2503
--------------------------------------	----------

Office of Toxic Substances (OTS)

Exposure Evaluation Division	382-3873
Assessment Division	382-3442

DATA BASES (Section 5)

Office of Toxic Substances (OTS)

Management Support Division	382-3546
-----------------------------	----------

REGULATORY STATUS, STANDARDS, AND CRITERIA (Sections 6 and 7)

Office of Air Quality Planning and Standards (OAQPS)

Strategies and Standards Division	
Research Triangle Park, NC	629-5504 (919-541-5504)

Office of Drinking Water (ODW)

Criteria and Standards Division	472-5016
---------------------------------	----------

Office of Water Regulations and Standards (OWRS)

Criteria and Standards Division	755-0100
---------------------------------	----------

Effluent Guidelines Division	426-2571
------------------------------	----------

Office of Solid Waste (OSW)

State Programs and Resources	
Recovery Division	755-9107

SPILL CLEAN-UP AND DISPOSAL (Section 8)

NOTE: For Emergencies call the National Response Center at 1-800-424-8802
(1-800-426-2675 from the Baltimore/Washington area).

Office of Emergency and Remedial Response (OERR)

Emergency Response Division	245-3045
-----------------------------	----------

Oil and Hazardous Materials Spills Branch

Edison, NJ, Region II	340-6634 (201-321-6634)
-----------------------	-------------------------

Office of Solid Waste (OSW)

Hazardous and Industrial Waste Division

755-9187

ANALYTICAL TECHNIQUES (Section 9)

Environmental Monitoring Systems Lab (EMSL)

Air Analysis

Research Triangle Park, NC

629-2454 (919-541-2454)

Water Analysis

Cincinnati, OH

684-7311 (513-684-7311)

Waste Analysis

Las Vegas, NV

545-2137 (702-798-2137)

GENERAL IPP COMMENTS, CORRECTIONS OR QUESTIONS

Office of Toxic Integration

Chemical Information and
Analysis Program

382-2249

APPENDIX A

Criteria and Standards, Their Derivation, Use, and Limitations

The Agency is often required to respond to environmental emergencies or incidents for which established protocols are not relevant. In some cases, when no traditional regulatory health criteria or action level exist, the Agency may fashion an approach using professional judgement, borrowing from standards/guidelines developed for similar circumstances. If the existing standards and criteria are to be applied correctly, the assumptions and methods used in deriving them must be taken into account. This Appendix contains a short description of the methods used to derive the standards and criteria listed in the IPP documents (Section 7).

Clean Air Act (CAA)

National Ambient Air Quality Standards (NAAQS)--Sections 108 and 109 of the CAA authorizes EPA to set levels at which air pollutants can safely be tolerated and to establish NAAQS. Control strategies (implementation plans) for emission sources are developed on a State-by-State basis. NAAQS are based on air quality criteria documents which reflect the latest knowledge concerning effects on the public health. To develop primary NAAQS, EPA must: (1) specify the significance of health effects; (2) identify sensitive populations, (e.g., asthmatics, heart patients, children, etc.); (3) determine probable adverse health effect levels in sensitive persons; and (4) estimate the level below the probable effect level which provides an adequate margin of safety. See 40 CFR 50 for NAAQS issued to date.

New Source Performance Standards (NSPS)--Under Section 111 of the CAA, EPA may issue NSPS to regulate air pollutants from new stationary sources which endanger the public health or welfare. In many cases, NSPS are set by EPA to facilitate the achievement of NAAQS; NSPS regulate emissions from specific categories of pollution sources rather than "air quality." NSPS are published in 40 CFR 60.

National Emission Standards for Hazardous Air Pollutants (NESHAPs)--Hazardous air pollutants are defined under Section 112 of the CAA as those that cause an increase in mortality or an increase in serious irreversible or incapacitating reversible illness. NESHAPs may apply to one particular stationary source or to several categories of sources. The basic approach used in the development of NESHAPs has been to identify an ambient level sufficient to protect public health and then relate emissions to this level by the use of meteorological dispersion estimates. The procedure used to determine what ambient concentrations allow an "ample margin of safety" varies with the pollutant of concern.

For suspected carcinogens, such as vinyl chloride, EPA assumes that no level of exposure is toxicologically insignificant (44 FR 58642). Therefore, EPA requires emission on reduction for vinyl chloride to the lowest achievable by use of the best available control technology (40 FR 59534). See 40 CFR 61 for published list.

Clean Water Act (CWA)

Section 311--Reportable Quantities for Hazardous Substances--Under CWA Section 311, 297 compounds have been designated as hazardous substances (40 CFR 116) and reportable quantities (RQs) have been assigned (40 CFR 117). The RQs assigned are all essentially based on acute aquatic toxicity. [EPA further screened candidates for listing under Section 311 on the basis of discharge potential.] Other criteria for selection adopted in 40 CFR 116 (acute toxicity in mammals and plants) have not yet been employed by the Agency. To date, EPA has relied exclusively on the 96-hour LC50 toxicity test (i.e., the concentration likely to kill 50 percent of the fish population within 96 hours) to assign reportable quantities. Reportable quantities vary from 1.0 pound for substances which are the most highly toxic to aquatic life ($LC50 < 1\text{ ppm}$) up to 5000 pounds for substances which are practically nontoxic ($100\text{ ppm} < LC50 < 500\text{ ppm}$). The reportable quantities of 10 pounds, 100 pounds, and 1000 pounds correspond to aquatic toxicity (LC50) ranges of 0.1 to 1 ppm, 1 to 10 ppm, and 10 to 100 ppm respectively (43 FR 10492).

If the reportable quantity is reached in a discharge, the regulations under Section 311 specify requirements for notification and prescribe penalty provisions. The regulations apply only to discharges of RQs in any 24-hour period; thus, RQ levels are set to control short-term nonroutine discharges of hazardous substances (44 FR 50775). No consideration is given to water body characteristics. In addition, discharges of mixtures and solutions are subject to the regulations only if a component hazardous substance is discharged in a quantity equal to or greater than its RQ (44 FR 50767).

Due to the passage of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund), the Agency is in the process of assigning RQs for newly designated hazardous substances and adjusting the RQs previously assigned under the CWA Section 311. RQ values set under Superfund regulations will use other criteria in addition to aquatic toxicity. However, until EPA sets other reportable quantities, RQs for CERCLA are the same as RQs established for Section 311 of the CWA, where applicable. For all other hazardous substances not covered under Section 311, the statutory RQs under Section 102(b) of CERCLA are set at 1.0 pound unless and until they are superceded by EPA regulations.

Water Quality Criteria (45 FR 79318)--Pursuant to Section 304(a)(1) of the CWA, EPA published water quality criteria (WQC) for the 65 pollutants that Congress, in the 1977 amendments to the Act, designated as toxic under Section 307(a)(1). The WQC reflect the latest scientific knowledge on the relationship between pollutant concentrations and environmental and human health effects. Criteria values do not consider the economic or technological feasibility of attainment; they are based on a scientific assessment of environmental and human health effects. WQC have no direct regulatory impact.

Two different types of WQC are calculated: one to protect aquatic life and other to protect human health. The human health criteria are based on three types of biological end points: carcinogenicity, toxicity (adverse effects other than carcinogenicity), and organoleptic effects

(taste and odor). Because EPA has regarded carcinogenicity as a non-threshold phenomenon, "safe" or "no-effect" levels for carcinogens could not be established. Consequently, WQC for carcinogens are presented as a range of pollutant concentrations associated with corresponding incremental risks of 10^{-4} , 10^{-5} and 10^{-6} (i.e., one out of 10,000, one out of 100,000, and one out of 1,000,000 respectively). The lifetime risk assumes a person is continuously exposed to the carcinogenic agent. In most cases, the data for a quantitative estimate of carcinogenic response are from lifetime animal studies; human studies were used in the few cases where the data were sufficient.

For compounds that do not exhibit a carcinogenic response, a threshold assumption is used in deriving criteria. These criteria are based upon Acceptable Daily Intake (ADI) levels and are generally derived using no-observed-adverse effect-level (NOAEL) data from animal studies. The ADI is calculated using safety factors (in accordance with the National Research Council recommendations) of 10 to 1000 depending on the quality and quantity of data. In instances where insufficient data are available on a chemical's toxicological effects, criteria may be based on its organoleptic characteristics. This type of criterion may also be established if the level based on organoleptic effects is lower than the level calculated from toxicological data.

The basic assumptions used for these calculations are that a 70 kilogram male will consume two liters of water per day, plus 6.5 grams per day of freshwater and estuarine fish and shellfish products. An average bioconcentration factor for the chemical in aquatic animals is used to estimate potential exposure due to ingestion of the fish or shellfish.

Aquatic life criteria were developed to protect most aquatic life. These criteria specify maximum and 24 hour average values in order to provide protection from acute and chronic toxicity. Specific aquatic life criteria have not been developed for some toxic pollutants due to insufficient data. In these cases, descriptions of apparent threshold levels are presented in order to convey an estimate of the toxicity in the absence of specific criteria.

An explanation of the guidelines used in developing aquatic and human health criteria may be found in the Federal Register (45 FR 79318).

Safe Drinking Water Act (SDWA)

Drinking Water Standards*--Pursuant to Section 1412 of the SDWA, EPA has promulgated National Interim Primary Drinking Water Standards for certain toxic pollutants in finished drinking water (40 CFR 141). Maximum contaminant levels (MCLs), which specify the maximum level permitted, are based on consideration of a range of factors including not only health effects, but also the technological and economic feasibility for removal of the substance from the supply (40 FR 59566). For treated drinking water supplies serving 25 or more people, States

* See: National Interim Primary Drinking Water Regulations, EPA-570/9-76-003, Office of Drinking Water (1976).

must control toxics down to levels at least as stringent as MCLs. EPA is also required to establish revised primary drinking regulations based on currently available information and treatment techniques.

The MCLs were based on an assumed consumption of two liters of water per day. Total environmental exposure was also considered in order to take into account the fact that drinking water may be a minor source of a contaminant in an average person's intake.

In the absence of formal drinking water standards, ODW has developed Health Advisories (HAs) on various pollutants. The advisories are called Suggested-No-Adverse-Response-Levels (SNARLs). EPA-SNARLs are not legally enforceable standards, although they may lead ultimately to the issuance of MCLs. Normally, EPA-SNARLs are issued for 1-day, 10-day, and longer-term exposure (where data exists) but do not consider possible carcinogenic risks. EPA-SNARLs are provided on a case-by-case basis in emergency situations such as spills and accidents.

One-day SNARLs are calculated for a 10 kg body weight child who consumes one liter of water per day. Minimal-effect-doses or no-adverse-effect-levels obtained from animal studies are used in conjunction with an appropriate safety factor (10 to 1000). Ten-day SNARLs are usually calculated by dividing one day SNARLs by 10. Longer-term SNARLs require information on effects produced from long-term exposure.

Resource Conservation and Recovery Act (RCRA)

EP Toxicity--A solid waste is classified as hazardous under RCRA if the waste exhibits the characteristics of the extraction procedure (EP) toxicity using specified test methods. The EP tests for the presence of any of 14 specified toxic materials at levels equal to or greater than the maximum level specified (40 CFR 261.24). The EP was designed in an attempt to identify wastes likely to leach hazardous concentrations of toxic chemicals into groundwater. The maximum levels specified were set at 100 times the MCL issued under the SDWA. (See 45 FR 33066 for a discussion of the rationale for using a 100-fold attenuation factor.)

Exclusion Limits for Acutely Hazardous Wastes--Chemicals designated as acutely hazardous under RCRA are subject to regulations in very small quantities. Provisions apply only to pure chemicals and associated containers, liners, and contaminated soils or spill residues (40 CFR 261.33(e)). EPA has set a general exclusion limit for generators of less than a total of 1000 kg/month hazardous waste; i.e.; the disposal of up to 1000 kg/month is not subject to RCRA Subtitle C requirements. However, for acutely hazardous wastes, the exclusion is set at 1 kg (2.2 lbs.) for the chemical (with other amounts specified for associated containers, etc.).

Acutely hazardous wastes are considered so hazardous that, unlike most wastes, they present a substantial hazard whether or not they are properly managed. Specifically, such a waste has been found to be fatal to humans in low doses, or, in the absence of human toxicity data, the chemical has been found to have a high acute toxicity in mammals (i.e., an oral LD50 of less than 50 mg/kg or inhalation LC50 of less than 2 mg/liter in rats, or a dermal LD50 of less than 200 mg/kg in rabbits).

Also included are chemicals which are otherwise capable of causing or contributing to serious or incapacitating adverse health effects, e.g., explosives (see 45 FR 331060).

Occupational Safety and Health Standards (OSHA)

OSHA Standards--In accordance with Section 6 of the Occupational Safety and Health Act (OSH Act), OSHA has promulgated exposure standards for designated air contaminants in the workplace (29 CFR 1910.1000 to 1910.1045). OSHA relied on two primary criteria to designate chemical substances for regulation: health effects and technical/economic feasibility. When carcinogenicity of a chemical served as a criterion for standards, OSHA generally established standards at the lowest feasible level. Technical feasibility may include engineering technology, work practices, or personal protective gear.

OSHA standards are designed to assure, to the extent feasible, that no employee suffers material impairment of health or functional capacity. Standards protect workers for up to 10-hour workdays, 40-hour workweeks over a working lifetime. OSHA standards are usually issued as 8-hour time weighted averages (TWA); in some cases, ceiling or maximum levels are listed in addition to (or in place of) 8-hour TWAs. Levels set by 8-hour TWAs may be exceeded, but cumulative exposures for 8-hours must not exceed the TWA. Maximum ceiling values cannot be exceeded at any time.

NIOSH Recommended Standards--The National Institute for Occupational Safety and Health (NIOSH) provides recommended standards to OSHA which are based on health effects. OSHA must then weigh these recommendations along with other considerations such as feasibility and means of implementation in developing regulatory standards. Therefore, NIOSH recommended standards have no regulatory force. Although the prevention of adverse health effects is the primary basis for recommended standards, the levels must also be measurable by available analytical techniques and sufficient technology must exist to permit compliance.

Neither OSHA Standards, nor NIOSH Recommended Standards are designed for the population-at-large and any extrapolations beyond the occupational environment may not be warranted.

American Conference of Governmental Industrial Hygienists (ACGIH)--ACGIH has issued and continues to update Threshold Limit Values (TLVs) for airborne contaminants which represent levels posing no health hazard to workers. TLVs refer to time-weighted levels for a 8-hour workday and 40-hour workweek. They are guides for use in the control of health hazards and should not be used as fine lines between safe and dangerous concentrations. TLVs do not necessarily relate to systemic toxicity, but may also be set on the basis of eye or skin irritation, narcosis, nuisance, or other forms of stress. In cases where there is a lack of data, TLVs may be set on the basis of consensus best professional judgement. Thus, it would be dangerous to utilize TLVs as a basis for comparison of the systemic toxicity of chemicals. ACGIH TLVs are merely recommendations and carry no regulatory authority.

Food, Drug, and Cosmetic Act (FDCA)

Pesticide Tolerance Levels--The powers originally granted to FDA to establish tolerances for pesticides were transferred to EPA in 1970 (35 FR 15623). In general, no raw agricultural commodity which bears or contains a pesticide chemical may be marketed in interstate commerce unless EPA has set a tolerance (i.e., maximum permissible level). The pesticide must be registered under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) before a tolerance may be set.

Approved pesticides are listed along with maximum levels permitted on specific crops in 40 CFR 180.101 through 180.379. The FDCA specifically requires that EPA consider the usefulness and necessity of the chemical. The level of tolerance is based on a broad cost/benefit analysis which examines the economic, environmental, and health effects resulting from use of the pesticide chemical (21 U.S.C. Section 346).

Food Additives and Color Additives--Except for food additives "generally recognized as safe" (GRAS), FDA must certify an additive and safe conditions/concentrations for use must be issued. Generally, the maximum permissible level of an additive must be 1 percent or less of the concentration found to produce no effect in experimental animals. Additives usually cannot be approved, nor safe tolerances set, if they are carcinogenic (the Delaney clause). However, carcinogenic color additives may still be used in external drugs and cosmetics if its use in those products does not induce cancer. Regulations covering food additives are published in 21 CFR 172 to 178; regulations covering color additives are listed in 21 CFR 73 and 74.

Other Tolerance/Action Levels--In contrast to the food and color additive regulations, FDA must first prove a cosmetic contains a "poisonous or deleterious substance" which is hazardous under conditions of normal use before it can be regulated. Under the FDCA, FDA may also regulate "poisonous and deleterious substances" in foods (and food packaging) if the substance "may render it injurious to health." FDA may issue tolerances permitting the presence of such substances if the substance cannot be avoided by good manufacturing practice and the tolerance is sufficient for protecting public health, taking into account the extent to which the presence of the substance cannot be avoided (21 CFR 109.6).

If possible technological changes may change the appropriateness of a tolerance level, then FDA may issue an informal action level. Action levels do not carry the same legal force as formal regulatory tolerances. Thus, food is considered "adulterated" and may be barred from interstate commerce merely if FDA demonstrates that a tolerance has been exceeded. When proceeding against a food with residues that are higher than an action level, however, the FDA must defend the action level itself in court.

Bottled Drinking Water Standards--the SDWA contains a provision which amends the FDCA by adding Section 410 to cover bottled drinking water. Based on the MCLs issued under the SDWA, FDA has set identical limits in bottled drinking waters (21 CFR 103.35).

Consumer Product Safety Act (CPSA)

Under CPSA, the CPSC regulates consumer products which present an unreasonable risk of injury (16 CFR 1201 to 1404). The product may be banned, or special labeling may be required. The standards are based on health effects data (human and animal exposure studies), the degree and nature of risk involved, the significance of exposure, and economic considerations. Thus, the CPSC must consider the degree of risk, the number of products involved, the public need for the product, and economic effects of the rule.

The CPSC may also regulate hazardous products under the older Federal Hazardous Substances Act (FHSA) which had been administered by FDA. For various reasons the CPSC tends to regulate hazardous substances under the CPSA. For example, the CPSC decided to regulate asbestos in consumer patching compounds under the CPSA because the procedure is shorter, more public participation is allowed, and the CPSA provides additional incentives to comply in the form of civil penalties (42 FR 63354). CPSC also adopted this strategy for lead in paint (41 FR 33637) and chlorofluorocarbon propellants (42 FR 21807).