UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT

EPA-330/2-80-031

PINE RIVER CONTAMINATION SURVEY

St. Louis, Michigan
(June 2-6, 1980)

October 1980

NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
Denver, Colorado

EPA

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Russell W. Forba

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EXECUTIVE SUMMARY

INTRODUCTION

A survey conducted in 1974* by the Michigan Department of Natural Resources (DNR) indicated severe contamination of the Pine River sediments in the St. Louis, Michigan Reservoir** and below the Velsicol Chemical Corporation (VCC) plant site. Several organic compounds were identified in the study including: DDT and associated analogs (total expressed as DDT: 293 mg/kg), phthalates (19.5 mg/kg), polybrominated biphenyls (PBB : 9.0 mg/kg), and oils (19,000 mg/kg). Flesh analyses of Pine River fish showed high levels of PBB (0.87 mg/kg), polychlorinated biphenyls (PCB 1254: 1.99 mg/kg), and total DDT (1.65 mg/kg). A Michigan Department of Public Health warning against consumption of Pine River fish from St. Louis 60 km downstream to the confluence with the Chippewa River was issued in November 1974, because of PBB contamination. This warning was renewed in 1976 and still remains in effect.

In a publication* dated June 15, 1979, concerning the contaminated Pine River the Michigan DNR recommended the following: (1) The St. Louis dam should be maintained in sound condition and precautions taken in any extensive drawdown to reduce the possibility of flushing polluted sediment downstream in the Pine River. (2) Dredging in the St. Louis impoundment and the Pine River directly below the impoundment should not be permitted without approved disposal of contaminated dredge spoils and without taking precautions to prevent contaminant flushing downstream.

In a meeting on February 27, 1980, between USEPA and Michigan DNR personnel concerning the Velsicol Chemical Corporation, St. Louis plant site, the National Enforcement Investigations Center (NEIC) was requested

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* "Biological Survey of the Pine River 1974 and 1978 Water Quality Division" - Michigan Department of Natural Resources, June 15, 1979. Publication No. 4833-5159.

** Reservoir is adjacent to VCC plant site.

by EPA Region V, Enforcement Division to conduct a limited sampling survey of the Pine River. Objectives of this survey were to:

- Document the contamination contributed to the Pine River by the Velsicol Chemical Corporation;
- Determine additional information needed to assess remedial action for the contaminated Pine River.

SUMMARY

Thirteen sediment samples and 14 water samples were collected June 2 to 6, 1980 from the Pine River between the Cheeseman Road bridge and the St. Louis Municipal wastewater treatment plant outfall to document contamination of the Pine River.

Polybrominated byphenyl (PBB), hexabromobenzene (HBB), DDT and analogs, and tris(2,3-dibromopropyl)phosphate (Tris) analyses, as well as, a limited organic scan were conducted on collected samples. An elutriate test [Appendix A] was conducted on two sediment samples (RSS-12 and RSS-13) for DDT and analogs, PBB, and HBB [Appendix B].

The literature was searched to determine toxicity data and adverse health effects of the substances identified in the samples.

Based on the pollutants found in the Pine River and sediments, additional information necessary to assess feasible remedial action is identified.

CONCLUSIONS

Sediment in the Pine River Reservoir at St. Louis, Michigan is contaminated by DDT and analogs (44,000 μg/g max), PBB (270 μg/g max), HBB (540 μg/g max), chlorobenzene (2,000 μg/g max), and oils. The DDT, PBB, and HBB can be attributed directly to former Velsicol Chemical Corporation plant site operations.

The Pine River water does not contain measureable concentrations of HBB, PBB, and DDT. Elutriate testing under laboratory conditions showed that these materials do not readily desorb from the sediments to the water. However, Michigan DNR data shows that Pine River fish have accumulated DDT and PBB above tolerance levels for human consumption.

Information needed before any remedial action can be taken includes the following:

- The vertical and areal distribution and magnitude of contaminated sediments in the St. Louis Reservoir.
- The extent and magnitude of DDT, PBB, and HBB contamination in the Pine River sediments below the St. Louis Reservoir.
- The current levels of contaminants in the Pine River biota.
- Alternative remedial methods to contain or remove the contaminants.
- The environmented impact of the remedial methods (including no action).
- Approved disposal areas for contaminated dredge spoils, if dredging is a viable alternative.

RECOMMENDATION

The Velsicol Chemical Corporation should determine the extent and magnitude of contamination in the Pine River and Pine River Reservoir, and propose alternative methods to EPA/DNR for protecting the Pine River environment.

TECHNICAL ANALYSIS

BACKGROUND

The Pine River is located in central Michigan and flows eastward 160 km to the Saginaw Valley to join the Chippewa River at Midland. The Chippewa River eventually discharges to Saginaw Bay (Lake Huron) at Bay City, Michigan. The average flow of the river at Alma, Michigan (9 km upstream of the St. Louis municipal dam) is 213 ft^3/sec. A maximum flow rate of 4,400 ft^3/sec, a 30-day low flow of 34 ft^3/sec, and a 30-day high flow of 1,580 ft^3/sec have been recorded.

The watershed is mainly agricultural except for the population centers of Alma and St. Louis located about 100 km from the Pine River headwaters. The river is impounded at Alma and St. Louis. Major rehabilitation of the St. Louis concrete gravity power dam, constructed in 1901, was started in December 1977 and completed in May 1979. The dam is now used not only to generate electricity but for flood control. The operator has a practical reservoir level control of 6 ft ranging from a MSL elevation of 714 ft to 720 ft with an average operating elevation of 718 ft. The reservoir level (MSL elevation) during the NEIC survey was approximately 718 ft.

Present or former wastewater dischargers to the Pine River include the Velsicol Chemical Corporation, Total Petroleum, the Lobdell-Emery Manufacturing Company, Alma Products Company, and the City of St. Louis and the City of Alma wastewater treatment plants.

Of particular interest in this study is the Velsicol Chemical Corporation, formerly the Michigan Chemical Company, which began as a bromine and salt extraction facility obtaining brine from local wells. Over the years the company has produced DDT (1945-1959), calcium chloride, magnesium compounds, rare earth compounds, and more recently flame retardants and industrial bromides including PBB (1970-1974), HBB (1971-1976), and Tris. In September 1978, VCC ceased production at the site and subequently has been

systematically removing materials and equipment from the property. Any DDT, HBB, PBB, and Tris found in Pine River sediments can be attributed to the VCC plant site operations since this site is the only location in the Pine River watershed where these compounds were produced.

STUDY METHODS

During the June 2 to 6, 1980 survey, NEIC personnel collected water and sediment samples from the Pine River at St. Louis, Michigan [Figure 1]. Water samples were collected in 1-gallon glass containers using a battery operated vacuum pump with teflon tubing [Table 1 describes sampling stations]. All water samples were iced and shipped by common air carrier to the NEIC laboratory in Denver, Colorado. Sediment cores [Table 2] were collected in 2 ft long, 1-½ in. I.D., acetone rinsed, stainless steel core tubes. The cores were secured with teflon-lined caps after sediment collection. The sediment samples were iced and transported to the Denver laboratory by NEIC personnel where the cores were extruded from the tubes and logged [Table 3]. NEIC Chain-of-Custody procedures were followed throughout the investigation.

DDT, PBB, and HBB analyses in addition to a limited organic scan were conducted on all water samples and 10 sediment samples (RSS-1 to RSS-10). The 10 sediment samples were also analyzed for Tris. Analytical procedures and associated quality control information are described in Appendix B. An elutriation test to determine the relative flux rates of PBB, HBB, and DDT from sediment to water was conducted [Appendix A] on samples collected at two stations (RSS-12 and RSS-13).

The published literature was searched to determine the toxicity and health effects of the identified compounds. The Registry of Toxic Effects of Chemical Substances (RTECS) and the Toxiology Information Online (TOXLINE) were the primary sources of information [Appendix C].

In view of the analytical and toxicology findings, additional studies were proposed to assess alternative remedial actions to contain or remove contaminated sediments from the Pine River.

PAGE NOT

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Table 1

RIVER WATER SAMPLING STATIONS (RWS) LOCATIONS
PINE RIVER
St. Louis, Michigan
June 2 to 6, 1980

Sampling[a] Station	Date of Sampling	Time of Sampling	Location Description
RWS-1			Midstream, 12 m north of Cheeseman Road bridge.
01	6/3/80	1040	
02	6/5/80	1040	
RWS-2			5 m east of Devon Road in small stream entering the Pine River immediately south of the Route 46 bridge.
01	6/3/80	1110	
02	6/5/80	1417	
RWS-3			Midstream, 12 m north of Route 46 bridge.
01	6/3/80	1120	
02	6/5/80	1124	
RWS-4			6 m from the end of the VCC plant site jetty and 70 m from the north shoreline on a transect running northwestward from the end of the jetty.
01	6/3/80	1142	
02	6/5/80	1205	
RWS-5			30 m from the end of the VCC plant site jetty and 46 m from the north shoreline on transect running northwestward from the end of the jetty.
01	6/3/80	1130	
02	6/5/80	1210	
RWS-6			52 m from end of the VCC plant site jetty and 24 m from the north shoreline on transect running northwestward from the end of the jetty.
01	6/3/80	1115	
02	6/5/80	1220	
RWS-7			30 m below the City of St. Louis municipal dam spillway, 3 m from east shore of Pine River.
01	6/3/80	1400	
02	6/5/80	1440	

a All River Water Samples (RWS) were collected at a 2-ft depth except RWS-2, collected in a small stream at a 2-in depth and RWS-7 collected in the river rapids below the St. Louis power dam at a 6-in depth.

Table 2

RIVER SEDIMENT SAMPLING (RSS) LOCATIONS
PINE RIVER
St. Louis, Michigan
June 2 to 6, 1980

Sampling Station	Date of Sampling	Time of Sampling	Location Description
RSS-1	6/2/80	1400	Mid-river on westward extention of Hazel Avenue, southeast of City of St. Louis water tower.
RSS-2	6/2/80	1428	34 m east of the mouth of the stream entering near the intersection of Route 46 and Devon Drive south of the Route 46 bridge.
RSS-3	6/2/80	1518	200 m north of the Route 46 bridge, 36 m west of the VCC plant site shoreline.
RSS-4	6/2/80	1540	37 m west of the south water intake pump.
RSS-5	6/2/80	1555	25 m northwest of the point of land protruding into the Pine River next to the disposal pit in the rotary kilns area of the VCC plant site.
RSS-6	6/2/80	1615	31 m from the south shore and 107 m from the north shore on a transect running north-south across the Pine River at the VCC plant site east boundary.
RSS-7	6/2/80	1715	49 m from the south shore and 89 m from north shore on a transect running north-south across the Pine River at the VCC plant site east boundary.
RSS-8	6/2/80	1655	92 m from the south shore and 46 m from the north shore on a transect running north-south across the Pine River at the VCC plant site east boundary.
RSS-9	6/2/80	1648	112 m from the south shore and 26 m from the north shore on a transect running north-south across the Pine River at the VCC plant site east boundary.
RSS-10	6/3/80	1420	Downstream of the St. Louis municipal dam, 5 m from shore directly opposite the City of St. Louis municipal wastewater treatment plant outfall.
RSS-11	6/5/80	1100	Same as RSS-1.
RSS-12	6/5/80	1145	Same as RSS-5.
RSS-13	6/5/80	1150	Same as RSS-7.

Table 3

SEDIMENT CORE DESCRIPTIONS
PINE RIVER
St. Louis, Michigan
June 2 to 6, 1980

Station	Water Depth	Total Core Length	Core Segments	Core Description
RSS-1	3 ft	7 in.	0-2.5 in.	Gray-brown sludge-like material iwth fine sand.
			2.5-5 in.	Hard black layer of plant detritus.
			5-7 in.	Well sorted gray sand.
RSS-2	1 ft	12 in.	0-6 in.	Gray-brown sandy silt.
			6-8 in.	Black sludge layer.
			8-12 in.	Gray-brown sandy silt.
RSS-3	7 ft	7 in.	0-7 in.	Well sorted gray-brown medium-grained sand.
RSS-4	6 ft	10 in.	0-3 in	Dark gray silty sand.
			3-9 in.	Black sludge layer.
			9-10 in.	Plant detritus and silty sand.
RSS-5	4 ft	11 in.	0-4 in	Gray-brown fine-grained silt.
			4-4.5 in	Banded gray-brown and white layers.
			4.5-5 in.	Black layer fine clay-sized particles.
			5-6 in.	White layer-fine material.
			6-6.5 in.	Gray-black hard deposit.
			6.5-9 in.	White-gray sludge
			9-11 in.	Brown to black plant detritus.
RSS-6	4 ft	23 in.	1-3 in.	Black to gray-black sludge.
			3-5 in. A[a]	Green-brown sludge.
			5-7.5 in.	Black sludge
			7.5-8 in	White layer fine-grained material.
			8-13.5 in.	Gray silt with white bands.
			13.5-18 in. B[a]	Gray silt.
			18-23 in.	Gray-brown mixed silt and organic detritus.
RSS-7	4 ft	10 in.	0-1.5 in.	Dark brown fine silt.
			1.5-2 in.	Gray-white band.
			2 in.	Black (organic) sand.
			3-6 in.	Gray silt.
			6-8 in.	Black (organic) sand.
			8-10 in	Organic detritus and medium-grained sand grading upward into silt
RSS-8	5 ft	8 in.	1-5 in.	Brown medium-grained sand quite odoriferous (petroleum smell).
			5-8 in.	Dark gray-black fine-grained sand and silt.
RSS-9	6 ft	18 in.	1-9 in. A	Black chemical sludge material with whitish-gray bands.
			9-18 in. B	Gray sludge.
RSS-10	1 ft	4 in.[b]	-	Top 4 inches of sediment gray sand.
RSS-11	3 ft	8 in.	0-8 in.	Gray-black medium-grained well sorted sand.
RSS-12	4 ft	13-½ in.	0-4 in.	Dark gray-brown silty sand.
			4-6 in.	Banded zone, gray white-gray
			6-8.5 in	Black sludge and plant detritus.
			8.5-12 in.	Dark gray-brown silt.
			12-13.5 in.	Black plant detritus.
RSS-13	4 ft	16 in	0-8.5 in.	Black sludge grading downward into gray silty sand.
			8.5-10.5 in.	Gray-brown poorly sorted silty sand with plant detritus.
			10.5-13.5 in	Gray-black sludge with plant detritus.
			13.5-15 in.	Gray fine-grained sand.
			15-16 in.	Red-brown plant detritus.

a A denotes top portion and B the bottom portion of cores which were divided into sections for chemical analysis (RSS-6 and RSS-9).

b Core sample was not collected at RSS-10 because of thin sediment layer in this part of the River. A sample was scooped out of the top 4 inches of the river bed using an acetone rinsed steel shovel.

ANALYTICAL RESULTS

Fourteen river water samples (RWS) and 13 sediment samples (RSS) were collected by NEIC personnel during the June 2 to 5, 1979, Pine River survey. All water samples and 10 sediment samples (RSS-1 to RSS-10) were analyzed for PBB, HBB, DDT, its analogs, and subjected to a limited organic scan. Sediment samples RSS-1 to RSS-10 were also analyzed for Tris. For analysis, sediment samples RSS-6 and RSS-9 were each divided in two sections. Three sediment cores were collected for elutriation testing of PBB, HBB, and DDT [Appendix A], although only two of the cores (RSS-12 and 13) were used in the test (concentration of contaminants in the upstream sample (RSS-11) were too low for testing).

HBB, PBB, or DDT analogs were not detected in any of the river water samples. However, the RWS-6-01 and RWS-6-02 contained 3.5 μg/l and 2.7 μg/l methoxychlor, respectively. The origin of this compound in the water samples is not known.

All of the cores were contaminated to some degree by DDT and its analogs with four samples containing over 2,000 μg/g (RSS-6A*, 6B*, 7, 9A). A maximum DDT concentration of 44,000 μg/g (4.4%) was found in RSS-6B. PBB levels of over 70 μg/g were found in three samples (RSS-6A, 7, and 8) with a maximum of 270 μg/g found in RSS-6A. HBB was found in concentration exceeding 20 μg/g in four samples (6A, 7, 8, and 9A) with a maximum of 540 μg/g found in RSS-6A. Tris was identified at quantifiable level (240 μg/g) in only one sediment sample (RSS-6A). Chlorobenzene was identified in several samples (RSS-6A, 6B, 7, 8, and 9A) with a maximum concentration of 2,000 μg/g found in RSS-6B. Several other organic contaminants were identified including dichlorobenzene isomers, trichlorobenzene, 4,4-dichlorobenzophenone, and several hydrocarbons associated with petroleum compounds. As can be seen, the most highly contaminated sediment samples were

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* 'A' designates top of sediment core sample; 'B' designates bottom.

found in cores collected in the lower end of the St. Louis Reservoir adjacent to the VCC plant site. Sediment cores collected upstream of the Route 46 bridge were relatively uncontaminated by DDT, HBB, and PBB.

Only one sediment sample was collected below the St. Louis Reservoir dam and, although PBB, HBB, and DDT were identified in this sample, they were at much lower concentrations than in the reservoir sediment. Sediment sample analysis results are shown on Table 4.

Elutriation testing under laboratory condition showed very little desorption of DDT, PBB, or HBB from the reservoir sediments. A small amount of p,p-DDT was detected in the water from the static phase of the testing. However, the amounts desorbed was less than 0.01% of the amount present in the sediment.

Table 4

RIVER SEDIMENT SAMPLES (RSS)
ORGANICS CONTENT (μg/g)
PINE RIVER, ST. LOUIS, MICHIGAN
June 2 to 6, 1980

Station Number	RSS-1	RSS-2	RSS-3	RSS-4	RRS-5	RSS-6A	RSS-6B	RSS-7	RSS-8	RSS-9A	RSS-9B	RSS-10	Detection Limits[a]
Chemical[b]													
Total DDT	0 06	0.09	0 045	0.37	2.62	4,700	44,000	2,210	13.3	3,400	0.01	0.80	
p,p'-DDT	ND[c]	0.01	0 02	ND	0.40	2,000	24,000	1,200	5.5	1,900	ND	0.41	0.008
o,p'_DDT	ND	ND	0.01	ND	0.20	650	17,000	760	0.59	1,300	ND	0 07	0.008
p,p'-DDE	0.02	0.03	0.005	0.09	0.62	260	1,300	11	1.4	80	0.01	0 06	0 004
p,p'-DDD	0.04	0.05	0.01	0.28	1.4	1,800	1,400	340	5.8	110	ND	0.26	0.004
PBB	ND	ND	ND	0.38	0.29	270	ND	7 8	1.4	ND	ND	0.03	0.02
HBB	ND	0.01	ND	0.08	0.13	540	ND	190	31	20	ND	0.30	0.01
Tris	ND	ND	ND	ND	ND	240	ND	ND	ND	ND	ND	ND	1
Chlorobenzene	ND	ND	ND	ND	ND	40	2,000	4	2	200	ND	ND	0 1
1,2,4-trichlorobenzene	ND	ND	ND	ND	ND	ND	60	ND	ND	ND	ND	ND	0.1
p-dichlorobenzene	ND	ND	ND	ND	ND	ND	100	ND	ND	ND	ND	ND	0.1
o-dichlorobenzene	ND	ND	ND	ND	ND	ND	30	ND	ND	ND	ND	ND	0.1
4,4-dichlorobenzophenone	ND	ND	ND	ND	ND	7	ND	ND	ND	ND	ND	ND	0.2
Confirmed Total Hydrocarbons[d]	ND	ND	ND	7	ND	8	ND	ND	20	10	ND	ND[b]	

a The detection limits are as given except for RSS-6B where PBB = 48 μg/g, HBB = 240 μg/g, and Tris = 15 μg/g; and for RSS-9A where PBB = 5μg/g.
b Chlorostyrene isomers were identified by their excellent match with library spectra in RSS-6A, RSS-6B, RSS-7, and RSS-9A. However, these compounds could not be confirmed or quantified because standards were not available.
c Not detected
d Additional hydrocarbon compounds associated with the presence of petroleum compounds were found in RSS-1, RSS-2, RSS-5, RSS-6A, RSS-8, RSS-9A, and RSS-9B. No attempt was made to confirm or quantify most of these compounds due to lack of standard or chromatographically unresolved peaks resulting in poor spectra.

TOXICITY AND HEALTH EFFECTS

Thirteen halogenated compounds and numerous hydrocarbon compounds were identified in sediment samples from the Pine River at St. Louis, Michigan. Of the 13 compounds, 7 are listed as priority pollutants and 4 are listed as hazardous substances under Section 311 of the Federal Water Pollution Control Act [Table 5].

DDT and PBB, found in high concentrations, in the sediments have exhibited numerous human and animal health effects. PBB ingestion by farm animals in Michigan caused interference with reproduction and liver function, promotion of nervous disorders, teratogenic effects, and mortality of some livestock. DDT is classified as a human carcinogen by the USEPA Cancer Assessment Group (CAG) and has exhibited central nervous system, neoplastic, and mutagenic effects on laboratory animals. DDT is extremely toxic to aquatic invertebrates in concentrations as low as 0.12 μg/l*. DDT also bioaccumulates readily. Studies by the National Water Quality Laboratory in Duluth, Minnesota exhibited bioaccumulation of DDT in fish of 100,000 times. Because of this bioaccumulation effect up the food chain, DDT can quickly accumulate in concentrations rendering fish unfit for human consumption.

Tolerance limits for human consumption of PBB or DDT in fish have not been established. However, tolerance limits in beef for PBB (0.3 mg/kg fat weight basis) and DDT (5.0 mg/kg fat weight basis) have been established. Maximum concentrations of PBB and DDT found in Pine River fish collected during a 1974 Michigan DNR survey were 0.87 mg/kg and 1.67 mg/kg, respectively (wet weight basis). These concentrations would equate to 19.6 mg/kg

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* Eisler, R. Acute Toxicity of Organochlorine and Organophosphorus Insecticides to Estuarine Fishes. Bureau of Sport Fisheries and Wildlife, U.S. Department of Interior, Technical Report No. 16, 1970.

Table 5

PRIORITY POLLUTANTS
PINE RIVER SEDIMENTS
ST. LOUIS, MICHIGAN
June 2 to 6, 1980

Chlorobenzene[a]
o-dichlorobenzene[a]
p-dichlorobenzene[a]
1,2,4-trichlorobenzene
1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD)
1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE)
1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane(p,p'DDT)[a]

a Hazardous substances as defined by Section 311 of Federal Water Pollution Control Act.

PBB and 37.2 mg/kg DDT fat weight basis employing the wet weight to fat ratios used by Hesse and Powers.* Both PBB and DDT fat weight concentrations in the Pine River fish collected by Michigan DNR are several times greater than the tolerance limits for human consumption of beef.

Presently a warning against human consumption of Pine River fish from St. Louis to the Chippewa River is in effect. This ban is unlikely to be lifted in the near future because of the extremely high levels of PBB and DDT in the Pine River fish.

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* Hesse, J. L. and Power, R. H., Polybrominated Biphenyl (PBB) Contamination of the Pine River, Gratiot, and Midland Counties, Michigan. Environmental Health Perspectives, vol. 23, pp. 19-25.

EVALUATION OF FINDINGS

Analyses of sediment samples collected by NEIC personnel showed high levels of DDT, PBB, and HBB in the St. Louis Reservoir from the Route 46 bridge to the municipal dam. Elutriation testing under laboratory conditions showed these major contaminants of concern are bound tightly with the sediment and do not desorb and solubilize readily. Water sample analyses showed levels of these contaminants to be below the detectable limit, supporting the elutriation testing data. However, fish tissue analyses performed by Michigan DNR show high levels (over the tolerance limits for human consumption) of PBB and DDT evoking a ban against consumption of Pine River fish.

If the contaminated sediments are left in the Pine River, levels of PBB and DDT in fish may remain above tolerance limits for human consumption for an unknown period of time. However, removal of sediment may re-entrain sediment particles with the adsorbed contaminants and have an acutely toxic impact on aquatic invertebrates downstream of St. Louis and may spread the contaminants further down the watershed.

Because of the chronic bioaccumulation problem of DDT and PBB in the Pine River fish, alternatives for removing or containing the contaminated Pine River sediments should be studied. However, the environmental impact of any sediment containment or removal method must be considered in developing any feasible remedial action.

APPENDICES

A ELUTRIATION STUDY, PINE RIVER SEDIMENTS

B SUMMARY OF ANALYTICAL METHODOLOGY

C TOXIC DATA COMPILATION METHODS

APPENDIX A

ELUTRIATION STUDY
PINE RIVER SEDIMENTS

PINE RIVER SEDIMENTS
ST. LOUIS, MICHIGAN

Purpose: To determine the extent to which organic compounds leach from sediment into aqueous media under both static and dynamic conditions. The static conditions will simulate conditions in a reservoir and dynamic conditions will simulate leaching from a river.

Test Format: The tests will closely follow the Elutriate Test Procedure of the Corps of Engineers (attached).

a) Background Testing. Three 25 g aliquots of sediment will be analyzed in triplicate to determine the baseline concentration of organic compounds. A solvent blank will also be analyzed with this set.

b) Dynamic Testing. A 25 gm aliquot of sample will be weighed into a 500 ml Erlenmeyer flask and 100 ml of distilled water added. The temperature of the water will be recorded before it is added. The sediment plus water will be vigorously shaken on a wrist action shaker for 30 minutes. After shaking, the suspension will be allowed to settle for 1 hour. After settling, the supernatant will be decanted into a centrifuge bottle and centrifuged to reduce the suspended solids concentration. After centrifugation, the supernatant will be filtered through a 0.45μ membrane filter to yield the final solution for analysis. This solution will be extracted and analyzed according to the NEIC Procedure for Organohclorine Pesticides in Water. This test will be done in triplicate. In addition, a blank, consisting of 100 ml of distilled water, will be analyzed. The concentration of organic compounds which have eluted into the aqueous phase will be reported.

c) Static Testing. The static testing will differ from the dynamic testing in only one aspect. Instead of continuous shaking, the sediment and water will be vigorously shaken initially for 1 minute and then held immobile for 24 hours. The supernatant will then be centrifuged and the procedure for dynamic testing followed. This test will also be done in triplicate and a blank will be analyzed.

Samples to be Tested. Three sediment samples were collected for the leaching study: RSS-11, RSS-12, and RSS-13. These correspond in location to three samples which have already been analyzed: RSS-1, RSS-5, and RSS-7 respectively. The attached table gives the analytical results for RSS-1, -5 and -7. The GC/MS data showed mainly alkanes (probably from petroleum products) in RSS-1 and RSS-5. RSS-7 contained alkanes, a small amount (c.a. 8 ng of chlorobenzene) and a significantly higher concentration of DDT-related compounds. The leaching study will be done only for DDT-related compounds, since those are the most significant components of the sample. Since the sentivity and precision of GC/MS is less than EC/GC techniques, only EC/GC will be used. RSS-11, which shows virtually no contamination will not be subjected to the leaching study. The other two samples, RSS-12 and RSS-13, will be tested. Twenty five grams of RSS-12 will be used but due to the much higher concentration of organics in RSS-7, only five grams of this sample will be used. It is anticipated that these tests will take approximately 3 weeks to complete.

d) Analytical Methodology - See Methods for Organochlorine Pesticides in Water and Sediment [Appendix B].

Table I. Results of Triplicate Analysis of Sediment Samples

	RSS-11A ug/g	RSS-11B ug/g	RSS-11C ug/g	Avg.
p,p'-DDT	ND	ND	ND	ND
o,p'-DDT	ND	ND	ND	ND
p,p'-DDE	0.005	0.008	0.008	0.007
p,p'-DDD	0.007	ND	ND	ND
HBB	ND	0.03	ND	0.03
PBB	ND	ND	ND	ND

	RSS-12A ug/g	RSS-12B ug/g	RSS-12C ug/g	Avg.
p,p'-DDT	0.075	0.19	0.18	0.15
o,p'-DDT	0.023	0.023	0.022	0.023
p,p'-DDE	0.17	0.16	0.17	0.17
p,p'-DDD	0.31	0.32	0.27	0.30
HBB	0.18	0.17	0.16	0.17
PBB	0.60	0.64	0.51	0.58

	RSS-13A ug/g	RSS-13B ug/g	RSS-13C ug/g	Avg.
p,p'-DDT	$8.0X10^3$	$7.1X10^3$	$7.0X10^3$	$7.4X10^3$
o,p'-DDT	$4.9X10^3$	$4.4X10^3$	$5.9X10^3$	$5.1X10^3$
p,p'-DDE	380	320	410	370
p,p'-DDD	440	490	500	480
HBB	50	51	83	61
PBB	22	21	17	20

PINE RIVER SEDIMENTS
ST. LOUIS, MICHIGAN

Purpose: To determine the extent to which organic compounds leach from sediment into aqueous media under both static and dynamic conditions. The static conditions will simulate conditions in a reservoir and dynamic conditions will simulate leaching from a river.

Test Format: The tests will closely follow the Elutriate Test Procedure of the Corps of Engineers (attached).

a) Background Testing. Three 25 g aliquots of sediment will be analyzed in triplicate to determine the baseline concentration of organic compounds. A solvent blank will also be analyzed with this set.

b) Dynamic Testing. A 25 gm aliquot of sample will be weighed into a 500 ml Erlenmeyer flask and 100 ml of distilled water added. The temperature of the water will be recorded before it is added. The sediment plus water will be vigorously shaken on a wrist action shaker for 30 minutes. After shaking, the suspension will be allowed to settle for 1 hour. After settling, the supernatant will be decanted into a centrifuge bottle and centrifuged to reduce the suspended solids concentration. After centrifugation, the supernatant will be filtered through a 0.45μ membrane filter to yield the final solution for analysis. This solution will be extracted and analyzed according to the NEIC Procedure for Organohclorine Pesticides in Water. This test will be done in triplicate. In addition, a blank, consisting of 100 ml of distilled water, will be analyzed. The concentration of organic compounds which have eluted into the aqueous phase will be reported.

c) Static Testing. The static testing will differ from the dynamic testing in only one aspect. Instead of continuous shaking, the sediment and water will be vigorously shaken initially for 1 minute and then held immobile for 24 hours. The supernatant will then be centrifuged and the procedure for dynamic testing followed. This test will also be done in triplicate and a blank will be analyzed.

Samples to be Tested. Three sediment samples were collected for the leaching study: RSS-11, RSS-12, and RSS-13. These correspond in location to three samples which have already been analyzed: RSS-1, RSS-5, and RSS-7 respectively. The attached table gives the analytical results for RSS-1, -5 and -7. The GC/MS data showed mainly alkanes (probably from petroleum products) in RSS-1 and RSS-5. RSS-7 contained alkanes, a small amount (c.a. 8 ng of chlorobenzene) and a significantly higher concentration of DDT-related compounds. The leaching study will be done only for DDT-related compounds, since those are the most significant components of the sample. Since the sentivity and precision of GC/MS is less than EC/GC techniques, only EC/GC will be used. RSS-11, which shows virtually no contamination will not be subjected to the leaching study. The other two samples, RSS-12 and RSS-13, will be tested. Twenty five grams of RSS-12 will be used but due to the much higher concentration of organics in RSS-7, only five grams of this sample will be used. It is anticipated that these tests will take approximately 3 weeks to complete.

d) Analytical Methodology - See Methods for Organochlorine Pesticides in Water and Sediment [Appendix B].

Table I. Results of Triplicate Analysis of Sediment Samples

	RSS-11A ug/g	RSS-11B ug/g	RSS-11C ug/g	Avg.
p,p'-DDT	ND	ND	ND	ND
o,p'-DDT	ND	ND	ND	ND
p,p'-DDE	0.005	0.008	0.008	0.007
p,p'-DDD	0.007	ND	ND	ND
HBB	ND	0.03	ND	0.03
PBB	ND	ND	ND	ND

	RSS-12A ug/g	RSS-12B ug/g	RSS-12C ug/g	Avg.
p,p'-DDT	0.075	0.19	0.18	0.15
o,p'-DDT	0.023	0.023	0.022	0.023
p,p'-DDE	0.17	0.16	0.17	0.17
p,p'-DDD	0.31	0.32	0.27	0.30
HBB	0.18	0.17	0.16	0.17
PBB	0.60	0.64	0.51	0.58

	RSS-13A ug/g	RSS-13B ug/g	RSS-13C ug/g	Avg.
p,p'-DDT	8.0×10^3	7.1×10^3	7.0×10^3	7.4×10^3
o,p'-DDT	4.9×10^3	4.4×10^3	5.9×10^3	5.1×10^3
p,p'-DDE	380	320	410	370
p,p'-DDD	440	490	500	480
HBB	50	51	83	61
PBB	22	21	17	20

Table II. Results of Dynamic Leaching Test

	RSS-12A leachate ug	RSS-12B leachate ug	RSS-12C leachate ug
p,p'-DDT	ND	ND	ND
o,p'-DDT	ND	ND	ND
p,p'-DDE	ND	ND	ND
p,p'-DDD	ND	ND	ND
HBB	ND	ND	ND
PBB	ND	ND	ND

	RSS-13A leachate ug	RSS-13B leachate ug	RSS-13C leachate ug
p,p'-DDT	ND	ND	ND
o,p'-DDT	ND	ND	ND
p,p'-DDE	ND	ND	ND
p,p'-DDD	ND	ND	ND
HBB	ND	ND	ND
PBB	ND	ND	ND

Table III. Results of Static Leaching Test

	RSS-12A leachate ug	RSS-12B leachate ug	RSS-12C leachate ug
p,p'-DDT	ND	ND	ND
o,p'-DDT	ND	ND	ND
p,p'-DDE	ND	ND	ND
p,p'-DDD	ND	ND	ND
HBB	ND	ND	ND
PBB	ND	ND	ND

	RSS-13A leachate ug	RSS-13B leachate ug	RSS-13C leachate ug
p,p'-DDT	0.4	ND	1.5
o,p'-DDT	ND	ND	ND
p,p'-DDE	ND	ND	ND
p,p'-DDD	ND	ND	ND
HBB	ND	ND	ND
PBB	ND	ND	ND

Table IV. Detection Limits

	Sediment ug/g	Leachate ug
p,p'-DDT	0.008	0.2
o,p'-DDT	0.008	0.1
p,p'-DDE	0.004	0.1
p,p'-DDD	0.004	0.1
HBB	0.01	0.2
PBB	0.02	1.0

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MRD Lab

DREDGED MATERIAL RESEARCH PROGRAM

MISCELLANEOUS PAPER D-76-17

ECOLOGICAL EVALUATION OF PROPOSED DISCHARGE OF DREDGED OR FILL MATERIAL INTO NAVIGABLE WATERS

INTERIM GUIDANCE FOR IMPLEMENTATION OF SECTION 404(b)(1) OF PUBLIC LAW 92-500 (FEDERAL WATER POLLUTION CONTROL ACT AMENDMENTS OF 1972)

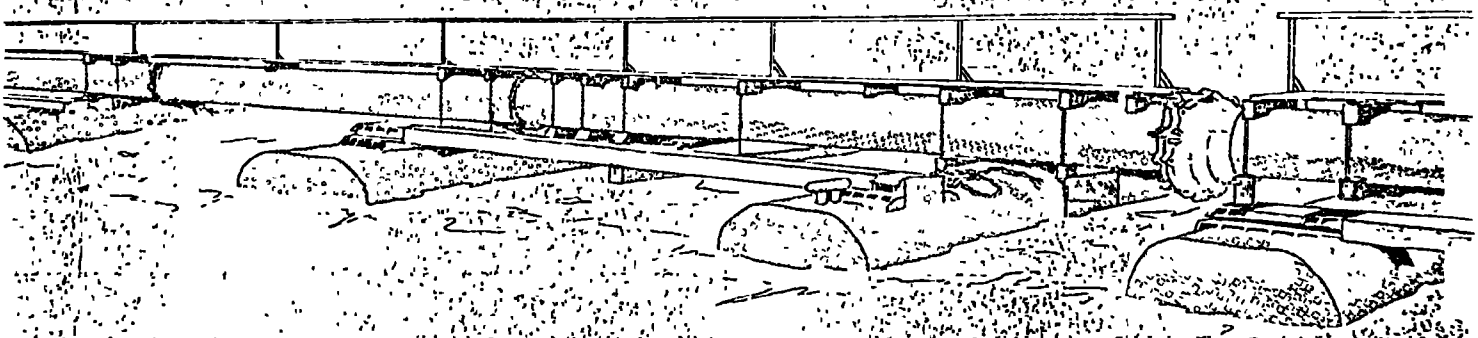
by

Environmental Effects Laboratory
U. S. Army Engineer Waterways Experiment Station
P. O. Box 631, Vicksburg, Miss. 39180

May 1976

Final Report

Approved For Public Release, Distribution Unlimited



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APPENDIX A: ELUTRIATE TEST PROCEDURE

Number of Samples

1. The number of sediment and water samples to be taken from the dredging site for replicate analyses must be carefully considered because of the extremely heterogeneous nature of samples of this type. Also, the necessary number of replicate analyses of composite disposal site water samples must be carefully considered because of the comparatively low background concentrations of some constituents in samples of this type.

Sample Collection and Preservation

Water

2. Collection should be made with appropriate noncontaminating water-sampling devices. Collect a 2-gal representative water sample at both the dredging site and the disposal site. If the samples are to be analyzed for trace organics or for a large number of constituents, a proportionately larger initial sample should be collected. The samples must be stored in plastic bottles or in glass storage containers if trace organic analyses are to be performed on the samples.

3. The samples should be stored immediately at 2 to 4°C. The samples should never be frozen. The storage period should be as short as possible to minimize changes in the characteristics of the water. It is recommended that samples be processed within one week of collection.

Sediment

4. Sediment samples from the dredging site should be taken with a grab sampler or corer in such a manner to ensure that their characteristics are representative of the proposed dredging site. Approximately 1 gal of sediment should be collected; if the samples are to be analyzed for trace organics or a large number of constituents, a proportionately larger initial sample should be collected. The samples should be placed in airtight plastic bags or jars or in glass storage containers if trace organic analyses are to be performed on the samples. Care should be taken to ensure that the containers are completely filled with sample and that air bubbles are not trapped in the container.

5. The samples should be stored immediately at 2 to 4°C. The samples must never be frozen. The storage period should be as short as possible to minimize changes in the characteristics of the sediment. It is recommended that samples be processed within one week of collection.

Apparatus

6. The following items are required. Prior to use, all glassware, filtration equipment, and filters should be washed with 5 to 10 percent (or stronger) hydrochloric acid (HCl) and then rinsed thoroughly with deionized water.

a. Acid-rinsed plastic bottles for collection of water samples.

b. Plastic jars or bags ("Whirl-Pak," plastic freezer containers, etc.) for collecting dredged or fill material samples.

c. Laboratory shaker capable of shaking 2-litre flasks at

approximately 100 excursions/min. Box type or wrist-action shakers are acceptable.

d. Several 1-litre graduated cylinders.

e. Large (15 cm) powder funnels.

f. Several 2-litre large-mouth graduated Erlenmeyer flasks.

g. Vacuum or pressure filtration equipment, including vacuum pump or compressed air source, and an appropriate filter holder capable of accomodating 47, 105, or 155-mm-diameter filters.

h. Membrane filters with a 0.45μ pore-size diameter should be used. The filters should be soaked in 5M HCl for at least 2 hr prior to use.

i. Centrifuge capable of handling six 1- or 0.5-litre centrifuge bottles at 3,000 to 5,000 rpm. International Model K or Sorval Super Speed are acceptable models.

j. Wide-mouth, 1-gal capacity glass jars with Teflon-lined screw-top lids should be used for sample containers when samples are to be analyzed for trace organics. (It may be necessary to purchase jars and Teflon sheets separately; in which case, the Teflon lid liners may be prepared by the laboratory personnel.)

Test Procedure

7. The stepwise test procedure is given below.

a. Subsample a minimum volume of 1 litre each of dredging site and disposal site water. If it is known in advance that a large number of measurements are to be performed, the size of each subsample

should be increased to meet the anticipated needs.

b. Filter an appropriate portion of the disposal site water through an acid-soaked 0.45μ pore-size membrane filter that has been prerinsed with approximately 100 ml of disposal site water. The filtrate from the rinsing procedure should be discarded.

c. Analyze the filtered disposal site sample for the major constituents as soon as possible using acceptable procedures.[1,2,3] If necessary, the samples may be stored at 2 to 4°C after preservatives have been added. The filtered water samples may be frozen with no apparent destruction of sample integrity.

d. Repeat steps a, b, and c with dredging site water.

e. Subsample approximately 1 litre of sediment from the well-mixed original sample. Mix the sediments and unfiltered dredging site water in a volumetric sediment-to-water ratio of 1:4 at room temperature (22 ± 2°C). This is best done by the method of volumetric displacement.[4] One hundred ml of unfiltered dredging site water is placed into a graduated Erlenmeyer flask. The sediment subsample is then carefully added via a powder funnel to obtain a total volume of 300 ml. (A 200-ml volume of sediment will now be in the flask.) The flask is then filled to the 1000-ml mark with unfiltered dredging site water, which produces a slurry with a final ratio of one volume sediment to four volumes water. If the volume of water required for analysis exceeds 700 to 800 ml, the initial volumes should be proportionately increased (e.g., mix 400 ml of sediment and 1600 ml disposal site water). Alternately, several 1-litre dredged material/dredging site

water slurries may be prepared as outlined above and the filtrates combined to provide sufficient water for analysis.

f. (1) Cap the flask tightly with a noncontaminating stoppper and shake vigorously on an automatic shaker at about 100 excursions per min for 30 min. A polyfilm-covered rubber stopper is acceptable for minimum contamination.

(2) During the mixing step given in paragraph 5f(1), the oxygen demand of the dredged material may cause the dissolved oxygen concentration in the elutriate to be reduced to zero. This change can alter the release of chemical contaminants from dredged material to the disposal site water and reduce the reproducibility of the elutriate test.[5] If it is known that anoxic conditions (zero dissolved oxygen) will not occur at the disposal site or if reproducibility of the elutriate test is a potential problem, the mixing may be accomplished by using the compressed air mixing procedure instead of the mechanical mixing described in paragraph 5f(1). After preparation of the elutriate slurry, an air-diffuser tube is inserted almost to the bottom of the flask. Compressed air should be passed through a deionized water trap and then through the diffuser tube and the slurry. The flow rate should be adjusted to agitate the mixture vigorously for 30 min. In addition, the flasks should be stirred manually at 10-min intervals to ensure complete mixing.

g. After shaking or mixing with air, allow the suspension to settle for 1 hr.

h. After settling, carefully decant the supernatant into

appropriate centrifuge bottles and then centrifuge. The time and rpm's during centrifiguration should be selected to reduce the suspended solids concentration substantially and therefore shorten the final filtration process. After centrifugation, vacuum or pressure filter approximately 100 ml of sample through a 0.45 u membrane filter and discard the filtrate. Filter the remainder of the sample to give a clear final solution (the standard elutriate) and store at 4°C in a clean noncontaminating container in the dark.

i. Analyze as soon as possible for major constituents using accepted procedures.[1,2,3]

j. Prepare and test the elutriate in triplicate and report the average concentration of the three replicates as the concentration in the standard elutriate.

APPENDIX IV
PINE RIVER, St. Louis, Mich.
June 2-6, 1980

Table I. Results of Triplicate Analysis of Sediment Samples

	RSS-11A ug/g	RSS-11B ug/g	RSS-11C ug/g	Avg.
p,p'-DDT	ND	ND	ND	ND
o,p'-DDT	ND	ND	ND	ND
p,p'-DDE	0.005	0.008	0.008	0.007
p,p'-DDD	0.007	ND	ND	ND
HBB	ND	0.03	ND	0.03
PBB	ND	ND	ND	ND

	RSS-12A ug/g	RSS-12B ug/g	RSS-12C ug/g	Avg.
p,p'-DDT	0.075	0.19	0.18	0.15
o,p'-DDT	0.023	0.023	0.022	0.023
p,p'-DDE	0.17	0.16	0.17	0.17
p,p'-DDD	0.31	0.32	0.27	0.30
HBB	0.18	0.17	0.16	0.17
PBB	0.60	0.64	0.51	0.58

	RSS-13A ug/g	RSS-13B ug/g	RSS-13C ug/g	Avg.
p,p'-DDT	8.0×10^3	7.1×10^3	7.0×10^3	7.4×10^3
o,p'-DDT	4.9×10^3	4.4×10^3	5.9×10^3	5.1×10^3
p,p'-DDE	380	320	410	370
p,p'-DDD	440	490	500	480
HBB	50	51	83	61
PBB	22	21	17	20

APPENDIX A
PINE RIVER - St. Louis, Mich
June 2-6, 1980

Table II. Results of Dynamic Leaching Test

	RSS-12A leachate ug	RSS-12B leachate ug	RSS-12C leachate ug
p,p'-DDT	ND	ND	ND
o,p'-DDT	ND	ND	ND
p,p'-DDE	ND	ND	ND
p,p'-DDD	ND	ND	ND
HBB	ND	ND	ND
PBB	ND	ND	ND

	RSS-13A leachate ug	RSS-13B leachate ug	RSS-13C leachate ug
p,p'-DDT	ND	ND	ND
o,p'-DDT	ND	ND	ND
p,p'-DDE	ND	ND	ND
p,p'-DDD	ND	ND	ND
HBB	ND	ND	ND
PBB	ND	ND	ND

APPENDIX A
PINE RIVER - ST LOUIS, MICH.
June 2-6, 1980

Table III. Results of Static Leaching Test

	RSS-12A leachate ug	RSS-12B leachate ug	RSS-12C leachate ug
p,p'-DDT	ND	ND	ND
o,p'-DDT	ND	ND	ND
p,p'-DDE	ND	ND	ND
p,p'-DDD	ND	ND	ND
HBB	ND	ND	ND
PBB	ND	ND	ND

	RSS-13A leachate ug	RSS-13B leachate ug	RSS-13C leachate ug
p,p'-DDT	0.4	ND	1.5
o,p'-DDT	ND	ND	ND
p,p'-DDE	ND	ND	ND
p,p'-DDD	ND	ND	ND
HBB	ND	ND	ND
PBB	ND	ND	ND

APPENDIX A
PINE RIVER, ST. LOUIS, MICH
June 2-6, 1980

Table IV. Detection Limits

	Sediment ug/g	Leachate ug
p,p'-DDT	0.008	0.2
o,p'-DDT	0.008	0.1
p,p'-DDE	0.004	0.1
p,p'-DDD	0.004	0.1
HBB	0.01	0.2
PBB	0.02	1.0

APPENDIX B

SUMMARY OF ANALYTICAL METHODOLOGY

SUMMARY OF ANALYTICAL METHODOLOGY

I. DDT's, DDE, DDD, HBB, PBB

A. Water Samples

Samples were serially extracted with 15% CH_2Cl_2/hexane at a neutral pH. The extracts were dried and filtered by passing through Na_2SO_4 and concentrated to 10 ml in a Kuderna-Danish (K-D) apparatus. The extracts were screened and quantitated using electron capture gas chromatography. If necessary, the extracts were cleaned up before quantitation using a alumina adsorption column. The procedure is described in the NEIC "Method for Organochlorine Pesticides in Environmental Water Samples."

B. Sediment Samples

Sediment samples were sieved through a 2 mm mesh sieve. Sieved samples were serially extracted with acetone and hexane and the combined extracts dried over Na_2SO_4 and concentrated to 10 ml in a K-D. The extracts were screened and quantitated using electron capture gas chromatography. If necessary, the extracts were cleaned up before quantitation using an alumina column. The procedure is described in the NEIC "Method for Organochlorine Pesticides in Soil and Sediment."

II. TRIS

A. Sediments

Samples were serially extracted with acetone. The acetone extract was combined with a large volume of water and the TRIS extracted with CH_2Cl_2. The extracts were dried and filtered by passing through Na_2SO_4 and then exchanged into hexane and concentrated to 10 ml in a K-D. The extract was cleaned up using a Florisil adsorption column, exchanged into methanol and analyzed by HPLC. The procedure is described in the NEIC "Method for TRIS (2,3-dibromopropyl) phosphate in Soil and Sediments."

III. ORGANIC CHARACTERIZATION AND PRIORITY POLLUTANT PROCEDURES

A. Sample Preparation

1. Water Samples - Extractables:

Samples were extracted with CH_2Cl_2 at a neutral pH. The extracts were dried and concentrated with the addition of acetone to 1 ml. The resultant extract concentrates were subjected to GC and GC/MS analyses. This procedure is in the method "Neutral Extraction Technique for Organics Analysis, NEIC-March 1979." To monitor the general performance of the method, each sample was spiked with 300 μg/l of α, α, α-Trifluoro-m-cresol and 100 μg/l of D_{10}-Biphenyl. These "surrogate" spike recoveries were monitored to show the overall efficiency of the preparation procedures.

2. Sediment Samples - Extractables:

Soil samples were sieved through a 2 mm mesh sieve. Sieved samples were repeatedly extracted with acetone and hexane. The extracts were dried over Na_2SO_4 and concentrated to 10 ml in a K-D. The extraction method is in "Method for Organochlorine Pesticides in Soil and Sediment."

B. Analytical Procedures

1. Extractable Organics:

An aliquot of sample extracts, in acetone, was injected into a gas chromatographic column. The eluting components were detected by a mass spectrometer. Identifications were made by comparison of the sample mass spectra to the mass spectra of pure compounds within specific GC retention-time windows. Quantification was by measurement of the area of specific ion fragments of each component. Retention time and response references were made to the internal standard. The detailed procedure is in "Base/Neutrals, Acids, and Pesticides - Method 625", Federal Register, Monday, December 3, 1979. Starting at section 11.

2. Identification of Unknowns:

The samples contained many nonpriority pollutant components. The mass spectra of these compounds were compared to the EPA/NIH/NBS 25000 spectra library. The best "hits" were determined by computer spectra matching programs and they were manually evaluated to determine the best probable identification. Where standards were available, they were analyzed under identical conditions and the suspected components verified or denied. If no standard was available, the best "hits" were reported as possibly present.

METHOD FOR ORGANOCHLORINE PESTICIDES IN ENVIRONMENTAL WATER SAMPLES

1. SCOPE AND APPLICATION

1.1 This method is an adaptation of that described in ref. 1 and covers the determination of various organochlorine pesticides, including some pesticidal degradation products and related compounds in industrial effluents. Such compounds are composed of carbon, hydrogen, and chlorine, but may also contain oxygen, sulfur, phosphorus, nitrogen or other halogens.

1.2 The following compounds may be determined individually by this method with a sensitivity of at least 1 μg/liter: BHC, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, DDE, DDD, DDT, methoxychlor, endosulfan, mirex, trifluralin, endrin aldehyde, and endosulfan sulfate. Under favorable circumstances, Strobane, toxaphene, chlordane (tech) and others may also be determined. The usefulness of the method for other specific pesticides must be demonstrated by the analyst before any attempt is made to apply it to sample analysis.

1.3 When organochlorine pesticides exist as complex mixtures, the individual compounds may be difficult to distinguish. High, low, or otherwise unreliable results may be obtained through misidentification and/or one compound obscuring another of lesser concentration. Provisions incorporated in this method are intended to minimize the occurrence of such interferences.

2. SUMMARY

2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and/or the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through use of column chromatography and liquid-liquid partition, methods for elimination of non-pesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, microcoulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per liter.

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

3. INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurements of organochlorine pesticides. Sample clean-up procedures are generally required and may result

in the loss of certain organochlorine pesticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Polychlorinated Biphenyls (PCB's) - Special attention is called to industrial plasticizers and hydraulic fluids such as the PCB's which are a potential source of interference in pesticide analysis. The presence of PCB's is indicated by a large number of partially resolved or unresolved peaks which may occur throughout the entire chromatogram. Particularly severe PCB interference will require special separation procedures (2,3).

3.4 Phthalate Esters - These compounds, widely used a plasticizers, respond to the electron capture detector and are a source of interference in the determination of organochlorine pesticides using this detector. Water leaches these materials from plastics, such as polyethylene bottles and tygon tubing. The presence of phthalate esters is implicated in samples that respond to electron capture but not to the microcoulometric or electrolytic conductivity halogen detectors or to the flame photometric detector.

3.5 Organophosphorus Pesticides - A number of organophosphorus pesticides, such as those containing a nitro group, e.g., parathion, also respond to the electron capture detector and may intefere with the determination of the organochlorine pesticides. Such compounds can be identified by their response to the alkali flame ionization or flame photometric detectors.

3.6 Anaerobic extracts may contain gross interference due to the presence of sulfur compounds. This interference can be removed by reacting the extract with a small amount of metal-

lic mercury to precipitate the sulfur compounds. After alumina column cleanup, the sulfur interferences are confined to the first fraction, and only this fraction need be reacted with metallic mercury (4).

4. APPARATUS AND MATERIALS

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options:

- 4.2.1 Electron Capture - Radioactive (tritium or nickel 63)
- 4.2.2 Microcoulometric Titration
- 4.2.3 Electrolytic Conductivity

4.3 Recorder - Potentiometric strip chart (10 in) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

- 4.4.1 Tubing - Pyrex (180 cm long x 4 mm ID)
- 4.4.2 Glass Wool - Silanized
- 4.4.3 Solid Support - Gas-Chrom Q (60-80 mesh)
- 4.4.4 Liquid Phases - Expressed as Weight percent coated on solid support.
  - 4.4.4.1 OV-101, 3%
  - 4.4.4.2 OV-210, 5%
  - 4.4.4.3 OV-17, 3% or any column yielding equivalent separation

4.5 Kuderna-Danish (K-D) Glassware (Kontes)

- 4.5.1. Snyder Column - three ball (macro)
- 4.5.2 Evaporative Flasks - 500 ml
- 4.5.3 Receiver Ampuls - 10 ml, graduated

4.6 Chromatographic Column - pyrex (approximately 340 mm long x 20 mm ID) with coarse fritted place on bottom (Kontes

K422000) modified to include a reservoir for 50 ml of solvent and fitted with a ball joint.

4.7 Micro Syringes - 10, 25, 50 and 100 µl

4.8 Separatory Funnels - 125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.9 Graduated cylinders - 100, 250 and 1000 ml.

4.10 Florisil - PR Grade (60-100 mesh); purchase activated at 1250 F and store in dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130°C in foil-covered glass container.

4.11 Alumina, Basic, Brockman Activity I; 80-200 mesh. The amount of water needed for proper deactivation is determined by the elution pattern for a technical chlordane standard. A 1.75% deactivation is usually sufficient to yield the correct elution pattern (see Table IV).

5. REAGENTS, SOLVENTS, AND STANDARDS

5.1 Ferrous Sulfate - (ACS) 30% solution in distilled water.

5.2 Potassium Iodide - (ACS) 10% solution in distilled water.

5.3 Sodium Chloride - (ACS) Saturated solution in distilled water (pre-rinse NaCl with hexane).

5.4 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.5 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned at 300 °C for 4 hours).

5.6 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.7 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.7.1 Must contain 2% alcohol and be free of peroxides by following test: To 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution. Shake

and let stand one minute. No yellow color should be observed in either layer. Alternately the peroxide test may be done with EM Quant™ Ether Peroxide - Test stacks. The peroxide level must be less than 1.5 ppm.

5.7.2 Decompose either peroxides by adding 40 g of 30% ferrous sulfate solution to each liter of solvent. CAUTION: Reaction may be vigorous if the solvent contains a high concentration of peroxides.

5.7.3 Distill deperoxidized ether in glass and add 2% ethanol.

5.8 Acetonitrile, Hexane, Methylene Chloride, Petroleum Ether (boiling range 30-60°C) - nanograde,redistill in glass if necessary.

5.9 Pesticide Standards - Reference grade: sources

5.9.1 Quality Assurance Section, Environmental Toxicology Division, EPA, HERL, Research Traingle Park, N.C. 27711, MD-69

5.9.2 Pesticides Reference Standards Section, Bldg 048 Range 3 and 3rd Street, BARC, West, Beltsville, MD 20705

5.9.3 Nanogens, P.O. Box 1025, Watsonville, CA 95076

6. CALIBRATION

6.1 Gas chromatographic operating conditions are considered acceptable if a Standard Mix B elutes from the GC with correct retention times and sensitivity. Standard Mix B consists of 0.025 µg/ml lindone, 0.050 µg/ml heptachlor, 0.075 µg/ml aldrin, 0.100 µg/ml γ chlordane, 0.125 µg/ml dieldrin, 0.250 µg/ml o, p'-DDT and 0.250 µg/ml p,p'-DDT

in hexane. The chromatographic conditions chosen should yield at least 30% full-scale deflection for all of the components of Std. Mix B (see Figures 1 through 3). For all quantitative measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full-scale.

6.2 Standards are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several standard pesticides are shown in Figures 1, 2 and 3 and provide reference operating conditions for recommended columns.

6.3 The elution order and retention ratios of various organochlorine pesticides are provided in Table I, as a guide. The sensitivity of these compounds is given in Table II.

7. QUALITY CONTROL

7.1 Replicate and spiked sample analyses are recommended as quality control checks. At a minimum, one replicate and one spiked analysis should be included per 20 sample analyses. If less than 20 sample analyses are required, one duplicate and one spiked analysis should still be included. Data for recovery of specific organochlorine pesticides from water is given in Table III.

7.2 In addition, one method blank is required per 20 sample analyses. If less than 20 sample analyses are required, one method blank should still be included.

7.3 One sample should be injected in replicate into the gas chromatograph per 20 samples analyzed. If less than 20 sample analyses are required, a replicate GC injection should still be made.

8. SAMPLE PREPARATION

8.1 Shake the sample if suspended matter is present and adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 Quantitatively transfer 1 liter of sample into a two-liter separatory funnel. Less sample may be analyzed if necessary, with the realization that detection limits will be affected.

9. EXTRACTION

9.1 Add 60 ml of 15% methylene chloride in hexane (v:v) to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter beaker. Pour the organic layer into a 250 ml beaker. Return the water phase to the separatory funnel. Rinse the one-liter beaker with a second 60 ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Transfer the combined solvent extract to a 500 ml Kuderna-Danish evaporative concentrator by passing it through a funnel plugged with glass wool and filled with sodium sulfate which has been prewashed with hexane.

9.4 Concentrate the extract to 10 ml in the K-D evaporator on a hot water bath.

9.5 Analyze by gas chromatography unless a need for cleanup is indicated (see Section 10).

10. CLEAN-UP AND SEPARATION PROCEDURES

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether clean-up is required. When these interfere with measurement of the pesticides, or affect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition - This procedure is used to isolate fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125 ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30 ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix throughly for 30-45 seconds. Extract with two 100 ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100 ml portions of distilled water. Discard the water layer and pour the hexane layer into a 500 ml K-D flask

through a funnel plugged with glass wool and filled with sodium sulfate which has been pre-washed with hexane. Rinse the separatory funnel and column with three 10 ml portion of hexane.

10.2.4 Concentrate the extracts to 10 ml in the K-D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further clean-up is indicated.

10.3 Florisil Column Adsorption Chromatography

10.3.1 Adjust the sample extract volume to 10 ml with hexane.

10.3.2 Prepare a 20 mm I.D. column that contains 4 inches (after settling) of activated Florisil topped with 0.5 inch anhydrous sodium sulfate.

10.3.3 Pre-elute the column with 50-60 ml of petroleum ether. Just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract onto the column. Just prior to exposure of the sodium sulfate layer to air, add the first eluting solvent, 200 ml of 6% ethyl ether in petroleum ether. Collect the eluate in a 250 ml beaker. Perform the second elution with 200 ml of 15% ethyl ether in petroleum ether, the third elution with 200 ml of 50% ethyl ether-petroleum ether, and the fourth elution with 200 ml fo 100% ethyl ether. (See Eluate Composition 10.3.6).

10.3.4 Concentrate the eluates to 10 ml in a K-D in a hot water bath. Fifty mls of petroleum ether must be added to the fourth fraction prior to concentration to eliminate the ethyl ether from the concentrated extract.

10.3.5 Analyze by gas chromatography.

10.3.6 Eluate Composition - The composition of the eluate should be checked for each new batch of Florisil with a standard mix consisting of gamma-BHC (lindane) heptachlor, endosulfan A and B. If the composition of the eluate varies from that given below, the amount of Florisil used in the column should be altered i.e., an increase in the amount of Florisil will increase the amount of solvent needed to elute compounds from the column. The majority of the compound should elute in the fraction listed below.

6% Eluate

Aldrin	DDT
BHC	Heptachlor
Chlordane	Heptachlor Epoxide
DDD	Lindane
Endosulfan A	Mirex
Toxaphene	PCB's
DDE	Methoxychlor

15% Eluate	50% Eluate
Endrin	Endosulfan B
Dieldrin	
Phthalate esters	

Certain thiophosphate pesticides will occur in each of the above fractions as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (5).

10.4 Alumina Column Adsorption Chromatography (6).

10.4.1 Adjust the sample extract volume to 10 ml with hexane.

10.4.2 Prepare a 15 cm (after settling) x 2 cm column of properly deactivated alumina (see 4.11). The alumina should be settled by tapping the column.

10.4.3 Pre-eluate the column with 40-50 ml of hexane. Adjust the flow of the solvent through the column to 5 ml/min with air. Just prior to exposure of the alumina surface to air, quantitatively transfer the sample extract to the column using several hexane washes. This transfer should be done without disturbing the surface of the alumina.

10.4.4 Just prior to the exposure of the alumina surface to air, add 50 ml of a 10% ethyl ether in hexane solution. Collect the eluate in a 50 ml beaker. Ten 50 ml fractions are collected in like manner and each fraction is concentrated to 10 ml on a hot plate under a gentle stream of air.

10.4.5 Analyze by gas chromatography.

10.4.6 Eluate Composition. --The composition of the eluate should be checked for each new batch of alumina with a technical chlordane standard. If the composition of the eluate varies from that given in Table IV, the amount of water added to the alumina should be altered, i.e., an increase in the amount of water will decrease the amount of solvent needed to elute compounds from the column.

11. CALCULATION OF RESULTS

11.1 Determine the pesticide concentration by using the absolute calibration procedure described below:

(1) $$\text{Micrograms/liter} = \frac{(A)\ (B)\ (V_t)}{(V_i)\ \ (V_s)}$$

$$A = \frac{\text{ng standard}}{\text{Standard area}}$$

B = Sample aliquot area

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

V_s = Volume of water extracted (ml)

12. REPORTING RESULTS

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

REFERENCES

1. "Method for Organochlorine Pesticides in Industrial Effluents", Natinal Pollutant Discharge Elimination System, Appendix A, Federal Register, 38, No. 75, Pt. II.

2. Monsanto Methodology for Arochlors - Analysis of Environmental Materials for Biphenyls, Analytical Chemistry Method 71-35, Monsanto Company, St. Louis, Missouri, 63166, 1970.

3. "Method for Polychlorinated Biphenyls in Industrial Effluents," Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, 45268, 1973. (Also NPDES, Appendix A, Fed. Reg., 38, No. 75, Pt. II.)

4. Goerlitz, D.F. and Law, L.M., "Notes on the Removal of Sulfur Interferences from Sediment Extracts for Pesticide Analysis," Bulletin of Environmental Contamination and Toxicology, Vol. 6, No. 1, 1971.

5. "Pesticide Analytical Manual," U.S. Dept. of Health, Education and Welfare, Food and Drug Administration, Washington, D.C., Vol. I, 211.14 (d).

6. Boyle, H.W., Burttschell, R.H., and Rosen, A.A., "Infrared Identification of Chlorinated Insecticides in Tissues of Poisoned Fish," Organic Pesticides in the Environment, Advances in Chemistry Series, No. 60, A.C.S., Washington, D.C., 1966.

Table I

Retention Times of Organochlorine Pesticides
Relative to Aldrin

Liquid Phase	3% OV-101	3% OV-17	5% OV-210	3% OV-225
Solid Support	2 mm x 6' glass on 60/80 GCQ	4 mm x 6' glass on 60/80 GCQ	2 mm x 6' glass on 60/80 GCQ	2 mm x 6' glass on 80/100 GCQ
Column Temperature	180°C	200°C	200°C	200°C
Flow Rate[a] (ml/min)	25	60	37	32
Pesticide	RRT	RRT	RRT	RRT
α-BHC	0.40	0.45	0.68	0.87
B-BHC	0.44	0.49	0.96	2.94
γ-BHC (lindane)	0.48	0.53	0.83	1.24
δ-BHC	0.50	0.54	1.54	0.53
heptachlor	0.80	0.82	0.88	0.90
heptachlor epoxide	1.26	1.19	1.71	2.11
γ chlordane	1.44	1.38	1.64	2.52
Endosulfan A	1.60	1.47	2.16	2.40
α chlordane	1.62	1.50	1.64	NA[b]
dieldrin	1.88	1.73	2.55	3.24
p,p' DDE	1.96	1.68	1.78	2.79
endrin	2.11	1.89	2.97	3.82
endosulfan B	2.20	1.93	3.72	6.82
o,p' DDT	2.64	2.25	2.22	3.92
p,p' DDD	2.52	2.10	2.94	6.70
endrin aldehyde	2.52	2.10	5.76	5.39
endosulfan sulfate	2.99	2.46	8.42	15.03
p,p' DDT	3.37	2.77	3.18	6.38
methoxychlor	5.31	4.01	4.60	12.96
aldrin (min absolute)	3.80	2.28	1.74	4.92

[a] Argon 10% methane. RRT for other columns are given in reference 1, Table I.

[b] NA - Value not available.

Table II

SENSITIVITY OF ORGANOCHLORINE PESTICIDES USING ELECTRON CAPTURE (EC) DETECTOR

Instrument	Tracor MT-220
Liquid Phase	3% OV-17
Solid Support	4 mm x 6' glass 60/80 GCQ
Column Temperature	200°C
Flow Rate	81.6 ml/min
Injection Size	2 µl

Pesticide	conc. (µg/ml)	att.	peak height (mm)
Lindane	0.025	8	79
Heptachlor	0.05	8	113
Aldrin	0.075	8	140
γ-Chlordane	0.10	8	132
Dieldrin	0.125	8	136
o,p' DDT	0.250	8	95
p,p' DDT	0.250	8	92
α-BHC	0.05	8	256+
endosulfan A	0.10	8	77
p,p' DDE	0.10	8	104
endosulfan B	0.10	8	60
DDD	0.10	8	46
endosulfan sulfate	0.50	8	215
β-BHC	0.050	8	79
Heptachlor Epoxide	0.100	8	134
Endrin	0.100	8	58
Endrin Aldehyde	0.100	8	31

Table III

RECOVERY DATA FOR SELECTED ORGANOCHLORINE PESTICIDES
(EXTRACTION FROM WATER ONLY)

Compound	Spiking Level (μg)	Number of Determinations	Average % Recovery	Standard Deviation
lindane	0.25	12	110	8.3
heptachlor	0.50	12	89	7.6
aldrin	0.75	12	91	12.4
γ-chlordane	1.00	12	97	2.5
dieldrin	1.25	12	100	3.8
o,p' DDT	2.50	12	98	6.4
p,p' DDT	2.50	11	109	5.5
DDD	1.00	11	100	14.8
Endosulfan A	1.00	12	99	4.3
Endosulfan B	1.00	12	95	6.0
α-BHC	0.50	9	102	3.8
p,p' DDE	1.00	12	98	4.1
Endosulfan sulfate	5.00	11	107	11.6
β-BHC	0.50	8	103	5.2
heptachlor epoxide	1.00	9	99	6.2
endrin	1.00	7	115	12.2
endrin aldehyde	1.00	8	89	7.2

Table IV

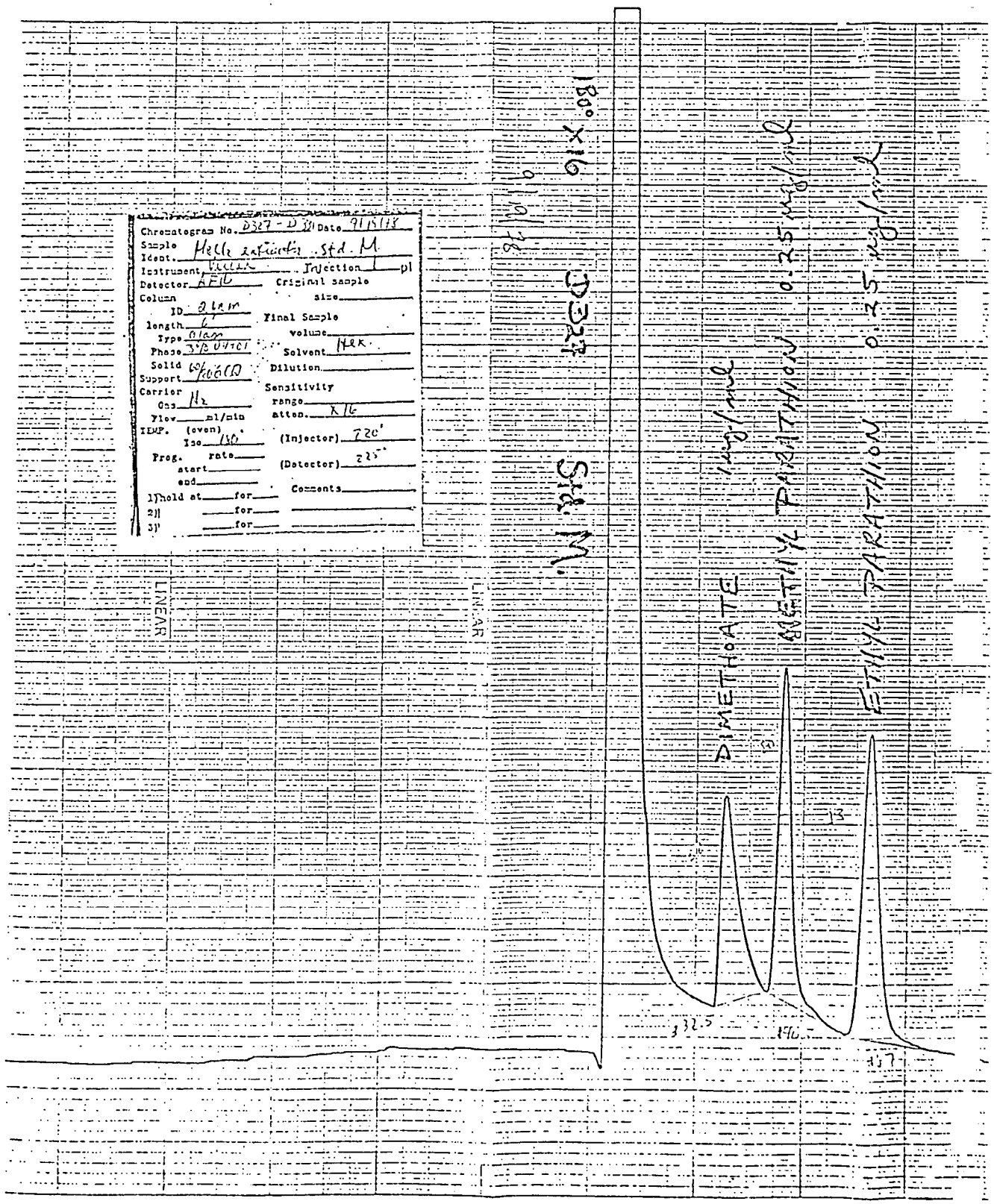
ORDER OF ELUTION OF CHLORINATED INSECTICIDES FROM ALUMINA ADSORPTION COLUMN[a] (6)

Insecticide	50 ml Eluate Fractions - % of Total Recovered										% Recovery
	1	2	3	4	5	6	7	8	9	10	
DDE	95	5									94
Aldrin	93	7									97
Heptachlor	75	25									96
Tech. Chlordane	30	30	35	5							99
Toxaphene	15	55	30	Trace							93
DDT	5	95									94
γ-Chlordane		2	80	18							99
α-Chlordane			95	5							97
DDD			60	40							93
Lindane			35	65							40
Endrin				45	55						95
Heptachlor Epoxide				35	50	15					95
Dieldrin						20	40	20	15	5	96
Methoxyclor						5	30	50	10	5	96
Aroclor 1242	100										100
Aroclor 1248	98	2									100
Aroclor 1254	95	5									100
Aroclor 1260	95	5									100
Lindane	(Acid Alumina)				25	60	15				100
Lindane	(Neutral Alumina)			3	75	20	2				91

a 9/1 Hexane/Ethyl Ether Eluting Solvent.

FIGURE 1. EC/GC, 3% OV-17

FIGURE 2. AFID, 3% OV-101

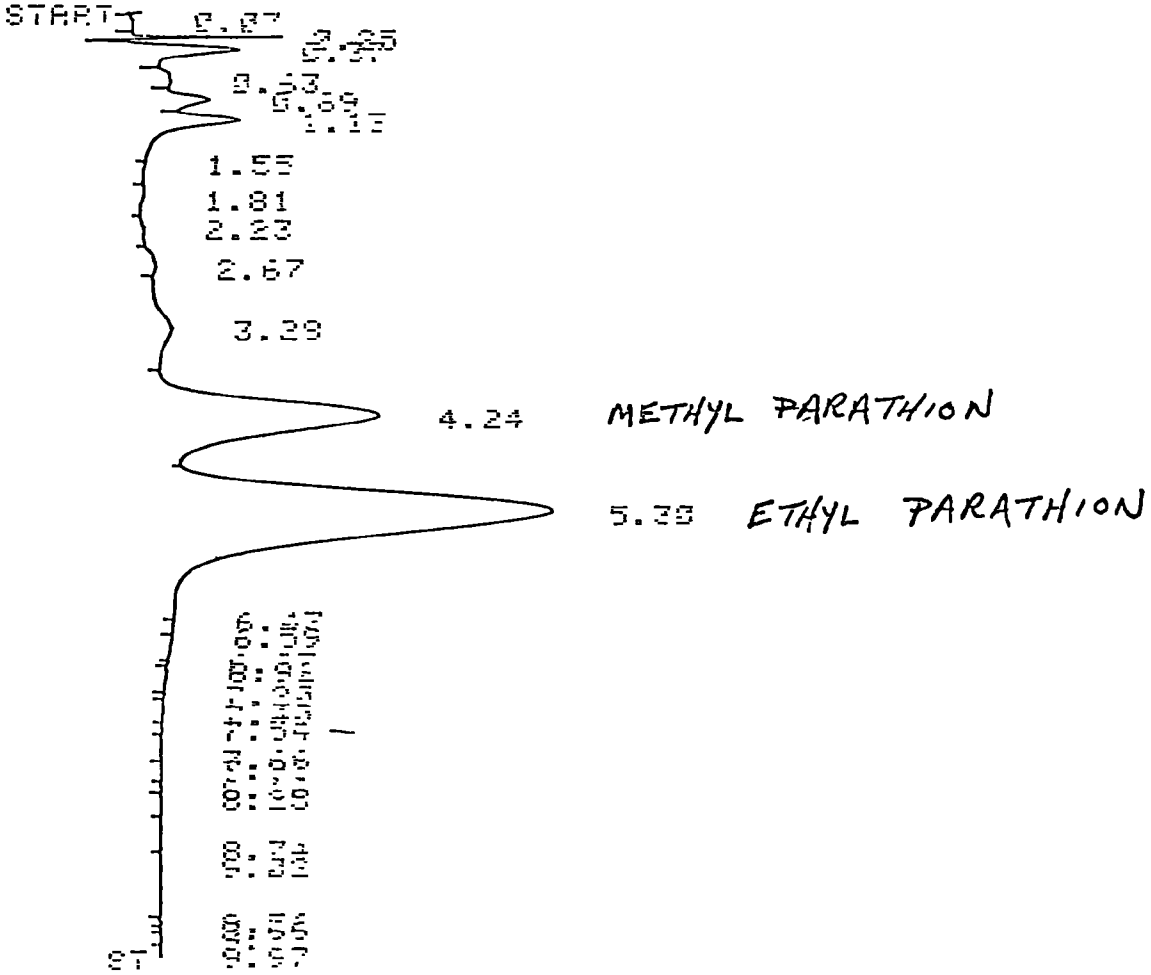


TEMP1	400	320	280
TIME1	0.00		
OVN TEMP	400	335	225
AUX TEMP	420	320	320

CHT SPD	1.27	
EPO	12.9	
ATTN 2^	10	
AUX SGNL	+3	
SLP SENS	0.10	
AREA REJ	10020	
FLOW A	3.2	2.2
FLOW B	34.7	34.2

10.00 STOP

FIGURE 3.
EC/GC, 5% OV-210



HP RUN # 35 JAN/17 78 TIME 21:41:47
BOTTLE 38
AREA %

RT	AREA	AREA %
0.25	46322	0.742
0.37	147320	2.360
0.63	104500	1.674
0.89	172950	2.771
1.13	286720	4.593
1.55	65500	1.050
1.81	93100	1.495
2.23	103300	1.655
2.67	150470	2.410

ANALYTICAL DATA REPORTING SHEET

PROJECT 624, VELSICOL, ST. LOUIS, MICHIGAN

TABLE IV, GENERAL ORGANICS DATA, QUALITY CONTROL DATA, WATER

STATION NUMBER	DATE	TIME	HBB ug/l	PBB ug/l	p,p'-DDT ug/l	o,p'-DDT ug/l	p,p'-DDE ug/l	p,p'-DDD ug/l	TRIS ug/l
BLANK 1			ND *	ND	ND	ND	ND	ND	NA **
BLANK 2			ND	ND	ND	ND	ND	ND	NA
BLANK 3			ND	ND	ND	ND	ND	ND	NA
DM-6			ND	ND	ND	ND	ND	ND	ND
DM-6 duplicate			ND	ND	ND	ND	ND	ND	ND
DM-6 spike (% recovery)			90%	75%	NA	NA	90%	NA	NA
DP5-01			ND	ND	0.4	ND	1.2	ND	NA
DP5-01 duplicate			ND	ND	0.2	ND	1.0	ND	NA
DP5-01 spike (% recovery)			NA	80%	70%	NA	NA	85%	NA
* NOT DETECTED									
DETECTION LIMITS			0.2	1	0.2	0.1	0.1	0.1	0.2
** NOT ANALYZED									

ANALYTICAL DATA REPORTING SHEET

PROJECT 624, VELSICOL, ST. LOUIS, MICHIGAN

TABLE III, GENERAL ORGANICS DATA, QUALITY CONTROL DATA, WATER

STATION NUMBER	DATE	TIME	HBB ug/l	PBB ug/l	p,p'-DDT ug/l	o,p'-DDT ug/l	p,p'-DDE ug/l	p,p'-DDD ug/l	TRIS ug/l
SS-20			ND	ND	1.5	0.7	1.0	0.5	.24
SS-20 duplicate			ND	ND	1.8	1.0	1.0	0.5	NA
SS-20 spike (% recovery)			NA	NA	86%	85%	100%	110%	91%
WPS 01			ND	ND	ND	ND	ND	ND	ND
WPS-01 duplicate			ND	ND	ND	ND	ND	ND	ND
WPS-01 spike			NA	NA	110%	90%	98%	NA	93%
BLANK I			NA	NA	NA	NA	NA	NA	ND
BLANK II			NA	NA	NA	NA	NA	NA	ND
BLANK III			NA	NA	NA	NA	NA	NA	ND

METHOD FOR ORGANOCHLORINE PESTICIDES IN SOIL AND SEDIMENT

1. SCOPE AND APPLICATION

1.1 This method is an adaptation of that described in reference 1 and covers the determination of various organochlorine pesticides, including some pesticidal degradation products and related compounds in soil. Such compounds are composed of carbon, hydrogen, and chlorine, but may also contain oxygen, sulfur, phosphorus, nitrogen or other halogens.

1.2 The following compounds may be determined individually by this method with a sensitivity of at least 0.05 µg/g: BHC, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, DDE, DDD, DDT, methoxychlor, endosulfan, mirex, trifluralin, endrin aldehyde, and endosulfan sulfate. Under favorable circumstances, Strobane, toxaphene, chlordane (tech.) and others may also be determined. The usefulness of the method for other specific pesticides must be demonstrated by the analyst before any attempt is made to apply it to sample analysis.

1.3 When organochlorine pesticides exist as complex mixtures, the individual compounds may be difficult to distinguish. High, low, or otherwise unreliable results may be obtained through misidentification and/or one compound obscuring another of lesser concentration. Provisions incorporated in this method are intended to minimize the occurrence of such interferences.

2. SUMMARY

2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and/or the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through use of column chromatography and liquid-liquid partition, methods for the elimination of non-pesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separation and may be corroborated through the use of two or more unlike columns. Detection and measurement are best accomplished by electron capture, microcoulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per gram of dry sample.

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

3. INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interference under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 The interferences in soil and sediment samples are high and varied and often pose great difficulty in obtaining accurate and precise measurement of organochlorine pesticides. Sample clean-up procedures are generally required and may result in the loss of certain organochlorine pesticides. Therefore,

great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in soil and sediment samples.

3.3 Polychlorinated Biphenyls (PCB's) - Special attention is called to industrial plasticizers and hydraulic fluids such as the PCB's which are a potential source of interference in pesticide analysis. The presence of PCB's is indicated by a large number of partially resolved or unresolved peaks which may occur throughout the entire chromatogram. Particularly severe PCB interferences will require special separation procedures (2,3).

3.4 Phthalate Esters - These compounds, widely used as plasticizers, respond to the electron capture detector and are a source of interference in the determination of organochlorine pesticides using this detector. Water leaches these materials from plastics, such as polyethylene bottles and tygon tubing. The presence of phthalate esters is implicated in samples that respond to electron capture but not to the microcoulometric or electrolytic conductivity halogen detectors or to the flame photometric detector.

3.5 Oganophosphorus Pesticides - A number of organophosphorus pesticides, such as those containing a nitro group, eg, parathion, also respond to the electron capture detector and may interfere with the determination of the organochlorine pesticides. Such compounds can be identified by their response to the alkali flame ionization or flame photometric detectors.

3.6 Anaerobic extracts have gross interferences due to the presence of sulfur compounds. This interference can be removed by reacting the extract with a small amount of metallic mercury to precipitate the sulfur compounds. After alumina

column cleanup, the sulfur interferences are confined to the first fraction, and only this fraction need be reacted with metallic mercury. (4)

4. APPARATUS AND MATERIALS

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options:

- 4.2.1 Electron Capture - Radioactive (tritium or nickel 63)
- 4.2.2 Microcoulometric Titration
- 4.2.3 Electrolytic Conductivity

4.3 Recorder - Potentiometric strip chart (10 in) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

- 4.4.1 Tubing - Pyrex (180 cm long x 4 mm ID)
- 4.4.2 Glass Wool - Silanized
- 4.4.3 Solid Support - Gas-Chrom Q (60-80 mesh)
- 4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.
  - 4.4.4.1 OV-101, 3%
  - 4.4.4.2 OV-210, 5%
  - 4.4.4.3 OV-17, 3% or any column yielding equivalent separation.

4.5 Kuderna-Danish (K-D) Glassware (Kontes)

- 4.5.1 Snyder Column - three ball (macro)
- 4.5.2 Evaporative Flasks - 500 ml
- 4.5.3 Receiver Ampuls - 10 ml, graduated

4.6 Chromatographic Column - Pyrex (approximately 340 mm long x 20 mm ID) with coarse fritted plate on bottom. (Kontes K422000) modified to include a reservoir for 50 ml of solvent

4.7 Micro Syringes - 10, 25, 50 and 100 µl.

4.8 Separatory Funnels - 125 ml and 1000 ml with Teflon stopcock.

4.9 Micro-pipets - disposable (140 mm long x 5 mm ID).

4.10 Graduated cylinders - 500 ml.

4.11 Beakers - 50 and 250 ml.

4.12 Wrist Action shaker

4.13 Erlenmeyer flask - 500 ml.

4.14 Graduated cylinders - 100, 250 and 1000 ml.

4.15 Florisil - PR Grade (60-100 mesh); purchase activated at 1250 F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130 C in foil-covered glass container.

4.16 Alumina, Basic; Brockman Activity I; 80-200 mesh. The amount of water needed for proper deactivation is determined by the elution pattern for a technical chlordane standard. A 1.75% deactivation is usually sufficient to yield the correct elution pattern (see Table IV).

5. REAGENTS, SOLVENTS, AND STANDARDS

5.1 Ferrous Sulfate - (ACS) 30% solution in distilled water.

5.2 Potassium Iodide - (ACS) 10% solution in distilled water.

5.3 Sodium Chloride - (ACS) Saturated solution in distilled water (pre-rinse NaCl with hexane).

5.4 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.5 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned @ 400 C for 4 hrs.).

5.6 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water

5.7 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.7.1 Must contain 2% alcohol and be free of peroxides by following test: To 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution.

4.8 Separatory Funnels - 125 ml and 1000 ml with Teflon stopcock.

4.9 Micro-pipets - disposable (140 mm long x 5 mm ID).

4.10 Graduated cylinders - 500 ml.

4.11 Beakers - 50 and 250 ml.

4.12 Wrist Action shaker

4.13 Erlenmeyer flask - 500 ml.

4.14 Graduated cylinders - 100, 250 and 1000 ml.

4.15 Florisil - PR Grade (60-100 mesh); purchase activated at 1250 F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130 C in foil-covered glass container.

4.16 Alumina, Basic; Brockman Activity I; 80-200 mesh. The amount of water needed for proper deactivation is determined by the elution pattern for a technical chlordane standard. A 1.75% deactivation is usually sufficient to yield the correct elution pattern (see Table IV).

5. REAGENTS, SOLVENTS, AND STANDARDS

5.1 Ferrous Sulfate - (ACS) 30% solution in distilled water.

5.2 Potassium Iodide - (ACS) 10% solution in distilled water.

5.3 Sodium Chloride - (ACS) Saturated solution in distilled water (pre-rinse NaCl with hexane).

5.4 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.5 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned @ 400 C for 4 hrs.).

5.6 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water

5.7 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.7.1 Must contain 2% alcohol and be free of peroxides by following test: To 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution.

consists of 0.025 µg/ml lindane, 0.050 µg/ml heptachlor, 0.075 µg/ml aldrin, 0.100 µg/ml δ chlordane, 0.125 µg/ml dieldrin, 0.250 µg/ml o,p' DDT and 0.250 µg/ml p,p' DDT in hexane. The chromatographic conditions chosen should yield at least 30% full scale deflection for all of the components of Std. Mix B [see Figures 1 thru 3]. For all quantitative measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full scale.

6.2 Standards are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several standard pesticides are shown in Figures 1, 2, and 3 and provide reference operating conditions for the recommended columns.

6.3 The elution order and retention ratios of various organochlorine pesticides are provided in Table I as a guide. The sensitivity of these compounds to detection by EC is given in Table II.

7. QUALITY CONTROL

7.1 Replicate and spiked sample analyses are recommended as quality control checks. At a minimum, one replicate and one spiked analysis should be included per 20 sample analyses. If less than 20 sample analyses are required, one duplicate and one spiked analysis should still be included. Data for recovery of specific organochlorine pesticides from soil is given in Table III

7.2 In addition, one method blank is required per 20 sample analyses. If less than 20 sample analyses are required, one method blank should still be included.

7.3 One sample should be injected in replicate into the gas chromatograph per 20 samples analyzed. If less than 20 samples analyses are required, a replicate GC injection should still be made.

8. SAMPLE PREPARATION

8.1 Separate water from sample, if necessary, by decantation or centrifugation. Analyze water using the "Method for Organochlorine Pesticides in Environmental Water Samples."

8.2 Sieve the soil and sediment sample through a 2 mm mesh sieve to remove rocks and other foreign material: sediment samples may require air drying before sieving to facilitate the procedure.

8.3 Weigh approximately 10 gm of the sieved sample into a weighed beaker. Record the weight. Place in a 105°C oven overnight and reweigh for moisture determination. Calculation:

$$\frac{\text{wt water}}{\text{wet sample}} \quad \frac{A - C}{A - B} \times 100 = \%\ \text{moisture}$$

A = weight of beaker + wet sample
B = weight of beaker
C = Weight of beaker + dry sample

8.4 Weigh 25-50 gm of sample into a 500 ml Erlenmeyer flask. Add water, if necessary, to adjust the moisture content of the sample to a 15% minimum.

9. EXTRACTION

9.1 Add 40 ml of acetone to the sample and shake vigorously for 20 minutes using a wrist action shaker. Add 80 ml of hexane and shake for an additional 10 minutes.

9.2 Allow the sample to settle and decant the solvent into a 1 liter separatory funnel

9.3 Repeat the extraction by adding 20 ml of acetone to the sample and shaking for 20 minutes, followed by 80 ml of hexane with an additional 10 minutes of shaking.

9.4 Allow the sample to settle, decant the solvent and combine with the solvent from the first extraction.

9.5 Add 500 ml of water to the separatory funnel containing the combined extracts and gently mix for 1 minute. Collect the organic solvent layer which contains hexane in a 250 ml beaker. This backwashing removes the acetone and other polar impurities from the extract.

9.6 Extract the resulting water layer with 25 ml of hexane. Combine the hexane extract with the extract from 9.5. Discard the water layer.

9.7 Prepare a funnel plugged with glass wool and filled with sodium sulfate. Remove interferes from the glass wool and sodium sulfate by washing with 30-50 ml of hexane. Pass the combined hexane extracts through the funnel and into a 500 ml Kuderna-Danish evaporative concentrator.

9.8 Concentrate the extract in the K-D evaporator on a hot water bath to a volume of 10 ml.

9.9 Analyze by gas chromatography unless a need for a cleanup is indicated. [See Section 10].

10. CLEAN-UP AND SEPARATION PROCEDURES

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether clean-up is required. When these interfere with measurement of the pesticides, or affect column life or detector sensitivity, proceed as directed below

10.2 Acetonitrile Partition - This procedure is used to isolate fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by

this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125 ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30 ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30-45 seconds. Extract with two 100 ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100 ml portions of distilled water. Discard the water layer and pour the hexane layer into a 500 ml K-D flask through a funnel plugged with glass wool and filled with anhydrous sodium sulfate which has been prewashed with hexane. Rinse the separatory funnel and column with 10 ml portions of hexane.

10.2.4 Concentrate the extracts to 10 ml in the K-D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further clean-up is indicated.

10.3 Florisil Column Adsorption Chromatography

10.3.1 Adjust the sample extract volume to 10 ml with hexane.

10.3.2 Prepare a 20 mm I.D. column that contains 4 inches (after settling) of activated Florisil topped with a 0.5 inch anhydrous sodium sulfate.

10.3.3 Pre-elute the column with 50-60 ml of petroleum ether. Just prior to exposure of the sodium sulfate layer to air, quantitatively transfer the sample extract into the column. Just prior to exposure of the sodium sulfate layer to air, add the first eluting solvent, 200 ml of 6% ethyl ether in petroleum ether. Collect the eluate in a 250 ml beaker. Perform the second elution with 200 ml of 15% ethyl ether in petroleum ether, the third elution with 200 ml of 50% ethyl ether-petroleum ether, and the fourth elution with 200 ml of 100% ethyl ether. [See Eluate Composition 10.3.6].

10.3.4 Concentrate the eluates to 10 ml in a K-D in a hot water bath. Fifty mls of petroleum ether must be added to the fourth fraction prior to concentration to eliminate the ethyl ether from the concentrated extract.

10.3.5 Analyze by gas chromatography.

10.3.6 Eluate Composition - The composition of the eluate should be checked for each new batch of Florisil with a standard mix consisting of gramma-BHC (lindane), heptachlor, and Endosulfan A and B. If the composition of the eluate varies from that given below, the amount of Florisil used in the column should be altered i.e., an increase in the amount of Florisil will increase the amount of solvent needed to elute compounds from the column. The majority of the compounds should elute in the fraction listed below.

6% Eluate	
Aldrin	DDT
BHC	Heptachlor
Chlordane	Heptachlor Epoxide
DDD	Lindane

DDE	Methoxychlor
Endosulfan A	Mirex
Toxaphene	PCB's

15% Eluate	50% Eluate
Endrin	Endosulfan B
Dieldrin	
Phthalate Esters	

Certain thiophosphate pesticides will occur in each of the above fractions as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (5).

10.4 Alumina Column Adsorption Chromatography ([6])

10.4.1 Adjust the sample extract volume to 10 ml with hexane.

10.4.2 Prepare a 15 cm (after setting) x 2 cm column of properly deactivated alumina [see 4.16]. The alumina should be settled by tapping the column.

10.4.3 Pre-elute the column with 40-50 ml of hexane. Just prior to exposure of the alumina surface to air, quantitatively transfer the sample extract to the column using several hexane washes. This transfer should be done without disturbing the surface of the alumina.

10.4.4 Just prior to the exposure of the alumina surface to air, add 50 ml of a 10% ethyl ether in hexane solution. Collect the eluate in a 50 ml beaker. Ten 50 ml fractions are collected in like manner and each fraction is concentrated to 10 ml on a hot plate under a gentle stream of air.

10.4.5 Analyze by gas chromatography.

10.4.6 Eluate Composition. The composition of the eluate should be checked for each new batch of alumina with

a technical chlordane standard. If the composition of the eluate varies from that given in Table IV, the amount of water added to the alumina should be altered, i.e. an increase in the amount of water will decrease the amount of solvent needed to elute compounds from the column.

11. CALCULATION OF RESULTS

11.1 Determine the pesticide concentration by using the absolute calibration procedure described below. Concentration is reported in terms of the dry weight of the sample.

(1) $$\text{Micrograms/gram} = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (W_s)\ (1.00-M)}$$

$A = \frac{\mu g \text{ standard}}{\text{Standard area}}$

B = Sample aliquot area

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

W_s = Weight of sample extracted (g)

$M = \frac{\%\ \text{moisture}}{100}$

12. REPORTING RESULTS

12.1 Report results in micrograms per gram without correction for recovery data. When duplicate and spiked samples are analyzed all data obtained should be reported.

REFERENCES

1. Goerlitz, D.F. and Law, L.M., "Determination of Chlorinated Insecticides in Suspended Sediment and Bottom Material," Journal of the AOAC, Vol. 57, No. 1, 1974.

2. Monsanto Methodology for Arochlors - Analysis of Environmental Materials for Biphenyls, Analytical Chemistry Method 71-35, Monsanto Company, St. Louis, Missouri, 63166, 1970.

3. "Method for Polychlorinated Biphenyls in Industrial Effluents" Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, 45268, 1973 (Also NPDES, Appendix A, Fed. Reg., 38, No. 75, Pt. II).

4. Goerlitz, D.F. and Law, L.M., "Notes on the Removal of Sulfur Interferences from Sediment Extracts for Pesticide Analysis," Bulletin of Environmental Contamination and Toxicology, Vol. 6, No. 1, 1971.

5. "Pesticide Analytical Manual," U.S. Dept. of Health, Education, and Welfare, Food and Drug Administration, Washington, D.C., Vol. I, 211.14 (d).

6. Boyle, H.W. Burttschell, R.H., and Rosen, A.A., "Infrared Identification of Chlorinated Insecticides in Tissues of Poisoned Fish," Organic Pesticides in the Environment, Advances in Chemistry Series, No. 60, A.C.S. Washington, D.C., 1966.

TABLE I

Retention Times of Organochlorine Pesticides
Relative to Aldrin

Liquid Phase Solid Support Column Temperature Flow Rate*(ml/min)	3% OV-101 2 min x 6' glass on 60/80 GCQ 180°C 25	3% OV-17 4 mm x 6' glass on 60/80 GCQ 200°C 60	5% OV-210 2 mm x 6' glass on 60/80 GCQ 200°C 37
Pesticide	RRT	RRT	RRT
α-BHC	0.40	0.45	0.68
B-BHC	0.44	0.49	0.96
γ-BHC (lindane)	0.48	0.53	0.83
δ-BHC	0.50	0.54	1.54
heptachlor	0.80	0.82	0.88
heptachlor epoxide	1.26	1.19	1.71
γ chlordane	1.44	1.38	1.64
Endosulfan A	1.60	1.47	2.16
α chlordane	1.62	1.50	1.64
dieldrin	1.88	1.73	2.55
p,p' DDE	1.96	1.68	1.78
endrin	2.11	1.89	2.97
endosulfan B	2.20	1.93	3.72
o,p' DDT	~~2.57~~ 2.64	2.25	2.22
DDD	2.52	2.10	2.94
endrin aldehyde	2.52	2.10	5.76
endosulfan sulfate	2.99	2.46	8.42
p,p' DDT	3 37	2.77	3.18
methoxychlor	5.31	4.01	4.60
aldrin (min absolute)	3.80	2 38	1.74

* Argon 10% methane. RRT for other columns are given in reference 1, Table I.

TABLE II

Sensitivity of Organochlorine Pesticides
Using Electron Capture (EC) Detector Tracor MT 220

Instrument	Tracor MT-220
Liquid Phase	3% OV-17
Solid Support	4 mm x 6' glass on 60/80 GCQ
Column Temperature	200°C
Flow Rate (ml/min)	81.6 ml/min
Injection Size	2 µl

Pesticide	Conc. ug/ml	Att	Peak Height (mm)
Lindane	0.025	8	79
Heptachlor	0.05	8	113
Aldrin	0.075	8	140
γ-Chlordane	0.10	8	132
Dieldrin	0.125	8	136
o,p' DDT	0.250	8	94
p,p' DDT	0.250	8	92
α-BHC	0.05	8	256+
Endosulfan A	0.10	8	77
p,p' DDE	0.10	8	104
Endosulfan B	0.10	8	60
DDD	0.10	8	46
Endosulfan Sulfate	0.50	8	215
B-BHC	.050	8	79
Heptachlor Epoxide	.100	8	134
Endrin	.100	8	58
Endrin Aldehyde	.100	8	31

TABLE III

Recovery Data for Selected Organochlorine Pesticides from Soil

Compound	Spiking Level (μg)	# Determinations	Average % Recovery	Standard Deviation
Lindane	0.25	3	94	0.5
Heptachlor	0.25	3	91	1.2
Aldrin	0.75	3	94	0.8
γ Chlordane	1.00	3	94	1.2
Dieldrin	1.25	3	93	0.5
o,p' DDT	2.5	3	96	1.9
p,p' DDT	2.5	3	105	2.6
DDD	1.0	3	106	4.3
Endosulfan A	1.0	3	102	3.3
Endosulfan B	1.0	3	99	5.0
α-BHC	0.50	3	92	2.6
p,p' DDE	1.0	3	103	3.3
Endosulfan Sulfate	5.0	3	83	2.9
B-BHC	5.0	3	95	1.4
Heptachlor Epoxide	1.0	3	98	0.5
Endrin	1.0	3	98	2.0
Endrin Aldehyde	1.0	3	79	1.9

Table IV

ORDER OF ELUTION OF CHLORINATED INSECTICIDES FROM ALUMINA ADSORPTION COLUMN[a] (6)

Insecticide	50 ml Eluate Fractions - % of Total Recovered										% Recovery
	1	2	3	4	5	6	7	8	9	10	
DDE	95	5									94
Aldrin	93	7									97
Heptachlor	75	25									96
Tech. Chlordane	30	30	35	5							99
Toxaphene	15	55	30	Trace							93
DDT	5	95									94
γ-Chlordane		2	80	18							99
α-Chlordane			95	5							97
DDD			60	40							93
Lindane			35	65							40
Endrin				45	55						95
Heptachlor Epoxide				35	50	15					95
Dieldrin						20	40	20	15	5	96
Methoxyclor						5	30	50	10	5	96
Aroclor 1242	100										100
Aroclor 1248	98	2									100
Aroclor 1254	95	5									100
Aroclor 1260	95	5									100
Lindane	(Acid Alumina)				25	60	15				100
Lindane	(Neutral Alumina)			3	75	20	2				91

a 9/1 Hexane/Ethyl Ether Eluting Solvent.

ANALYTICAL DATA REPORTING SHEET

PROJECT 624, VELSICOL, ST. LOUIS, MICHIGAN

TABLE IV, GENERAL ORGANICS DATA, RIVER, SEDIMENT

Based on dry weight

STATION NUMBER	DATE	TIME	HBB µg/g	PBB µg/g	p,p'-DDT µg/g	o,p'-DDT µg/g	p,p'-DDE µg/g	p,p'-DDD µg/g	TRIS µg/g
RSS-1	6-2-80	1400	ND*	ND	ND	ND	0.02	0.04	ND
RSS-2	6-2-80	1428	0.01	ND	0.01	ND	0.03	0.05	ND
RSS-3	6-2-80	1518	ND	ND	0.02	0.01	0.005	0.01	ND
RSS-4	6-2-80	1540	0.08	0.38	ND	ND	0.09	0.28	ND
RSS-5	6-2-80	1555	0.13	0.29	0.40	0.20	0.62	1.4	ND
RSS-6A	6-2-80	1615	540	270	2000	650	260	1800	240
RSS-6B	6-2-80	1615	<240	<48	24000	17000	1300	1400	<15
RSS-7	6-2-80	1715	190	7.8	1100	760	11	340	ND
RSS-8	6-2-80	1655	31	1.4	5.5	0.59	1.4	5.8	ND
RSS-9A	6-2-80	1648	20	<5	1900	1300	80	110	ND
RSS-9B	6-2-80	1648	ND	ND	ND	ND	0.01	ND	ND
RSS-10	6-3-80	1420	0.30	0.03	0.41	0.07	0.06	0.26	ND
DETECTION LIMITS			0.01	0.02	0.008	0.008	0.004	0.004	1
*NOT DETECTED									

ANALYTICAL DATA REPORTING SHEET

PROJECT 624, VELSICOL, ST. LOUIS, MICHIGAN

TABLE III, GENERAL ORGANICS DATA, QUALITY CONTROL DATA, SEDIMENT

STATION NUMBER	DATE	TIME	HBB	PBB	p,p'-DDT	o,p'-DDT	p,p'-DDE	p,p'-DDD	TRIS
RSS-2			0.01	ND	0.01	ND	0.03	0.05	ND
RSS-2 duplicate			0.03	ND	0.02	ND	0.03	0.06	ND
RSS-2 spike (% recovery)			NA*	NA	76%	71%	NA	86%	NA
RSS-9B			ND	ND	ND	ND	0.01	ND	ND
RSS-9B spike (% recovery			NA	NA	NA	NA	NA	NA	88%
Blank 2	**	6-13-80	+		+		+		NA
Blank 3		7-10-80	ND	ND	ND	ND	ND	ND	NA
Blank 4		7-14-80	ND	ND	ND	ND	ND	ND	NA
Blank I		NA	NA	NA	NA	NA	NA	NA	ND
Blank II		NA	NA	NA	NA	NA	NA	NA	ND
Blank III		NA	NA	NA	NA	NA	NA	NA	ND

* NOT ANALYZED

** Blank high due to contamination from high-level samples (RSS-6A, 6B, 7 and 9A) Analyses repeated

***** RESULT QUALIFIERS *****

PNQ PRESENT BUT NOT QUANTIFIED
THE SUBJECT PARAMETER WAS PRESENT IN THE SAMPLE AT A LEVEL GREATER THAN THE LOWER LIMIT OF DETECTION FOR RELIABLE QUANTIFICATION, BUT NO QUANTIFIABLE RESULT COULD BE DETERMINED

PBL PRESENT BELOW LOWER LIMIT OF DETECTION FOR RELIABLE QUANTIFICATION
THE SUBJECT PARAMETER WAS PRESENT IN THE SAMPLE, BUT WAS NOT QUANTIFIED

NAI NOT ANALYZED DUE TO INTERFERENCE
THIS PARAMETER WAS NOT DETERMINED BECAUSE AN UNCONTROLLABLE INTERFERNCE WAS PRESENT

NA NOT ANALYZED
THE SAMPLE WAS NOT ANALYZED FOR THIS COMPONENT

ND NOT DETECTED
THIS COMPONENT WAS NOT DETECTED OR IDENTIFIED IN THE SAMPLE

********* FOOTNOTES *********

1 QUANTITATIVE MEASUREMENTS FOR VOLATILES REPRESENT SAMPLE CORRECTED FOR ANY CONTAMINATION DETECTED IN THE FIELD BLANK

2 %RECOVERY OUTSIDE THE RANGE OF [% AVERAGE RECOVERY +- 2(STD DEV)]

3 COMPONENT CONCENTRATION EXCEEDED LINEAR DYNAMIC RANGE OF MASS SPEC THE QUANTITATIVE MEASUREMENT FOR THIS COMPOUND REPRESENTS THE LEAST AMOUNT OF COMPOUND PRESENT

4 NOMINAL LOWER LIMIT OF DETECTION FOR QUANTIFICATION OF COMPOUNDS PRESENT IN 1 LITER OF WATER EXTRACTED, CONCENTRATED TO 1 MILLILITER (B/N/A)

5 NOMINAL LOWER LIMIT OF DETECTION FOR QUANTIFICATION OF COMPOUNDS IN 20 MILLILITERS OF LIQUID EXTRACTED INTO 5 MILLILITERS OF ORGANIC SOLVENT (HAZ)

6 NOMINAL LOWER LIMIT OF DETECTION FOR QUANTIFICATION OF COMPOUNDS IN 20 GRAMS OF SOLID EXTRACTED, CONCENTRATED TO 5 MILLILITERS OF ORGANIC SOLVENT (HAZ)

7 NOMINAL LOWER LIMIT OF DETECTION FOR QUANTIFICATION OF COMPOUNDS IN 5 MILLILITERS OF WATER PURGED WITH A CONSTANT VOLUME OF HELIUM (VOA)

METHOD FOR TRIS (2,3-DIBROMOPROPYL) PHOSPHATE IN SOIL AND SEDIMENTS

Extraction

1. Weigh-out a 25g portion of sample into a 250 ml erlenmeyer flask, add 60 ml of acetone to the flask and shake vigorously for 15 minutes using a wrist action shaker.

2. Allow the sample to settle and decant the solvent into a 1-liter separatory funnel containing 500 ml of distilled/deionized H_2O.

3. Repeat steps 1-2.

4. Mix the contents of the separatory funnel for approximately 15-20 seconds.

5. Extract the water with 3 successive 60 ml portions of CH_2Cl_2, combining the extracts in an erlenmeyer flask.

6. Prepare a funnel plugged with glass wool and filled with anhydrous Na_2SO_4. Remove interferences from the glass wool and sodium sulfate by washing with 30-50 ml of CH_2Cl_2. Pass the combined CH_2Cl_2 extracts through the funnel and into a 500 ml Kuderna-Danish evporative concentrator.

7. Concentrate the extract in the K-D evaporator on a hot H_2O bath to a volume of 100-150 ml.

8. Add 100 ml of hexane to the K-D evaporator containing the CH_2Cl_2 extract and continue to concentrate the extract to a volume of 10 ml.

Clean-up - Separation

Florisil Column Adsorption Chromatography

1. Prepare a 20 mm I.D. column that contains 20g of activated florisil topped with a 0.5 inch layer of anhydrous Na_2SO_4.

2. Pre-Elute the column with 50-60 ml of petroleum ether. Just prior to exposure of the Na_2SO_4 layer to air, quantitatively transfer the sample extract onto the column. Just prior to exposure of the Na_2SO_4 layer to air, add the first eluting solvent, 200 ml of 6% ethyl ether in petroleum ether. Collect the eluate in a 250 ml erlenmeyer flask. Perform the second elution with 200 ml of 15% ethyl ether in petroleum ether, the third elution with 400 ml of 50% ethyl ether in petroleum ether (use a 500 ml erlenmeyer to collect this fraction), and the fourth elution with 200 ml of 100% ethyl ether. The Tris will elute within the 50% and 100% fractions, so the first two fractions collected may be discarded.

3. Quantitatively transfer the 50% and 100% fractions to separate 500 ml round-bottom flasks. To each flask add 40 ml of CH_3OH and a teflon boiling chip.

4. Exchange the Tris from the ethyl ether/petroleum ether extracts into the CH_3OH by evaporating off the solvents using a rotary-evaporator under vacuum and a hot H_2O bath set to 50°C. Evaporate to a final volume of less than 5 ml.

5. Quantitatively transfer the extract to a graduated centrifuge tube and bring up to a volume of 5 ml with CH_3OH.

6. Transfer the extract to a clean screw-cap type vial fitted with a teflon-liner.

7. Store the extract in a refrigerator until it can be analyzed for Tris by HPLC.

8. Eluate composition - 91-95% of the Tris will elute with the 50% ethyl ether-petroleum ether fraction, while the remaining Tris will elute with the 100% ethyl ether fraction. The composition of the eluate should be checked for each new batch of Florisil with a known amount of Tris.

See Method For Organochlorine Pesticides in Soil and Sediment - Table V for Quality Control data

0.12.5 2

NEUTRAL EXTRACTION TECHNIQUE FOR ORGANICS ANALYSIS

March 1979

1.0 Scope and Application

1.1 This procedure is applicable to the analysis of water and wastewater samples for a broad spectrum of organic pollutants.

2.0 Summary of Method

2.1 Water and wastewater samples are extracted with CH_2Cl_2 (dichloromethane) at a neutral pH. The extract is dried and concentrated with the addition of acetone or iso-octane to exchange solvents. The resultant extract concentrate is subjected to GC and GC/MS analysis to identify and quantitate the organic pollutants present.

3.0 Sample Handling and Preservation

3.1 Prior to extraction, samples are refrigerated and extracted as soon as possible, generally within 48 hours. Samples may be held 5 days or more if necessary.

4.0 Definitions and Comments

5.0 Interferences

5.1 Solvents, glassware and reagents could be sources of contamination. Therefore, reagent blanks must be prepared contacting the solvent with all potential sources of contamination. This blank should then be processed through the same analytical scheme as the associated samples.

5.2 Typical interferences from reagents are: 4-methyl-4-hydroxy-2-pentanone (diacetone alcohol) from acetone and phthalate esters from Na_2SO_4, cyclohexene from dicholormethane.

6.0 Apparatus

6.1 Separatory funnels: 2 l and 4 l glass with glass or teflon stoppers and stopcocks. No stopcock grease used.

6.2 Drying column: All glass 3 cm x 50 cm with attached 250 ml reservoir.

6.3 Concentrator: 250 or 500 ml Kuderna-Danish evaporative concentrator equipped with a 5 or 10 ml receiver ampule and a 3 ball Snyder column.

7.0 Reagents

7.1 Extraction solvent: Pesticide analysis grade CH_2Cl_2 (dichloromethane) (Burdick and Jackson or equivalent)

7.2 Exchange solvents

7.2.1 Exchange solvent: Pesticide analysis grade acetone (Burdick and Jackson or equivalent)

7.2.2 Exchange solvent: Iso-octane suitable for pesticide analysis (Burdick and Jackson or equivalent)

7.3 Drying agent: Analytical reagent grade granular anhydrous Na_2SO_4 (sodium sulfate). Washed with CH_2Cl_2 prior to use.

7.4 Glass wool that has been extracted with CH_2Cl_2 prior to use.

7.5 6N NaOH for pH adjustment.

7.6 6N HCl for pH adjustment.

7.7 pH paper for pH measurement.

8.0 Procedure

8.1 If low concentrations of pollutants are expected, measure 3 l of sample for extraction. Otherwise, one liter is sufficient.

8.2 Measure and record the initial pH. Adjust the pH to 6-8 if necessary, and record the adjusted pH.

8.3 Extract the sample with 3 successive extractions of 100, 50 and 50 ml of CH_2Cl_2 for 1 liter samples and 200, 100, 100 ml of CH_2Cl_2 for 3 liter samples.

If emulsions form, use a wire or stirring rod to break it, pass the emulsion through glass wool or centrifuge if necessary. Combine the extracts and measure the volume recovered. 85 percent constitutes an acceptable recovery.

8.4 Place a glass wool plug in a drying column and add ca 10 cm of Na_2SO_4. Wash the Na_2SO_4 with at least 50 ml of CH_2Cl_2. Pour the combined extract through the column. Follow with 100 ml of acetone. Collect the CH_2Cl_2 and acetone and transfer to a KD assembly. Add 2 ml of iso-octane for 1 liter extracts and 5 ml iso-octane for 3 liter extracts.

8.5 Concentrate on a hot water bath at 80 - 90°C until the extract stops boiling. Quantitatively transfer the receiving tube contents to a graduated centrifuge tube. Adjust the volume to 2 or 5 ml by either adding more iso-octane or evaporating the excess iso-octane under a gentle stream of carbon filtered air. Transfer to a 12 ml vial and cap with a teflon lined cap. (Note: The final extract volume should depend on the sample. Extracts containing high concentrations of pollutants may only require concentrations to 5 ml while cleaner samples may require a final volume of 2 ml).

9.0 Quality Control Procedures

9.1 Reagent blanks are prepared by contacting an equivalent amount of solvent with reagents and glassware in order to detect contaminants.

9.2 Duplicate extractions are prepared by thoroughly mixing a sample, splitting it into two aliquots, extracting and analyzing each aliquot. Duplicate extractions measure the precision of the overall analytical scheme.

9.3 Spiked samples are prepared by thoroughly mixing a sample, splitting into two aliquots, spiking one with the compounds of interest, extracting and analyzing each aliquot. The sample should be spiked with the compounds of interest at levels between 50 and 200% of the original concentration. Spikes measure the accuracy of the method.

9.4 These audits are done for two samples for batches of 20 or less samples and one sample for each additional 20 samples.

10.0 Calculations

10.1 Solvent Recovery:
% recovery = Volume recovered (ml)*100/volume added (ml)

10.2 Pollutant Recovery:

$$\% \text{ recovery} = \frac{(\text{Concentration measured} - \text{initial concentration})*100}{\text{Concentration added}}$$

11.0 Precision and Accuracy

11.1 Table I is a summary of the results of analysis of 4 samples of tap water spiked at 100 ug/l with each component for each exchange solvent. Individual recoveries reflect the accuracy of the analysis for each component. Overall, the average bias is -19 and -17 percent for the acetone and iso-octane exchange solvents respectively.

11.2 The table also shows the precision of the analysis for each component for each exchange solvent. The average percent standard deviations for acetone and iso-octane exchange solvents are 28 and 15 percent respectively. These data show that use of iso-octane as an exchange solvent improves the precision of the analysis.

The precision of the recoveries across components is also enhanced by the use of iso-octane vs. acetone. This is shown by the standard deviations of the overall average component recoveries of 14 and 35 percent respectively.

12.0 References

(1) "An EPA GC/MS Procedural Manual - Review Copy", Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

Table I - Recovery of organic compounds at 100 ppb from tap water.
Data collected in February 1979.

Compound Name	Acetone Exchange Mean[a] Recovery	Acetone Exchange Recovery Rel. St. Dev.	Iso-Octane Exchange Mean Recovery	Iso-Octane Exchange Recovery Rel. St. Dev.
Bis(2-chloroethyl) ether	92	24	95	12
1,3-Dichlorobenzene	76	21	83	17
1,4-Dichlorobenzene	78	18	82	11
1,2-Dichlorobenzene	80	18	84	13
Hexachloroethane-nitrobenzene	90	21	103	10
Isophorone	97	17	111	7
1,2,4-Trichlorobenzene	82	15	86	15
Naphthalene	88	19	97	16
Hexachlorobutadiene	68	17	50	18
2-Chloronaphthalene	84	20	92	12
Acenaphthalene	80	17	89	10
Dimethyl Phthalate	100	26	82	33
Acenaphthene	82	16	92	9
2,4-Dinitrotoluene	88	29	92	22
Fluorene	69	17	88	7
Diethyl Phthalate	83	23	82	12
n-Nitrosodiphenylamine (Diphenyl Amine)	68	32	90	13
4-Bromodiphenyl Ether	60	21	87[b]	11
Hexachlorobenzene	54	16	94	27
Phenanthrene	54	16	80	18
Anthracene	50	29	70	15
Di-n-Butyl Phthalate	66	53	76	13
Fluoranthene	49	48	65	19
Pyrene	56	44	68	15
Butylbenzyl Phthalate	230[b]	18	54	26
Ethylhexyl Phthalate	118[c]	83	67	15
Average	81	28	83	15
Standard deviation	35		14	

[a] Mean recovery is average of 4 analyses.

[b] Average determined from 3 analyses.

[c] Average determined from 2 analyses.

ORGANIC CHARACTERIZATION
QUALITY CONTROL REPORT

Table II

PROJECT 624 STATION RSS 1 SEQUENCE spike DATE 6/2/80 TIME 1400 TAC# ____

DESCRIPTION River sediment sample - upstream near St Louis water tower - mid stream

NAME	DUPLICATES UNITS ____ FIRST	SECOND	%DIFFERENCE	SPIKE UNITS ug/g LEVEL	%RECOVERY
Bromobenzene				20	50
1,2,4-trimethyl benzene				20	65
Sec. butyl bromide				20	50
p-dibromobenzene				20	50
3,5-dichlorophenol				60	50
Diethyl phthalate				20	100
Diphenyl amine				20	65
1,1-diphenyl hydrazine				20	110
Di-n-butyl phthalate				20	65
4,4-dibromo biphenyl				20	60

%DIFFERENCE = 2 * 100 * (SECOND - FIRST)/(SECOND + FIRST)
%RECOVERY = 100 * RECOVERED/LEVEL

ORGANIC CHARACTERIZATION
QUALITY CONTROL REPORT

Table II (Cont.)

PROJECT 624 STATION RS58 SEQUENCE dup. DATE 6/3/80 TIME 1655 TAG# 1645

DESCRIPTION On transect 150' from north shore.

NAME	DUPLICATES UNITS ug/g FIRST	SECOND	%DIFFERENCE	SPIKE UNITS ____ LEVEL	%RECOVERY
undecane	4	---	100		
dodecane	---	6	100		
tridecane	4	6	40		
tetradecane	4	5	20		
pentadecane	5	5	0		
hexadecane	---	3	100		
heptadecane	3	5	50		
chlorobenzene	2	---	100		
o,p-DDD	PNQ	PNQ			
p,p-DDD	PNQ	PNQ			

%DIFFERENCE = 2 * 100 * (SECOND - FIRST)/(SECOND + FIRST)
%RECOVERY = 100 * RECOVERED/LEVEL

ORGANIC CHARACTERIZATION
QUALITY CONTROL REPORT

Table II (Cont.)

PROJECT 624 STATION ~~Spike~~ RW56 SEQUENCE 02 DATE 6/5/80 TIME 12:30 TAC# 1568

DESCRIPTION 80' from north shore on transect off Jetty

NAME	DUPLICATES UNITS ____ FIRST	SECOND	%DIFFERENCE	SPIKE UNITS ug/l LEVEL	%RECOVERY
1,2,4-trichlorobenzene	------	------	------	125	32
Isophorone	------	------	------	125	40
Acenaphthene	------	------	------	125	40
2,4-dinitrotoluene	------	------	------	125	80
Di-n-butyl phthalate	------	------	------	125	80
Pyrene	------	------	------	125	80
Phenol	------	------	------	125	24
2-Chlorophenol	------	------	------	125	32
2,4-dinitrophenol	------	------	------	250	-0-
Pentachlorophenol	------	------	------	250	-0-
------	------	------	------	------	------
------	------	------	------	------	------
------	------	------	------	------	------
------	------	------	------	------	------
------	------	------	------	------	------

%DIFFERENCE = 2 * 100 * (SECOND - FIRST)/(SECOND + FIRST)
%RECOVERY = 100 * RECOVERED/LEVEL

ORGANIC CHARACTERIZATION
QUALITY CONTROL REPORT

Table II (Cont.)

PROJECT 6024 STATION SS 25 SEQUENCE spike DATE 6/4/80 TIME 1710 TACH ____

DESCRIPTION 60 ft. east of WP 5 between rare earth barrels & NW corner of dredge pond.

NAME	DUPLICATES UNITS ____ FIRST	SECOND	%DIFFERENCE	SPIKE UNITS ug/g LEVEL	%RECOVERY
Bromobenzene	------	------	------	20	55
1,3,4-trimethylbenzene	------	------	------	20	55
sec butyl bromide	------	------	------	20	50
p-dichlorobenzene	------	------	------	20	50
3,5-dichlorophenol	------	------	------	60	38
diethyl phthalate	------	------	------	20	90
diphenylamine	------	------	------	20	55
1,1-diphenylhydrazine	------	------	------	20	60
Di-n-butyl phthalate	------	------	------	20	85
4,4-dibromobiphenyl	------	------	------	20	50
----------	------	------	------	------	------
o,p DDT	* P&Q	P&Q	------	------	------
p,p DDT	P&Q	P&Q	------	------	------
o,p DDD	ND	P&Q	------	------	------
----------	------	------	------	------	------

P&Q = present and quantitated

Spike considered as duplicate in order to determine presence of DDT & DDD

%DIFFERENCE = 2 * 100 * (SECOND - FIRST)/(SECOND + FIRST)
%RECOVERY = 100 * RECOVERED/LEVEL

ORGANIC CHARACTERIZATION
QUALITY CONTROL REPORT

Table II (Cont.)

PROJECT 624 STATION SS24 SEQUENCE dup DATE 6/4/80 TIME 1655 TAC# 1795

DESCRIPTION 25 ft. east of DIM-6 next to intake pump

NAME	DUPLICATES UNITS _____ FIRST	SECOND	%DIFFERENCE	SPIKE UNITS _____ LEVEL	%RECOVERY
no compds detected & quantitated					
o,p - DDT	*P&Q	PNQ			
p,p - DDT	P&Q	PNQ			
o,p - DDD	---	PNQ			

* P&Q = present and quantitated

%DIFFERENCE = 2 * 100 * (SECOND - FIRST)/(SECOND + FIRST)
%RECOVERY = 100 * RECOVERED/LEVEL

***** RESULT QUALIFIERS *****

PNQ PRESENT BUT NOT QUANTIFIED
THE SUBJECT PARAMETER WAS PRESENT IN THE SAMPLE AT A LEVEL GREATER THAN THE LOWER LIMIT OF DETECTION FOR RELIABLE QUANTIFICATION, BUT NO QUANTIFIABLE RESULT COULD BE DETERMINED

PBL PRESENT BELOW LOWER LIMIT OF DETECTION FOR RELIABLE QUANTIFICATION
THE SUBJECT PARAMETER WAS PRESENT IN THE SAMPLE, BUT WAS NOT QUANTIFIED

NAI NOT ANALYZED DUE TO INTERFERENCE
THIS PARAMETER WAS NOT DETERMINED BECAUSE AN UNCONTROLLABLE INTERFERNCE WAS PRESENT

NA NOT ANALYZED
THE SAMPLE WAS NOT ANALYZED FOR THIS COMPONENT

ND NOT DETECTED
THIS COMPONENT WAS NOT DETECTED OR IDENTIFIED IN THE SAMPLE

********* FOOTNOTES *********

1 QUANTITATIVE MEASUREMENTS FOR VOLATILES REPRESENT SAMPLE CORRECTED FOR ANY CONTAMINATION DETECTED IN THE FIELD BLANK

2 %RECOVERY OUTSIDE THE RANGE OF [% AVERAGE RECOVERY +- 2(STD DEV)]

3 COMPONENT CONCENTRATION EXCEEDED LINEAR DYNAMIC RANGE OF MASS SPEC THE QUANTITATIVE MEASUREMENT FOR THIS COMPOUND REPRESENTS THE LEAST AMOUNT OF COMPOUND PRESENT

4 NOMINAL LOWER LIMIT OF DETECTION FOR QUANTIFICATION OF COMPOUNDS PRESENT IN 1 LITER OF WATER EXTRACTED, CONCENTRATED TO 1 MILLILITER (B/N/A).

5 NOMINAL LOWER LIMIT OF DETECTION FOR QUANTIFICATION OF COMPOUNDS IN 20 MILLILITERS OF LIQUID EXTRACTED INTO 5 MILLILITERS OF ORGANIC SOLVENT (HAZ)

6 NOMINAL LOWER LIMIT OF DETECTION FOR QUANTIFICATION OF COMPOUNDS IN 20 GRAMS OF SOLID EXTRACTED, CONCENTRATED TO 5 MILLILITERS OF ORGANIC SOLVENT (HAZ)

7 NOMINAL LOWER LIMIT OF DETECTION FOR QUANTIFICATION OF COMPOUNDS IN 5 MILLILITERS OF WATER PURGED WITH A CONSTANT VOLUME OF HELIUM (VOA)

8. LLD is the lower limit of detection.

9. Detection limit based upon the response of a straight chain saturated hydrocarbon of MW 250.

MCBD-1X0-1

TOXICITY OF COMPOUNDS
PINE RIVER
St. Louis, Michigan

Compound Name	Molecular Formula	Chemical Abstracts Service No.	Aquatic Toxicity[a]	Other Toxicity Data[b]						Exposure Limits[e]
				Route of Entry - Species	Type of Dose	Dose	Duration[c]	Effects[d]		
Benzene, Chloro-	C_6H_5Cl	108-90-7[f]	TLm 96: 100-1 ppm	Oral-rat	LD50:	2,910 mg/kg				TLV (air). 75 ppm
				Subcutaneous-rat	LDLo.	7,000 mg/kg				
				Oral-rabbit	LD50:	2,830 mg/kg				OSHA std (air). TWA 75 ppm
				Intraperitoneal-rat	LDLo.	7,400 mg/kg				
				Intraperitoneal-guinea pig	LDLo:	4,100 mg/kg				
				Inhalation-mouse	LCLo:	15 gm/m³				
Benzene, 1,2-dichloro-	$C_6H_4Cl_2$	95-50-1[f]		Oral-human	LDLo	500 mg/kg				TLV (air): 50 ppm
				Oral-rat	LD50:	500 mg/kg				
				Inhalation-rat	LCLo:	821 ppm	7H			OSHA std (air) Cl 50 ppm
				Intraperitoneal-rat	LD50	840 mg/kg				
				Intravenous-mouse	LDLo	400 mg/kg				
				Oral-rabbit	LD50:	500 mg/kg				
				Intravenous-rabbit	LDLo.	250 mg/kg				
				Oral-guinea pig	LDLo:	2,000 mg/kg				
				Inhalation-guinea pig	LCLo:	800 ppm	24H			
				Eye-rabbit		100 mg	30 sec	Mild Irritation		
Benzene, 1,4-dichloro-	$C_6H_4Cl_2$	106-46-7[f]		Oral-human	LDLo:	500 mg/kg				TLV (air): 75 ppm
				Oral-human	TDLo·	300 mg/kg		Systemic Irritation		
				Eye-human		80 ppm				OSHA std (air): TWA 75 ppm
				Oral-rat	LD50:	500 mg/kg				
				Intraperitoneal-rat	LD50.	2,562 mg/kg				
				Oral-mouse	LD50	2,950 mg/kg				
				Subcutaneous-mouse	LD50.	5,145 mg/kg				
				Oral-guinea pig	LDLo	2,800 mg/kg				
				Unreported-man	LDLo:	221 mg/kg				
Benzene, 1,2,4-trichloro-	$C_6H_3Cl_3$	120-82-1[f]	TLm 96 10-1 ppm	Oral-rat	LD50:	756 mg/kg				TLV (air): 5 ppm
				Oral-mouse	LD50:	766 mg/kg				
				Intraperitoneal-mouse	LDLo.	500 mg/kg				
				Skin-rabbit		1,950 mg	13WI	Moderate Irritation		
Benzophenone, 4,4'- Dichloro-	$C_{13}H_8Cl_2O$	90-98-2		Intraperitoneal-mouse	LD50:	200 mg/kg				
Ethane, 1,1-Dichloro-2,2-Bis(p-Chlorophenyl)- [DDD]	$C_{14}H_{10}Cl_4$	72-54-8[f]		Oral-human	LDLo:	5,000 mg/kg				
				Oral-rat	LD50.	113 mg/kg				
				Oral-rat	TDLo:	54 gm/kg	78WC	Equivocal Tumorigenic Agent		
				Oral-mouse	TDLo:	39 gm/kg	2YC	Neoplastic		
				Skin-rabbit	LD50:	1,200 mg/kg				
				Bacteria-S. Marcescens-mouse		1,500 mg/kg		Mutation		

TOXICITY OF COMPOUNDS
PINE RIVER
St. Louis, Michigan

Compound Name	Molecular Formula	Chemical Abstracts Service No.	Aquatic Toxicity[a]	Other Toxicity Data[b]						Exposure Limits[e]
				Route of Entry	Species	Type of Dose	Dose	Duration[c]	Effects[d]	
Ethylene, 1,1-Dichloro-2,2-Bis(p-Chlorophenyl)-[DDE]	$C_{14}H_8Cl_4$	72-55-9[f]		Oral-rat		LD50	880 mg/kg			
				Oral-mouse		LDLo	200 mg/kg			
				Oral-mouse		TDLo:	28 gm/kg	80WC	Neoplastic	
				Oral-mouse		TD.	17 gm/kg	78WC	Carcinogenic	
				Lymphocyte-somatic cells-mouse			40 mg/L	4H	Mutation	
				Oral-mouse		TDLo:	9,700 mg/kg	78WC	Carcinogenic	
Ethane, 2-(o-Chlorophenyl)-2-(p-Chlorophenyl)-1,1,1-Trichloro-[o,p'-DDT]	$C_{14}H_9Cl_5$	789-02-6		Oral-mouse		LDLo:	1,000 mg/kg			
Ethane, 1,1,1-Trichloro-2,2-Bis(p-Chlorophenyl)-[p,p'-DDT]	$C_{14}H_9Cl_5$	50-29-3[f]	TLm 96 under 1 ppm	Oral-infant		LDLo.	150 mg/kg			TLV (air) 1mg/m^3
				Oral-human		TDLo:	6 mg/kg		Central Nervous System	OSHA std (air) TWA 1 mg/m^3 (skin)
				Unreported-man		LDLo:	221 mg/kg			
				Oral-rat		LD50:	113 mg/kg			
				Oral-rat		TDLo:	14 gm/kg	80WC	Neoplastic	
				Skin-rat		LD50:	1,931 mg/kg			
				Intraperitoneal-rat		LD50:	225 mg/kg			
				Subcutaneous-rat		LD50.	1,500 mg/kg			
				Intravenous-rat		LDLo.	30 mg/kg			
				Oral-mouse		LD50:	135 mg/kg			
				Oral-mouse		TDLo:	73 mg/kg	26WC	Carcinogenic	
				Intraperitoneal-mouse		LD50:	280 mg/kg			
				Subcutaneous-mouse		TDLo:	200 mg/kg	40WI	Carcinogenic	
				Oral-dog		LDLo:	300 mg/kg			
				Intravenous-dog		LDLo.	75 mg/kg			
				Intravenous-monkey		LDLo·	50 mg/kg			
				Oral-cat		LDLo:	250 mg/kg			
				Intravenous-cat		LDLo:	40 mg/kg			
				Oral-rabbit		LD50·	250 mg/kg			
				Skin-rabbit		LD50:	300 mg/kg			
				Subcutaneous-rabbit		LD50·	250 mg/kg			
				Intravenous-rabbit		LDLo.	50 mg/kg			
				Oral-guinea pig		LD50:	150 mg/kg			
				Skin-guinea pig		LD50:	1,000 mg/kg			
				Subcutaneous-guinea pig		LD50.	900 mg/kg			
				Oral-chicken		LDLo	300 mg/kg			
				Subcutaneous-frog		LD50	35 mg/kg			
				Oral-domestic		LDLo:	300 mg/kg			
				Lymphocyte-somatic cells-human			200 ug/l	72H	Mutation	
				Oral-rat			100 mg/kg		Mutation	
				Oral-monkey		LD50:	200 mg/kg			
				Oral-mouse		TD	11 gm/kg	78WC	Equivocal Tumorigenic Agent	

TOXICITY OF COMPOUNDS
PINE RIVER
St. Louis, Michigan

Compound Name	Molecular Formula	Chemical Abstracts Service No.	Aquatic Toxicity[a]	Other Toxicity Data[b]						Exposure Limits[e]
				Route of Entry	Species	Type of Dose	Dose	Duration[c]	Effects[d]	
Methoxychlor	$C_{16}H_{15}Cl_3O_2$	72-43-5		Oral-human		LDLo·	6,430 mg/kg			
				Skin-human		TDLo:	2,414 mg/kg			
				Oral-rat		TDLo	2,000 mg/kg	6-15D (preg)	Teratogenic	
				Oral-rat		LD50:	5,000 mg/kg			
				Oral-rat		TDLo:	2,000 mg/kg	6-15D (preg)	Teratogenic	
				Intrapentoneal-vat		LDLo	500 mg/kg			
				Oral-mouse		LD50.	1,850 mg/kg			
1-Propanol, 2,3,- Dibromo-	$C_3H_6Br_2O$	96-13-9		Intraperitoneal-mouse		LDLo:	125 mg/kg			
Styrene, chloro-	C_8H_7Cl	1331-28-8		Skin-rabbit			10 mg	24H	Irritation	TLV (air): 50 ppm
				Eye-rabbit			500 mg		Irritation	
				Oral-rat		LD50:	5,200 mg/kg			
				Skin-rabbit		LD50·	20 gm/kg			

HBB

PBB.

TRIS
tris(2,3-dibromopropyl) phosphate

TOXICITY OF COMPOUNDS
PINE RIVER
St. Louis, Michigan

a Aquatic Toxicity: TLm 96: 96-hour static or continuous flow standard protocol, in parts per million (ppm)

b Type of Dose
- LD50 - lethal dose 50% kill
- LCLo - lowest published lethal concentration
- LC50 - lethal concentration 50% kill
- LDLo - lowest published lethal dose
- TDLo - lowest published toxic dose
- TCLo - lowest published toxic concentration
- TD - toxic dose

c Duration
- M - minute,
- H - hour
- D - day
- W - week
- Y - year
- C - continuous
- I - intermittent

d Effects
- Blood - Blood effects; effect on all blood elements, electrolytes, pH, protein, oxygen carrying or releasing capacity.
- Carcinogenic - Carcinogenic effects, producing cancer, a cellular tumor the nature of which is fatal, or is associated with the formation of secondary tumors (metastasis).
- Central Nervous System - Includes effects such as headaches, tremor, drowsiness, convulsions, hypnosis, anesthesia.
- Eye - Irritation, diplopia, cataracts, eye ground, blindness by affecting the eye or the optic nerve.
- Gastrointestinal - diarrhea, constipation, ulceration
- Irritation - Any irritant effect on the skin, eye or mucous membrane.
- Mutation - Transmissible changes produced in the offspring
- Neoplastic - The production of tumors not clearly defined as carcinogenic.
- Psychotropic - Exerting an effect upon the mind.
- Pulmonary - Effects on respiration and respiratory pathology.
- Systemic - Effects on the metabolic and excretory function of the liver or kidneys.
- Teratogenic - Nontransmissible changes produced in the offspring.
- Equivocal Tumorigenic Agent - those studies reporting uncertain, but seemingly positive results.

e Exposure Limits.
- NR - not reported
- NIOSH - National Institute for Occupational Safety and Health
- OSHA - Occupational Safety and Health Act of 1970
- TWA - time-weighted average concentration
- TLV - threshold limit value
- Cl - ceiling
- Pk - peak concentration

f This chemical has been selected for priority attention as point source water effluent discharge toxic pollutant (NRDC vs Train consent decree)

APPENDIX C

TOXIC DATA COMPILATION METHODS

TOXIC DATA COMPILATION METHODS

Fourteen compounds were identified in the water and/or sediment samples collected during the Pine River Investigation. Seven of the fourteen compounds are listed as priority pollutants.

To obtain toxicity and health effects information for the 14 compounds, two main sources were used. Those compounds for which toxic information was not located are listed in the conclusion.

REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS)

RTECS contains toxicity data for about 37,000 substances, but does not presently include all chemicals for which toxic effects have been found. Chemical substances in RTECS have been selected primarily for the toxic effect produced by single doses, some lethal and some non-lethal. Substances whose principal toxic effect is from chronic exposure are not presently included. Toxic information on each chemical substance was compiled from published medical, biological engineering, chemical and trade information.

The RTECS search yielded information on 12 of the 14 compounds.

TOXICOLOGY INFORMATION ONLINE (TOXLINE)

The Toxline data base, a computerized bibliographic retrieval system for toxicology, contains 692,394 records taken from material published in primary journals, was also searched. It is part of the MEDLARS system from the National Library of Medicine and is composed of 11 subfiles:

1. Chemical-Biological Activities, 1965-
   (Taken from Chemical Abstracts, Section 1-5, Sections 62-64, Section 8 - Radiation Biochemistry, Section 59 - Air Pollution and Industrial Hygiene, and Section 60 - Sewage Wastes.)

2. Toxicity Bibliography, 1968-
   (A subset of Medline)

3. Pesticides Abstracts, 1966-
   (Compiled by the Environmental Protection Agency and formerly known as Health Aspects of Pesticides Abstracts Bulletin.)

4. International Pharmaceutical Abstracts, 1970-
   (Product of the American society of Hospital Pharmacists)

5. Abstracts on Health Effects of Environmental Pollutants, 1972-
   (Comprised of profiles from BIOSIS data bases only)

6. Hayes File on Pesticides, 1940-1966
   (A collection of more than 10,000 citations to published articles on the health aspects of pesticides)

7. Environmental Mutagen Information Center File, 1960-
   (Prepared at the Environmental Mutagen Information Center, Oak Ridge National Laboratory, Tennessee.)

8. Toxic Materials Information Center File, 1971-1975
   (Prepared at the Oak Ridge National Laboratory, Oak Ridge, Tennessee.)

9. Tetratology File, 1960-1974
   (Closed subfile of citations on tetratology)

10. Environmental Tetratology Information Center File, 1950-
    (From the Oak Ridge National Laboratory, Oake Ridge, Tennessee)

11. Toxicology/Epidemiology Research Projects, October 1978-
    (Projects selected from the Smithsonian Science Information Exchange - SSIE data base.)

The Toxline search yielded 7,539 citations from the 14 compounds, providing support to the toxic data from RTECS.

ADDITIONAL SOURCES

Additional sources searched to locate toxic information were: (1) Merck Index; (2) Toxicology Data Bank (TDB) from the National Library of Medicine, which currently contains information on 2,514 substances; (3) Oil and Hazardous Materials Technical Assistance Data System (OHMTADS), an EPA file containing toxic data for about 1,000 compounds.

COMPOUNDS NOT LOCATED

Specific toxic data from RTECS were not located for the following compounds detected in the water and/or sediment samples:

HBB (Hexabromobenzene)
PBB (Polybrominated Biphenyls)

However, there is an abundance of information in the published literature (EPA reports, laboratory animal toxicity studies, aquatic studies and epidemiological studies) on the adverse effects of these 2 compounds.

Hexa bromo biphenyl DV5330000 RTECS.
skn irbt - LD_{50} = 5 g/kg.
Octa bromo biphenyl DV5700000
LD_{50} rat p.o. = 2800 mg/kg