ESTIMATING RELEASES AND WASTE-TREATMENT EFFICIENCIES FOR THE TOXIC CHEMICAL RELEASE INVENTORY FORM

Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986

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- p. 3-14 Example 3-7 illustrates use of an engimeering calculation, not an emission factor, to estimate releases to air from material storage.
- p. B-4 Center of page under the Claussius-Clapeyron equation. Grams or pounds should be divided by molecular weight, not multiplied, to convert to g-moles.
- p. B-8 The vapor pressure for 1,2-Dibromoethane, CAS No. 106-93-4, should be 11.7 mm Hg instead of 1117 mm Hg.
- p. B-12 The vapor pressure of 10 mm Hg at 31°C for sulfuric acid, CAS No. 7664-93-9, is incorrect. This value was obtained from the 62nd edition of the CRC Handbook of Chemistry and Physics. A more appropriate value is 0.0117 mm Hg at 30°C for 90% H₂SO₄ concentrations (Perry's Chemical Engineering Handbook) or less than 0.001 mm Hg for 93-98% concentrations at ambient temperature (NIOSH Pocket Guide to Chemical Hazards).

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SECTION 1

INTRODUCTION

Under a new Federal law, the Emergency Planning and Community Right-to-Know Act of 1986, certain chemical manufacturers, processors, and users are required to report total annual releases of listed toxic chemicals to air, water, and land. These reporting requirements, which are outlined in Section 313 of Title III of Superfund Amendments and Reauthorization Act of 1986 (SARA), specify that both routine and accidental releases be reported.

The regulations that implement this reporting requirement describe its applicability in detail. In summary, your facility is subject to the reporting requirements if all of the following apply:

- o It has 10 or more full-time employees.
- It conducts manufacturing operations (i.e., if it is included in Standard Industrial Classification Codes 20 through 39).
- It manufactures, processes, or in any other way uses any of the listed toxic chemicals in amounts greater than the threshold quantities.

The threshold quantities for manufacturers and processors are as follows:

- ° 75,000 pounds during the 1987 calendar year
- ° 50,000 pounds during the 1988 calendar year
- 25,000 pounds during the 1989 calendar year and in subsequent years

The threshold quantities for users are as follows:

° 10,000 pounds during the 1987 calendar year and in subsequent years

Each facility must complete and file the Toxic Chemical Release Inventory Reporting Form (hereinafter referred to as "Form") for each listed chemical or listed chemical category for which it meets or exceeds the preceding thresholds. For chemical categories based on metal content (e.g., copper compounds), releases of the metal, in whatever form, are to be reported (even

though the thresholds for amounts manufactured, processed, or used are based on the metal <u>compounds</u>). For other chemical categories (e.g., glycol ethers), total releases of all members of the category are to be reported.

The Form(s), which are to be filed by July of each year, cover the preceding calendar year. For example, Form(s) filed by July 1988 will cover the 1987 calendar year. Facilities are urged to consult the Code of Federal Regulations (40 CFR Part 372) to determine their legal responsibilities under Section 313 of Title III of SARA.

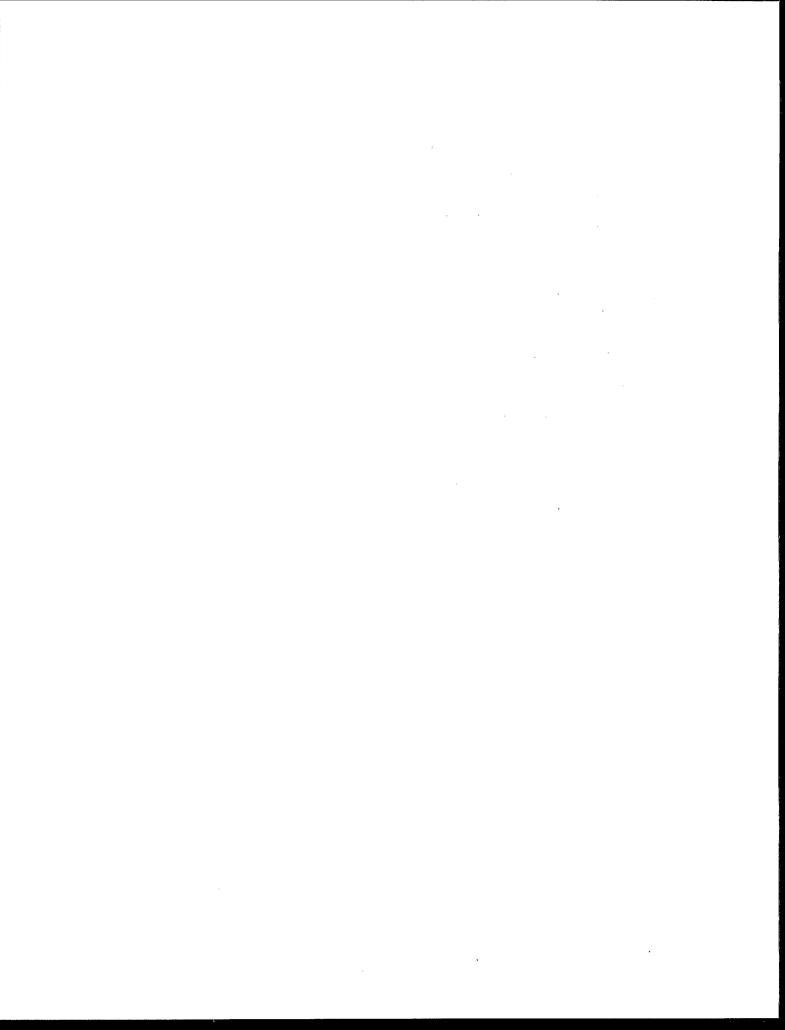
This manual provides an overview of the general methods that may be used to estimate releases subject to the reporting requirements. Examples of the application of most of the methods discussed are also included. Where possible, the manual indicates which method is likely to provide the most accurate estimate. The manual focuses on processes that may be present in facilities within Standard Industrial Classification Codes 20 through 39. It does not include methods specific to commercial service establishments, waste sites, mobile sources, etc. Sources of additional information on release estimation are also provided.

This manual is not intended to cover all possible situations; many types of releases may require case-by-case analysis and simply cannot be covered herein. Neither is its purpose to describe and/or recommend monitoring/analytical programs that might be used to generate data for completing the Form(s). Although no monitoring is required to comply with the reporting requirements, facilities are urged to use monitoring data (which may have been gathered under other regulatory programs or research efforts) wherever possible and to initiate the monitoring of waste streams, particularly where estimation techniques may be complex and result in estimates of limited accuracy.

Most users of chemicals subject to the reporting requirements will not need many of the estimation techniques covered here. In some cases, a single calculation based on available monitoring data may yield the only release estimate needed to meet the reporting requirements. In others, a few calculations based on chemical and/or physical properties may suffice. The U.S. Environmental Protection Agency (EPA) believes that many affected facilities will be able to meet the reporting requirements based on methods discussed

herein. The Agency also recognizes, however, that complex chemical manufacturing processes, "unique" uses, and other special situations present difficulties that cannot be covered here. In addition to this manual, EPA is developing other guidance manuals aimed at some specific industry segments that process or use many of the listed chemicals. The intent of these manuals is to provide industry-specific guidance for estimating toxic emissions. (Reference numbers will be provided when the documents are available.)

Section 2 of this manual presents an overview of the information that must be reported and the various types of analyses that a facility can use. Sections 3, 4, and 5 describe methods specific to estimating air releases, water releases, and "solid" waste releases, respectively. Section 6 briefly describes procedures that may be used for estimating accidental releases. Examples are provided throughout the manual to illustrate sources of information, manipulation of data, and calculation procedures. Section 7 presents a set of examples for estimating overall releases from an individual facility.



OUTLINE FOR SECTION 2 GENERAL PRINCIPLES AND CONSIDERATIONS

- 2.1 Data to be Reported
- 2.2 Sources of Wastes/Releases
- 2.3 An Overview of the Analysis
- 2.4 Definitions of Major Approaches
- 2.5 Some Observations on the Use of Data
- 2.6 Which Approach to Use
 - 2.6.1 Fugitive Air Emissions
 - 2.6.2 Point Source Air Emissions
 - 2.6.3 Releases to Wastewater
 - 2.6.4 Releases in Solids, Slurries, and Nonaqueous Liquids

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SECTION 2

GENERAL PRINCIPLES AND CONSIDERATIONS

This section briefly describes the data that a facility must report and discusses information that is necessary for the facility to generate the data required to complete the Form. If you have not already familiarized yourself with the Form and the reporting requirements, it would be helpful to do so before proceeding.

2.1 DATA TO BE REPORTED

Items 5 and 6 in Part III of the Form require the following releases of the chemical be reported (in pounds per year):

- To air from fugitive or nonpoint sources
- To air from stack or point sources
- ° To water directly discharged to a receiving stream
- ° In wastes that are injected underground
- To land on site (including landfills, surface impoundments, or landspreading)
- To water discharged to a publicly owned treatment works (POTW)
- ° In other wastes transferred offsite for treatment or disposal.

Quantities reported on the Form should reflect the amounts of chemical released after any onsite treatment and are specific to the chemical, metal, or chemical category subject to reporting. These quantities should <u>not</u> reflect the total quantity of waste or constituents of the waste that are <u>not</u> subject to the reporting requirements.

Part III, Item 7, of the Form requires reporting of the percentage by which any onsite treatment of any wastes containing the listed chemical

reduces the amount of that <u>chemical</u> in the wastestream (weight percent reduction). The instructions for the Form specify how to list the treatment method, by code, and the concentration of the chemical in the waste prior to treatment.

2.2 SOURCES OF WASTES/RELEASES

All sources of wastes should be considered in estimating releases of a chemical from your facility. Sources include but are not limited to the following:

Fugitive air sources

- Volatilization from open vessels, waste-treatment facilities, spills, and/or shipping containers
- Leaks from pumps, valves, and/or flanges
- Building ventilation systems

Stack or point air sources

- Vents from reactors and other process vessels
- Storage tank vents
- Stacks or vents from pollution control devices, incinerators, etc.

Water sources

- Process steps
- Pollution control devices
- Washings from vessels, containers, etc.
- Storm water (if your permit includes storm water sources of a listed chemical)

Solids, slurries, and nonaqueous liquid sources

- ° Filter cakes, and/or filter media
- Distillation fractions
- Pollution control wastes such as baghouse particulates, absorber sludges, spent activated carbon, and/or wastewater treatment sludge
- Spent catalysts
- Vessel or tank residues (if not included under water sources)
- Spills and sweepings
- Off-specification product
- Spent solvents
- Byproducts

Accidental or nonroutine releases should also be included in the release totals, and are not to be listed separately. The quantities that are to be

reported in Part III of the Form should be the total of the releases of the listed chemical from the various individual release points of waste streams for each medium (i.e., air, water, and land). For example, fugitive air emissions estimated separately for leaks, open vessels, and spills would be added and entered under "Fugitive or Nonpoint Air Emissions."

So that consideration of all of the possible points/sources of release is ensured prior to making the release estimate, it will be useful to prepare or refer to simplified flow diagrams for those processes involving the listed chemical; for example, for a polymerization process that uses a listed chemical, a schematic of the major pieces of equipment in which the polymerization is carried out, the associated storage vessels, and the treatment steps for wastes containing the solvent would be helpful in assessing possible release points/sources. If the chemical is made or used in multiple processes, the quantities to be reported are the total releases for all processes; a flow diagram for each process would also be helpful.

2.3 AN OVERVIEW OF THE ANALYSIS

The level of detail of the analysis and the level of effort required depend on your specific circumstances. Before data needs are described and before methods are outlined for estimating quantities to be entered on the Form, it should be noted that many (if not most) processors and users will have only one or two releases of a given chemical to report. Further, if monitoring data are available for that release, simple multiplication of the concentration of the chemical in the waste by the volume of the waste released may yield an acceptable estimate.

The following are examples of this "simple" solution:

- A furniture maker uses a listed solvent in coating furniture. The solvent evaporates in a drying area, from which it is ducted to a discharge stack and is then released into the air without treatment. In this case, the release estimate would simply be the amount of solvent present in the coating(s) purchased (adjusted for any inventory change). This value would be entered on the Form under point source emissions to air.
- A food processor uses an an aqueous cleaning solution that contains a listed, nonvolatile component to wash down food processing equipment. In this case, the quantity of cleaning solution used multiplied by the concentration of the nonvolatile component in the

cleaning solution would be used as an estimate of the release, say to a POTW (assuming that it does not undergo treatment prior to discharge). This amount would be entered in Part III, Item 6.1, "Discharge to POTW."

- The manufacture of a chemical compound in solution generates a solid filter cake that is land-filled on site. The filter cake contains a listed chemical. The release of the listed chemical would be estimated by multiplying the concentration of that chemical in the filter cake by the quantity of the filter cake landfilled in the reporting year. This estimate would then be entered in Part III, Item 5.5, "Releases to Land," with the code DO2 for landfills (these codes can be found in the instructions for completing the Form).
- A processor of copper-containing compounds has measured the concentration of copper in wastewater to comply with a water discharge permit. The copper concentration times the daily volume of wastewater times the number of days on which discharge occurs yields the release estimate. This estimate would be entered in Part III, Item 5.3, "Discharge to Water."

In all of the above situations, readily available data on the volume of the chemical manufactured, processed, or used and data from the measurement of the concentration of the chemical in the waste were all that was needed to estimate a release. Of course, careful scrutiny of the process(es) at the facility is necessary to ensure that no sources are overlooked. For example, discarded containers of unused coating or water used to wash a filter press may be additional sources in the first and third examples, respectively.

The task will be somewhat more complicated when, for example, there are several waste streams, treatment is used, or wastewater is discharged but the chemical in the wastewater has not been measured. The following are examples of slightly more complex situations:

A paint formulator incorporates a listed pigment into coatings. The formulator has determined that there are two sources of release for the listed pigment: 1) fine solids emitted to air from a milling step, and 2) solvent cleaning wastes that are sent to an off-site location for incineration. In this case, total release would be equal to the amount of pigment used (purchases adjusted for inventory changes) minus the amount of pigment sold in the product (the concentration of the pigment in the coating multiplied by the weight of coating solid). Because two wastes are involved, it is necessary to apportion the total release between them. It is unlikely that "fugitive" solids to air will have been measured; therefore, the best approach may be to estimate the amount of cleaning waste (perhaps based on the known volume of the waste

shipped offsite, the concentration of coating in the waste, and the concentration of the pigment in the coating). The release quantity in cleaning wastes calculated from these estimates would be entered in Part II, Item 2, "Transfer to Offsite Location," and could then be subtracted from the total release estimate to yield the "fugitive air emissions" (which should be entered in Part III, Item 5.1). The code "M50" for "Incineration/Thermal Treatment" would be entered with the location and address of the off-site incineration facility.

The processor of copper-containing compounds, discussed earlier, precipitates solids from wastewater generated by the process. In addition to the discharge mentioned previously, some precipitate is shipped to a waste broker. This additional copper release may be estimated by multiplying the volume of waste shipped by the concentration of copper in the waste. This release estimate would be entered in Part II, Item 2. The type of disposal (transfer to a waste broker) would be indicated by entering the code "M91". Treatment efficiency may be specified in Part III, Item 7 (Code CO9 for chemical precipitation). Treatment efficiency may be calculated by dividing the amount of copper in solids by the total amount of copper (the amount of copper in solids plus the amount in the treated water). The resulting fraction would be multiplied by 100 to obtain a percentage reduction of copper in water resulting from the treatment (precipitation step). The concentration of copper in the influent would simply be the total copper in the two "releases" divided by the wastewater volume. (Alternatively, copper concentration in influent water may have been measured.)

Calculations will be more complicated when a volatile material is made or used and air emissions must be estimated for leaks, vents, etc., or when no data are available on water releases and the water comes from several points in the process.

- The manufacture of a solvent uses a continuous process that involves a reactor, distilation columns, pumps, compressors, miles of piping, and hundreds of fittings as well as associated storage tanks and pollution control devices. Generally, the air release points will not have been monitored, and no "emission factor(s)" for the process will be available to facilitate estimating releases for the process as a whole (emission factors are discussed further in Subsection 2.4). Estimates of air releases must then be based on the other calculation techniques. Section 3 discusses other calculation techniques and presents a subsection on calculating air releases.
- The manufacture of a chemical generates wastewater during the reaction step. This wastewater is separated for treatment prior to discharge. Additional wastewaters arising from product washings and pollution control equipment are all combined in a central treatment system. The amount of chemical released can be estimated

by considering the losses from each part of the process and then using mass balances and engineering calculations (defined in Subsection 2.4). Obviously, the larger the number of sources, the more difficult it will be to estimate the total release.

2.4 DEFINITIONS OF MAJOR APPROACHES

The preceding examples illustrated four basic approaches to estimating releases after release points have been identified. These approaches are defined here:

- Calculations based on measured concentrations of the chemical in a waste stream and the volume/flow rate of that stream.
- Mass balance around entire processes or pieces of process equipment. The amount of a chemical leaving a vessel equals the amount entering. If input and output or "product" streams are known (based on measured values), a waste stream can be calculated as the difference between input and product (any accumulation/depletion of the chemical in the equipment, e.g., by reaction, must also be accounted for).
- Emission factors, which (usually) express releases as a ratio of amount released to process or equipment throughput. Emissions factors, which are commonly used for air emissions, are based on the average measured emissions at several facilities in the same industry.
- Engineering calculations and/or judgment based on physical/chemical properties and relationships such as the ideal gas law.

A single release estimate may involve the use of more than one of these estimation techniques; for example, when a mass balance is used to estimate the amount of wastewater leaving a process, and water solubility is used to calculate the maximum amount of chemical in that wastewater.

Estimates may be based on analogy. The emission factor approach relies heavily on your determination that your process is analogous to the process for which data were used to derive the factor. The use of any published data (for example, on the effectiveness of wastewater treatment for a chemical or on the releases from a papermaking plant) implies that the treatment schemes of processes are analogous to those you are using. Extreme caution should be used in the application of an analogy, especially from one facility to another.

2.5 SOME OBSERVATIONS ON THE USE OF DATA

You may be able to estimate a release in several ways based on the various sets of data that are available. If this is the case, you will have to make a decision as to which estimate to report based on the expected accuracy of each. Assuming that equally valid and equally accurate data are available for each of the preceding approaches, the following caveats should be noted:

- Data on the actual released waste will generally provide a better estimate than data on the waste before treatment (to which a treatment efficiency must be applied).
- Data on the aggregate stream are preferable to data on the several streams that make up the aggregate.
- Data on the specific chemical are preferable to data on an analogue.
- Data on the chemical for a specific process are preferable to published data on similar processes. In fact, data on the treatment efficiency for a close analogue chemical treated at a specific facility will probably provide a better estimate than published data on the actual chemical, as operating conditions vary greatly from plant to plant. It may be easier to make a good chemical analogy based on physical/chemical properties than to make a process analogy.

Data (for example, on the concentration of chemical in wastewater) may be available as a range of measured values. In this case, the average value of all measurements should be used for data specific to the facility as it operated in the reporting year, unless it can be demonstrated that some data points can be disregarded. If operating conditions varied during the year (e.g., the listed chemical was used periodically or new equipment was installed at midyear), releases should be estimated for each set of conditions (e.g., 3 months during which the chemical was used, 9 months during which it was not), and these values should be added. Representative data taken during the reporting year should be used. You should, however, consider whether including data from previous years might improve the estimate because so few samples are taken each year.

With regard to published data on other processes, the average for facilities/equipment/operating conditions most closely analogous to the one in question should be used.

2.6 WHICH APPROACH TO USE

Selection of the best approach to estimating releases depends on the circumstances at your facility. Available information on a process may be the single most important factor in determining how to proceed. This subsection provides some general guidelines on the most effective approach(es), assuming that information is available to complete the analysis. It is organized according to type of release.

2.6.1 Fugitive Air Emissions

Measurement data on fugitive air emissions will rarely be available. Furthermore, the fugitive emissions from most single sources is small compared with the total volume of chemical handled; therefore, inaccuracies in measurements of input and output can totally mask the magnitude of the release if mass balance is attempted (an exception is the example of all solvent volatilized after application of a coating). For this reason, the use of emission factors is a major method for estimating fugitive air emissions. This approach requires the following:

- A published factor (usually reported as pounds emitted per pound of chemical processed or pounds emitted per piece of equipment, such as a valve).
- The amount of chemical handled at a facility and/or a count of the valves, pumps, etc., for which emission factors are available.

Specific emission factors are available for only a few processes as a whole (see Table 3-5 in Section 3 entitled "Availability of Chemical-Specific Emission Factors for Various Processes"), and these process-specific factors can only be applied to processes that are very similar to the one for which the factor was developed.

Volatilization equations can also be used for open vessels or for spills. This approach, however, requires that the vapor pressure of the chemical at the appropriate temperature, its molecular weight, and the open surface area be known or estimated (see Sections 3 and 6).

2.6.2 Point Source Air Emission

Point-source air emissions are enclosed; thus, such releases are much more likely to have been measured (as compared with fugitive air emissions)

This permits calculations based on available data on the concentration and flow rate of the emission. For example, multiplication of the measured benzene concentration by the measured flow rate of air through a vent yields the quantity of benzene being released. Unavailability of analytical techniques for determining airborne concentration of many of the chemicals on the list limits this approach. When this is the case, total hydrocarbon analysis can be used to set an upper limit to the estimate.

Emission factors specific to some point sources (e.g., the reactor vent for ethylene dichloride production) are available and should be used if monitoring data are not available.

When these approaches are not possible, estimates for point sources must be based on mass balance calculations or on engineering calculations, design data, etc. Point sources such as storage tanks will usually require a calculation based on physical properties of the chemical, the throughput, and the configuration of the storage tank. (See Section 3 for example of storage tank release calculations.)

2.6.3 Releases to Wastewater

Many of the listed chemicals for which your facility may be subject to reporting requirements may be controlled under Federal, State, and/or local regulations. Frequently, wastewater discharges will have been monitored. If this is the case, release can be calculated directly. In fact, your discharge permit and Discharge Monitoring Reports may contain sufficient information to support any needed calculations (i.e., concentration of the listed chemical in the discharge and the wastewater flow rate). Multiplication of the measured concentration by the measured flow will yield an estimate of the release.

When monitoring data for the listed chemical are not available at your facility, the following approaches may be applicable (in approximate order of preference):

- Identifying individual process points that contribute to water discharge, performing a mass balance calculation around each to determine individual releases, and then totaling them.
- Conducting a mass balance around the process as a whole. For example, input of dye equals output on dyed fabric plus output in

wastewater (individual sources of that water need not be estimated). This approach is most appropriate if the only release of the listed chemical is through a wastewater stream.

Ousing discharge data on the listed chemical from similar facilities. This approach is particularly useful if the industry has been studied by EPA's Office of Water Regulations and Standards and an Effluent Guidelines Background Document containing release estimates or typical waste stream concentrations for that industry is available.

2.6.4 Releases in Solids, Slurries, and Nonaqueous Liquids

Some of these wastes may be regulated as hazardous wastes under the Resource Conservation and Recovery Act (RCRA). Information in the permit and manifests for disposing of the waste provide a basis for estimating released quantities of a listed chemical. Frequently, however, the concentration of individual chemicals that make up a waste will not have been measured. In this case, the concentration of the listed chemical will have to be determined, either by measurement or by an estimation method based on mass balance, engineering calculations, etc.

For nonhazardous wastes in this category, the volume or total weight of the waste should be readily derivable from shipping records, a count of waste containers, etc. Again, the important factor to determine is the concentration of the listed chemical.

Unfortunately, there are no solid waste emission factors and little published data on concentrations of chemicals in such wastes. When monitoring data are not available for a waste, mass balance and engineering calculation approaches will be necessary.

OUTLINE FOR SECTION 3

ESTIMATING RELEASES TO AIR

- 3.1 Sources of Releases to Air and Release Estimation Methods
 - 3.1.1 Process Vents
 - 3.1.2 Releases From Material Handling, Storage, and Loading
 - 3.1.3 Fugitive Emissions
 - 3.1.4 Releases to Air From Wastewater Treatment and Solid Waste Disposal
- 3.2 Air Pollution Control Equipment and Treatment Efficiency
 - 3.2.1 Combustion
 - 3.2.2 Adsorption
 - 3.2.3 Absorption
 - 3.2.4 Condensation
 - 3.2.5 Particulate Collection Devices

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SECTION 3

ESTIMATING RELEASES TO AIR

Air emissions can originate from a wide variety of sources and therefore are usually not centrally collected before being discharged; as a consequence, each source or category of sources must be evaluated individually to determine the amount released. Often, releases to air are reduced by the use of air pollution control devices, and the effectiveness of the control devices must be accounted for in the calculation of the release estimate. This section provides various methods for estimating releases to air and for determining the efficiency of pollution control devices. A bibliography of reports pertaining to releases and efficiency of the various pollution control devices is provided at the end of this section. These reports present more specific emission data on various industries.

3.1 SOURCES OF RELEASES TO AIR AND RELEASE ESTIMATION METHODS

Releases to air from industrial processes can be broadly categorized as follows: point sources, such as stacks and vents, and fugitive sources, which are not contained or ducted into the atmosphere. Whether a source is considered a point or fugitive source depends on whether the release is contained in a duct or stack before it enters the atmosphere. Table 3-1 lists common air emission sources that should be considered when estimating releases. Examples in the following subsections illustrate the emission estimation methods described in Section 2 for air emission sources. The examples presented in this section and throughout the manual are for purposes of illustration only; they are not meant to predict actual releases.

3.1.1 Process Vents

In general, process vents are the main air exhaust devices in a manufacturing or processing operation functioning under normal conditions; however, emergency venting devices on unit operations, such as relief valves, are also

TABLE 3-1. SOURCE CATEGORIES FOR COMMON RELEASES TO AIR

(1)	(2)	(3)	(4)
Process vents	Secondary sources	Fugitive sources	Handling, storage, and loading
Reactors Distillation system	Pond evaporation Cooling tower evaporation	Flanges/connectors Valves	Breathing losses Loading/unloading
Vacuum systems	Wastewater treatment	Pump seals	Line venting
Baghouses or precipi- tators	facilities	Compressor seals Sample connections	Packaging/container loading
Combustion stacks		Open-ended lines	
Blow molding		Pressure relief	
Spray drying		devices (e.g., rupture disks)	
Curing/drying		Lab hoods	,
Scrubbers/absorbers		Process sampling	·
Centrifuges		Equipment inspection	
Extrusion operations		Equipment cleaning	
Pressure safety valves		Equipment maintenance	
Manual ventings	4	Blowing out pipelines Storage piles	

NOTE: Process vents are usually point sources. Secondary sources are usually not contained and are considered fugitive sources.

Storage tank emissions are considered as point sources; other loading and unloading releases could be categorized as either point or fugitive sources, depending on whether the releases are ducted.

grouped under process vents. The methods that can be used to estimate releases to air from a process vent are discussed here; they include measurement, mass balance, emission factors, engineering calculations, or a combination of these methods. Several examples are given to illustrate the basic principles of each technique.

<u>Measurement</u>. Measurement is the most straightforward means of estimating releases.* The pollutant concentration and flow rate from a process vent during typical operating conditions, if available, can be used to calculate releases. Total annual releases are based on the plant operating schedule for the year.

 $\underline{\text{Example } 3\text{--}1}$ - Use of measurement data to estimate releases to air from a process vent:

Step 1. Assemble data from emission measurement task.

Measurements are taken at the oxychlorination vent of a plant producing dichloroethylene at its normal operating rate. The vent gas velocity is measured and an average of 26 ft/s is obtained. The measured average concentration of dichloroethylene is 0.22 gram/cubic meter (g/m^3) after correction to $70^\circ F$. The vent gas temperature is measured to be $200^\circ F$. The diameter of the vent is 1 foot.

Step 2. Calculate volumetric flow of vent gas stream.

The next step in estimating emissions using this information is to calculate the vent gas flow rate. The product of the velocity and the stack cross-sectional area will be the actual volumetric flow.

Volumetric flow = Gas velocity x area

Area = $3.14 \times (diameter)^2/4$

Volumetric flow = $\frac{26 \text{ ft}}{\text{second}} \times 3.14 \text{ (1 ft)}^2/4 = \frac{20.41 \text{ ft}^3}{\text{second}} \text{ at } 200^{\circ}\text{F}$

Step 3. Calculate annual releases.

The dichloroethylene concentration, 0.22 g/m^3 , was reported at a standard temperature, 70°F. The actual emission rate is derived by making a volume correction to account for the difference between standard and actual

Emission measurement is a complex procedure requiring specialized equipment and personnel trained in chemical analysis and flow measurement. The description of sampling procedures is beyond the scope of this document. The EPA emission test procedures for regulated compounds are described in the Code of Federal Regulations, 40 CFR 60, Appendix A, July 1986.

vent gas absolute temperatures and multiplying the concentration by the vent gas flow rate.

Actual emission rate = Volumetric flow x concentration

$$= \frac{20.41 \text{ ft}^3}{\text{second}} \times \frac{0.22 \text{ g}}{\text{cubic meter}} \times \frac{2.205 \times 10^{-3} \text{ lb}}{\text{gram}} \times \frac{0.028 \text{ m}^3}{\text{cubic foot}}$$
$$\times \frac{(70^{\circ}\text{F} + 460)^{\circ}\text{R}^*}{(200^{\circ}\text{F} + 460)^{\circ}\text{R}} \times \frac{3600 \text{ seconds}}{\text{hour}} = 0.80 \text{ lb per hour}$$

During this test period, the average plant production was 10 tons of product per hour. From the calculated mass emission rate, the loss is 0.080 lb/ton of product (0.80 lb/h ÷ 10 tons/h). On an annual basis, the atmospheric release is determined for a production rate of 20,000 tons/year as follows:

Annual release =
$$\frac{20,000 \text{ tons}}{\text{year}} \times \frac{0.08 \text{ lb}}{\text{ton}} = 1603 \text{ lb per year}$$

= 1600 pounds per year.

NOTE:

This calculation assumes that the measured emissions are representative of the actual emissions at all times. This may not always be the case. Ideally, using a continuous emission monitor to measure and record releases would provide the most representative data and provide a basis for calculating an average concentration.

Gaseous concentrations also are frequently expressed in parts per million (ppm) by volume; i.e., a volume of the constituent in a million volumes of vent gas. In this case, the vent gas volume must be multiplied by the concentration and this value divided by the molar volume** (adjusted to the vent gas temperature) and multiplied by the compound's molecular weight to obtain the mass emission rate.

Some vent streams contain large amounts of water vapor (10 to 20 percent by volume), and the actual vent gas rate includes this volume of vapor. Concentrations of chemicals in the gas, however, are frequently expressed on a dry basis. For an accurate release rate, the vent gas rate should be corrected for its moisture content by multiplying by [1 minus the fraction of water vapor]. The resulting dry volume can then be multiplied by the chemical's concentration.

^{*} Absolute temperatures must be used in making volume-temperature corrections based on the ideal gas law. Thus, 460 must be added to degrees Fahrenheit and 273 to degrees Centigrade to obtain an absolute temperature expressed in degrees Rankine or Kelvin, respectively.

^{**} The molar volume of any gaseous compound is 359 ft³/lb-mole at 32°F or 492°R.

Mass Balance. As defined in Section 2, mass balance provides a means of accounting for all the inputs and outputs of a chemical in a process. A mass balance is useful for estimating releases when measured release data are not available and when other inlet and output streams are quantified. The amounts entering and/or leaving a process are either measured or estimated. A mass balance can be performed on the process as a whole or on a subprocess. Individual operations within the process usually must be evaluated.

<u>Example 3-2</u> - Use of a mass balance to estimate releases to air from a process vent:

Step 1. Draw a diagram, label all streams, and list input and output values.

Consider a unit process that uses Chemical X to produce a product. In a year, 10,000 lb of Chemical X is used to produce 24,000 lb of a product containing 25 percent of Chemical X by weight. The input consists of 8000 lb of purchased Chemical X and 2000 lb that is collected from recycling. This process generates 5 tons or 10,000 lb of solid waste containing 15 percent (1500 lb) of Chemical X. The only other unit process stream is a process vent, which emits an unknown amount of Chemical X to the atmosphere. Figure 3-1 presents a schematic of this hypothetical unit process.

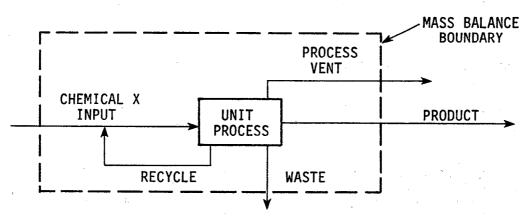


Figure 3-1. Hypothetical unit process using Chemical X.

Step 2. Set up equations with input streams equal to ouput streams.

Considering the quantities of Chemical X in all streams that enter or leave the process, the amount of Chemical X that is lost through the process vent on an annual basis can be estimated as follows:

Input = Amount purchased (8000 1b)

Output = Product (24,000 lb x 25%) + waste (10,000 lb x 15%) + process vent loss (unknown)

Input = Output

8000 lb Chemical X = 6000 lb + 1500 lb + process vent loss

Process vent loss = 8000 - 6000 - 1500 = 500 lb Chemical X per year

NOTE:

In this example, suppose that an error of 5 percent was made in the quantity of materials purchased; i.e., the input of Chemical X into the process was thought to be 8400 lb rather than the actual 8000 lb. Substituting 8400 lb of Chemical X into the mass balance equation yields an air emission of 900 lb (i.e., an 80 percent error). This illustrates the sensitivity of emission estimates based on mass balances to small errors in raw material and product quantities. Care must be taken to ensure that accurate values of raw materials and product quantities are available before a mass balance is used to make release estimates.

<u>Emission Factors</u>. A third technique for estimating air releases from process vents involves the use of emission factors. One type of emission factor relates a quantity of a pollutant to some process-related parameter or measurement. The amount of pollutant per quantity of product is frequently used.

 $\underline{\text{Example } 3\text{--}3}$ - Use of an emission factor to estimate releases to air from a process vent:

Step 1. Assemble emission factor information from literature.

Hydrofluoric acid is being produced by reacting fluorspar with sulfuric acid. The emission factor given in EPA Publication AP- 42^1 is 50 pounds of fluoride per ton of acid product. The plant produced 55,000 tons of acid in the past year.

Step 2. Calculate releases.

In the absence of more accurate information (such as measurement data, etc.), the uncontrolled fluoride emissions from the process would be calculated as follows:

$$\frac{55,000 \text{ tons}}{\text{year}} \times \frac{50 \text{ lb}}{\text{ton}} = 2,750,000 \text{ lb per year}$$

Based on information in AP-42, the use of a water scrubber to control releases would reduce emissions to 0.2 lb of fluorides per ton of acid. Emissions after control would thus be:

$$\frac{55,000 \text{ tons}}{\text{year}} \times \frac{0.2 \text{ lb}}{\text{ton}} = 11,000 \text{ lb per year}$$

NOTE:

Releases from other unit processes could be calculated in a similar manner, and the amounts from all unit processes would be summed to estimate the total release from the plant. When emission control devices (i.e., air pollution control devices) are used to reduce emissions, atmospheric releases are estimated by multiplying the uncontrolled emission by the quantity (1 minus the fractional control efficiency).

Many air emission factors are expressed in terms of total volatile organic compounds (VOC) or particulates rather than a single chemical compound. Emission factors for VOC's are available in "VOC Emission Factors for the NAPAP Emission Inventory," EPA 600/7-86-052, December 1986. These data can be used with actual process vent measurements of volatile organics or particulates to estimate emissions of a specific compound. The "Volatile Organic Compound (VOC) Species Data Manual" also provides information on numerous air emission sources, which allows the user to estimate releases of specific toxic compounds based on the total amount of VOC's emitted from a particular source. Similarly, the "Receptor Model Source Composition Library" provides information relating metals emissions to total particulate emissions for different release sources. 4

 $\underline{\text{Example } 3\text{--}4}$ - Use of emission factors to determine releases of a specific chemical to air:

Step 1. Assemble emission factor information from literature.

Air emissions from the blast furnace of a primary lead smelting facility are controlled by a fabric filter system. In Section 7.6 of AP-42 (Primary Lead Smelting), an emission factor for uncontrolled releases of particulate is given as 361 lb per ton of lead produced. Also in this section, a particulate removal efficiency range of 95 to 99 percent is provided for fabric filter control devices used for primary lead smelting operations.

Step 2. Calculate particulate releases.

Assuming the fabric filter system is 97 percent efficient, the particulate emission factor is reduced to:

 $(1.00 - 0.97) \times \frac{361 \text{ lb particulate}}{\text{ton lead produced}} = 10.83 \text{ lb particulate per ton of lead}$

Thus, an annual production of 31,500 tons of lead will result in the emission of 341,145 lb of particulate (10.83 \times 31,500).

Step 3. Calculate specific chemical releases.

The "Receptor Model Source Composition Library" is used to determine the amount of toxic compounds emitted. Source Profile No. 29302 gives a typical chemical composition for particulate matter sampled downstream of a fabric filter controlling emissions from a primary lead smelting blast furnace. Based on this information, annual emissions of individual toxic compounds can be calculated by multiplying the respective chemical composition by the total particulate 341,145 lb/yr. The specific compounds found according to this data source, their respective percentages of the total particulate matter, and their resultant annual emissions are summarized below.

Compound	Percentage of particulate	Annual emissions, lb	Report, 1b
Chromium	0.02	68.2	70
Nickel	0.06	204.7	200
Copper	0.35	1,194.0	1,200
Zinc	15.2	51,854.0	52,000
Cadmium	23.1	78,804.5	79,000
Lead	30.7	104,731.5	105,000

Emission factors have been developed for a number of processes and pollutants. The bibliography at the end of this section lists literature sources containing emission factors for some industries. The source of an emission factor must be carefully evaluated to determine that it is applicable to the process vent in question at your facility. The Journal of the Air Pollution Control Association deals primarily with the subject of air emissions and controls. Appendix E lists industries for which emission factors have been published in EPA's Publication AP-42, "Compilation of Air Pollutant Emission Factors."

Another good source of air emission factors is a series of reports published by the EPA on locating and estimating emissions for specific toxic chemicals. Reports for 13 chemicals are currently available. All are listed in the Bibliography under "U.S. Environmental Protection Agency" and are identifiable by the number series "EPA 450/4-84-007a through m."

Engineering Calculations. When parameters related to emissions cannot be directly measured, emissions may be estimated or inferred through engineering calculations and/or measurement of other secondary parameters (i.e., physical/chemical properties of the materials involved, design information on the unit operation for which the estimate is being made, or

emission information from similar processes). Engineering calculations are generally used to "fill in" information needed for one of the other emission estimation methods.

Information derived from equipment design, such as fan curves, vessel capacities, operating temperatures, and operating pressures, can be used to estimate gaseous flow rates. Physical/chemical information derived from the ideal gas law, vapor pressure, and equilibrium relationships can frequently be applied when estimating gaseous concentrations of a particular compound.

A common approach to calculating the concentration of a compound in the vapor phase over a liquid is to determine its partial pressure. The partial pressure of a compound divided by the total pressure of the gas stream is equal to the mole fraction of the compound (X_{AG}) in the stream. The following paragraphs discuss two methods of determining the partial pressure of a compound in a gas stream at equilibrium. Even though equilibrium may not occur for the process under consideration at your facility, these methods can provide approximate results.

In dilute aqueous solutions (i.e., when gases are dissolved in low concentrations in water), the partial pressure of the gas above the liquid surface (P_A) is equal to the mole fraction of the compound dissolved in the liquid (x_{AL}) multiplied by Henry's law constant (H); $P_A = x_{AL}$ H. Thus, if the Henry's Law constant can be estimated or found in the technical literature for the solution temperature, the partial pressure of a gas above this liquid can be estimated by multiplying the mole fraction in solution by the constant H at the solution temperature. This relationship, however, is only valid for dilute aqueous solutions.

The partial pressure of a compound in the vapor phase over a solution (organic or aqueous) also may be estimated by multiplying its mole-fraction in the solution by the vapor pressure it exerts when it is pure; i.e.

$$P_A = x_{AL} P^O$$
 (Raoult's Law)

where P^0 = vapor pressure of pure liquid

 x_{AL} = mole fraction of that liquid in solution

 P_A = partial pressure exerted by that compound in the vapor phase over the solution

This equation is valid only for ideal solutions, however, and should only be used to make an approximation. At equilibrium, the partial pressure divided by the total pressure $(P_{\overline{I}})$ will give the mole fraction in the gas stream.

$$\frac{P_A}{P_T}$$
 = XAG = mole fraction of A in gas phase

<u>Example 3-5</u> - Use of engineering calculations to estimate releases to air from a process vent:

Step 1. Assemble process composition information.

A process vessel containing 5 wt. percent A, 15 wt. percent B, and 80 wt. percent C is vented to the atmosphere. The discharge rate through the vent has been measured at 5 ft^3 per minute at 70°F. The process tank is in service 200 days/yr. At 32°F, 1 lb-mole of the gas occupies 359 ft^3 .

Step 2. Calculate composition of vented gas.

Assuming equilibrium between air and liquid in the tank, the emissions of A are calculated by using the following equations:

$$X_{AL} = \text{mole fraction}_{A} = \frac{\frac{\text{wt. } \% \text{ A}}{\text{MW}_{A}}}{\frac{\text{wt. } \% \text{ A}}{\text{MW}_{A}} + \frac{\text{wt. } \% \text{ B}}{\text{MW}_{B}} + \frac{\text{wt. } \% \text{ C}}{\text{MW}_{C}}}$$
(1)

where MW = molecular weight of compound
 wt. % = percent by weight

$$P_{A} = X_{AL} P^{O}$$
 (2)

where P^{0} = vapor pressure of A at ambient temperature

$$\frac{P_A}{14.7} = \text{fraction of A in gaseous phase, } X_{AG}$$
 (3)

Equation 3 calculates the fraction of \boldsymbol{A} in the gaseous phase at standard temperature and pressure.

Step 3. Calculate annual release.

To calculate the annual release, multiply the following factors:

$$X_{AG} \times \frac{5 \text{ ft}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{h}} \times \frac{24 \text{ h}}{\text{day}} \times \frac{200 \text{ operating days}}{\text{yr}} \times (\frac{P_T}{14.7}) \times \frac{P_T}{14.7}$$

 $\frac{1b\text{-mole}}{359 \text{ ft}^3} \frac{(32^{\circ}\text{F} + 460)^{\circ}\text{R}}{(70^{\circ}\text{F} + 460)^{\circ}\text{R}} \times \frac{(\text{MW})}{1b\text{-mole}} = \text{pounds of chemical A emitted per year}$

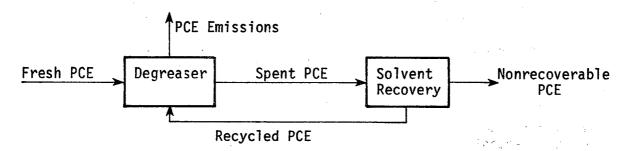
where $P_T/14.7$ is a correction for the pressure at the vent. P_T may be assumed to be 14.7 in the absence of pressure measurement data.

A combination of the previous methods often can be used to estimate air releases. The following example demonstrates the combined use of an emission factor, a mass balance, and an engineering calculation.

Example 3-6 - Use of an emission factor, mass balance, and an engineering calculation to estimate releases to air from a process vent:

Step 1. Layout process and obtain process information.

Perchloroethylene (PCE) is emitted from open-top vapor degreasing processes via evaporation. The emission factor for this process has been determined to be 0.78 lb per pound of PCE entering the degreaser. The PCE entering the degreaser consists of recycled PCE and fresh PCE makeup. Spent PCE from the degreaser is sent to solvent recovery, where 75 percent is estimated to be recovered and subsequently recycled. The 25 percent that is not recovered is sent offsite for disposal.



To determine how much PCE is emitted from the degreaser, one needs to determine the pounds of PCE emitted per pound of <u>fresh</u> PCE used; the amount of fresh PCE used should be ascertainable from the <u>facility</u>'s records. This factor can be calculated if the amount of PCE recycled per pound of fresh PCE used is known. A mass balance approach can be used to calculate the necessary emission factor.

Step 2. Set up mass balance around degreaser.

Using a basis of 1 lb of fresh PCE entering the degreaser and letting X = pounds of PCE recycled per pound of fresh PCE used, set up a mass balance around the degreaser. The total amount into the degreaser equals (1 + X). A material balance around the degreaser is made to determine the spent PCE rate.

Step 3. Set up mass balance around solvent recovery system.

Knowing that 75 percent of the spent PCE is recycled, a mass balance around the solvent recovery process can be expressed as follows:

```
Input = Output

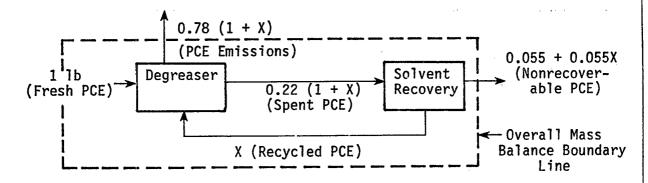
Spent = recycled + nonrecoverable

0.22 (1 + X) = 0.75 [0.22 (1 + X)] + nonrecoverable

0.055 + 0.055X = nonrecoverable PCE
```

Step 4. Set up mass balance around entire process.

An overall mass balance around the entire process can be used to solve for X:



Step 5. The PCE emitted per 1b of fresh PCE can then be calculated.

```
PCE emissions = 0.78 (1 + X)
= 0.78 (1 + 0.20)
= 0.94 lb per pound of fresh PCE
```

Total annual emissions of PCE would be 0.94 times the total amount of fresh PCE consumed annually.

3.1.2 Releases From Material Handling, Storage, and Loading

Releases of chemicals from material handling, storage, and loading may result from both breathing and working losses. Breathing losses are due to vapor expansion and contraction, which force vapor from a tank or vessel. Expansion and contraction are caused by temperature and atmospheric pressure fluctuations. Working losses occur when the tank or vessel is filled or emptied.

These types of releases are generally estimated by the use of emission factors and engineering calculations. The U.S. EPA publication "Compilation of Air Pollutant Emission Factors" (AP-42)¹ provides equations for estimating air emissions from organic liquid storage and handling operations. These equations contain factors that depend on tank parameters and service conditions. For convenience, the storage tank equations and factors are provided in Appendix C. For emissions from loading operations (tank trucks, barges, etc.), use equations and factors in Table 3-2.

TABLE 3-2. CALCULATING LOADING LOSSES FOR VOLATILE ORGANIC LIQUIDS 1

$$L_L = 12.46 \frac{SPM}{T}$$

where

 L_1 = release in pounds/1000 gal of liquids loaded

P = liquid vapor pressure, psia (see chemical handbook or Appendix B)

M = molecular weight (see chemical handbook or Appendix B)

T = liquid temperature, °R (°F + 460)

S = Saturation factor depending on carrier and mode of operation as shown below:

Cargo carrier	Mode of operation	S factor
Tank trucks and tank cars	Submerged loading of a clean cargo tank	0.50
	Splash loading of a clean cargo tank	1.45
	Submerged loading: normal dedicated service	0.60
	Splash loading: normal dedi- cated service	1.45
•	Submerged loading: dedicated vapor balance service	1.00
	Splash loading: dedicated vapor balance service	1.00
Marine vessels	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

Example 3-7 - Use of an emission factor to estimate releases to air from material storage:

Step 1. Assemble tank and product data.

The following calculations are for a 10,000-gallon, white, fixed-roof tank that holds 1,1,1-trichloroethane at an average temperature of 60°F. The tank is 10 feet in diameter and 17 feet high. On the average, the tank is half full and has a throughput of 2000 gallons per month, or 24,000 gallons per year. The average diurnal (day and night) temperature change is 20°F. Ambient pressure is 1 atmosphere or 14.7 psi. Chemical handbook data show that 1,1,1-trichloroethane has a molecular weight of 133 and a vapor pressure of 1.6 psi at 60°F. The vapor pressure may be estimated by plotting temperature against vapor pressures obtained from handbooks and selecting the pressure at the given temperature.

Step 2. Use Equation 1 for calculating breathing losses from Appendix C:

$$L_{\rm B} = 2.26 \times 10^{-2} M_{\rm V} \left(\frac{P}{P_{\Delta} - P}\right)^{0.68} {\rm D}^{1.73} {\rm H}^{0.51} {\rm \Delta T}^{0.50} {\rm F}_{\rm P} {\rm CK}_{\rm C}$$
 (1)

where L_R = fixed roof breathing loss (lb/yr)

 P_A = average atmospheric pressure at tank location (psia)

P = true vapor pressure at bulk liquid conditions (psia), see Note 2 in Appendix C

D = tank diameter (ft)

H = average vapor space height, including roof volume correction
 (ft), see Note 3 in Appendix C

 ΔT = average ambient diurnal temperature change (°F)

 F_p = paint factor (dimensionless), see Table 4.3-1 in Appendix C

C = adjustment factor for small diameter tanks (dimensionless), see Figure 4.3-4 in Appendix C

 K_C = product factor (dimensionless), see Note 4 in Appendix C

Step 3. Calculate each of the factors and insert into Equation 1.

 $M_V = 133$

 $P_{\Delta} = 14.7 \text{ psia}$

P = 1.6 psia

D = 10 ft

 $H = (17 \text{ ft})(\frac{1}{2}) \text{ since the tank is half full}$

 $\Delta T = 20^{\circ} F$

 $F_p = 1$ since tank is white

C = 0.51 obtained from Figure 4.3-4 in Appendix C

 $K_c = 1$ since this is an organic liquid (as per Appendix C)

Substituting these values in Equation 1 yields

$$L_{\rm B} = 2.26 \times 10^{-2} (133) \left(\frac{1.6}{14.7 - 1.6}\right)^{0.68} (10)^{1.73} (8.5)^{0.51} (20)^{0.5} (1)(0.51)(1)$$
 (1) = 262.5 pounds/year

Working losses can be estimated by using Equation 2 in Appendix C.

$$L_W = 2.40 \times 10^{-5} M_V PVNK_N K_C$$
 (2)

where L_W = fixed roof working loss (1b/year)

 M_V = molecular weight of vapor in storage tank (lb/lb-mole); see Note 1 to Equation 1 in Appendix C

P = true vapor pressure at bulk liquid temperature (psia); see Note 2 to Equation 1 in Appendix C

V = tank capacity (gal)

N = number of turnovers per year (dimensionless)

$$N = \frac{\text{Total throughput per year (gal)}}{\text{Tank capacity, V (gal)}}$$

 K_N = turnover factor

 K_{C} = product factor

Again, calculate each of the factors and insert into Equation 2:

 $M_V = 133$

P = 1.6 psia

V = 10,000 gallons

 $N = \frac{24,000 \text{ gallons used}}{10,000-\text{gallon capacity}}$

 $K_N = 1$ obtained from Figure 4.3-7 in Appendix C

 $K_C = 1$ since this is an organic liquid (as per Appendix C)

Substituting these values into Equation 2 yields:

$$L_W = (2.40 \times 10^{-5})(133)(1.6 \text{ psia})(10,000 \text{ gallons})(\frac{24,000 \text{ gallons}}{10,000 \text{ gallons}})(1)(1)$$

= 122.6 pounds/year

Total losses due to handling = $L_B + L_W = 262.5 + 122.6 = 385.1$ pounds/year Report 390 lb/yr

The density of 1,1,1-trichloroethane is 11.2 pounds per gallon. Annual throughput is 24,000 gallons or 269,000 pounds. The calculated annual release is 385 pounds. A mass balance could not determine a 385-pound loss in 269,000 pounds handled. Consequently, the use of emission factors is an appropriate method for estimating tank releases.

NOTE:

If the storage tank in the this example contained a mixture of materials A and B, the air releases could be calculated in a similar manner given the mole fractions of the components in the liquid phase (X_{A_i} and X_{B_i}) and the vapor pressure of the pure components (P_A^0 and P_B^0). The molecular weight and vapor pressure used in the calculation of breathing and working losses would be calculated as:

Molecular weight =
$$M_V = (M_A) \times (\frac{P_A^o X_{AL}}{P_t^o}) + (M_B) \times (\frac{P_B^o X_{BL}}{P_t^o})$$

True vapor pressure =
$$P_t^0 = (P_A^0)(X_{AL}) + (P_B^0)(X_{BL})$$

These values would be used in the previous equation to calculate total emissions. Each component would be released in proportion to its mole fraction in the gas phase (X_{AG} and X_{BC}) in the tank, which can be calculated as:

$$X_{AG} = \frac{P_A^O X_{AL}}{P_t^O}$$

The gaseous mole fractions must be converted into weight fraction (in gas phase) by use of the following equation:

$$W_{AG} = \frac{X_{AG} M_{A}}{X_{AG} M_{A} + X_{BG} M_{B}}$$

The weight fraction of component A in the gaseous air emissions can then be multiplied by the total pounds of emissions per year as previously calculated.

3.1.3 Fugitive Emissions

Fugitive emissions are those emissions that are not released through a stack, chimney, vent, or other confined vent stream. These releases include process leaks, evaporation from open processes and spills, and raw material and product loading and unloading losses. Whenever possible, fugitive emissions should be calculated by the use of data available from direct measurement. Fugitive emissions, however, often have to be estimated by the use of emission factors or engineering calculations because they are too diffuse and/or dilute to be measured directly, or they are too small relative to the amounts of material processed to permit the use of a mass balance. This is particularly true of hazardous and/or toxic air pollutants. An EPA report entitled "Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models" provides methods for the estimation of emissions from container loading, storage, and cleaning; waste treatment and disposal operations; and equipment leaks in the synthetic organic chemical manufacturing industry.

<u>Uncaptured Process Releases</u>. One basis for estimating process fugitive releases is the use of plant air measurement data. Health and safety regulations may require measurements of regulated air pollutant concentrations on

either an absolute or not-to-exceed basis. These data could provide a basis for determining fugitive emissions. Occupational standards themselves, however, should not be used to calculate emissions; only actual measurements taken to ensure compliance with the standards should be used.

<u>Example 3-8</u> - Use of measurement data to estimate the potential release to air from an uncaptured process:

Step 1. Determine basis for estimating releases and assemble necessary data.

Employee exposure to benzene should not exceed 1 ppm as an 8-hour time-weighted average. A plant has an alarm system that responds to 0.2 ppm benzene and a ventilation system that exhausts 20,000 acfm of room air at 70°F. If the alarm has not sounded during the course of the year and the plant operates 24 hours per day, 330 days per year, a conservative estimation of benzene fugitive releases could be performed as follows:

Step 2. Calculate releases.

Benzene releases per year would be calculated as follows:

$$\frac{20,000 \text{ ft}^3}{\text{minute}} \times \frac{60 \text{ minutes}}{\text{hour}} \times \frac{24 \text{ hr}}{\text{day}} \times \frac{330 \text{ days}}{\text{year}} \times \frac{0.2 \text{ ft}^3 \text{ benzene}}{10^6 \text{ ft}^3 \text{ air}} = 1900.8 \text{ ft}^3$$

The density of benzene vapor is 0.2 $1b/ft^3$, and the annual release would be less than:

$$\frac{1900 \text{ ft}^3 \text{ benzene}}{\text{vear}} \times \frac{0.2 \text{ lb}}{\text{ft}^3} = 380 \text{ lb of benzene per year}$$

Report 380 lb of benzene/year. This value thus serves as an upper limit of potential releases.

Leaks in Vessels, Pipes, Valves, etc. The accepted method of estimating releases from leaks in vessels, pipes, and valves is to use emission factors. Various factors are available to estimate releases due to leaks in process streams carrying hydrocarbon vapors, light liquids (more volatile than kerosene, i.e., a vapor pressure greater than 0.1 psia at 100°F), or heavy liquids (equal to or less volatile than kerosene). These factors can also be used to estimate fugitive emissions in other industries that process hydrocarbon streams.

For convenience, data to estimate releases from leaks are included in Appendix Tables D-1 and D-2. These data are based on information in EPA

Publication EPA-450/3-86-002, entitled "Emission Factors For Equipment Leaks of VOC and HAP." This report addresses fugitive emissions and reductions due to scheduled operation and maintenance procedures.

The EPA has also published a protocol for use in estimating emissions from equipment leaks entitled "Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and HAP." This protocol provides for the use of EPA's average emission factors, along with equipment component counts or screening data for calculating fugitive emission rates. The emission factors used in this approach are based on typical refinery and synthetic organic chemical manufacturing plants.

<u>Example 3-9</u> - Use of emission factors to estimate releases to air from leaks in vessels, pipes, and valves:

Step 1. Compile an inventory of fittings and appurtenances that may leak organic compounds.

A chemical plant uses benzene (a light liquid with a vapor pressure greater than 2 psia) and has six pipe valves, three open-end valves, four flanges, two pumps, one compressor, and one pressure-relief valve. The plant operates 24 hours a day, 250 days a year. Average factors from Appendix D-1 are used to estimate fugitive emissions.

Step 2. Review maintenance schedule and select appropriate emission factors based on leak rates.

The following calculation uses light liquid service factors and units of pounds per hour from Appendix D:

```
(6 x 0.016) (pipe valves)

+ (3 x 0.0037) (open-end valves)

+ (4 x 0.0018) (flanges)

+ (2 x 0.11) (pumps)

+ (1 x 0.5) (compressor in vapor service)

+ (1 x 0.23) (pressure-relief valves in vapor service)
```

= 1.064 pounds per hour

$$\frac{1.064 \text{ lb}}{\text{hour}} \times \frac{24 \text{ h}}{\text{day}} \times \frac{250 \text{ days}}{\text{year}} = 6384 \text{ pounds per year}$$

Report 6400 lb/yr

NOTE:

In this example, an average value of the emission factors was used. The factors cover a range, and a higher or lower value might be more appropriate if the number of leaks are identified through a leak detection screening study.

3.1.4 Releases to Air From Wastewater Treatment and Solid Waste Disposal

Secondary emissions of volatile compounds to the air may occur from the onsite treatment of aqueous or solid waste. The bulk of secondary emissions are estimated to result from the handling, pretreatment, and final treatment (primarily biological treatment) of aqueous wastes. Other sources include surface impoundments, landfilling, and incineration of liquid and solid waste.

Estimating releases of volatile compounds from disposal is complex and requires detailed knowledge of the compound's parameters and the disposal procedure. Table A-2 in Appendix A presents data on the fate of some toxic compounds in secondary wastewater treatment plants, including the percentage of the compound in the influent that is volatilized to air. These data, however, should be used only when operating conditions are similar to those under which the data were derived.

Analytical models have been developed by EPA's Office of Air Quality Planning and Standards (OAQPS) to estimate emissions of volatile organic compounds via various pathways from emission sources at hazardous waste disposal sites. These models are discussed in a draft EPA report entitled "Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models," dated December 1987. To make reasonable estimates of volatile releases, one must know which pathways predominate for a given chemical, type of waste site, and set of meteorological conditions. Models have been developed for the following emission sources:

- Nonaerated impoundments (which include quiescent surface impoundments and open-top tanks)
- Aerated impoundments (which include aerated surface impoundments and aerated tanks)
- Disposal impoundments (which include nonaerated disposal impoundments)

- Land treatment
- ° Landfills

Computerized methods for applying these emission models are being developed by EPA. Models for aerated and nonaerated impoundments, lagoons, landfills, wastepiles, and land treatment facilities have been installed in an integrated spreadsheet program, CHEMDAT4, which allows a user to calculate the partitioning of volatile compounds among various pathways depending on the particular parameters of the facility of interest. The EPA report includes a diskette containing the program for use on an IBM PC and a user's guide.

3.2 AIR POLLUTION CONTROL EQUIPMENT AND TREATMENT EFFICIENCY

Air pollutants entering an air control device may undergo one or more of the following: 1) they may be transferred from the air stream to another medium, 2) they may be modified to a less toxic state, 3) they may be destroyed through combustion and/or dissociation, or 4) they may pass through untreated. The physical characteristics of the pollutant to be removed generally determine which type of control device is used. Table 3-3 presents a summary of air pollution control techniques used to control some of the various pollutants of concern.

Estimates of releases to air must take into account the control equipment efficiency. This efficiency should be based on the amount of pollutant removed from the air inlet stream of the control device by destruction, by modification, or by transfer to another medium.

Percent efficiency =
$$\frac{X \text{ inlet - } X \text{ outlet}}{X \text{ inlet}} \times 100$$

where X inlet = Total mass of pollutant X flowing to the air inlet of the control device in a given year

X outlet = Total mass of pollutant X flowing from the air outlet of the control device in a given year

The amount of pollutant transferred to and subsequently released in another medium (solid or water) would be included in the releases of that particular pollutant in that medium.

TABLE 3-3. TECHNIQUES FOR CONTROLLING SELECTED AIR POLLUTANTS³

Catalytic incineration ^a	Thermal incineration ^a	Boilers/process heaters ^a	Flares ^a	Absorption
Acrylic acid Acrylonitrile Benzene Butadiene Cumene Ethylene dichloride Ethylene oxide Phenol	Acrolein Acrylonitrile Aniline Benzene Benzyl chloride Butadiene Epichlorohydrin Ethylene dichloride Formaldehyde Methyl chloroform Perchloroethylene/ trichloroethylene Polychlorinated bipheyhyls Toluene Toluene diisocyanate Vinylidene chloride	Butadiene ^a Cumene Ethylbenzene/styrene Ethylene oxide Formaldehyde Phenol Propylene oxide	Acetaldehyde Acrolein Acrylic acid Acrylonitrile Allyl chloride Butadiene Chloromethanes Chloroprene Cumene Ethylbenzene/ styrene Ethylene oxide Formaldehyde Methyl methacrylate Propylene oxide	Acetaldehyde ^C Acrylonitrile Acrylic acid Allyl chloride Aniline Benzene Benzyl chloride ^C Butadiene Carbon tetrachloride Chlorobenzene Chloromethanes ^C Chloroprene Epichlorohydrin Ethylbenzene/ styrene Ethylene dichloride Ethylene oxide Methyl chloroform Perchloroethylene/ trichloroethylene Phenol Phosgene Propylene/oxide Vinylidene chloride Xylene

(continued)

Adsorption	Condensation	Fabric filters	Wet scrubbing	Electrostatic precipitators	Cyclones
Acrylonitrile Aniline Benzene Carbon tetrachloride/ perchloroethylene Chlorobenzene Chloroform Ethylene dichloride Methyl chloroform Methyl methacrylate Methylene chloride Phenol Naphthalene Phosgene Styrene Toluene Toluene diisocyanate Trichloroethylene Vinyl chloride Vinylidene chloride Vinyl chloride Vinyl chloride Xylene	Acetaldehyde Acrylic acid Acrylonitrile Allyl chloride Aniline Benzene Benzyl chloride Butadiene Carbon tetrachloride Chlorobenzene Chloromethanes Chloroprene Ethylbenzene/sty- rene Ethylene dichloride Ethylene oxide Formaldehyde Methyl chloroform Methyl methacrylate Perchloroethylene Phenol Toluene Toluene Toluene diisocyanate Vinylidene chloride Xylene	Cadmium Chromium Copper Nickel	Cadmium Chlorobenzene Chromium Nickel Toulene diisocyanate	Cadmium Chromium Copper Nickel	Cadmium Copper Nickel

^a Combustion techniques.

b Refers to 1,3 butadiene.

^C Possible control technique.

d Chloromethanes include methylene chloride, chloroform, and carbon tetrachloride. Individual compound is listed whenever specific information is available.

The best basis for an efficiency estimate is a measurement or test, a mass balance calculation, or a combination of measurement and mass balance calculations. If such data are not available, comparison of "controlled" and "uncontrolled" emission factors for the pollutant (chemical) of concern, engineering calculations, data on the operating parameters of the control device, or vendor data and/or guarantees that reflect actual operating conditions may be used. It is important to use data that reflect efficiency achieved during typical operations, not the theoretical optimum efficiency.

In the absence of typical operating data, treatment efficiency data cited in the open literature for a similar process may be used as an approximate guide. Figure 3-2 can be used to help estimate treatment efficiencies by identifying the expected emission reduction from the application of each control technique on the basis of the total VOC (volatile organic compound) concentration in the inlet stream. Without actual source test data for a specific emission stream and control system, the removal efficiency can be assumed to equal total VOC removal efficiency if the chemical is a volatile organic compound (not a particulate, metal, PCB, etc.). For example, up to 95 percent reduction can be achieved for incineration of a gas stream containing 50 ppm styrene. Some potential sources of air efficiency data are listed in the bibliography at the end of this section. Other potential sources of information include air pollution journals. Unfortunately, many complex variables enter into the calculation of efficiency, and actual measurement is the best way to determine efficiency.

Adsorption, absorption, condensation, particulate collection (cyclones, fabric filters, electrostatic precipitators, and scrubbers), and combustion equipment are the major categories of control devices that can be used to reduce toxic air emissions. Each technique is briefly discussed in the following subsections.

3.2.1 Combustion

Combustion is widely applicable for control of air emissions of combustible organic compounds. The combustion device can be a thermal or catalytic incinerator, a boiler or process heater, or a flare. Combustion can destroy organic pollutants through oxidation, which forms water vapor and carbon

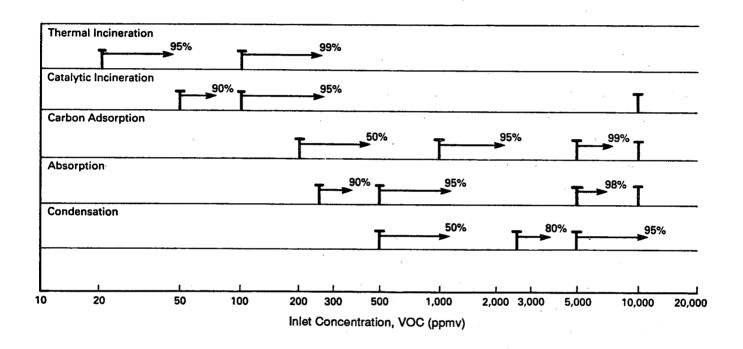


Figure 3-2. Percent reduction ranges for add-on control devices.⁷ Represents <u>maximum</u> achievable reduction for the corresponding inlet concentration.

dioxide. Any other elements in the organic compound will also be emitted as an oxide or acid gas; e.g., chlorine will be emitted as hydrogen chloride.

Thermal incinerators rely on high temperature, sufficient pollutant residence time, and adequate turbulence to ensure high destruction efficiencies. Catalytic incinerators operate at somewhat lower temperatures as a catalyst promotes the oxidation. Information on destruction efficiency of specific organic compounds is limited. Most volatile organic compounds are rapidly destroyed at temperatures over 1400°F; some compounds, however (e.g., halogenated hydrocarbons), require higher temperatures.

While destroying one air pollutant, incineration may create other pollutants that require further treatment for removal from flue gases. For example, an incinerator that effectively destroys trichloroethylene may create hydrogen chloride, which is then removed by flue gas scrubbing. The Toxic Release Inventory Form(s) should indicate the destruction of trichloroethylene and any resulting release, the release of hydrogen chloride, and the amount of HCl in any wastewater or slurry resulting from scrubbing.

Waste and purged gaseous organic compounds are also commonly destroyed by flaring when it is not economical to recover the heat value of the gases, and the control process upset vent gases. Although flaring is widely applied, information on the air pollutant destruction efficiencies is limited. A 98 percent destruction efficiency can be achieved for flares provided they operate under the conditions listed in Table 3-4.

TABLE 3-4. OPTIMAL OPERATING CONDITIONS FOR FLARES

Type of flare	Exit velocity, V (ft/sec)	Heating value, H _T of gas stream ^a (Btu/scf)
Steam-assisted	$V < 60$ $60 \le V < V_{max}(1)$ $V < 400$	$H_{T} \ge 300$ $300 < H_{T} < 1000$ $H_{T} > 1000$
Non-assisted		$H_{T} \ge 200$ $200 < H_{T} < 1000$ $H_{T} > 1000$
Air-assisted	V < V _{max(2)}	H _T > 300

a Heating value of total gas stream (not just listed chemical).

Notes:
$$V_{max(1)} = e^{\begin{bmatrix} 1.424 + 0.00118 & (H_T) \end{bmatrix}}$$
 or log $V_{max(1)} = 1.424 + 0.00118 & (H_T)$
 $V_{max(2)} = 28.54 + 0.087 & H_T$

H_T should be calculated at conditions of 25°C (77°F) and 1 atmosphere (14.7 psia). For information on measurement and calculation of operating exit velocity and heating value of gas stream, consult 40 CFR 60.18 (July 1986).

Flares with values of less than 300 Btu/scf (steam- or air- assisted flares) or 200 Btu/scf (nonassisted flares) may or may not achieve 98 percent destruction. For example, a steam-assisted flare burning a volatile organic compound subject to reporting could be considered to have a 98 percent efficiency for that compound if its exit velocity and Btu value of the gas stream were within one of the three operating conditions listed for this type of flare. This would allow an estimate of the treatment efficiency in absence of other data for the compound.

Another combustion technique that may be used as a control device for toxic air pollutants is to inject the pollutants into process heaters or boilers. Waste streams may provide supplemental fuel or may even be the primary fuel in some operations.

3.2.2 Adsorption

In an adsorption process, a pollutant is adsorbed on the surface of the adsorbent until its capacity is reached. Common adsorbent materials used are activated carbon, resins, and molecular sieve materials. The adsorbent can then be regenerated. The pollutant is released in a more concentrated form, which is recovered or treated by further processing. The particular adsorption/regeneration process and the pollutant and its associated process parameters determine further processing steps, which can include incineration or condensation and decantation so that the chemical can be recovered for recycling or disposal. Although adsorption is effective in the removal of various toxic chemicals from air, the regeneration and further processing steps may transfer some of the toxic substance to water or to solid waste streams, which must be considered releases to these media. Typically, the adsorption capacity increases with the molecular weight of the VOC being adsorbed. In addition, unsaturated compounds are generally more completely adsorbed than saturated compounds, and cyclical compounds are more easily adsorbed than

linearly structured materials. Also, the adsorption capacity is enhanced by lower operating temperatures and higher concentrations. The VOC's characterized by low vapor pressures are more easily adsorbed than those with high vapor pressures.

3.2.3 Absorption

Absorption as a method of treating an emission is a physical or chemical process that transfers a component(s) from a gas stream to a liquid. Although often used to recover products or raw materials, absorption can also serve as an emission control device. In this capacity, absorption has been used to control alcohols, acids, chlorinated and fluorinated compounds, aromatics, esters, and aldehydes. Absorption devices can be used separately or in conjunction with other air pollution control equipment, e.g., to provide additional pollutant removal after incineration or after condensation. Liquids are used as the absorbent; therefore, a media transfer of toxic pollutants can occur. In general, more soluble compounds are removed with greater efficiency. Liquid-to-gas ratios, liquid temperature, and column height are also important parameters affecting efficiency.

3.2.4 Condensation

Condensation is used as a control technique for some organic compounds. It cools the gas stream and transforms the gaseous compound to a liquid. Like absorption, condensation is one of the primary techniques used for product recovery; however, it is also used as an air-pollution-control device. Control of storage and process emissions is a common application. Condensers are frequently used in series with other control equipment, including absorbers, incinerators, and adsorbers.

3.2.5 Particulate Collection Devices

Electrostatic precipitators (ESP's), fabric filters, wet scrubbers, and cyclones or mechanical collectors are the four devices commonly used to remove particulate matter from air streams. These devices are widely applied in the metal processing industries, where they control many of the Title III, Section 313, metals and other solids. Gaseous compounds are not collected by these devices unless they adsorb on a solid particle or react with water in a scrubber. Vendors of particulate control equipment, when supplied with

sufficient data on flow rates, particle size distribution, etc., will guarantee the removal efficiency of their equipment. Any process variations that affect particle size, particle density, and gas velocity, however, will generally affect the removal efficiency of particulate control devices. In some applications, the solid particulate collected by these devices is recycled to a process, in which case they may be considered part of a unit process as opposed to air-pollution-control equipment. Otherwise, the collected particulate is disposed of and has the potential to create liquid or solid waste problems. Collection efficiency can be readily determined through a simple mass balance if one knows the inlet flow rate and concentration of particulate and can measure the amount of material collected by the device. In this case, the fractional efficiency is equal to the amount collected divided by the amount entering.

<u>Cyclones/Mechanical Collectors</u>. Cyclones are seldom used as the sole or primary means of particulate collection, but they often serve as "first stage" air-cleaning devices that are followed by other methods of particle collection. Cyclone collection efficiency is probably more susceptible to changes in particulate characteristics (i.e., process variation) than are other types of devices. Therefore, care should be taken in the use of design efficiency to estimate actual operating conditions. Although very little compound-specific collection data are available, cyclone operation is dependent on physical parameters (particle size, density, velocity) as opposed to the chemical nature or properties of the material being collected. Thus, within reason, it may be possible to obtain and transfer efficiency data from known applications to unknown applications on processes with physically similar particulate and gas flows.

<u>Fabric Filters</u>. When properly designed and operated, fabric filters or baghouses are efficient collection devices, even for small particles. Vendor information is often a good source of collection efficiency information, as most units are designed for specific applications. As in the case of cyclones, fabric filter performance is affected by process variations that affect the gas stream and by other variables, such as temperature and gas dew point. The particle collection mechanisms of these filters (like those of

cyclones) usually depend solely on physical as opposed to chemical properties; thus, data from known applications may be transferable.

<u>Electrostatic Precipitators</u>. Electrostatic precipitators remove from gas streams particles that have been electrically charged. They are not used to collect organic solids because of combustibility potential. Efficiency data are limited with the exception of ESP's applied to combustion processes. The collection efficiency of an ESP depends on the physical characteristics of the particulate and the gas stream, as well as on the electrical resistivity of the pollutant to be collected. Electrical resistivity, in turn, can be affected by temperature, which may vary in some processes.

<u>Wet Scrubbers</u>. Wet scrubbers are used to collect organic as well as inorganic particulate matter and reactive gases. Scrubbers, which often use water as the scrubbing medium, have the inherent potential of creating releases in the liquid medium. Like some other particulate collection equipment devices, scrubber designs are based on physical parameters, so available efficiency data may be transferrable. The key factors in scrubber performance are particle size and scrubber pressure drop. As shown in Figure 3-3 for a venturi-type scrubber, a high particle removal efficiency can be achieved for larger particles and at higher pressure drops across the device.

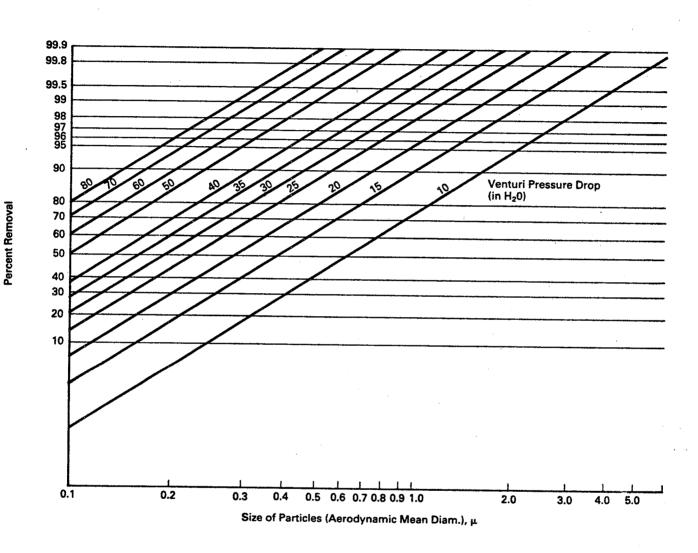


Figure 3-3. Venturi scrubber collection efficiencies. 7

SECTION 3 REFERENCES

- 1. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors, Volume I: Stationary Point and Area Sources. Fourth Edition. AP-42, September 1985.
- 2. U.S. Environmental Protection Agency. VOC Emission Factors for NAPAP Emission Inventory. EPA 600/7-86-052, December 1986.
- 3. U.S. Environmental Protection Agency. Volatile Organic Compound (VOC) Species Data Manual. Second Edition. EPA-450/4-80-015. Research Triangle Park, North Carolina. 465 pp. 1980.
- 4. Carl, J. E., et. al., Receptor Model Source Composition Library. EPA-450/4-85-002. November 1984.
- 5. U.S. Environmental Protection Agency. Survey of Perchloroethylene Emission Sources. EPA-450/3-85-017, June 1985.
- 6. U.S. Environmental Protection Agency. Hazardous/Toxic Air Pollutant Control Technology, A Literature Review. EPA-600/2-84-194, December 1984.
- 7. U.S. Environmental Protection Agency, Control Technologies for Hazardous Air Pollutants. EPA/625/6-86/014. September 1986.
- 8. Perry, R. H., and C. H. Chilton. Chemical Engineer's Handbook. Fifth Edition. New York. McGraw-Hill. 1973.

SECTION 3 BIBLIOGRAPHY

Documents 4 through 17 contain detailed information on the certain process industries, their emission sources, development and use of emission factors, control devices and their efficiency, as well as qualitative data on other emission sources. Documents 4 through 16 are chemical-specific, whereas Document 17 covers mostly VOC's, particulates, and other criteria pollutants. It does have some chemical-specific emission factors.

Document 1 is a compilation summary of chemical-specific emission factors, which includes a summary of factors found in Documents 4 through 16. Document 18 is a summary of the criteria pollutant emission factors from Document 17 and other data sources.

Table 3-5 has been prepared to aid users of this guidance to find information on chemical-specific emission factors for their industry. Although specific chemicals mentioned in the industry categories may not be on the Section 313 list, the documents cover emissions of listed 313 chemicals from the process. The industries for which particulate and VOC emission factors are available in Document 17 are listed in Appendix E. Industries covered by Document 18 are too numerous to list here, but are similar to those covered by Document 17.

The NTIS documents can be obtained from:

National Technical Information Service (NTIS) 5285 Port Royal Road Springfield, Virginia 22161 (703) 487-4650

Docu- ment No.	Document	NTIS No.	NTIS price as of June 1987
1	Preliminary Compilation of Air Pollutant Emission Factors for Selected Air Toxic Com- pounds. EPA 450/4-86-010a, April 1987	PB 87-183414	\$13.95
2	Hydrogen Chloride and Hydrogen Fluoride Emission Factors for the NAPAP Emission Inventory. EPA 600/7-85-041, January 1986	PB 86-134020	\$13.95
3	Ammonia Emission Factors for the NAPAP Emission Inventory. EPA 600/7-87-001, January 1987	PB 87-152336	\$13.95

Docu- ment			NTIS price as of
No.	Document	NTIS No.	June 1987
	Locating and Estimating Air Emissions from Sources of:		
4	Acrylonitrile. EPA 450/4-84-007a, March 1984	PB 84-200609	\$13.95
5	Carbon Tetrachloride. EPA 450/4-84-007b, March 1984	PB 84-200625	\$18.95
6	Chloroform. EPA 450/4-84-007c, March 1984	PB 84-200617	\$18.95
7	Ethylene Dichloride. EPA 450/4-84-007d, March 1984	PB 84-239193	\$13.95
8	Formaldehyde. EPA 450/4-84-007e, March 1984	PB 84-200633	\$18.95
9	Nickel. EPA 450/4-84-007f, March 1984	PB 84-210988	\$18.95
10	Chromium. EPA 450/4-84-007g, July 1984	PB 85-106474	\$24.95
11	Manganese. EPA 450/4-84-007h, September 1984	PB 86~117587	\$18.95
12	Phosgene. EPA 450/4-84-007i, September 1985	PB 86-117595	\$13.95
13	Epichlorohydrin. EPA 450/4-84-007j, September 1985	PB 86-117603	\$13.95
14	Vinylidene Chloride. EPA 450/4-84-007k, September 1985	PB 86-117611	\$13.95
15	Ethylene Oxide. EPA 450/4-84-0071, September 1986	PB 87-113973	\$13.95
16	Chlorobenzenes. EPA 450/4-84-007m, September 1986	PB 87-189841	\$18.95
17	Compilation of Air Pollutant Emission Factors-AP-42, Volume 1. Stationary Point and Area Sources, Fourth Edition. (Also available from: Supt. of Documents Government Printing Office Washington, D.C. 20402 (202) 783-3238 GPO Stock No. 055-000-00251-7 Price: \$20.00)	PB 86-124906	\$60.95

Docu- ment No.	Document	NTIS No.	NTIS price as of June 1987
- 1, -, - , -	Supplement A to Fourth Edition of AP-42	PB 87-150959	\$36.95
18	Criteria Pollutant Emission Factors for the 1985 NAPAP Emissions Inventory. EPA 600/7-87-015, May 1987	PB 87-198735	\$24.95
19	VOC Species Data Manual. EPA 450/4-80-015, 1980	PB 81-119455	\$36.95
20	Receptor Model Source Composition Library. EPA 450/4-85-002, November 1984	PB 85-228823	\$30.95
21	Emission Factors for Equipment Leaks of VOC and HAP. EPA 450/3-86-002, January 1986	PB 86-171527	\$13.95
22	Evaluation of Control Technologies for Hazardous Air Pollutants, Volume I, Technical Report. EPA 600/7-86-009a, 1986	PB 86-167020	\$30.95
23	Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models. U.S. EPA Office of Air Quality Planning and Standards, Emission Standards Division (MD-13), Research Triangle Park, North Carolina 27711. Phone (919) 541-5671	Not available from NTIS	
24	Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and HAP. U.S. EPA Office of Air Quality Planning and Standards, December 1987. David Markwodt, Chemicals and Petroleum Branch (MD-13), Research Triangle Park, North Carolina 27711. Phone (919) 541-5411		,

TABLE 3-5. AVAILABILITY OF CHEMICAL-SPECIFIC EMISSION FACTORS FOR VARIOUS PROCESSES

Industry/process	No. for chemical-specific emission factor
CHEMICAL PROCESS INDUSTRY	
Ammonia synthesis Petroleum refineries Coke manufacture Sodium dichromate manufacture Chromic acid manufacture Acrylonitrile manufacture Fluorocarbon 22 manufacture Methane chlorination process Ethylene oxide manufacture Pesticide manufacture Perchloroethylene manufacture Ethylene dichloride manufacture Vinyl chloride monomer manufacture	3, 17 1, 3, 8 3, 9, 17 1, 9 1, 9 1, 4 1, 6 1, 15 1, 16 1, 5, 6, 7, 14 1, 5, 6, 7
Methyl chloroform manufacture Ethylene amines manufacture Trichloroethylene manufacture Vinylidene chloride manufacture Ethyl chloride manufacture Carbon tetrachloride manufacture Fluorocarbon 11 and 12 manufacture Pharmaceutical manufacture Chlorobenzene manufacture Dye/pigment manufacture 3,4-Dichloroaniline manufacture Chlorinated solvent manufacture Caprolactam manufacture	1, 7 1, 7 5, 6, 7, 14 7, 14 1, 7 1, 5 1, 5 1, 5 1, 16 1, 16 1, 16 1, 16 1, 16 1, 16 1, 16 1, 16
Phenol manufacture Propylene oxide manufacture Hydrogen chloride manufacture Hydrogen fluoride manufacture Formaldehyde manufacture Hexamethylene tetramine manufacture Pentaerythritol manufacture 1,4-Butanediol manufacture Trimethylol propane manufacture Phthalic anhydride manufacture Solid urea manufacture Phosgene manufacture Toluene diisocyanate manufacture Substituted phenyl urea manufacture Epichlorohydrin manufacture	2 2, 17 2, 17 1, 8 1, 8 1, 8 1, 8 1, 8 1, 8 1, 17 1, 12 1, 12 1, 12 1, 12 1, 13

(continued)

TABLE 3-5 (continued)

Industry/process	No. for chemical-specific emission factor
CHEMICAL PROCESS INDUSTRY (continued)	
Batch process using epichlorohydrin as feedstock	1, 13
Adipic acid manufacture	17, 18
Carbon black manufacture	17
Chlorine manufacture	1, 17
Phosphoric acid manufacture	<u>17</u>
Sulfuric acid manufacture	17
Lead alkyl compound manufacture	17
Maleic anhydride manufacture	17
Ammonium nitrate manufacture Ammonium sulfate manufacture	17 17
Manganese chemicals manufacture	1, 11
Polysulfide rubber production	1, 7
Vinylidene chloride polymerization plants	1, 14
Formaldehyde resin production	1, 8
Polyacetal resin production	1, 8
Polycarbonate production	1, 12
Epoxy resin production	1, 13
METALLURGICAL INDUSTRY	
Nickel production	1, 9
Nickel ore mining and smelting	1, 9
Nickel matte refining	1, 9
Steel production	1, 9, 10, 11
Ferrous and nonferrous metals production	1, 9
Chromite ore refining	1, 10
Ferrochrome plants Cast iron production	1, 10 1, 11
Nonferrous alloy production	1
Primary lead smelting	ī
Beryllium alloy stamping, drawing, molding	1
Beryllium metal fabrication Gray iron production	1, 17
Zinc smelting	1
Copper smelting	1, 17
Cadmium refining	1
Secondary lead smelting	1, 17
Steel scrap	1
Primary aluminum production	1, 2, 17
Primary mercury ore processing	1

(continued)

TABLE 3-5 (continued)

Industry/process	No. for chemical-specific emission factor
METALLURGICAL INDUSTRY (continued)	
Secondary mercury processing Metallurgical vanadium processing Manganese ore beneficiation, transport, storage Manganese ferroalloy production Manganese metal and manganese oxide production Iron and steel foundries Lead type production	1 1 11 1, 11 1, 11
FOOD AND AGRICULTURAL INDUSTRY	
Cropland spreading of livestock wastes Beef cattle feed lots Fertilizer manufacture and use Grain fumigation Phosphate fertilizer production Fish processing plants	3 3, 17 3 1, 5, 7 2, 17 17
MINERAL PRODUCT INDUSTRY	
Cement plants Refractory industry Asbestos milling, processing Glass production Ceramics Brick manufacture Glass fiber manufacture Frit smelting Lead glass manufacture Asphalt concrete plant Hot mix asphalt plant	1, 9, 11 1, 10 1, 10 1 1 17 17 17 17 17 17 18
MISCELLANEOUS INDUSTRY/PROCESS	
Integrated circuit board manufacture Battery manufacture Functional fluids use Textile dyeing Vapor degreasing Conveyorized degreasing Photoresist stripping	1, 8 1, 9, 17 16 16 1

TABLE 3-5 (continued)

Industry/process	No. for chemical-specific emission factor
MISCELLANEOUS INDUSTRY/PROCESS (continued)	
Cooling water systems Loading/storage of gasoline Use of epoxy resins Tank and drum solvent cleaning Burning cotton ginning waste Waste treatment, storage, and disposal Wastewater treatment operations	1, 6, 9, 10 1, 7 1, 13 17 1 1, 11 1, 16
Explosives manufacturing Can soldering (lead) Lead cable covering Ammunition manufacture	17 17 17 17

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OUTLINE FOR SECTION 4

ESTIMATING RELEASES IN WASTEWATER

- 4.1 Sources of Wastewater and Methods for its Disposal
 - Direct Discharge to Surface Waters 4.1.1
 - 4.1.2 Discharge to a Public 4.1.3 Underground Injection Discharge to a Publicly Owned Treatment Works

 - 4.1.4 Surface Impoundments
 - 4.1.5 Land Treatment
- 4.2 Calculating Releases From Wastewater
 - 4.2.1 Direct Measurement
 - 4.2.2 Wastewater Release Calculations by Mass Balance
 - 4.2.3 Emission Calculations Using Release Data From Other Facilities in Same Industry
 - 4.2.4 Engineering Estimates
- 4.3 Estimating Treatment Equipment Efficiency

SECTION 4

ESTIMATING RELEASES IN WASTEWATER

At most facilities, wastewater from individual process sources is centrally collected and discharged from one point. This greatly simplifies the task of estimating releases of toxic materials to water because it decreases to one or a few the number of discharge streams for which releases must be estimated. Nevertheless, in some situations it may be necessary to estimate releases in wastewater from individual sources.

A facility that discharges or has the potential to discharge water containing toxic and/or hazardous wastes probably operates under the terms of Federal, State, and/or local permits. The permit(s) usually require measurements of the water volume and analyses of some generalized wastewater parameters [e.g., biological oxygen demand (BOD) and total suspended solids (TSS)]. Occasionally, releases for which the permit requires analyses and those subject to reporting will be similar. In these instances, releases can be calculated by straightforward multiplication of the volume of wastewater released by the concentration of the chemical released. The permit(s) also often require that the wastewater be treated before its discharge to minimize releases.

The following subsections present some of the various sources of waste-water and methods of wastewater disposal. Also discussed are methods for calculating releases of compounds subject to reporting in wastewater and estimating efficiencies of wastewater treatment devices.

4.1 SOURCES OF WASTEWATER AND METHODS FOR ITS DISPOSAL

Releases of toxic chemicals can originate from a wide variety of wastewater sources. Table 4-1 lists some of the more common sources and processes that generate wastewater. Unlike air emissions, wastewater from individual sources in a facility are usually centrally collected and combined for discharge at one or a few points. Methods of wastewater disposal are presented in Table 4-2 and are discussed briefly in the following subsections.

TABLE 4-1. TYPICAL WASTEWATER SOURCES

Untreated process wastewater
Miscellaneous untreated wastewater - equipment washdown,
steam jet condensate, cooling water
Decantates or filtrates
Cleaning wastes
Steam stripping wastes
Acid leaching solutions
Spent plating, stripping, or cleaning baths
Spent scrubber, absorber, or quench liquid
Off-spec, discarded products or feedstock
Distillation side cuts
Cyclone or centrifuge wastes
Spills, leaks, vessel overflows

TABLE 4-2. METHODS OF WASTEWATER DISPOSAL

Direct discharge to surface waters

Discharge to a publicly owned treatment works

Underground injection

Surface impoundments

Land treatment

4.1.1 <u>Direct Discharge to Surface Waters</u>

Many facilities discharge wastewater directly to nearby bodies of water; this action requires a National Pollutant Discharge Elimination System (NPDES) permit. The permit usually requires monitoring of the wastewater discharge flow and the concentrations of various constituents within the

wastewater (usually generalized constituents such as BOD and TSS). Monitoring is usually not required for most of the individual chemicals or compounds. When such monitoring is required, wastewater flow rate and concentration data collected for the NPDES permit can be used to calculate wastewater releases directly.

4.1.2 Discharge to a Publicly Owned Treatment Works (POTW)

Many facilities discharge their wastewater to POTW's. In some cases, a POTW may require pretreatment of wastewater and/or monitoring of the flow rate and the concentration of various constituents. If a POTW requires monitoring of a chemical or compound subject to reporting, releases of that chemical or compound in the wastewater can be calculated by multiplying the reported concentration by the flow rate. On the Toxic Chemical Release Inventory Form, discharge to a POTW is considered a transfer to an offsite location.

4.1.3 Underground Injection

In some situations, wastewater containing hazardous and/or toxic wastes may be injected beneath the earth's surface in locations where it is unlikely to contaminate ground water. Injection operations are usually controlled by RCRA permitting procedures that require maintaining records of the volumes and analyses of the wastes injected. From this information, quantities of listed chemicals and/or compounds that are disposed of in this manner can be directly calculated.

4.1.4 Surface Impoundments

A surface impoundment is a natural topographic depression, man-made excavation, or diked area formed primarily of earthen materials (although it may be lined with man-made materials), which is designed to hold an accumulation of liquid wastes or wastes containing free liquids. Examples of surface impoundments are holding, storage, settling, and elevation pits, ponds, and lagoons. If the pit, pond, or lagoon is intended for storage or holding without discharge, it is considered to be a surface impoundment used as a final disposal method under Section 313 Reporting. The operation of surface impoundments is usually controlled by RCRA permits, which require maintaining records of the volume and concentration of hazardous wastes disposed of.

This information can be used for direct calculation of the quantity of a listed chemical and/or compound disposed of in this manner. This disposal method is considered a release to land; however, listed chemicals in the impoundment may be released to air by volatilization, collected as sludge and removed, or biodegraded. Any releases from the impoundment should be accounted for in release totals to air, water, land, or offsite disposal.

4.1.5 Land Treatment

Land treatment is a disposal method in which wastewater is applied onto or incorporated into soil. These operations are usually controlled by RCRA permits with conditions that regulate the volumes of wastewater to be treated, the concentrations of hazardous and/or toxic materials it contains, and the frequency of land application, and also require a ground-water monitoring program. This information can be used to calculate the quantity of a listed chemical and/or compound disposed of in this manner. Chemicals and/or compounds in the wastewater are released to the soil or to air (by volatilization). On the Toxic Chemical Release Inventory Form, this disposal method is considered a "release to land."

4.2 CALCULATING RELEASES IN WASTEWATER

Quantities of listed chemicals and/or compounds released to the environment in wastewater can be calculated by summing the releases from individual operations or by determining releases from a central wastewater discharge point (if available). The latter method is preferred because it involves the direct measurement or estimation of the flow of the discharge stream, and the concentrations of chemicals and/or compounds it contains. The following subsections describe the use of direct measurement, mass balance, release data from other facilities in the industry, and engineering calculations to estimate releases of listed chemicals and/or compounds in wastewater. No general compilation of emission factors is available for release in wastewater as it is for releases to air; however, in some instances, information from other facilities in the industry can be applied to estimate releases in wastewater.

4.2.1 Direct Measurement

Direct measurement can be used to calculate releases in wastewater from individual processes or from a central discharge point. This method involves

multiplying the wastewater flow rate by the concentration of the chemical or compound of concern. The following two items describe direct measurement of wastewater releases based on average measured values and multiple measured values, respectively.

Releases Based on Total Annual Volume and Average Measured Concentration. If a wastewater stream has a relatively constant daily flow rate and the measured concentrations of listed the chemicals and/or compounds in the stream do not vary greatly or are well characterized, average values for flow rate and concentration can be used to calculate releases.

 $\underline{\text{Example 4-1}}$ - Use of direct measurement to estimate releases in wastewater:

Step 1. Gather process information and monitoring data.

A stream containing an average acetaldehyde concentration of 500 milligrams per liter is sent to an onsite treatment system at a rate of 5 gal/min. The stream leaving the treatment system at 5 gal/min contains 25 milligrams of acetaldehyde per liter. If the plant operates 24 hours per day, 330 days per year, the quantity of acetaldehyde entering and leaving the treatment system can be calculated, assuming no net loss of water or acetaldehyde by evaporation to air. Also, the treatment system efficiency can be calculated.

Step 2. Calculate the quantity of acetaldehyde entering and leaving the system.

Volume =
$$\frac{5 \text{ gal}}{\text{minute}} \times \frac{60 \text{ min}}{\text{hour}} \times \frac{24 \text{ h}}{\text{day}} \times \frac{330 \text{ days}}{\text{year}} = \frac{2.376 \text{ million gal}}{\text{year}}$$

Into system:
$$\frac{2.376 \text{ million gal}}{\text{year}} \times \frac{500 \text{ mg}}{\text{liter}} \times \frac{3.78 \text{ liters}}{\text{gallon}} \times \frac{1 \text{ lb}}{453,000 \text{ mg}}$$
$$= \frac{9913.11 \text{ lb}}{\text{year}}$$

From system:
$$\frac{2.376 \text{ million gal}}{\text{year}} \times \frac{25 \text{ mg}}{\text{liter}} \times \frac{3.78 \text{ liters}}{\text{gallon}} \times \frac{1 \text{ lb}}{453,000 \text{ mg}}$$
$$= \frac{495.66 \text{ lb}}{\text{year}}$$

Step 3. Calculate treatment system efficiency.

Treatment system efficiency:
$$\frac{9913.11 - 495.66}{9913.11} \times 100 = 94.99\%$$

Report 95%.

Releases Based on Calculated Annual Volume and Average Concentration
From Scheduled Periodic Water Analyses. Even though a facility has regularly scheduled wastewater sampling and analyses to determine flow rates and toxic pollutant concentrations before and after treatment, both flow rates and concentrations may vary considerably. Daily release rates are calculated by multiplying the flow rate times the concentration. These daily emission rates can be averaged to yield an annual release rate if the sample timing and frequency accurately represent the discharge.

<u>Example 4-2</u> - Use of direct measurement to estimate releases in wastewater:

Step 1. Gather wastewater flow and concentration data from NPDES permit.

The NPDES Permit of a leather tanning facility requires daily monitoring of wastewater flow volume and biweekly analysis of a daily composite sample of this discharge for total chromium. The total chromium analytical results for the year are presented below.

Step 2. Calculate releases for those days in which a chromium analysis was performed.

The total chromium releases (in pounds per day) to water for a given day at this facility are calculated by multiplying the daily flow (in million gallons per day) by the total chromium concentration (in micrograms per liter) times a conversion factor (8.34×10^{-3}) .

Discharge flow rate, 10 ⁶ gal/day	Total chromium, ug/liter	Releases, lb/day	
0.415	918	3.177	
0.394	700	2.300	
0.417	815	2.834	
0.440	683	2.506	
0.364	787	2.389	
0.340	840	2.382	
0.457	865	3.297	
0.424	643	2.274	
0.463	958	3.699	
0.414	681	2.351	
0.476	680	2.699	

(continued)

Discharge flow rate, 10 ⁶ gal/day	Total chromium, ug/liter	Releases, lb/day
0.431	627	2.254
0.369	807	2.484
0.392	729	2.383
0.323	964	2.597
0.302	722	1.818
0.358	566	1.690
0.322	510	1.370
0.330	630	1.734
0.322	630	1.692
0.408	652	2.218
0.442	649	2.392
0.356	69 5	2.063
0.390	758	2.465
0.423	658	2.321
0.487	970	3.940
	Averag	je 2.435

Step 3. Calculate annual releases.

Based on an average daily release of 2.44 1b over the year and 250 days of discharge during the year, the yearly total chromium discharged to water is:

$$\frac{2.435 \text{ lb}}{\text{day}} \times \frac{250 \text{ days}}{\text{year}} = 609 \text{ lb per year}$$

Report 610 1b per year.

Permit requirements or detection limits of analytical procedures (particularly after treatment) may produce an analytical result, such as the concentration of a toxic and/or hazardous pollutant, expressed as less than a certain value. For example, a copper concentration may be reported as less than 5 micrograms per liter (5 parts per billion). In this case, a common practice is to use a value of one-half the detection limit in calculating an average concentration. Based on the data set available, this may or may not be the best procedure for evaluating results. Any procedure used must take into account the number of analyses available, the distribution of data, and the detection limit.

Example 4-3 - Use of direct measurement to estimate releases in wastewater:

Step 1. Gather analytical results and determine average value.

The results of 10 copper analyses are expressed in micrograms per liter:

The average concentration is $\frac{1(6) + 1(10) + 1(8) + 7(5/2)}{10} = \frac{4.2 \text{ micrograms}}{1 \text{ iter}}$

=
$$4.2 \times 10^{-6}$$
 grams per liter

Step 2. Determine annual releases.

For an annual flow of 37.8 million liters (10 million gallons), the average discharge would be 4.2×10^{-6} grams/liter x 37.8 x 10^{6} liters/year = 159 grams/year or 0.35 lb/year.

4.2.2 Wastewater Release Calculations by Mass Balance

Wastewater releases from individual processes or a central discharge point can be estimated by the use of mass balances; however, care must be exercised because it is not always clear to which medium (air, water, or solid waste) the release occurs. In some cases, the contaminants in the wastewater volatilize and result in an air release, not a water release. During wastewater treatment, many contaminants settle out of the wastewater and are disposed of as solid waste. Also, as discussed previously, when mass balances are applied to very large operations, they are susceptible to large errors in release estimates as a result of even small errors in raw material or finished product quantities.

Example 4-4 - Use of a mass balance to estimate releases in wastewater:

Step 1. Gather purchasing and inventory data.

A plant buys 20,000 gal (75,800 liters) per year of a water-based cleaner that contains 0.5 lb/gal (60 g/liter) of 1,1,1-trichloroethane as an emulsion. No material is recovered and year-beginning and year-ending inventories are both 1000 gallons.

Step 2. Calculate annual releases.

Assume all trichloroethane is discharged into the plant wastewater and none evaporates into the air.

Annual emissions =
$$\frac{20,000 \text{ gal}}{\text{year}} \times \frac{0.5 \text{ lb}}{\text{gallon}} = \frac{10,000 \text{ lb}}{\text{year}}$$

If the plant wastewater undergoes treatment before discharge, releases would equal 10,000 lb/year multiplied by [1 minus the treatment efficiency] for trichloroethane. The quantity of trichloroethane removed during treatment is equal to the sum of the quantities volatilized to air, partitioned to sludge (solid waste), and chemically transformed or destroyed.

Example 4-5 - Use of a mass balance to estimate releases in waste-water:

Step 1. Gather production data.

A plant processes 220,000 lb per year of scrap containing an average of 12 percent silver. The plant recovers 26,000 lb of 100 percent silver metal.

Step 2. Calculate annual releases.

Emissions = Material In - Material Recovered

220,000 lb scrap x
$$\frac{0.12 \text{ lb silver}}{\text{lb scrap}}$$
 = 26,400 lb silver

26,400 lb silver in scrap - 26,000 lb silver recovered

= 400 lb discharged yearly

Again, any treatment of plant wastewater would result in a release adjusted for the treatment removal efficiency for silver.

4.2.3 Release Calculations Using Release Data From Other Facilities in the Same Industry

The wastewater bibliography at the end of this section lists some possible sources of information on wastewater emission and treatment for various processes and industries. This listing, which was compiled from a literature search of wastewater emissions and treatment efficiencies, is provided as a starting point for finding documented wastewater information concerning similar processes and industries. It does not represent a complete listing of available sources and those presented may not contain information pertaining to many of the listed toxic chemicals.

A listing of EPA development documents for effluent limitation guidelines and standards for particular industries is attached to the wastewater bibliography. These documents, which contain measured data on specific compounds (primarily the 129 priority pollutants) discharged by a particular industry, may serve as a source of emission data. A facility should use only data for operations and treatment methods similar to its own. These documents may not give direct emission factors, but they can provide other useful information, such as estimates of wastewater concentrations for specific chemicals.

In lieu of these documents, emission factors based on production or process throughput may be derived from information available in the technical literature or based on manufacturers' or vendors' data for a similar process. Information also may be available through trade and industrial organizations and associations.

In addition, technical journals sometimes contain information applicable to one's particular process or industry. The following journals deal with wastewater and wastewater treatment:

- Water Engineering and Management
- Journal of the Water Pollution Control Federation
- Water Technology
- Journal of the Environmental Engineering Division, ASCE
- Environmental Science and Technology
- Pollution Engineering
- Effluent and Water Treatment Journal
- Chemical Engineering

Because each individual processing or manufacturing facility is unique, great care must be taken when applying emission factors to ensure that the conditions under which the factor was developed apply to the facility in question.

4.2.4 Engineering Estimates

Estimates in lieu of direct measurements would not generally satisfy wastewater discharge permit requirements for any hazardous and/or toxic material. The permit would require monitoring and analyses that provide a basis for estimating releases.

Engineering estimates could be used, however, to calculate releases in wastewater from individual unit operations. Physical and chemical properties of the listed chemicals and/or compounds, such as water solubility, could be

used as a basis for estimating releases directly or in conjunction with one of the other release-estimation methods. Also, equipment parameters (e.g., pump flow capacity) could be used to estimate wastewater flow rates.

The solubility of most compounds in water is known, and this value can serve as a basis for the upper limit concentration of a chemical present in a wastewater stream; however, temperature, pressure, pH, and the presence of other compounds will affect solubility.

Measurement of a secondary or generalized parameter can also be used in an engineering estimate of releases in wastewater. Typically, the only measurements that can be used to calculate releases are those representing the particular chemical or compound of concern. In some situations, however, the concentration of a particular chemical in a wastewater can be related to generalized parameters, such as BOD, chemical oxygen demand (COD), or pH. For example, the wastewater generated from a particular process is known to contain only phenol, and a relationship has been established that indicates that the wastewater contains an average of 0.4 milligram per liter of phenol for every milligram per liter of COD. Based on this relationship, the concentration of phenol in the wastewater can be estimated by measuring the COD. A word of caution: if the wastewater contains other compounds that will influence the measurement of the generalized parameter, the relationship between the chemical of concern and the generalized parameter will vary. Under these circumstances, this estimation technique cannot be used.

The pH parameter can be used to estimate the concentration of an acid or base if it is known that the acid or base is the only compound in the wastewater affecting pH; however, this situation is rare. When it does occur, the acid or base disassociation constant can be used with the pH measurement to calculate the concentration of the acid or base in solution. The reader is urged to consult a general chemistry textbook for details of this calculation.

Example 4-6 - Use of engineering calculations to estimate releases in wastewater:

Step 1. Diagram process.

In the production of ethylene dichloride (EDC) by the oxygen process (oxychlorination), a decanter is used to separate EDC from H₂O formed

during the reaction step. The decanted H_2O stream is then discharged to a POTW along with wastewater from the entire facility.

Step 2. Make engineering assumptions to estimate chemical concentration in process streams.

To estimate the quantity of EDC emitted to the POTW from this particular operation, the following engineering calculations will be used to develop a mass balance around the decanter:

engineering calculation: The reaction stoichiometry dictates that equal molar portions of EDC and water are contained in the stream entering the decanter (Stream No. 1). As such, the composition of Stream No. 1 is known.

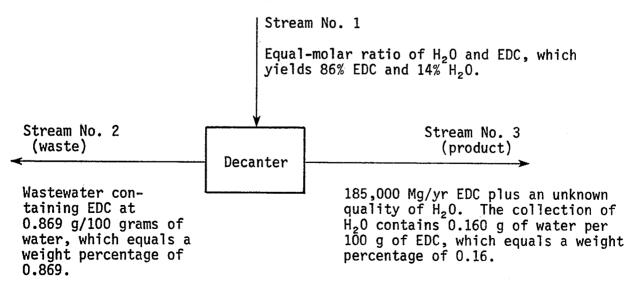
1 mole EDC = 97 grams; 1 mole H_2O = 18 grams

1 mole EDC + 1 mole H_2O = 115 grams

EDC weight percentage = $\frac{99}{115}$ grams x 100 = 86 percent

- Engineering calculation: The solubility of EDC in water is 0.869 gram per 100 grams. Assuming equilibrium in the decanter, this solubility represents the concentration of EDC in the wastewater stream (Stream No. 2). Also, the solubility of water in EDC is 0.160 gram per 100 grams. This solubility represents the concentration of $\rm H_2O$ in the EDC product stream (Stream No. 3).
- Step 3. Perform mass balance around the process.

This facility is known to produce 185,000 Mg/year (megagrams per year) of EDC. By combining this with the engineering calculations above, the following mass balance can be performed.



Mass Balance:

Total: Stream No. 1 (Mg/yr) = Stream No. 2 (Mg/yr) + Stream No. 3 (Mg/yr)

From the EDC production rate, it is known that:

Stream No. 3 = $185,000 \text{ Mg EDC/yr} + X \text{ Mg H}_2\text{O/yr}$

The quantity of $\rm H_2O$ in Stream No. 3 is determined by using the solubility of $\rm H_2O$ in EDC:

$$X = \frac{0.160 \text{ gram H}_20}{100 \text{ grams EDC}} \times \frac{185,000 \text{ Mg EDC}}{\text{year}} \times \frac{10^6 \text{ grams EDC}}{1 \text{ Mg EDC}}$$

= 296 x
$$\frac{10^6 \text{ grams H}_20}{\text{year}}$$
 = $\frac{296 \text{ Mg H}_20}{\text{year}}$

: Stream No. 3 = $\frac{185,296 \text{ Mg}}{\text{year}}$

The total mass balance can be written as:

Eq. A: Stream No. 1 (Mg/yr) = Stream No. 2 (Mg/yr) +
$$185,296$$
 (Mg/yr)

EDC: Eq. B: (0.86) Stream No. 1 = (0.00869) Stream No. 2 + 185,000

$$\frac{\text{Eq. B}}{\text{Eq. A}}$$
 0.86 = $\frac{(0.00869) \text{ Stream No. 2 + 185,000 (Mg/yr)}}{\text{Stream No. 2 + 185,296 (Mg/yr)}}$

Solving for Stream No. 2 = 30,125 Mg/yr.

Step 4. Calculate total annual releases.

Therefore EDC emissions to the wastewater equal

$$(30,125 \text{ Mg/yr}) \times (0.00869) = 262 \text{ Mg/yr}$$

 $262 \text{ Mg/yr} \times 10^3 \text{ Kg/Mg} \times 2.2 \text{ lb/Kg} = 576,400 \text{ lb/year}$

Report 576,000 lb/year.

Example 4-7 - Use of engineering calculations to estimate releases in wastewater:

Step 1. Gather process information and analytical data.

Ethyl acrylate is used to make a water-soluble acrylic polymer in a batch process. The polymerization reactor is cleaned after each batch, and some unreacted ethyl acrylate is released in wastewater. The reactor

volume is 10,000 gallons, and eight batches are processed per day for 250 days per year. Based on laboratory analyses, it is known that the reactor product mixture contains 1.2 percent ethyl acrylate and has an approximate specific gravity of 1.02.

Step 2. Using an engineering assumption, calculate annual releases from the process.

Based on a study of equipment cleaning practices, the amount of residue left in tanks after emptying can be estimated as 1 percent.* The amount of ethyl acrylate released to the wastewater through cleaning residue from the reactor can be estimated as follows:

$$\frac{8 \text{ batches}}{\text{day}} \times \frac{250 \text{ days}}{\text{year}} \times \frac{10,000 \text{ gallons}}{\text{batch}} \times \frac{8.34 \text{ lb H}_20}{1 \text{ gallon}}$$

$$\times \frac{1.02 \text{ lb reactor product}}{1.00 \text{ lb H}_20} \times \frac{0.010 \text{ lb residue}}{1 \text{ lb reactor product}}$$

Step 3. Calculate total annual releases from the entire facility.

The wastewater from this activity is treated along with the wastewater for the entire facility before discharge. It is estimated that an additional 10,000 pounds of ethyl acrylate is discharged to the wastewater from other sources in the facility. If the wastewater treatment process provides 80 percent removal of ethyl acrylate, the yearly discharge of ethyl acrylate from the facility to water would be:

$$\left[\frac{20,416 \text{ lb}}{\text{year}} + \frac{10,000 \text{ lb}}{\text{year}}\right] \times \left[\frac{100-80}{100}\right] = 6083 \frac{\text{lb}}{\text{year}}$$

Report 6100 lb/year.

From "Releases During Cleaning of Equipment." Prepared by PEI Associates, Inc., for the U.S. Environmental Protection Agency Office of Pesticides and Toxic Substances, Washington, D.C. Contract No. 68-02-4248. June 30, 1986. The reactor product mixture in this example would have a relatively high viscosity. For lower-viscosity materials, a table is presented in Section 5 (Table 5-2), which relates residue quantities to the capacity of tanks and drums based on unloading method, vessel material, and bulk fluid material. If the information in Table 5-2 cannot be applied to a particular situation or material, 1.0 percent is a common estimate for residue quantities.

<u>Example 4-8</u> - Use of engineering calculations to estimate releases in wastewater:

In batch dyeing processes for textiles or leather, unexhausted dye is released during the draining of the dye batch and subsequent rinsings of the fabric or leather. An estimate of the amount of dye released to wastewater can be made if the degree of exhaustion for the particular dye is known. It is best to use exhaustion data as measured for the dye under actual plant operating conditions, but in the absence of such data, literature values (or manufacturers data) could be utilized. The type of fabric being dyed, the dyeing temperatures, and other operating parameters may greatly influence the degree of exhaustion and should be taken into account when using exhaustion data from other sources. An example for calculating releases for a dye with the use of exhaustion data is as follows:

Step 1. Gather production information and process data from similar operations at other facilities

A facility consumed approximately 37,000 lb/yr of 30 percent active C.I. Disperse Yellow 3 dye in the paddle-dyeing of nylon carpets. The following is a list of exhaustion data for various substrates collected from dye manufacturers:

Dye Temperature and Exhaust Data for C.I. Disperse Yellow 3

Substrate	Dyeing Temperature, °F	Degree of Exhaustion, %	
Nylon carpet	190-212	80-90	
Nylon hosiery	180-205	75-90	
Acetate linings	160-190	68-90	

Step 2. Calculate annual releases.

Total yearly releases can be calculated by assuming that all the unexhausted dye is released in wastewater.

37,000 lb dye formulation \times 0.30 active dye per year \times 0.30 active dye not exhausted on fabric

= 2220 lb C.I. Disperse Yellow 3 released per year

Report 2200 lb/year.

If the wastewater is treated before being discharged from the facility, emissions would be reduced by a factor equal to the treatment efficiency for the dye in wastewater.

4.3 ESTIMATING TREATMENT EQUIPMENT EFFICIENCY

Toxic pollutants entering a wastewater treatment device may undergo one or more of the following fates: 1) transfer from the wastewater stream to another media (air or land), 2) modification to a less toxic state by chemical reaction, 3) destruction through biodegredation or chemical reaction, or 4) passing through untreated. Any releases of listed chemicals and/or compounds to air or land (via sludge disposal) resulting from the treatment of wastewater must be accounted for in the total quantity of releases to those media. Care must be taken to ensure that the quantity released to another medium is not also counted into the total quantity released to water. Table 4-3 lists some wastewater unit operations.

Wastewater treatment efficiency is based on the amount of a contaminant removed from the wastewater stream, either by destruction or modification of the pollutant or by transfer to another medium (air or solid).

Percentage efficiency =
$$\frac{X \text{ inlet - } X \text{ outlet}}{X \text{ inlet}} \times 100$$

where X inlet = total mass of pollutant X flowing to the wastewater treatment system in a given year

For toxic metals, release estimates and treatment efficiencies must be reported on the basis of the mass of the parent metal. For acids and bases, treatment efficiency is calculated based on the amount of acid or base neutralized.

Wastewater treatment systems are often made up of multiple-unit operations. In these instances, each unit operation in the system used to treat a particular chemical should be listed on Form R, and the boxes for sequential treatment marked. The range of influent concentration should only be provided for the first unit in the treatment sequence. Also, only the overall system treatment efficiency should be estimated. The efficiency of the system should be reported in the space provided for the last step of the system. For example, if acetone is present in a facility's wastewater that is treated by settling/clarification followed by aerobic biological treatment, portions of the acetone will be removed during both steps of the treatment sequence.

TABLE 4-3. UNIT OPERATIONS AND PROCESSES USED TO TREAT WASTEWATER

i. Chemical oxidation

Cyanide oxidation--alkaline chlorination

Cyanide oxidation--Electrochemical

Cyanide oxidation--Other

General oxidation (including disinfection) -- chlorination

General oxidation (including disinfection) -- ozonation

General oxidation (including disinfection) -- other

ii. Chemical precipitation (pH adjustment, flocculation, and settling)

Chemical precipitation--lime or sodium hydroxide

Chemical precipitation--sulfide

Chemical precipitation--other

iii. Chromium reduction

iv. Complexed metals treatment (other than pH adjustment)

v. Emulsion breaking

Emulsion breaking--thermal

Emulsion breaking--chemical

Emulsion breaking--other

vi. Adsorption

Carbon adsorption

Ion exchange

Resin adsorption

Other adsorption

vii. Stripping

Air stripping

Steam stripping

Other stripping

viii. Filtration

ix. Air flotation

x. Settling/clarification and oil skimming

xi. Biological treatment

Aerobic

Anaerobic

Facultative

Other

xii. Other wastewater treatment

Wet air oxidation

Neutralization

Equalization

Reverse osmosis (other than for recovery/reuse)

On the Toxic Chemical Release Inventory Reporting Form for acetone, both treatment codes should be entered separately, and the sequential treatment box should be checked for both. The acetone influent concentration range should be entered with the settling/clarification treatment method. The overall system treatment efficiency should be entered with the aerobic biological treatment method.

The efficiency of removing or destroying a specific compound varies widely depending on the design and operation of a system (e.g., retention time, inlet loading, biological activity). The best method for calculating treatment efficiency for an individual compound is by direct measurement of the treatment device's influent and effluent streams. A combination of measurement data and mass balances can be used to make reliable estimates based on actual operating conditions.

In lieu of operating data, it is best to refer to the EPA Development Documents for Effluent Limitation Guidelines for the facility's particular industry, which was discussed in Subsection 4.2.3. The next best source is information from the literature on treatment systems similar to those at the given facility (see Subsection 4.2.3). Obviously, the operating conditions under which the efficiency information was derived for a particular treatment system would have to be similar to those at the given facility.

Table A-1 in Appendix A contains numerous citations of wastewater treatment efficiency for specific compounds based on the wastewater stream. The data in this table were compiled and summarized from a literature search on pilot- and full-scale treatment systems.* The data in this table should be used with an awareness and understanding of test conditions involved. Facilities should use the removal data for a treatment system whose conditions are similar (type of waste, chemical concentration, suspended solids concentration, residence time) to the facility's own wastewater treatment system.

[&]quot;Estimation of Removal of Organic Chemicals During Wastewater Treatment, Draft Final Report," Versar Inc. Prepared for U.S. Environmental Protection Agency, Exposure Evaluation Division, Office of Toxic Substances, Washington, D.C. EPA Contract No. 68-02-3968, Task 867.148. September 30, 1986.

Table A-2 in Appendix A also presents wastewater treatment efficiencies for a number of chemicals; however, this information applies only to secondary biological wastewater treatment systems receiving relatively low concentrations of the particular toxic pollutant (\cong 500 parts per billion). It provides educated estimates on pollutant fate in the treatment system (i.e., volatilized to air, particularly to sludge, or biodegraded) from "Report to Congress on the Discharge of Hazardous Waste to Publicly-Owned Treatment Works."

Tables A-1 and A-2 do not have information on all of the chemicals subject to reporting. These tables should be used only when efficiency information cannot be obtained through any of the methods described above.

The following subsections describe briefly the general wastewater treatment methods presented in Table 4-3. *†

<u>Chemical Oxidation</u>. Chemical oxidation is a process that oxidizes compounds or ions to render them nonhazardous or to make them more amenable to subsequent removal or destruction processes. Species are oxidized by the addition of a chemical oxidizing agent that is itself reduced. Treatment efficiency is measured by dividing the quantity of a particular contaminant chemically modified by the quantity entering the process.

Chemical Precipitation. Chemical precipitation is a physicochemical process in which a dissolved contaminant is transformed into an insoluble solid to facilitate its subsequent removal from the liquid phase by sedimentation or filtration. The process usually involves 1) adjustment of pH to shift the chemical equilibrium to a point that no longer favors solubility; 2) addition of the chemical precipitant; and 3) flocculation, in which precipitate particles agglomerate into larger particles. Treatment efficiency is calculated by dividing the quantity of a particular contaminant removed from the wastewater by the quantity entering the process.

^{* &}quot;Briefing: Technologies Applicable to Hazardous Waste," Metcalf and Eddy, Inc. Prepared for U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, Ohio. May 1985.

[†] "Remedial Action at Waste Disposal Sites," (Revised), EPA/625/6-85/006, U.S. Environmental Protection Agency, Office of Research and Development, Hazardous Waste Engineering Laboratory, Cincinnati, Ohio. October 1985.

Chromium Reduction. Chemical reduction, which involves the transfer of reactive electrons from one compound to another, is used either to render compounds nontoxic or to enable compounds to undergo chemical destruction or physical removal. Metals, in particular hexavalent chromium, are reduced through the addition of a compatible reducing agent (for example, reduced sulfur compounds). Specific solution pH and agitation requirements must be met to ensure successful chemical reduction. Treatment efficiency is calculated by dividing the quantity of a particular contaminant chemically modified by the quantity entering the process.

Adsorption. Adsorption is the adherence of one substance to the surface of another by physical and chemical processes. Treatment of wastestreams by adsorption is essentially a process of transferring and concentrating contaminants (the adsorbate) from one medium (liquid or gas) to another (the adsorbent). The most commonly used adsorbent is activated carbon. Other adsorbents include specially manufactured resins. Ion exchange is a process whereby the toxic ions are removed from the aqueous waste by being exchanged with relatively harmless ions held by the ion exchange material. In each of these processes, treatment is achieved by transfer of contaminant compounds from wastewater to a solid phase. Treatment efficiency is measured by dividing the quantity of a particular contaminant removed from the wastewater by the quantity entering the process.

<u>Stripping</u>. Air stripping is a mass transfer process in which volatile contaminants in wastewater are transferred to gas streams. Typically, a wastewater stream will flow countercurrently to a forced air stream in a packed tower to maximize the transfer of volatile materials. The gas stream subsequently requires treatment before emission to the atmosphere.

Steam stripping essentially involves removing volatile constituents from an aqueous stream by steam heat. The volatile constituents are concentrated in a vapor or liquid solution that usually requires further treatment. In both steam and air stripping, pollutants are transferred from the wastewater to a gaseous or liquid stream, and efficiency is measured by dividing the quantity of particular constituents removed from the wastewater stream by the quantity entering the process.

Filtration. Filtration is a physical process whereby suspended solids are removed from solution by forcing the fluid through a porous medium. Granular media filtration is typically used for treating wastewater streams. The filter medium consists of a bed of granular particles (typically sand or sand with anthracite or coal). The bed is contained within a basin and is supported by an underdrain system that allows the filtered liquid to be drawn off while the filter media is retained in place. As water laden with suspended solids passes through the bed of filter medium, the particles become trapped on top of and within the bed.

Removal of toxic constituents in the wastewater is confined to the quantity of toxic constituents in the form of filterable suspended solids. The efficiency of the process is measured by dividing the mass of a particular chemical removed from the wastewater stream by the mass of that chemical entering the process.

<u>Air Flotation</u>. Air flotation is a gravity separation process in which the attachment of fine air bubbles to suspended solids or oils decreases the effective density of the material and thereby enhances gravity separation. Treatment efficiency is calculated by dividing the quantity of the contaminant removed from the wastewater by the quantity entering the process.

Settling/Clarification and Oil Skimming. Gravity separation is widely used as a waste treatment process for the removal of settleable suspended solids, oil and grease, and other material heavier or lighter than the carrying fluid (usually water). Grit chambers, clarifiers, American Petroleum Institute (API) separators, inclined plate settlers, and corrugated plate interceptors (CPI) are common forms of gravity separation devices used in wastewater treatment. Treatment efficiency is calculated by dividing the quantity of a particular contaminant removed from the wastewater by the quantity entering the process.

<u>Biological Treatment</u>. The function of biological treatment is to remove organic matter from the wastestream through microbial degradation. The most prevalent form of biological treatment is aerobic, i.e., in the presence of dissolved oxygen. In anaerobic treatment, biological degradation takes place in the absence of dissolved oxygen; in facultative treatment, biological degradation occurs with or without dissolved oxygen. In all of these processes,

contaminants are either destroyed, transferred to solid phase, or volatilized to air. Efficiency is measured by dividing the quantity of a particular contaminant removed from the wastewater (or destroyed) by the quantity entering the process.

Other Wastewater Treatment. Wet air oxidation is the aqueous-phase oxidation of dissolved or suspended organic or inorganic substances at elevated temperature (177° to 315°C) and pressure (300 to 3000 psi). Removal of the contaminants is accomplished by destruction. Neutralization involves combining either an acid or a base with wastewater to adjust liquid pH to acceptable levels. Acid and bases in the wastewater are chemically transformed during the process. Equalization is the method of controlling the concentration or "strength" of a wastewater before entering subsequent processes. Contaminants are neither destroyed nor removed, and as such, treatment efficiency is zero. Reverse osmosis is used to separate water from inorganic salts and some relatively high-molecular-weight organics. Pressure (typically 200 to 1200 psi) is used to force water from a solution through a semipermeable barrier (membrane) that will pass only certain components of a solution (the permeate) but is impermeable to most dissolved solids (both inorganic and organic).

SECTION 4 BIBLIOGRAPHY

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- U.S. Environmental Protection Agency. 1983. Health Assessment Document for Toluene. EPA-600/8-82-008f. Research Triangle Park, North Carolina. 427 pp.
- U.S. Environmental Protection Agency. 1985. Technical Support Document for Water Quality-Based Toxics Control. EPA-440-4-85-032. Washington, D.C.

EPA DEVELOPMENT DOCUMENTS FOR EFFLUENT LIMITATION GUIDELINES

The following list of development documents for effluent limitation guidelines (Table 4-4) is available from NTIS or the Government Printing Office if referenced by the appropriate number.

Requests can be submitted to:

National Technical Information Service (NTIS) 5285 Port Royal Road Springfield, Virginia 22161 Order Desk Telephone Number: (703) 487-4650 NTIS Accession Number is required when ordering NTIS Information Telephone Number: (703) 487-4600

Supt. of Documents Government Printing Office Washington, D.C. 20402 (202) 783-3238

All development documents are available for review and inspection at the EPA Regional Office Libraries listed in Table 4-5.

TABLE 4-4. DEVELOPMENT DOCUMENTS FOR EFFLUENT LIMITATION GUIDELINES FOR SELECTED CATEGORIES^a

Industrial point source category	Subcategory	EPA publication document No.	NTIS accession No.	GPO stock No.	
Aluminum forming	Aluminum forming	EPA 440/1-84/073 Vol. I Vol. II	PB84-244425 PB84-244433	-	
Asbestos manufac- turing	Building, construction, and paper	EPA 440/1-74/017a	PB238320/6	5501-00827	
	Textile, friction materials, and sealing devices	EPA 440/1-74/035a	PB240860/7	-	
Battery manufac- turing	Battery manufacturing	EPA 440/1-84/067 Vol. I Vol. II	PB85-121507 PB85-121515	<u>-</u>	
Builders' paper and board mills	Pulp, paper and paperboard, and builders' paper and board mills	EPA 440/1-82/025	PB83-163949	. ' -	
Canned and pre- served fruits and vegetables	Apple, citrus, and potato processing	EPA 440/1-74/027a	PB238649/8	5501-00790	
Canned and pre- served seafood	Catfish, crab, and shrimp	EPA 440/1-74/020a	PB238614/2	5501-00920	
processing	Fishmeal, salmon, bottom fish, sardine, herring, clam, oyster, scallop, and abalone	EPA 440/1-75/041a	PB256840/0	-	
Cement manufactur- ing	Cement manufacturing	EPA 440/1-74/005a	PB238610/0	5501-00866	
(continued)			•		

TABLE 4-4 (continued)

Industrial point source category	Subcategory	EPA publication document No.	NTIS accession No.	GPO stock No.	
Coil coating	Coil coating, Phase I	EPA 440/1-82/071	PB83-205542	-	
	Coil coating, Phase II - can- making	EPA 440/1-83/071	PB84-198647		
Copper forming	Copper	EPA 440/1-84/074	PB84-192459	-	
Dairy products processing	Dairy products processing	EPA 440/1-74/021a	PB238835/3	5501-00898	
Electroplating and metal finishing	Copper, nickel, chrome, and zinc	EPA 440/1-74/003a	PB238834/AS	5501-00816	
	Electroplating - pretreatment	EPA 440/1-79/003	PB80-196488	-	
<u>.</u>	Metal finishing	EPA 440/1-83/091	PB84-115989	-	
Ferroalloy	Smelting and slag processing	EPA 440/1-74/008a	PB238650/AS	5501-00780	
Fertilizer manu-	Basic fertilizer chemicals	EPA 440/1-74/011a	PB238652/AS	5501-00868	
facturing	Formulated fertilizer	EPA 440/1-75/042a	PB240863/AS	5501-01006	
Glass manufactur-	Pressed and blown glass	EPA 440/1-75-034a	PB256854/1	5501-01036	
ing	Insulation fiberglass	EPA 440/1-74/001b	PB238078/0	5501-00781	
	Flat glass	EPA 440/1-77/001c	PB238-907/0	5501-00814	
Grain mills	Grain processing	EPA 440/1-74/028a	PB238316/4	5501-00844	
	Animal feed, breakfast cereal, and wheat	EPA 440/1-74/039a	PB240861/5	5501-01007	

(continued)

TABLE 4-4 (continued)

Industrial point source category	Subcategory	EPA publication document No.	NTIS accession No.	GPO stock No.	
Inorganic chemi- cals manufacturing	Inorganic chemicals Phase I	EPA 440/1-82/007	PB82-265612		
	Inorganic chemicals Phase II	EPA 440/1-84/007	PB85-156446/XAB	-	
Iron and steel manufacturing	Iron and steel Volume I Volume II Volume III Volume IV Volume V Volume VI	EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024	PB82-240425a PB82-240433b PB82-240441c PB82-240458d PB82-240466e PB82-240474f	-	
Leather tanning	Leather tanning	EPA 440/1-82/016	PB83-172593		
Meat products and	Red meat processing	EPA 440/1-74/012a	PB238836/AS	5501-00843	
rendering	Renderer	EPA 440/1-74/031d	PB253572/2	-	
Metal finishing	Metal finishing	EPA 440/1-83/091	PB84-115989		
Metal molding and casting (foundries)	Metal molding and casting	EPA 440/1-85/070	PB86-161452/XAB	-	
Nonferrous metals forming	Nonferrous metals forming	EPA 440/1-84/019b Vol. I Vol. II Vol. III	PB83/228296 PB83/228304 PB83/228312	-	
Nonferrous metals manufacturing	Bauxite refining - aluminum segment	EPA 440/1-74/019c	PB238463/4	5501-00116	
(continued)					

TABLE 4-4 (continued)

Industrial point source category	Subcategory	EPA publication document No.	NTIS accession No.	GPO stock No.	
Nonferrous metals manufacturing	Primary aluminum smelting - aluminum segment	EPA 440/1-74/019d	PB240859/9	5501-00817	
(continued)	Secondary aluminum smelting - aluminum segment	EPA 440/1-74/019e	PB238464/2	5501-00819	
Organic chemical Organic chemicals manu manufacturing and ing and plastics and splastics and splastics and splastics fibers		EPA 440/1-87-009	Available from NTIS after publication (1/87)		
Petroleum refining	Petroleum refining	EPA 440/1-82/014	PB83-172569	-	
Pharmaceuticals	Pharmaceutical	EPA 440/1-83/084	PB84-180066	-	
Phosphate manu- facturing	Phosphorus-derived chemicals	EPA 440/1-74/006a	PB241018/1	5503-00078	
	Other non-fertilizer chemicals	EPA 440/1-75/043	-	••	
Porcelain enamel- ing	Porcelain enameling	EPA 440/1-82/072		-	
Pulp, paper, and paperboard	Unbleached kraft and semi- chemical pulp	EPA 440/1-74/025a	PB238833/AS	-	
	Pulp, paper and paperboard, and builders' paper and board mills	EPA 440/1-82/025	PB83-163949	~	
Rubber processing	Tire and synthetic	EPA 440/1-74/013a	PB238609/2	5501-00885	
	Fabricated and reclaimed rubber	.EPA 440/1-74/030a	PB241916/6	5501-01016	

(continued)

TABLE 4-4 (continued)

Industrial point source category	Subcategory	EPA publication document No.	NTIS accession No.	GPO stock No.	
Soaps and deter- gents	Soaps and detergents	EPA 440/1-74/018a	PB238613/4	5501-00867	
Sugar processing	Beet sugar	EPA 440/1-74/002b	PB238462/6	5501-00117	
	Cane sugar refining	EPA 440/1-74/002c	PB238147/3	5501-00826	
Textile mills man- ufacturing	Textile mills	EPA 440/1-82/022	PB83-116871		
Timber products processing	Wood furniture and fixtures	EPA 440/1-74/033a	-	-	
	Timber products processing	EPA 440/1-81/023	PB81-227282	-	

^a This list includes only "final" development documents for effluent limitations guidelines. For many industries, these documents are in the draft or proposal stage.

TABLE 4-5. EPA REGIONAL OFFICE LIBRARIES

Library
Environmental Protection Agency, Region I
John F. Kennedy Federal Bldg.
Boston, MA 02203

Library Environmental Protection Agency, Region II 26 Federal Plaza New York, NY 10278

Diane M. McCrary, Librarian Environmental Protection Agency, Region III Sixth & Walnut Streets - Curtis Bldg. Philadelphia, PA 19106

Library
Environmental Protection Agency, Region IV
365 Courtland Street, NE
Atlanta, GA 30065

Ms. Lou W. Tilley, Librarian Environmental Protection Agency, Region V 230 South Dearborn Street, Room 1420 Chicago, IL 60604

Library
Environmental Protection Agency, Region VI
1201 Elm Street, 1st International Bldg.
Dallas, TX 75270

Connie McKenzie, Librarian Environmental Protection Agency, Region VII 324 East 11th Street Kansas City, MO 64106

Dolores Eddy, Librarian Environmental Protection Agency, Region VIII 1860 Lincoln Street Denver, CO 80295

OUTLINE FOR SECTION 5

ESTIMATING RELEASES IN SOLID, SLURRY, AND NONAQUEOUS LIQUID WASTES

- 5.1 Source's and Disposal Methods for Solid, Slurry, and NonAqueous Liquid Wastes

 - 5.1.1 Landfilling5.1.2 Land treatment
 - 5.1.3 Underground injection
 - 5.1.4 Surface impoundments
- 5.2 Methods for Calculatiing Releases in Solid, Slurry, and NonAqueous Liquid Wastes
- 5.3 Estimating Treatment Equipment Efficiency
 - 5.3.1 Incineration
 - 5.3.2 Reuse as fuel
 - 5.3.3 Solidification
 - 5.3.4 Recovery of solvents and other organic chemicals

 - 5.3.5 Recovery of metals5.3.6 Sludge dewatering operations

SECTION 5

ESTIMATING RELEASES IN SOLID, SLURRY, AND NONAQUEOUS LIQUID WASTES

In the context of section 313 reporting requirements, the terms solid, slurry, and nonaqueous liquid refer to those wastes which are not gaseous waste or wastewater. Where a waste is a mixture of water and organic liquid, it is considered a wastewater unless the organic content exceeds 50 percent. Slurries containing water should be reported as solids if they contain appreciable amounts of settleable or dissolved solids such that the viscosity or density of the waste is considerably different from that of process wastewater. Throughout this document, "solid/slurry waste" refers to all solid, slurry, and nonaqueous liquid wastes.

Solid/slurry wastes originate from a wide variety of sources. Based on the physical and chemical characteristics of a particular solid waste, it can be treated and disposed of either individually by source or mixed with other wastes from a facility. Treatment and disposal can take place on site or at an approved off-site facility.

For a number of the listed toxic chemicals, generation, storage, transportation, treatment, and disposal of wastes are subject to RCRA regulations. The RCRA reporting requirements such as permits, manifests, and biennial reports can serve as a valuable source of information for the estimation of releases in solid/slurry wastes. In this section, sources and disposal methods for solid/slurry wastes are presented, along with associated release estimation techniques. Treatment methods and efficiencies are also discussed.

5.1 SOURCES AND DISPOSAL METHODS FOR SOLID, SLURRY, AND NONAQUEOUS LIQUID WASTES

Table 5-1 presents some generalized sources of solid/slurry wastes, and the following subsections describe disposal methods for these wastes. In

Spent solvents

Heavy ends - distillation residues

Heavy ends - miscellaneous

Light ends - condensable

Steam stripping wastes

Acid leaching solutions

Spent plating, stripping, or cleaning baths

Off-spec, discarded products or feedstock

Distillation side cuts

Residue in containers, liners, drums, cans, cleaning rags, gloves

Spills, leaks, vessel overflows

Precipitates or filtration residues

Spent activated carbon or other adsorber

Spent ion-exchange resins

Spent catalyst

Scrap metal

Solid scrap from finishing or trimming operations

Untreated solid waste

Equipment cleaning sludge (tank bottoms, heat exchangers)

Oven residue

Wastewater treatment sludges - biological

Wastewater treatment sludges - other

Treated organics

Treated solids

Oily waste from treated wastewater

most circumstances involving the disposal of the chemicals subject to reporting, these disposal methods will be controlled by RCRA permitting procedures. Therefore, quantities of the listed chemicals disposed of by these methods have the potential of being calculated directly from the information obtained for the permit. Incineration is not discussed as a disposal method because (for purposes of this report) it is included in treatment methods (see Subsection 5.3). Sometimes, solid/slurry wastes are discharged in wastewater (either to an onsite wastewater treatment facility or a POTW). In this instance, these wastes would be reported as part of the releases to water after accounting for any onsite removal.

5.1.1 Landfilling

Typically, the ultimate disposal method for solid wastes is landfilling. Any waste generating free liquids (based on EPA's "paint filter test") must be disposed of in some other fashion besides landfilling. For onsite landfills, volatilization of toxic chemicals from the landfill must be accounted for as a separate emission to air (see Section 3.1.4).

5.1.2 Land Treatment

Land treatment is a disposal method in which waste is applied onto or incorporated into soil. This disposal method is considered a release to land, but volatilization of toxic chemicals into air from this source must be accounted for.

5.1.3 <u>Underground Injection</u>

Analogous to underground injection of wastewater, "pumpable" solid/slurry wastes containing hazardous and/or toxic chemicals may be injected beneath the earth's surface, where they are unlikely to contaminate ground water.

5.1.4 <u>Surface Impoundments</u>

A surface impoundment is a natural topographic depression, man-made excavation, or diked area formed primarily of earthen materials (although some may be lined with man-made materials), which is designed to hold an accumulation of liquid wastes or wastes containing free liquids. Examples of surface

impoundments are holding, storage, settling, and elevation pits; ponds; and lagoons. If the pit, pond, or lagoon is intended for storage or holding without discharge, it is considered to be a surface impoundment used as a final disposal method under Section 313 reporting. This disposal method is considered a release to land; however, listed chemicals in the impoundment may be released to air by volatilization, collected as sludge and removed, or biodegraded.

5.2 METHODS FOR CALCULATING RELEASES IN SOLID, SLURRY, AND NONAQUEOUS LIQUID WASTES

Combinations of direct measurement, mass balance, and engineering calculations may be used to estimate environmental releases of listed chemicals from the disposal of solid/slurry wastes. A general compilation of emission factors for these wastes is not available. However, some emission factors may be found in trade journals and the literature for specific industries. The bibliography at the end of this section presents some potentially helpful references on solid and slurry wastes. This bibliography was developed from a literature search of solid/slurry waste emissions and treatment efficiencies. It is not a complete listing of available references on the subject and those listed may not contain information pertaining to all of the listed chemicals. Other potential sources of information include journals (such as Waste Age and World Wastes) that deal primarily with the subject of solid/slurry wastes.

The quantity of solid waste generated can be estimated from shipping invoices if the waste is sent offsite. Quantities can also be estimated by keeping track of the drums or tanks filled with waste prior to disposal.

For plants subject to the RCRA regulations (40 CFR Part 261 et seq.), the quantities of waste and its fate will have been reported on hazardous waste manifests. Generators of hazardous waste that ship their waste offsite will have completed biennial reports on EPA Form 8700-13A. The amount of waste disposed of each year is reported on this form, but its exact composition may not be known. Specific constituents in the waste may be available from chemical analyses performed to determine the hazardous nature of the

waste. These analyses may be performed by the generator or an offsite facility accepting the waste. The following examples illustrate the calculations for estimating annual releases.

 $\underline{\text{Example } 5\text{--}1}$ - Use of direct measurement to estimate releases in solid/slurry:

Spent degreasing sludges are disposed of by shipping to an off-site waste treatment facility. The specific release of methylene chloride can be estimated as follows.

Step 1. Gather information from RCRA permit.

From EPA Form 8700-13A, the quantity of waste identified by hazardous waste Number F001 is recorded as 50,000 gallons per year. The receiver of this waste has analyzed each shipment and determined that the methylene chloride content averages 10 percent by weight.

Step 2. Calculate annual releases.

The methylene chloride release (to off-site disposal) is calculated by multiplying the volume shipped by its density (8.5 lb/gal determined by weighing a known volume of waste) and by the weight percent of methylene chloride.

$$\frac{50,000 \text{ gal}}{\text{year}} \times \frac{8.5 \text{ lb}}{\text{gallon}} \times 10\% = \frac{42,500 \text{ lb}}{\text{year}}$$

Report 43,000 lb/year.

<u>Example 5-2</u> - Use of direct measurement to estimate releases in solid/slurry:

Step 1. Gather information on quantity and concentration of solid/slurry waste.

During the year, an electroplater shipped 7500 gallons of waste solution to a hazardous waste treatment, storage, and disposal facility (TSDF). The electroplater's analyses showed that the wastes contained an average of 87.4 grams of cyanide per liter of solution before treatment.

Step 2. Calculate annual releases.

Cyanide shipped to TSDF:

7500 gal x $\frac{3.785 \text{ liters}}{\text{gallon}}$ x $\frac{87.4 \text{ grams}}{\text{liter}}$ = 2,481,067.5 grams or $\frac{5458 \text{ lb}}{\text{year}}$

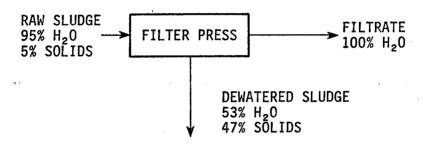
Report 5500 lb/year.

<u>Example 5-3</u> - Use of a combination of measurement, mass balance, and an engineering calculation to estimate releases in solid/slurry:

Step 1. Gather process and analytic information.

A tannery utilizes a filter press to dewater raw sludge from its wastewater treatment plant. The dewatered sludge is disposed of in an onsite landfill. Liquid filtrate from the filtering operation is recirculated to the wastewater treatment process. Several analyses for chromium have been made on the dewatered sludge and have yielded an average value of 100 mg total chromium/kg sludge. The quantity of dewatered sludge disposed multi- plied by this concentration will yield the quantity of chromium released to land from this source.

To calculate the quantity of dewatered sludge sent to the landfill, an engineering estimate and mass balance will be used. Moisture measurements of the raw and dewatered sludge show that these streams contain an average of 95 and 53 percent H₂O by weight, respectively.



Step 2. Make an engineering assumption to estimate the quantity of filtrate from the filter press.

It is known that the filter press has a filtration area of $100~\rm{ft^2}$ and operates an average of $10~\rm{hours}$ per day, $5~\rm{days}$ per week, and $50~\rm{weeks}$ per year. When designing the filter press, a filtration rate of $10~\rm{gal/h}$ per ft² of filtration area was used. With this information, the total amount of filtrate produced by the filter press can be estimated.

100 ft² x
$$\frac{10 \text{ gal filtrate}}{\text{hour }}$$
 x $\frac{10 \text{ hours}}{\text{day}}$ x $\frac{5 \text{ days}}{\text{week}}$ x $\frac{50 \text{ weeks}}{\text{yr}}$ x $\frac{8.34 \text{ lb water}}{1 \text{ gal of water}}$
= $\frac{20.85 \times 10^6 \text{ lb filtrate}}{\text{yr}}$

Step 3. Perform a mass balance around the process.

A mass balance can then be performed around the filter press to find the quantity of dewatered sludge produced per year. Total mass balance: (raw sludge) = (dewatered sludge) + (filtrate)

Eq. 1: Raw sludge = dewatered sludge + 20.85 x $\frac{10^6 \text{ lb}}{\text{yr}}$

Solids mass balance: Eq. 2: (0.05)(raw sludge) = (0.47)(dewatered sludge)

$$\frac{\text{Eq. 2}}{\text{Eq. 1}}: 0.05 = \frac{(0.47)(\text{dewatered sludge})}{(\text{dewatered sludge}) + 20.85 \times 10^6 \text{ lb/yr}}$$

: dewatered sludge = 2.482 x
$$\frac{10^6 \text{ lb}}{\text{yr}}$$

Step 4. Calculate annual releases.

To calculate the amount of chromium discharged to land:

 $\frac{100 \text{ mg total chromium}}{1 \text{ kg dewatered sludge}} = \frac{100 \text{ mg total chromium}}{10^6 \text{ mg dewatered sludge}} = \frac{100 \text{ lb total chromium}}{10^6 \text{ lb dewatered sludge}}$

$$\frac{100 \text{ 1b Cr}}{10^6 \text{ 1b dewatered sludge}} \times \frac{2.482 \times 10^6 \text{ 1b dewatered sludge}}{\text{yr}}$$

$$= \frac{248.2 \text{ lb Cr}}{\text{yr}}$$

Report 250 lb Cr/yr.

Example 5-4 - Use of an engineering calculation to estimate solid/slurry:

Step 1. Gather process information.

A semiconductor production facility uses 1,1,1-trichloroethane (1,1,1-TCE) to degrease semiconductors. The solvent is pumped into degreasing units from 55-gallon steel drums when needed. The empty drums are sent to an offsite drum cleaning facility for reclamation.

Step 2. Use an engineering estimate of the quantity of residue left in each drum.

To estimate the quantity of 1,1,1-trichloroethane sent to the drum cleaning facility as residue in the drums, the information in Table 5-2 can be utilized. This table provides results from experimentation on residue quantities left in drums and tanks when emptied. Results are presented as the mass percent of the vessel capacity, and are categorized based on unloading method, vessel material, and bulk fluid material properties (i.e., viscosity and surface tension).

TABLE 5-2. SUMMARY OF RESIDUE QUANTITIES FROM PILOT-SCALE EXPERIMENTAL STUDY^{a,b} (wt. percent of drum capacity)

		•		Material		
Unloading method	Vessel type	Value	Kerosene ^C	Water ^d	Motor oil ^e	Surfactant _f solution
Pumping	Steel drum	Range Mean	1.93 - 3.08 2.48	1.84 - 2.61 2.29	1.97 - 2.23 2.06	3.06 3.06
Pumping	Plastic drum	Range Mean	1.69 - 4.08 2.61	2.54 - 4.67 3.28	1.70 - 3.48 2.30	Not available
Pouring	Bung-top steel drum	Range Mean	0.244 - 0.472 0.404	0.266 - 0.458 0.403	0.677 - 0.787 0.737	0.485 0.485
Pouring	Open-top steel drum	Range Mean	0.032 - 0.080 0.054	0.026 - 0.039 0.034	0.328 - 0.368 0.350	0.089 0.089
Gravity drain	Slope-bottom steel tank	Range Mean	0.020 - 0.039 0.033	0.016 - 0.024 0.019	0.100 - 0.121 0.111	0.048 0.048
Gravity drain	Dish-bottom steel tank	Range Mean	0.031 - 0.042 0.038	0.033 - 0.034 0.034	0.133 - 0.191 0.161	0.058 0.058
Gravity drain	Dish-bottom glass- lined tank	Range Mean	0.024 - 0.049 0.040	0.020 - 0.040 0.033	0.112 - 0.134 0.127	0.040 0.040

From "Releases During Cleaning of Equipment." Prepared by PEI Associates, Inc., for the U.S. Environmental Protection Agency Office of Pesticides and Toxic Substances, Washington, D.C. Contract No. 68-02-4248. June 30, 1986.

The values listed in this table should only be applied to similar vessel types, unloading methods, and bulk fluid materials. At viscosities greater than 200 centipoise, the residue quantities can rise dramatically and the information on this table is not applicable.

^C For kerosene, viscosity = 5 centipoise, surface tension = 29.3 dynes/cm².

d For water, viscosity = 4 centipoise, surface tension = 77.3 dynes/cm².

e For motor oil, viscosity = 97 centipoise, surface tension = 34.5 dynes/cm².

f For surfactant solution viscosity = 3 centipoise, surface tension = 31.4 dynes/cm².

In this example, steel drums were pumped empty; of the four materials tested, 1,1,1-trichloroethane most resembles kerosene. As such, it can be estimated that each empty drum contains approximately 2.48 percent of the 1.1.1-trichloroethane in the drum.

Step 3. Calculate annual releases.

The yearly quantity of 1,1,1-trichloroethane sent to the drum reclaimer would be estimated as follows based on the use of 1.3249 as the specific gravity of 1,1,1-trichloroethane relative to $\rm H_2O$ at 1.00.

$$\frac{100 \text{ drums}}{\text{year}} \times \frac{55 \text{ gal}}{\text{drum}} \times \frac{8.34 \text{ lb H}_20}{\text{gal}} \times \frac{1.3249 \text{ lb 1,1,1-trichloroethane}}{\text{lb H}_20}$$

 $x = \frac{0.0248 \text{ lb residue}}{\text{lb solvent}} = 1507 \text{ lb of 1,1,1-trichloroethane residue per year}$

Report 1500 lb of 1,1,1-trichloroethane residue per year.

5.3 ESTIMATING TREATMENT EQUIPMENT EFFICIENCY

Toxic pollutants entering a solid/slurry waste treatment device will undergo one or more of the following fates: 1) transfer to a different media, 2) destruction through combustion, biodegredation, or chemical reaction, 3) modification to a less toxic state, 4) fixed in place or concentrated in the same waste media by transformation of the solid/slurry matrix, or 5) pass through untreated. In some instances, treatment is not provided to solid/slurry wastes before disposal. Table 5-3 presents a list of various solid/slurry waste treatment processes.

Efficiency for solid/slurry waste treatment devices is based on the amount of a contaminant removed from the solid/slurry waste, either through destruction, modification by chemical reaction, or transfer to air or water.

Percent efficiency =
$$\frac{X \text{ inlet - } X \text{ outlet}}{X \text{ inlet}} \times 100$$

where X inlet = total mass of pollutant entering the solid/slurry treatment system in a given year

The amount of a pollutant transferred and subsequently released to another media must be included with the total releases for that particular

TABLE 5-3. UNIT OPERATIONS AND TREATMENT PROCESSES USED TO TREAT SOLID, SLURRY, AND NONAQUEOUS WASTES

Incineration/thermal treatment

Liquid injection
Rotary kiln with liquid injection unit
Other rotary kiln
Two stage
Fixed hearth
Multiple hearth
Fluidized bed
Infra-red
Fume/vapor
Pyrolytic destructor
Wet air oxidation
Thermal drying/dewatering
Other incineration/thermal treatment

Reuse as fuel

Industrial kiln
Industrial furnace
Boiler
Fuel blending
Other

Solidification

Cement processes (including silicates)
Other pozzolanic processes (including silicates)
Asphaltic processes
Thermoplastic techniques
Other solidification processes

Recovery of solvents and other organic chemicals

Fractionation
Batch still distillation
Solvent extraction
Thin film evaporation
Other solvent recovery

Recovery of metals

Electrolytic metal recovery
Ion exchange (for metals recovery)
Reverse osmosis (for metals recovery)
Solvent extraction (for metals recovery)
Other metals recovery

Sludge dewatering operations

pollutant in that media. Of course this amount should be subtracted from the quantity of the pollutant released as a solid/slurry waste. Release estimates and treatment efficiencies for toxic metals must be based on quantities of parent metal.

The best method of estimating treatment efficiency is direct measurement of the inlet and outlet streams. Measurement of treatment efficiency may also be necessary for RCRA reporting requirements. The next best method would involve the use of a mass balance along with measurement of a secondary parameter. In lieu of these methods, efficiency estimates in the literature may be used provided that the cited treatment system is similar to the operation for which the estimate is being made.

Solid/slurry waste treatment devices usually fall within one of six categories (incineration, reuse as fuel, solidification, recovery of solvents, recovery of metals, and dewatering), based on the predominant method of contaminant removal. Frequently however, a solid/slurry waste treatment device will not fall into one of these categories and will more closely resemble a wastewater treatment process (see Section 4.3). The treatment process reported on the Toxic Chemical Release Inventory Form should most closely resemble the treatment process at the facility, regardless of how it may be categorized in this report.

The following subsections provide a brief description of each of the six categories of solid/slurry waste treatment devices.*

5.3.1 Incineration

Incineration is a controlled oxidation destruction process that uses combustion to destroy wastes with oxygen by converting the wastes to carbon dioxide, water, and other combustion products. The specific products of incineration (combustion) vary depending on the type of wastes that are burned. Typically, controls are required to reduce transfer of contaminants to the air. The efficiency of the incinerator should be based on the quantity of the compound in the input solid/slurry waste stream and the quantity of the compound in the ash.

5.3.2 Reuse as Fuel

Reuse as fuel involves the use of combustible organic wastes as substitutes or supplements for conventional fuels that are burned in industrial

processes. As in incineration, the organic waste is destroyed in flame combustion yielding essentially carbon dioxide and water. The efficiency of treatment through reuse as a fuel should be calculated as with incinerators.

5.3.3 Solidification

Solidification/stabilization is used to reduce the mobility of pollutants in the environment and thereby make disposal safer. Materials are mixed with wastes to immobilize the waste constituents chemically and physically. The process is usually applied to concentrated waste solids, sludges, and slurries; however, liquid wastes may also be treated. Separate techniques are usually applied to the solidification/stabilization of organic and inorganic wastes; however, several processes are available to immobilize both organic and inorganic pollutants with the same processes. In most of these treatment methods, the toxic component of the waste is neither destroyed nor transferred to a different media. Therefore, treatment efficiency as defined has no meaning for these processes and should be reported as zero on the Toxic Chemical Release Inventory Form.

5.3.4 Recovery of Solvents and Other Organic Chemicals

These treatment methods generally involve the separation of a particular organic compound or group of organic compounds from a dilute liquid waste stream. Removal is based on differences in physical properties (usually boiling point) between the desired product and the bulk of the waste stream. The recovered product is in nearly pure form, which enables it to be reused; whereas the original waste stream is depleted of its toxic component. Efficiency is based on the amount of the toxic component removed from the main input-output waste stream.

5.3.5 Recovery of Metals

Treatment processes for metals recovery use a combination of physical separation and chemical reaction methods to extract metals from a waste stream for reuse or disposal. Efficiency of these processes is based on the removal of the toxic metals from the main input-output waste stream.

^{*} Hazardous Waste, HW-122B, Background Document for Solvents to Support 40 CFR Part 268 Land Disposal Restrictions (Volume II). Analysis of Treatment and Recycling Technologies for Solvents and Determination of Best..., Pope-Reid Associates, Inc. EPA Contract No. 68-01-6892, January 1986.

5.3.6 Sludge Dewatering Operations

Dewatering operations are used to remove excess liquid from solid/slurry wastes. The liquid portion of the waste is separated from the solid by gravity settling, centrifugation, or filtration. Toxic chemicals in the waste entering the process exit in the liquid filtrate stream, remain in the dewatered solid, or both. For reporting purposes, treatment efficiency is based on the difference between the quantity of material entering the process and the quantity leaving in the dewatered solid. Because the goal of a dewatering process is usually volume reduction of the waste, efficiencies calculated in this manner may be low.

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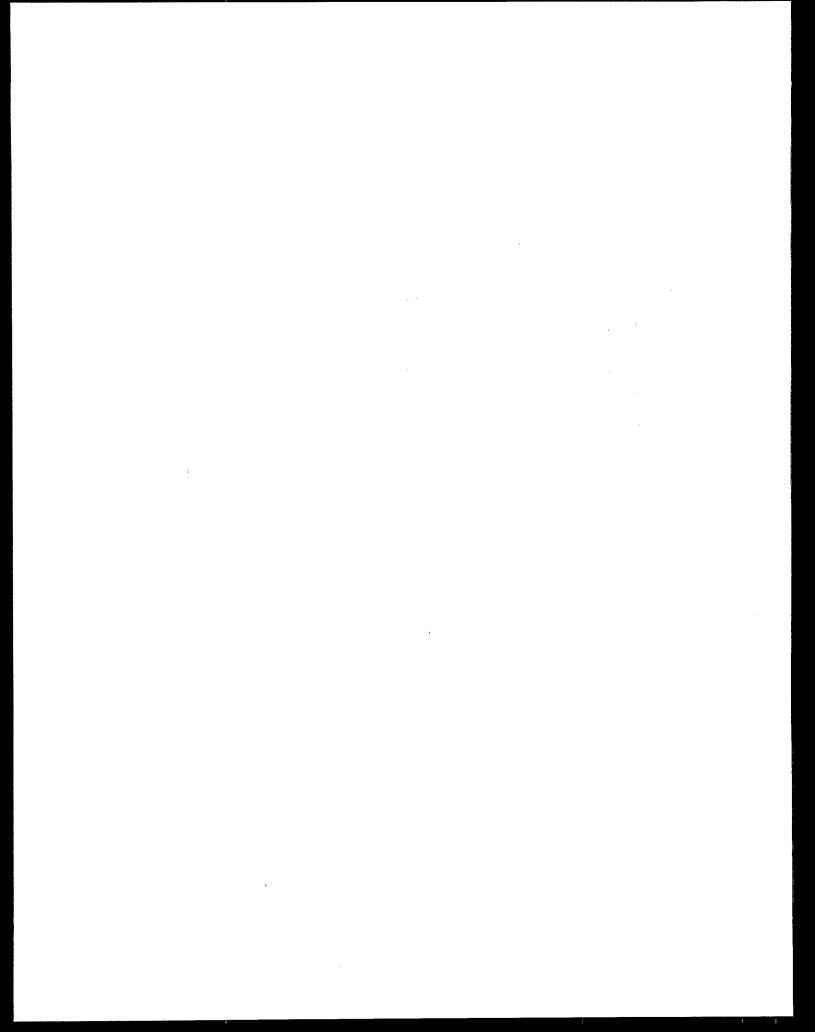
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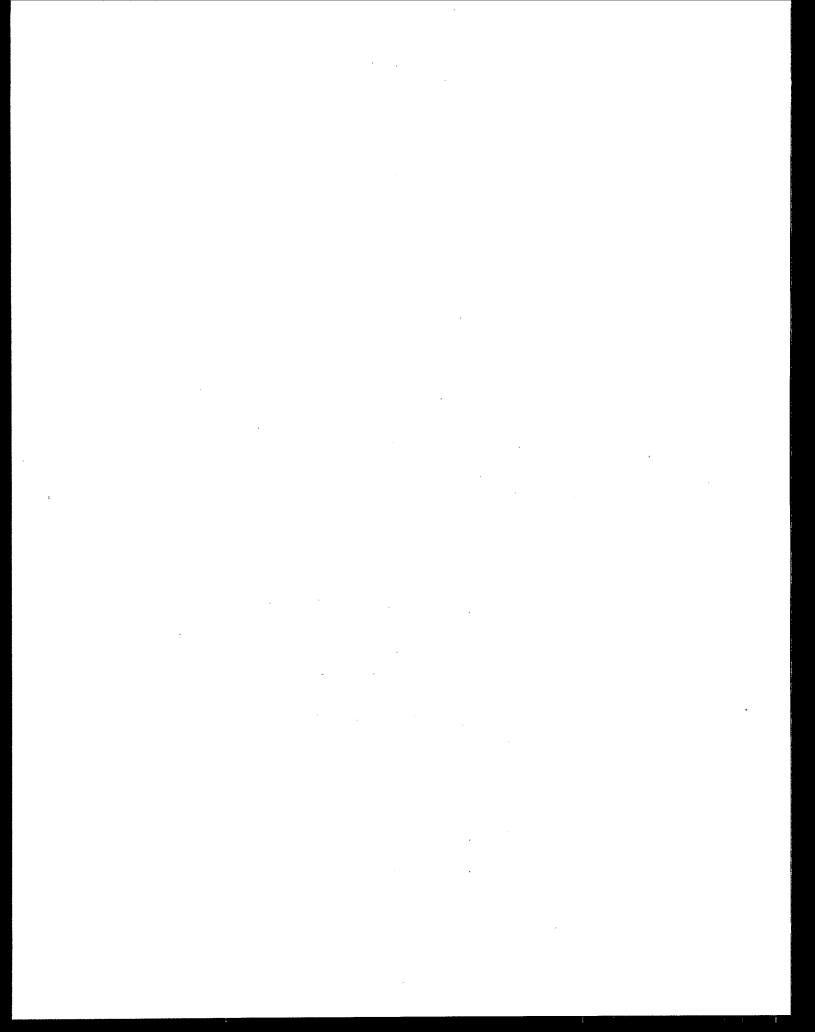


OUTLINE FOR SECTION 6 ESTIMATING ACCIDENTAL RELEASES

- 6.1 General Methods and Considerations
- 6.2 Equations for Modeling Release Rates

 - 6.2.1 Liquid Discharge 6.2.2 Fraction of Discharge Flashed 6.2.3 Vaporization Model 6.2.4 Two-Phase Discharge

 - 6.2.5 Gas Discharge



SECTION 6

ESTIMATING ACCIDENTAL RELEASES

In fulfillment of Section 313, Title III, reporting requirements, accidental releases of a listed chemical into the environment should be included in the release totals reported on the Form; they should not be listed separately. Accidental releases from a facility may be the result of spills, vessel overflows, tank overpressures, pipe ruptures, etc. Other regulations, such as Section 304 of Title III, CERCLA, or the Clean Water Act, may require the reporting of quantities of these releases, and these same data can also be used for Section 313 reporting purposes.

6.1 GENERAL METHODS AND CONSIDERATIONS

Because the volume of a spill or accidental discharge cannot always be measured easily, engineering judgment must be used to determine the best method for making the most accurate estimate. In lieu of direct measurement, a mass balance method could be used in some cases to estimate the amount of a chemical spill or leak; this would involve evaluating the difference in vessel inventory before and after the discharge occurred. Alternatively, equations in Section 6.2 can be used to calculate the release from an opening in the equipment containing the chemical, provided the area of the opening and physical properties of the material within the system are known. Users should try to calculate these types of releases by the best means available to obtain the most accurate estimate.

Spills should be reported as a release to water if, for example, the spilled chemical is washed down the sewer or into the waste treatment system after accounting for removal in treatment. If the spill is absorbed onto some material and landfilled, it should be reported as a release to land. Volatilization of the chemical may take place as it is discharged from equipment and/or after it is discharged to the ground. Equations are presented in

Section 6.2 to estimate the amount volatilized in either case. The amount volatilized should be included in any totals for fugitive air emissions reported on the Form, and this amount should be subtracted from the total spill to arrive at an amount, if any, disposed of in water or on land. Spilled liquid chemical may completely evaporate to air; therefore, the entire amount of this accidental release would be reported as a fugitive air emission.

6.2 EQUATIONS FOR MODELING RELEASE RATES

The methods described in this section were originally developed for the calculation of rates of chemical release for use in dispersion modeling to determine downwind concentrations. They provide a generation rate, which must then be multiplied by the duration of the release to yield the quantity released. The circumstances under which each method applies are described. As presented, the equations apply only for release of the pure compound, not for mixtures of chemicals. Estimating the release of a chemical in a mixture will require adjustments in the equation.

6.2.1 Liquid Discharge

For releases of liquids in enclosed systems that are refrigerated, are subject to a hydrostatic liquid head or internal pressure in excess of ambient atmospheric pressure, or are liquified gases, the liquid rate of discharge from an opening in the vessel can be estimated by using a model based on the Bernoulli flow equation. This model can also be used to analyze bottom pipe failures close to vessels containing saturated liquid under pressure, P_1 . This method assumes an incompressible flow through the opening and makes no allowances for the time dependency of the discharge as the pressure of liquid head falls.

$$W = C_d AD_e \left[\frac{288 g (P_1 - P_a)}{D_e} + 2gh \right]^{\frac{1}{2}}$$

where

W = discharge rate, lb/second

C_d = discharge coefficient, dimensionless for nozzles and orifices (may be available from vendor or manufacturer)

 C_d may be available from the equipment vendor or manufacturer, can be calculated by standard chemical engineering methods (see Perry's Chemical Engineering Handbook), or can be istimated by using:

 C_d = 0.97 nozzle type safety relief valves C_d^d = 0.81 openings on rupture discs C_d^d = 0.8 leakage from pipes connected to vessels C_d^d = 0.6 (conservative figure) used for hole in vessel

 $A = discharge area, ft^2$

 $D_p = density of liquid at conditions (T,P_1) of discharge, lb/ft³$

g = gravitational constant, 32.17 lb-ft/lb force-second²

 P_1 = absolute pressure of system, gauge pressure plus atmospheric, psia

 P_a = atmospheric pressure, psia (can assume 14.7 psia)

h = hydrostatic head pressure due to elevation or liquid depth, ft (if hydrostatic pressure already included in P_1 , then set h = 0)

To estimate the release of chemicals in a mixture, use the density of the mixture in the equation (instead of the density of the chemical), and then multiply the amount of mixture released by the weight fraction of the chemical of interest.

6.2.2 Fraction of Discharge Flashed

When a release of liquified gas or superheated liquid occurs, a portion of the discharge may flash immediately to form a vapor. The following equation calculates the fraction that will flash when the discharge contacts ambient air. If this fraction is less than 1, further dilution of the liquid spray with ambient air is necessary to complete vaporization of the remaining cold liquid; however, if F_{vap} is greater than 1, the liquid has evaporated completely before reaching atmospheric pressure.

$$F_{\text{vap}} = C_{\text{pl}} (T_{\text{l}} - T_{\text{b}})/H_{\text{vap}}$$

where

 F_{vap} = fraction of fluid vaporized, dimensionless

 c_{pl} = heat capacity of liquid at a constant pressure at temperature of system, Btu/1b-°F

 T_1 = temperature of liquid in system, °F

 T_h = boiling point of liquid at atmospheric pressure, °F

 H_{vap} = heat of vaporization, Btu/1b

This fraction can be multiplied by the generation rate obtained with equations in Subsection 6.2.1 (liquid discharge) or Subsection 6.2.4 (two-phase discharge) to obtain the quantity of chemical emitted to air as it is being discharged.

For a chemical in a mixture, use the boiling point and heat capacity of the chemical as before. The system temperature will be the same for all the chemicals in the mixture. Multiply the fraction flashed by the release rate calculated according to instructions for mixtures in Section 6.2.1.

6.2.3 Vaporization Model

A liquid chemical that is spilled onto the ground may spread out over an area, vaporize, and thus result in an air emission. A vaporization model developed by Clements can be used to estimate the rate of evaporation if the size (area) of the spill is known or can be estimated. This is a simple vaporization model, but other available spill models (TRC 1986) are more complex and may require more input data.

$$W = \frac{MKAP^{\circ}}{RT_{1}}$$

where.

W = vapor generation rate, lb/second

M = molecular weight of chemical

 $A = area of spill, ft^2$

 P° = vapor pressure of chemical, psia, at temperature T_1 [can assume 25°C (77°F) if not known]

R = universal gas constant, 10.73 psia-ft³/ $^{\circ}R$ -lb mole

 T_1 = temperature of liquid spilled, $^{\circ}R$ = $^{\circ}F$ + 460

K = gas-phase mass transfer coefficient, ft/second

$$K = 0.00438 \ (U)^{0.78} \left[\frac{D}{3.1 \times 10^{-4}} \right]^{2/3}$$

where D = diffusion coefficient for chemical in air, ft^2 /second U = Windspeed, miles/h

Diffusion coefficients can be found in chemical handbooks, usually in $cm^2/second$ (converted to $ft^2/second$ by multiplying $cm^2/second$ by 1.08 x 10^{-3}).

If D is not available, use the following equation instead to calculate ${\sf K}.$

$$K = 0.00438 (U)^{0.78} (\frac{18}{M})^{1/3}$$
, ft/second

For a chemical in a spilled mixture, use the partial pressure, P_A , for the chemical instead of the chemical's vapor pressure. See Section 3.1.1 to calculate P_A ; M and K remain chemical specific parameters.

6.2.4 Two-Phase Discharge

This method, which is based on the Fauske/Cude method, involves calculating the rate of discharge from two-phase (liquid-gas) critical flows. It is applicable to releases of saturated liquids stored under pressure at a temperature above the normal boiling point, and it is valid only if the calculated fraction of liquid flashing (see Section 6.2.2) is less than 1. This method assumes that the two phases (as discharged) are homogeneous and in mutual equilibrium. A simple empirical method, it yields approximate solutions. Alternative methods are required for more complex situations. The accuracy of this method is questionable for discharges involving long lengths of pipe where two-phase flow may develop within the line.

Two-phase critical flows can occur in failures of connections to the vapor space of vessels containing superheated liquids under pressure. They can also occur in failures of pipework containing superheated liquids remote from the vessel, where a fully developed critical flow would be established. Critical flow exists when velocity of the fluid attains sonic velocity, which can be determined by calculating the critical pressure ratio and using the

criteria presented in Subsection 6.2.5. Alternatively, the critical pressure can be assumed to be 55 percent of the system pressure, P_1 (World Bank 1985).

$$W = AC_d [288 Dm (P_1 - P_c)]^{\frac{1}{2}}, lb/second$$

where

W = generation rate

 $A = discharge area of opening, ft^2$

 C_d = discharge coefficient, dimensionless (see Subsection 6.2.1)

 P_c = critical pressure (P_c = 0.55P, for critical flow), psia

 P_1 = absolute pressure, gauge plus atmospheric, psia

 $g = 32.17 \text{ lb/sec}^2$

 $Dm = mean density of the two-phase mixture, <math>1b/ft^2$

$$Dm = 1/\left[\left(\frac{F_{vap}}{D_{v}}\right) + \left(\frac{1 - F_{vap}}{D_{1}}\right)\right]$$

where

F_{vap} = fraction of discharge vaporized (see Subsection 6.2.2), except values of C_p, T_b, and H_{vap} should be at system pressure, not atmospheric pressure

 $D_v = density of vapor at system temperature and pressure, <math>lb/ft^3$

 D_1 = density of liquid at system temperature and pressure, lb/ft^3

D, can be estimated by:

$$\frac{P_1 M}{RT_1} = D_V, 1b/ft^3$$

where
$$R = \frac{10.73 \text{ lb - psia}}{^{\circ}R - \text{ft}^{3}}$$

M = molecular weight

For a chemical in a mixture, the calculations are more complicated, but they can be performed with sufficient information and extra effort. The release rate of the mixture should first be calculated and then this value should be multiplied by the weight fraction of chemical in the mixture. To obtain the release rate of the mixture, use average molecular weight, M_{avg} , to calculate vapor density:

$$M_{avg} = X_{AG} M_A + X_{BG} M_B + \dots X_{IG} M_I$$

where

 M_{I} = molecular weight of chemical I X_{IG} = gas phase mole fraction of chemical I

$$X_{IG} = \frac{P_I \circ X_{IL}}{P_I}$$

where

 P_{I}° = vapor pressure of chemical I at system pressure, P_{I} X = liquid phase mole fraction P_{I} = system pressure, psia

See Section 3.1.1 to calculate X_{TI} from liquid-phase weight fractions.

 $\mathbf{D}_{\mathbf{l}}$ should be density of liquid mixture. Fraction vaporized should be calculated as follows:

$$F_{\text{vap}} = \text{wt. fraction}_{A} F_{\text{vap}_{A}} + \text{wt. fraction}_{B} F_{\text{vap}_{B}} \dots \text{wt. frac}_{I} F_{\text{vap}_{I}}$$

where $F_{\text{vap}}^{}$ = fraction of chemical I vaporized using $C_{\text{p}}^{}$, $T_{\text{b}}^{}$, $H_{\text{vap}}^{}$ for chemical at the system temperature and pressure

6.2.5 Gas Discharge

This method can be used to calculate discharge rates for gases from sources under pressure and assumes reversible adiabatic behavior. Ideal gas behavior is a reasonable assumption for all cases but very high (near critical) pressures.

The ratio of specific heats, k, is calculated as follows:

$$k = C_p/C_v$$

where

 $C_{\rm p}$ = heat capacity at constant pressure

 C_v = heat capacity at constant volume

(Specific units are not important but need to be the same for both.)

Critical pressure, P_c , is calculated as follows to estimate critical ratio, P_c/P , and P_c is then calculated by multiplying P_1 by the ratio.

$$P_{c} = P_{1} \left(\frac{2}{k+1} \right)^{-\frac{k}{k-1}}$$

where

P₁ = absolute system pressure, psia = gauge + atmospheric (14.7) pressure (or relief valve set pressure can be used if actual pressure is not known)

$$k = C_p/C_v$$

The critical pressure ratio is the largest ratio of downstream pressure to upstream pressure capable of producing sonic velocity. Critical flow will usually exist for most gases and vapor discharging through a safety valve or orifice.

First, it must be determined if flow is critical:

If $P_2 < P_C$, flow is critical (sonic) If $P_2 > P_C$, flow is subcritical (subsonic)

 P_2 = absolute pressure of downstream discharge flow, psia (for discharge to atmosphere, it is assumed to be 14.7 psia).

For critical flow:

$$W = 735 C_d A G P_1 \left(\frac{M}{RT}\right)^{\frac{1}{2}}$$

where

W = generation rate, lb/h

A = discharge area, in.²

 C_d = discharge coefficient, dimensionless (see Subsection 6.2.1)

G = gas constant, determined from k

$$G = 520 \left[k \left(\frac{2}{k+1} \right)^{\frac{k+1}{k-1}} \right]^{\frac{1}{2}}$$

 P_1 = absolute pressure upstream of discharge opening, psia (if unknown, relief device set pressure should be used).

M = molecular weight of chemical, 1b/1b-mole

R = universal gas constant, $10.73 \text{ psia-ft}^3/^{\circ}\text{R lb-mole}$

T = absolute temperature at inlet of discharge opening, °R = °F + 460 (system temperature)

For subcritical flow:

$$W = 735 C_d A P_1 \left(\frac{P_2}{P_1}\right)^{1/k} \left[\frac{Mk}{RT (k-1)} \left(1 - \left(\frac{P_2}{P_1}\right)^{k-1}\right)\right]^{\frac{1}{2}}$$

Definitions for the parameters are the same as for critical flow. For a chemical in a mixture, values of C_p , C_v , and M will have to be averaged by summing the product of each chemical property by its weight fraction in the gas. (See calculation for M_avg in Section 6.2.4.) The calculated release rate of the mixture in pounds/hour should then be multiplied by the weight fraction of the chemical of interest.

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OUTLINE FOR SECTION 7 AN OVERALL FACILITY EXAMPLE RELEASE CALCULATION

- 7.1 Atmospheric Releases
- 7.2 Wastewater Column Releases

SECTION 7

AN OVERALL FACILITY EXAMPLE RELEASE CALCULATION

This section presents an example illustrating the procedures used to estimate releases. The example involves a complex manufacturing process for producing acrylonitrile, which has air and water waste streams. Several methods of estimating the releases are shown.

This complex manufacturing process (illustrated in Figure 7-1) produces three listed chemicals: acrylonitrile (AN), acetonitrile, and hydrogen cyanide. It also uses ammonia as a raw material and sulfuric acid as a quenching aid, and produces ammonium sulfate as a byproduct. Separate toxic chemical release forms would be completed for each of these compounds. In this example, only the main product (AN) is discussed. Only routine releases occurring during normal operation are considered here; however, estimates of startup releases and any accidental releases would normally be included.

7.1 ATMOSPHERIC RELEASES

7.1.1 Absorber Vent B

Releases from this vent contain nitrogen, oxygen, unreacted propylene, other organic impurities present in the propylene feed, carbon monoxide, carbon dioxide, water, and small amounts of AN. Hydrogen cyanide and acetonitrile are other toxic compounds in this stream. This vent stream may be sent to a fume incinerator prior to discharge to the atmosphere.

Problem: Estimate AN emissions from the absorber Vent B.

Available data:

- Vent gas flow rate is 80,000 cubic feet per minute (measured) at 100°F and 1 atmosphere.
- Moisture content is 7 percent by volume (measured).
- AN concentration is 8 parts per million by volume on a dry basis (measured).

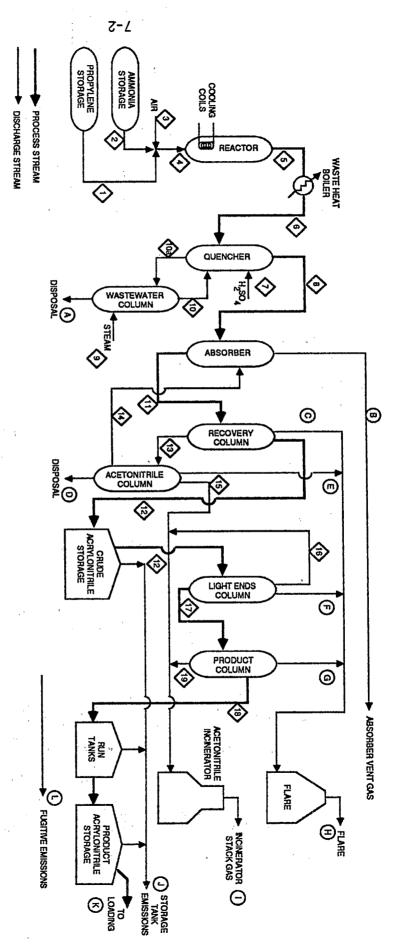


Figure 7-1. Acrylonitrile Production Process.*
*From EPA AP-450/4-84-007a, March 1984.

- Annual operating hours equal 7000, based on the operating log.
- Step 1: Calculate annual volume of gas discharged 80,000 ft³/min x 60 min/h x 7000 hours/yr = 3.36×10^{10} ft³/yr.
- Step 2: Calculate annual AN volume discharged on dry basis.

3.36 x 10^{10} ft³ gas/year x 8 x 10^{-6} parts AN/parts gas x (1 - 0.07) to correct to dry basis

 \times (70°F + 460)°R/(100°F + 460) °R to correct volume to 70°F

= 236,592 ft³ AN per year was a second of

Step 3: Calculate pounds of AN per year.

236,600 ft³ x 53.06 lb/lb-mole (molecular weight of AN) \div 387 ft³/lb-mole (the volume occupied by a lb-mole of gas at standard conditions) = 32.438 lb/yr

If the vent stream is controlled by a device such as a fume incinerator, use outlet measurements to estimate releases. If no monitoring data are available, apply a control efficiency based on design data for the incinerator to the value calculated in the example.

7.1.2 Product Recovery Column Vents, C, E, F, G, and H

Gaseous releases from the recovery column, light-ends column, product column, and the acetonitrile column are frequently tied together and vented to a flare. The fact that these streams are combined makes it possible to measure one flow and its concentration. Releases after the flare can only be estimated, however, because quantitative measurements cannot be made in the flare exhaust.

Problem: Estimate AN emissions from Vents C, E, F, G, and H.

Available data:

- The emission factor for all column vents is 5 g/kg of product (equivalent to 5 lb/1000 lb), based on published data in EPA publication 450/4-84-007a.
- ° 350 million 1b of AN was produced, based on your operating logs or product inventory data.

Step 1: Calculate AN emissions

5 lb emission/1000 lb production x 350 x 10^6 lb/yr production = 1.75×10^6 lb/yr

As an example of a control device applied to an air emission, assume that a flare is used with a destruction efficiency of 98 percent. Actual releases are:

1.75 x
$$10^6$$
 lb/yr x (1 - 0.98) = 35,000 lb/yr

The alternative of performing mass balances around the columns would be very difficult because of the number of streams involved. Several input and output values, each with an associated error, would be involved to estimate what is a relatively small release value compared with the process stream.

7.1.3 Storage Tank Releases

Releases of AN from storage tanks and loading operations depend primarily on the quantities handled and the number, size, and type of tanks. Release estimates are calculated according to procedures provided in EPA Publication AP-42. Section 4.3 (Appendix C).

Problem: Estimate annual AN releases from storage tanks.

Approach: Because monitoring data are not available, use equations presented in EPA Publication AP-42, Section 4.3.2. Here it is assumed that a fixed-roof tank is used. For floating-roof tanks, which are commonly used, other equations in this section of AP-42 should be used.

Equation for breathing loss:

$$L_B = 0.0226 \times M_V = \frac{P}{P_A - P}$$
 0.68 $D^{1.73} \times H^{0.51} \times \Delta T^{0.50} \times F_P CK_C$

 L_p = fixed-roof breathing loss, lb/yr

 M_V = molecular weight of vapor in storage tank, lb/lb-mole

 P_A = average atmospheric pressure at tank location, psia

P = true vapor pressure at bulk liquid conditions, psia

D = tank diameter, ft

H = average vapor space height, including roof volume correction, ft

 ΔT = average ambient diurnal temperature change, °F

 F_{p} = paint factor, dimensionless

C = adjustment factor for small diameter tanks, dimensionless.

 K_{C} = product factor, dimensionless

To complete the calculation in this example:

 $M_V = 53.6$ for acrylonitrile (see Appendix B)

P = 2.4 at 80°F (see Appendix B or standard chemical reference)

D = 30 ft for your tank (measured)

H = 6 ft for your tank (estimated)

 $F_p = 1.15$ for a white tank in poor condition (see Appendix C)

C = 0.89 for a small tank (Appendix C)

 $K_c = 1.0$ for acrylonitrile (Appendix C)

Inserting these values into the equation for $L_{\mbox{\footnotesize B}}$ produces the following result:

 $L_R = 1,635 \text{ lb/year}$

For 20 tanks of this size and type, uncontrolled releases due to breathing losses would be:

$$20 \times 1635 = 32,700 \text{ lb/year}$$

Report 33,000 lb/year

If scrubbers are used to reduce these emissions by 95 percent, the controlled releases would be:

$$\frac{32,700 \text{ lb}}{\text{year}} \times \frac{100 - 95}{100} = 1600 \text{ lb/year}$$

Problem: Estimate release due to working losses during tank filling.

Approach: Because monitoring data are not available, use equations in AP-42, Section 4.3.2. (See also Appendix C.)

$$L_W = 2.4 \times 10^{-5} M_V PVN K_N K_C$$

V = tank volume (gal) = 100,000

where L_{ij} = fixed roof tank working losses, lb/yr

 $N = turnovers per year = annual throughput <math>\div$ tank capacity $\cong 25$

 K_N = turnover factor = 1.0 (from Figure 4.3-7 in AP-42)

Other factors are the same as in the preceding $\boldsymbol{L}_{\boldsymbol{R}}$ equation.

$$L_W = 2.4 \times 10^{-5} \times 53 \times 2.4 \times 100,000 \times 20 \times 1.0 \times 1.0$$

= 6106 lb per year

For 20 tanks, total annual releases would be:

20 x 6106 = 122,120 lb per year (without emission controls)

Working losses are reduced by using scrubbers on the tank vents or by using floating-roof tanks. With a scrubber operating at 95 percent efficiency, the final release would be:

$$\frac{122,120 \text{ lb}}{\text{year}} \times \frac{100 - 95}{100} = 6105 \text{ lb per year}$$

7.1.4 Other Fugitive Releases

Emissions from loading operations and from leaks in valves, flanges, pumps, etc., also contribute to the overall annual AN release.

Problem: Estimate emissions from loading operations and from leaks in valves, flanges, pumps, etc.

Available data: Plant loading 51 x 106 gal/year

P = liquid vapor pressure = 2.4 psia

M = molecular weight = 53.6

T = liquid temperature (°F + 460°) = 540°R

Approach: Loading releases are estimated by the equations and data in AP-42, Section 4.4.

$$L_1 = 12.46 \text{ SPM}$$

 L_1 = releases in 1b/1000 gal of liquid loaded

S = Saturation factor (use 0.6 for submerged fill into tank truck or rail car)

$$L_1 = 12.46 \times 0.6 \times \frac{2.4 \times 53.6}{540^{\circ}R} = 1.78 \text{ lb per 1000 gal}$$

Total loading releases would be:

$$\frac{1.76 \text{ lb}}{1000 \text{ gal}} \times 51,000,000 \text{ gal} = ~90,828 \text{ lb per year}$$

The use of vapor balance loading would greatly reduce these releases.

Leaks from valves, flanges, pumps, etc. can be estimated from factors developed for the synthetic organic manufacturing processes (see Appendix D). The number of fittings in the plant and the service (i.e., gas, liquid, etc.) of each fitting must be known to make this estimate.

Available data:

Equipment

25 pumps in light-liquid service 500 pipeline valves in light-liquid service 100 pipeline valves in gas-vapor service 50 safety-relief valves in gas-vapor service

Approach: Use the following emission factors from Appendix D and multiply times the number of fittings associated with the factor.

Emission factor, lb/h per fitting	Fitting type				
0.11	Pumps in light liquid service				
0.016	Valves in light liquid service				
0.012	Valves in gas service				
0.23	Safety valves in gas service				

The total AN releases are the sum of these separate leaks, or:

$$25 (0.11) + 500 (0.016) + 100 (0.012) + 50 (0.23) = 23.45$$
 1b per hour

For 7000 hours of operation per year, annual releases would be:

$$\frac{7000 \text{ h}}{\text{year}} \times \frac{23.45 \text{ lb}}{\text{hour}} = ^{164,150} \text{ lb per year}$$

A good maintenance and inspection program would greatly reduce these average releases. If you have data on your leak rates, these data should be used.

7.1.5 Atmospheric Release Summary for AN

The following is a listing summarizing atmospheric releases of AN.

Process	rele	Stack ases, lb/yr	Fugitive releases, lb/yr		
Absorber Recovery columns after flare Storage (1635 + 6105) Loading		32,438 35,000 7,740	90,828		
Leaks Estimated total annual release of			<u>164,150</u>		
AN during normal operations	or	75,178 75,000 lb/yr (stack)	254,978 255,000 lb/yr (fugitive)		

7.2 WASTEWATER COLUMN RELEASES

Liquid discharge from the wastewater column contains small amounts of AN in addition to cyanide, sulfates, ammonia, and acetonitrile, which generally would go to wastewater treatment. Estimates of releases after treatment should be based on effluent measurements, if available. In the absence of such data, the amount of AN released can be estimated by calculating the amount of AN influent to treatment and then applying the efficiency of the treatment.

Problem: Estimate wastewater releases of AN

Approach: Measured flow data are available prior to treatment and will be used to calculate annual releases of AN. A treatment efficiency will then be applied to estimate actual plant releases.

- Average discharge flow = 500 gallons/min
- AN concentration = 150 parts per million by weight
- Annual operating hours = 7000

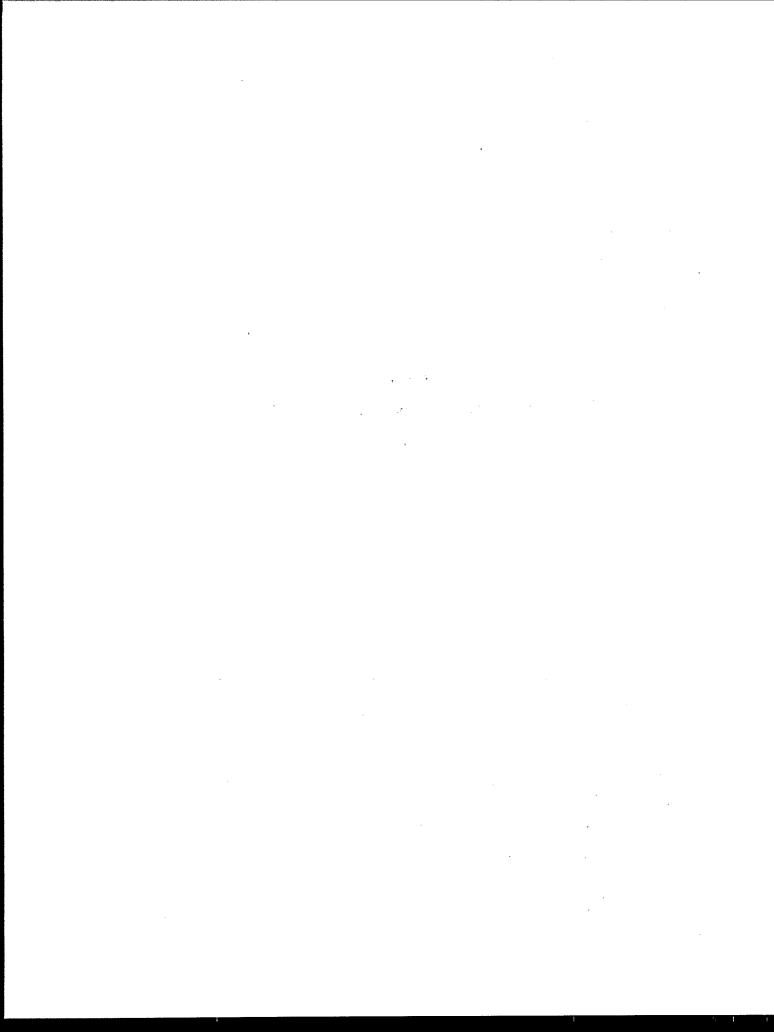
The AN releases to a wastewater treatment system are calculated by multiplying the flow by the concentration and the duration of release. Note that the density of water is 8.32 lb/gal at 70°F.

$$\frac{500 \text{ gal}}{\text{minute}} \times \frac{8.32 \text{ lb}}{\text{gallon}} \times \frac{150 \text{ parts}}{10^6 \text{ parts}} \times \frac{60 \text{ min}}{\text{hour}} \times \frac{7000 \text{ h}}{\text{year}} = 262,080 \text{ lb per year}$$

The treatment efficiency can be estimated based on published data for similar treatment at the appropriate influent concentration. As shown in Appendix D, AN can be reduced by 99.1 percent for an initial concentration

of 110 mg/liter (ppm) by the use of activated sludge treatment. Releases to surface water would then be:

$$\frac{262,000 \text{ lb to treatment}}{\text{year}} \times \frac{(100 - 99.1)}{100} = 2359 \text{ lb per year}$$
 or 2400 lb/year



APPENDIX A WASTEWATER TREATMENT EFFICIENCY DATA

Appendix A contains tables of information that allow the estimation of wastewater treatment efficiency for selected processes and compounds. The information provided should only be used when no other method of wastewater treatment efficiency is available. Extreme care must be taken to ensure that the data are applied only to systems operating under conditions similar to those used to develop the efficiency estimates.

Table A-1 contains numerous citations of wastewater treatment efficiency for specific compounds based on the type of treatment and source of the wastewater stream. The data in this table were compiled and summarized from a literature search in "Estimation of Removal of Organic Chemicals During Wastewater Treatment," Draft Final Report, Versar, Inc., prepared for the U.S. EPA, Exposure Evaluation Division, Office of Toxic Substances, Washington, D.C., EPA Contract No. 68-02-3968, Task 807.148, September 30, 1986. The original data are from research conducted on pilot- and full-scale treatment systems.

Data in the table should be used with an awareness and understanding of test conditions involved.

- Tests with the same chemical performed at different temperatures often showed thermally dependent differences in removal, with higher percentage removal values at higher temperatures.
- Longer retention times usually result in a higher rate of removal.
- Aeration often results in greater removal for various reasons:
 more agitation causes more contact between chemicals and cells;
 aeration adds more oxygen to the wastewater system, and oxidative
 microbial processes proceed more rapidly at higher oxygen levels;
 many of the organic compounds reviewed in the Summary Table are
 volatile, and aeration of the wastewater will accelerate the rate
 of chemical transport from the aqueous to the atmospheric compartment.

It is suggested that the user consult the references cited in Table A-1.

Facilities should use the removal data for a treatment system that has similar conditions (type of waste, chemical concentration, suspended solids concentration, and residence time) to the facility's own wastewater treatment system.

Table A-2 also presents wastewater treatment efficiencies for a number of chemicals. This information, however, applies only to secondary biological wastewater treatment systems receiving relatively low concentrations of the particular toxic pollutant (approximately 500 parts per billion). It provides educated estimates on pollutant fate in the treatment system (i.e., volatilized to air, partitioned to sludge, or biodegraded) extracted from "Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works," EPA/530-SW-86-004 (February 1986).

TABLE A-1. SELECTED WASTEWATER TREATMENT REMOVAL EFFICIENCIES^a

Chemical	Percent Removal	Waste Stream	Initial Chem Conc	Treatment	Scale	Temp C	Susp Solids Conc	Hydraulic Res. Time	Acclimation	Reference
Acetone	73.0		[Activated Sludge	Pilot	NR) HR	8 hrs	NR	Kincennon et al, no date
Acrolein	>85.7	Domestic Wastewater	700 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	7	NR I	Cormack and Hsu, 1983
Acrylonitrile	99.1	Synthetic Wastewater	110 mg/l	Activated Sludge	1	NR	į kr	NR	4 weeks	Kincannon et. al, 1983
Uniline	>99	Petroleum Refinery Waste	j ·	Activated Sludge	Full	HR	38 mg/L	NR	NR	Snider and Manning, 1982
Anthracene	>96.0	Coke processing plant	7.2 ug/l	Activated sludge	Full	HR	NR NR] NR	NR	Walters and Luthy, 1984
Anthracene	>99.0	Coke processing plant	85 ug/l	Activated sludge	Full	NR	NR NR	j NR	NR [Walters and Luthy, 1984
Anthracene	98.0	Coke processing plant	15 ug/l	Activated sludge	Full	NR	į NR	NR NR	HR	Walters and Luthy, 1984
Anthracene	97.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/t	7 days	NR	Petrasek et al, 1983
Benzene	99.40	i -	5 ug/l	Activated sludge	Pilot	NR	NR NR	SRT=5 days	NR	Bishop, 1982
Benzene	i >99	Coke Plant Effluent	6.1-9.8 mg/l	Activated Sludge	Pilot	NR	45 mg/l	j HR	NR	Osantowski and Hendriks, no dat
Benzene	i >99 i	Raw Wastewater	73 ug/l	Activated Sludge	Pilot	NR	j 2900 mg/l	7.5 hr	NR	Petrasek et. al.,1983b
Benzene	99.90	Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	NR	140 kg/day	30 min	1 ? [SCS Engineering, 1979
Benzene	>75.00	Domestic Wastewater	4 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	?	į HR į	Cormack and Hsu, 1983
Benzidine	0.00	Paper/Petrochemical Wastes	4 ug/l	Activated Sludge	Full	NR	į NR	NR NR	1 7 1	SCS Engineering, 1979
Butylbenzyl phthalate	>95.5	Domestic Wastewater	21-24 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	j ?	NR	Cormack and Hsu, 1983
Butylbenzyl phthalate	96.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/l	7 days	NR I	Petrasek et al, 1983a
Carbon Tetrachtoride	100.00	Industrial Wastewaters	1-2 ug/l	Activated Sludge	Full	NR	931 mg/l	NR NR	j nr j	Feiler, 1979
Carbon Tetrachloride	98.70	NR	50-200 ug/l	Activated Sludge	Pilot	NR	NR NR	NR NR	I NR I	Bishop, 1982
Carbon Tetrachloride	93.0	Pulp waste	I NR	Two stage bio.	Full	NR	i NR	12.0 hr	NR I	Leuenberger et al. 1985.
Carbon Tetrachloride	>99	Raw Wastewater	60 ug/l	Aeration Basin	Pilot	NR	2900 mg/l	7.5 hr	NR 1	Petrasek et al.,1983b
Carbon Tetrachloride	51.0	Acid waste	NR NR	Activated sludge	Pilot	NR	NR	8.0 hr	j NR j	Kincannon et al., no date
Carbon Tetrachloride (3)	99.90	Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	NR	i NR	30 min	1 7 1	SCS Engineering, 1979
Chlorobenzene	99.80	NR	50-200 ug/l	Activated Sludge	Pilot	NR	i NR	i NR	į NR į	Bishop, 1982
Chlorobenzene	97.60	Dyestuff Manufact Waste	0.55 mg/l	Activated Sludge	Full	NR	216 g/cu m	NR NR	į NR į	Keinath, 1984
Chlorobenzene	74.00	Domestic/Ind. Wastewater	NR	Secondary Treatment	Full	NR	HR	i NR	None	McCarty and Reinhard, 1980
Chlorobenzene	97.80	Dvestuff Manufact Waste	0.55 mg/l	Activated Sludge	Full	NR	216 g/cu m	į NR	i NR i	Keinath, 1984
Chlorobenzene	>99	Raw Wastewater	197 ug/l	Aeration Basin	Pilot	i nr	2900 mg/l	j 7.5 hr	j nr i	Petrasek et al.,1983b
Chloroform	>93.60	Domestic Wastewater	6-140 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	j ?	i NR i	Cormack and Hsu, 1983
Chloroform	65.0	Pulp waste) NR	Two stage bio.	Full	i NR	NR	12.0 hr	į NR į	Leuenberger et al. 1985.
Chloroform	85.0	Acid waste	NR NR	Activated sludge	Pilot	NR	i NR	8.0 hr	i NR i	Kincannon et al., no date
Chloroform	99.40	NR NR	50-200 ug/l	Activated Sludge	Pilot	NR	NR NR	NR NR	I NR I	Bishop, 1982
Chloroform	0-91	Primary Domestic Sewage	0-10 ug/l	Activated Sludge	Full	i NR	97 mg/l	į NR	NR I	Feiler, 1979
Chloroform	>97	Raw Wastewater	137 ug/l	Aeration Basin	Pilot	i NR	2900 mg/l	j 7.5 hr	NR I	Petrasek et al.,1983b
Chloroform	86.00	i	i	Activated Sludge	Pilot	NR	NR	8 hrs	i NR i	Kincannon et al, no date
Chloroform	99.90	Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	NR	140 kg/day	30 min	7	SCS Engineering, 1979
Chloroform	57-70	Industrial Wastewaters	30-36 ug/l	Activated Sludge	Full	NR	931 mg/l	NR NR	i NR i	Feiler, 1979
Chlorophenol,m	1	Paper/Petrochemical Wastes	0.9 ug/l	Activated Sludge	Full	NR	104-19,811 kg/day	NR	1 7 1	SCS Engineering, 1979
Di (2-ethylhexyl) phthalate (1)	>96.9	Domestic Wastewater	21-66 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	?	i NR i	Cormack and Hsu, 1983
Di (2-ethylhexyl) phthalate (1)	•	Industrial Wastewaters	32-36 ug/l	Activated Sludge	Full	NR	931 mg/l	NR NR	NR I	Feiler, 1979
Di (2-ethylhexyl) phthalate (1)		Trickling Filter Effl	NR NR	Secondary Treatment	Full	NR	NR	i NR	None	McCarty and Reinhard, 1980

(continued)

TABLE A-1 (continued)

**************************************		_	Initial	Treatment	Scale		Susp Solids	Hydraulic	Acclimation	Reference
Chemical	Percent Removal		Chem Conc	ii ea cineiic	J	C	Conc	Res. Time		
Di (2-ethylhexyl) phthalate (1)	62.00	Domestic/Ind. Wastewater		Secondary Treatment	Full	NR	NR	NR	None	McCarty and Reinhard, 1980
Di (2-ethylhexyl) phthalate (1)	•	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/l	7 days	NR	Petrasek et al, 1983a
Di (2-ethylhexyl) phthalate (1)		Paper/Petrochemical Wastes	2 ug/l	Activated Sludge	Full	NR	NR	NR	1 ?	SCS Engineering, 1979
Dibutylphthalate, n	55.00	Domestic/Ind. Wastewater	NR	Secondary Treatment	Full	NR	NR	NR NR	None	McCarty and Reinhard, 1980
Dibutylphthalate, n	94.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/l	7 days	NR	Petrasek et al, 1983a
Dibutylphthalate, n	>91.5	Domestic Wastewater	9-15 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	7	NR	Cormack and Hsu, 1983
Dibutylphthalate, n	83.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/l	7 days	NR	Petrasek et al, 1983a
Dichlorobenzene (1,2-)	98.80	Trickling Filter Effl	NR	Secondary Treatment	Full	NR	NR NR	NR	None	McCarty and Reinhard, 1980
Dichlorobenzene (1.2-)	>97.00	Domestic/Ind. Wastewater	NR I	Secondary Treatment	Full	₩R	NR NR	NR NR	None	McCarty and Reinhard, 1980
Dichlorobenzene (1.3-)	99.20	Dyestuff Manufact Waste	0.42 mg/l	Activated Sludge	Full	NR	850 g/cu m	j NR	NR	Keinath, 1984
Dichlorobenzene (1.3-)	98.50	Trickling Filter Effl	NR	Secondary Treatment	Full	NR	NR NR	NR	None	McCarty and Reinhard, 1980
Dichlorobenzene (1.3-)	93.30	Dyestuff Manufact Waste	18 ug/l	Activated Sludge	Full	NR	213 g/cu m	j NR	NR	Keinath, 1984
Dichlorobenzene (1,3-)	88.00	Domestic/Ind. Wastewater	NR	Secondary Treatment	Full	NR	NR NR	NR NR	None	McCarty and Reinhard, 1980
Dichlorobenzene (1,4-)	99.00	Trickling Filter Effl	NR I	Secondary Treatment	Full	. NR	NR NR	NR NR	None	McCarty and Reinhard, 1980
Dichlorobenzene (1,4-)	96.60	Dyestuff Manufact Waste	0.8 mg/l	Activated Sludge	Full	NR	850 g/cu m	NR	NR	Keinath, 1984
Dichlorobenzene (1,4-)	>99.00	Domestic/Ind. Wastewater	₩R	Secondary Treatment	Full	NR	NR NR	NR NR	None	McCarty and Reinhard, 1980
Dichlorobenzene (1,4-)	99.70	Dyestuff Manufact Waste	3.2 mg/l	Activated Sludge	Full	NR	216 g/cu m	NR	NR	Keinath, 1984
Dichlorobenzene (1,4-)	99.60	Dyestuff Manufact Waste	68 ug/l	Activated Sludge	Full	NR	213 g/cu m	NR NR	NR	Keinath, 1984
Dichlorobromomethane (5)	>99	Raw Wastewater	89 ug/l	Aeration Basin	Pilot	NR	2900 mg/l	7.5 hr	NR I	Petrasek et al.,1983b
Dichlorobromomethane (5)	95.70	NR .	50-200 ug/l	Activated Sludge	Pilot	MR	NR NR	NR NR	NR I	Bishop, 1982
Dichloroethane (1,2-)	>94.00	Domestic Wastewater	33-710 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	?	NR	Cormack and Hsu, :1983
Dichloroethylene (1,1-)	<99.5	NR NR	50-200 ug/l	Activated Sludge	Pilot	İNR	NR	NR NR	NR	Bishop, 1982
Dichloroethylene (1,1-)	>99	Raw Wastewater	79 ug/l	Aeration Basin	Pilot	NR	2900 mg/l	7.5 hr	NR	Petrasek et al.,1983b
Dichloromethane (6)	93.10	Dyestuff Manufact Waste	5.5 ug/l	Activated Sludge	Full	NR	216 g/cu m	NR NR	NR I	Keinath, 1984
Dichloromethane (6)	12.0		•	Activated Sludge	Pilot	NR) NR	8 hrs	NR	Kincannon et al, no date
Dichloromethane (6)	91.30	Dyestuff Manufact Waste	5.5 ug/l	Activated Studge	Full	j nr	216 g/cu m	NR NR	j NR	Keinath, 1984
Dichloromethane (6)	>97	Raw Wastewater	118 ug/l	Aeration Basin	Pilot	NR	2900 mg/l	7.5 hr	NR	Petrasek et al.,1983b
Dichloromethane (6)	98.90	NR NR	50-200 ug/l	Activated Sludge	Pilot	NR	NR NR	NR	NR	Bishop, 1982
Dichloromethane (6)	0-91	Industrial Wastewaters	6-14 ug/l	Activated Sludge	Full	NR	931 mg/l	NR	NR	Feiler, 1979
Dichloromethane (6)	>96.6	Domestic Wastewater	1-62 mg/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	7	NR	Cormack and Hsu, 1983
Dichloromethane (6)	90.60	Trickling Filter Effl	NR	Secondary Treatment	Full	NR	NR NR	NR NR	None	McCarty and Reinhard, 1980
Dichlorophenol (2,4-)	27.0	Pulp waste	i NR	Two stage bio.	Fult	NR	NR NR	12.0 hr	NR I	Leuenberger et al. 1985.
Dichloropropane (1,2-)	>98	Raw Wastewater	309 ug/l	Aeration Basin	Pilot	NR	2900 mg/l	7.5 hr.	NR	Petrasek et al.,1983b
Dichloropropane (1,2-)	96.10	NR NR	50-200 ug/l	Activated Sludge	Pilot	NR	NR NR	NR NR	NR I	Bishop, 1982
Dichloropropylene (4)		Dyestuff Manufact Waste	0.1 mg/l	Activated Sludge	Full	NR	213 g/cu m	NR NR	NR I	Keinath, 1984
Dichloropropylene (4)	•	Dyestuff Manufact Waste	0.13 mg/l	Activated Sludge	Full	NR	213 g/cu m	NR	NR I	Keinath, 1984
Diethyl phthalate		Paper/Petrochemical Wastes	6 ug/l	Activated Sludge	Full	MR	NR	NR NR	1 ? 1	SCS Engineering, 1979
Diethyl phthalate	97.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/t	7 days	j NR j	Petrasek et al, 1983a
Diethyl phthalate	>66.7	Domestic Wastewater	2-4 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	7	. j nr j	Cormack and Hsu, 1983
Diisobutyl phthalate	74.50		NR NR	Secondary Treatment	Full	NR	NR	i NR-	None	McCarty and Reinhard, 1980

TABLE A-1 (continued)

*****************	222752773773			****************	*******	******				***********************
Chemical	Percent Removal		Initial Chem Conc	Treatment	Scale		Susp Solids		Acclimation	Reference
	KCHOYAL	 	Chesa Conc	 	 	C	Conc	Res. Time	 	******************
Diisobutyl phthalate	93.00	Domestic/Ind. Wastewater	NR NR	Secondary Treatment	Full	NR	l HR	I NR	None	McCarty and Reinhard, 1980
Dimethyl phthalate	98.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	MR	430 mg/l	7 days	NR I	Petrasek et al, 1983a
Dimethyl phthalate	89.40	Trickling Filter Effl	NR	Secondary Treatment	Full	HR	NR NR	NR NR	None	McCarty and Reinhard, 1980
Dimethyl phthalate	93.00	Domestic/Ind. Wastewater	NR NR	Secondary Treatment	Full	MR	NR NR	NR NR	None	McCarty and Reinhard, 1980
Dimethyl phthalate	50.00	Paper/Petrochemical Wastes	2 ug/l	Activated Sludge	Full	MR	I NR	i HR	1 ? 1	SCS Engineering, 1979
Dimethyl phthalate	97.0	•	6 ug/l	Anaerob/aerob basins	Full	30-45	į NR	max=21 days	i nr i	SCS Engineering, 1979
Dimethylphenol (2,4)	98.9	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/l	7 days	i nr i	Petrasek et al. 1983a
Dimethylphenol (2,4-)	99.90	Paper/Petrochemical Wastes	15 ug/l	Activated Sludge	j Full	MR	104-19,811 kg/day	I NR	i ? i	SCS Engineering, 1979
Dinitrophenol (2,4-)	84.40	Dyestuff Manufact Waste	2.7 mg/l	Activated Sludge	j Full	NR	850 g/cu m	NR NR	i nr i	Keinath, 1984
Dinitrophenol (2,4-)	63.00	Synthetic Wastewater	130 mg/l	Activated Sludge	i i	MR	NR NR	NR NR	4 weeks	Kincannon et. al, 1983
Dinitrophenol (2,4-)	26.40	Dyestuff Manufact Waste	5.3 mg/l	Activated Sludge	j Full	NR	216 g/cu m	i NR	i NR i	Keinath, 1984
Dinitrotoluene (2,4-)	95.0	Petrochemical	8 ug/l	Anaerob/aerob basins	Full	30-45	NR	mex=21 days	i nr i	SCS Engineering, 1979
Dinitrotoluene (2,4-)	95.0	Petrochemical	8 ug/l	Anaerob/aerob basins	Full	30-45	I NR	max=21 days	I NR I	SCS Engineering, 1979
Dinitrotoluene (2,4-)	99.90	Paper/Petrochemical Wastes	390 ug/l	Activated Sludge	Full	HR	104-19,811 kg/day	NR	7	SCS Engineering, 1979
Dinitrotoluene (2,4-)		Paper/Petrochemical Wastes	390 ug/t	Activated Sludge	Full	NR	NR NR	NR	1 7	SCS Engineering, 1979
Diphenylhydrazine	99.0		73 ug/l	Anaerob/aerob basins	Full	30-45	NR NR	max=21 days	NR I	SCS Engineering, 1979
Diphenylhydrazine (1,2-)		Paper/Petrochemical Wastes	341 ug/l	Activated Sludge	Full	NR	NR NR	NR	7	SCS Engineering, 1979
Ethyl Benzene	>90	Petroleum refinery wastes		Activated sludge/AC	Full	NR	38 mg/l	NR NR	NR I	Snider and Manning, 1982
Ethyl Benzene,n	>90	Petroleum refinery wastes	i	Activated sludge/AC	Full	MR	38 mg/l	NR NR	NR I	Snider and Manning, 1982
Ethylbenzene	88.90		5 ug/l	Activated sludge	Pilot	NR	NR NR	SRT=5 days	NR I	Bishop, 1982
Ethylbenzene	i >99	Raw Wastewater	82 ug/l	Activated Sludge	Pilot	NR	2900 mg/l	7.5 hr	NR I	Petrasek et. al.,1983b
Ethylbenzene	72.00	Domestic/Ind. Wastewater	NR	Secondary Treatment	Full	NR	NR NR	NR	None	McCarty and Reinhard, 1980
Ethylbenzene	97.90	Trickling Filter Effl	NR.	Secondary Treatment	Full	NR	NR	NR NR	None .	McCarty and Reinhard, 1980
Ethylbenzene	0.0		¦ ''''	Activated Sludge	Pilot	NR	I NR	8 hrs	NR I	Kincannon et al, no date
Ethylbenzene	77-99	Ind. Wastewater	30-36 ug/l	Activated Sludge	Full	NR	931 mg/t	NR NR	NR I	Feiler, 1979
Heptachlor	93.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	1 430 mg/l	7 days	NR I	Petrasek et al. 1983
Hexachlorocyclopentadiene	•	Paper/Petrochemical Wastes	113 ug/l	Activated Sludge	Full	NR NR	NR	NR	7 1	SCS Engineering, 1979
Isopropanol	70.0		1 110 03/1	Activated Sludge	Pilot	MR	NR NR	8 hrs	NR I	Kincannon et al, no date
Lindane	67.00	Domestic/Ind. Wastewater	NR NR	Secondary Treatment	Full	NR	NR	NR NR	None	McCarty and Reinhard, 1980
Lindane	45.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR.	430 mg/l	7 days	NR I	Petrasek et al, 1983
Naphthalene	2.50	Dyestuff Hanufact Waste	4 ug/l	Activated Sludge	Full	NR	850 g/cu m	NR	NR I	Keinath, 1984
Naphthalene		Paper/Petrochemical Wastes	4 ug/l	Activated Studge	Full	NR	NR NR	NR NR	7	SCS Engineering, 1979
Naphthalene	>99.0	Coke processing plant	560 ug/l	Activated studge	- Full	NR	i NR	NR NR	NR I	Walters and Luthy, 1984
Naphthalene	>54.2	Domestic Wastewater	2-3 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	7	NR I	Cormack and Hsu, 1983
Naphthalene	>99.2	Dyestuff Manufact Waste	0.12 mg/l	Activated Studge	Full	NR	213 g/cu m	NR	I NR I	Keinath, 1984
Naphthalene	>99	Petroleum Refinery Waste	J. 1	Activated Studge	Full	NR	38 mg/t	NR	I NR I	Snider and Manning, 1982
Naphthalene	75.00	Domestic/Ind. Wastewater	NR	Secondary Treatment	Full	NR	JO MOJ/L	NR	None	McCarty and Reinhard, 1980
Naphthalene	99.0	Coke processing plant	69 ug/l	Activated studge	Full	NR NR	j nk I NR	I NR		
Naphthalene	99.0	Loke processing plant Municipal Sewage	59 ug/t 50 ug/t	Plug Flow A.S.	Pilot	NK NR		•	i NR j	Walters and Luthy, 1984
Naphthalene	94.70			, -			430 mg/l	7 days	NR I	Petrasek et al, 1983
naprilialette	74.70	Trickling Filter Effl	NR NR	Secondary Treatment	Fuli	NR	NR NR	NR NR	None	McCarty and Reinhard, 1980

TABLE A-1 (continued)

Chemical	Percent Removal	Waste Stream	Initial Chem Conc	Treatment	Scale		Susp Solids Conc	Hydraulic Res. Time	Acclimation	Reference ,
Naphthalene	1 >99.0	Coke processing plant	180 ug/l	Activated sludge	Full	NR	NR	NR	NR	Walters and Luthy, 1984
Nitrobenzene	99.60	Dyestuff Manufact Waste	0.66 mg/l	Activated Sludge	Full	NR	213 g/cu m) NR	NR I	Keinath, 1984
Nitrobenzene	74.00	Dyestuff Manufact Waste	0.35 mg/l	Activated Sludge	Full	NR	216 g/cu m) NR	NR	Keinath, 1984
Nitrophenol (2-)	14.30	Dyestuff Manufact Waste	7.7 ug/l	Activated Sludge	Full	NR	51 g/ cu m	NR NR	NR	Keinath, 1984
litrophenol (2-)	i 99.90 i	Paper/Petrochemical Wastes	9 ug/l	Activated Sludge	Full	NR	j nr	NR	7	SCS Engineering, 1979
litrophenol (2-)	99.90	Dyestuff Manufact Waste	9 ug/l	Activated Sludge	Full	NR	104-19,811 kg/day	NR NR	?	SCS Engineering, 1979
litrophenol, p	92.80	Dyestuff Manufact Waste	0.46 mg/l	Activated Sludge	j Full	NR	850 g/cu m	NR NR	NR	Keinath, 1984
I,N-Dimethylaniline	89.00	Petroleum Refinery Waste	j	Activated Sludge	Full	NR	38 mg/l	NR	NR	Snider and Manning, 1982
entachlorophenol	26.0	Pulp waste	NR I	Two stage bio.	Full	NR	NR	12.0 hr	NR	Leuenberger et al. 1985.
Pentachlorophenol	81.0	•	i	Plug-flow A.S.	Pilot	NR	j 430 mg/l	7 days	?	Petrasek et al, 1983a
Pentachlorophenol	40.00	Wood Preserving Effluent	5.5 mg/l	Activated Sludge	Pilot	25.00	69 mg/l	NR NR	NR	Jank and Fowlie, no date
Pentachlorophenol	58.00	Wood Preserving Effluent	3.6 mg/l	Activated Sludge	Pilot	26.00	69 mg/l	NR:	NR I	Jank and Fowlie, no date
Pentachlorophenol	35.00	Wood Preserving Effluent	5.5 mg/l	Activated Sludge	Pilot	27.00	69 mg/l	NR	NR -	Jank and Fowlie, no date
Pentachlorophenol	>96.4	Domestic Wastewater	28 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	7	NR I	Cormack and Hsu, 1983
Phenol	91.00	Indust. Creosote Waste	47 mg/l	Microb Treat. Tower	j Full	>10	116 mg/l	NR .	NR	Vela and Raiston, 1978
henol	94.60	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	i nr	227 mg/l	12 days	į NR į	Mahmud and Thanh, no date
henol	95.30	Refinery Wastes	16.2 mg/l	Cont Activated Sludge	Full	6.00	NR	7 hr	j NR j	Mahmud and Thanh, no date
henol	90.60	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	285 mg/l	1 day	NR	Mahmud and Thanh, no date
Phenol	95.90	Dyestuff Manufact Waste	3.2 mg/l	Activated Sludge	Full	NR	850 g/cu m	NR NR	, NR	Keinath, 1984
henol	90.70	Refinery Wastes	22.7 mg/l	Cont Activated Sludge	Full	6.00	i HR	7 hr	NR	Mahmud and Thanh, no date
henol	98.20	Refinery Wastes	18.5 mg/l	Cont Activated Sludge	Full	6.00	NR NR	7 hr	NR	Mahmud and Thanh, no date
henol	95.0	Municipal Sewage	50 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/l	7 days	NR	Petrasek et al, 1983a
henol	86.30	Refinery Wastes	19.9 mg/l	Cont Activated Sludge	Full	6.00	NR NR	7 hr	NR	Mahmud and Thanh, no date
henol	93.30	Refinery Wastes	13.5 mg/l	Cont Activated Sludge	Full	6.00	į nr	7 hr	-NR	Mahmud and Thanh, no date
Phenol	96.70	Refinery Wastes	19.6 mg/l	Cont Activated Sludge	Full	6.00	i nr	j 7 hr	NR I	Mahmud and Thanh, no date
henol	>86.7	Dyestuff Manufact Waste	0.150 mg/l	Activated Sludge	j Full	NR	213 g/cu m	NR NR	NR I	Keinath, 1984
henol	90.70	Refinery Wastes	21.2 mg/l	Aerated Lagoon	j Full	NR	250 mg/l	3 days	NR	Mahmud and Thanh, no date
henol	0-5	Ind. Wastewater	13-19 ug/l	Activated Sludge	Full	NR	931 mg/l	NR NR	NR	Feiler, 1979
henol	90.80	Refinery Wastes		Batch Activated Studge	Full	i nr	NR	10 hr	NR	Mahmud and Thanh, no date
henol	75.30	Refinery Wastes	20.3 mg/l	Cont Activated Studge	Full	6.00	NR "	j 7hr	į NR į	Mahmud and Thanh, no date
henol	98.00	Paper Mill/Petrochemical	0.02-97 mg/ml	Activated studge	Full	NR	i NR	j nr	i i	SCS Engineering, 1979
henol	94.10	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	245 mg/l	10 days	NR	Mahmud and Thanh, no date
henol	76.20	Refinery Wastes	20.6 mg/l	Cont Activated Sludge	Full	6.00	NR.	7 hr	NR I	Mahmud and Thanh, no date
henol	81.30	Refinery Wastes	20.3 mg/l	Cont Activated Sludge	Full	6.00	i NR	j 7hr	į NR į	Mahmud and Thanh, no date
henol	99.00		39.6 mg/l	Seq Batch Reactor	Full	24-26	NR NR	8-9 days	i NR i	Herzbrun et al, 1985
henol	97.40	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	265 mg/l	10 days	j ar j	Mahmud and Thanh, no date
henol	80.20	Refinery Wastes	21.2 mg/l	Cont Activated Sludge	Full	6.00	NR ·	7 hr	i NR i	Mahmud and Thanh, no date
henol	82.70	Refinery Wastes	21.6 mg/l	Cont Activated Sludge	Full	6.00	NR -	7 hr	i NR i	Mahmud and Thanh, no date
henol	80.20	Refinery Wastes	24.8 mg/l	Cont Activated Sludge	Full	6.00	•	7 hr	NR I	Mahmud and Thanh, no date
Phenol	86.20	Refinery Wastes	24.5 mg/t	Cont Activated Studge	1	6.00	•	7 hr	i NR i	Mahmud and Thanh, no date

TABLE A-1 (continued)

Chemical	Percent									HEISISSERSSENSSISSISSESSES
CHEMICEL	Removal		Initial Chem Conc	Treatment	Scale	Temp C	Susp Solids Conc	Hydraulic Res. Time	Acclimation	Reference
mt								†	÷	
Phenol	88.60	Refinery Wastes	23 mg/l	Cont Activated Sludge		6.00	NR NR	7 hr	NR [Mahmud and Thanh, no date
Phenol	92.80	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	290 mg/L	3 days	NR	Mahmud and Thanh, no date
Phenol	80,30	Refinery Wastes	20.2 mg/l	Cont Activated Sludge	Full	6.00	j hr	7 hr	NR	Mahmud and Thanh, no date
Phenol	>96.4	Domestic Wastewater	19-66 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	1 7	NR	Cormack and Hau, 1983
Phenol	99.90	Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	NR	140 kg/day	30 min	1 7 1	SCS Engineering, 1979
Phenol	93.70	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	260 mg/l	7days	j HR j	Mahmud and Thanh, no date
Phenol	99.90	Dyestuff Manufact Waste	4.9 mg/l	Activated Sludge	Full	NR	51 g/ cu m	NR NR	į NR į	Keinath, 1984
Phenol	96.30	Refinery Wastes	18.8 mg/l	Cont Activated Sludge	Full	6.00) NR	7 hr	į NR į	Mahmud and Thanh, no date
Phenol	88.30	Refinery Wastes	25.7 mg/l	Cont Activated Sludge	Full	6.00	j nr	7 hr	i HR i	Mahmud and Thanh, no date
Phenol	85,40	Refinery Wastes	20.3 mg/l	Cont Activated Sludge	Full	6.00	į nr	7 hr	j nr j	Mahmud and Thanh, no date
Phenol	26.00	Paper/Petrochemical Wastes	8 ug/l	Activated Sludge	Full	NR	104-19,811 kg/day	NR NR	i ? i	SCS Engineering, 1979
Phenot	93.50	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	282 mg/l	5 days	i nr i	Mahmud and Thanh, no date
Phenol	>99	Wood Preserving Effluent	0.16 mg/l	Activated Sludge	Pilot	27.00	69 mg/l	NR NR	i NR i	Jank and Fowlie, no date
Phenol	94.30	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	265 mg/l	5 days	i NR i	Mahmud and Thanh, no date
Phenol	j >99	Wood Preserving Effluent	0.16 mg/l	Activated Sludge	Pilot	26.00	69 mg/l	NR.	i NR i	Jank and Fowlie, no date
Phenol	94.60	Refinery Wastes	21.2 mg/l	Aerated Lagoon	Full	NR	260 mg/l	7 days	I NR I	Mahmud and Thanh, no date
Phenol	81.40	Refinery Wastes	18.1 mg/l	Cont Activated Sludge	Full	6.00	NR.	7 hr	NR I	Mahmud and Thanh, no date
Phenol	90-100	Coke Plant Effluent	655 mg/l	Activated Sludge	Pilot	NR	45 mg/l	NR.	I NR I	Osantowski and Hendriks, no date
Phenol	i>99 i	Wood Preserving Effluent	0.65 mg/l	Activated Sludge	Pilot	25.00	69 mg/l	NR NR	NR I	Jank and Fowlie, no date
Pyridine	i 65.00 i	Aqueous Solution	NR	AFNOR T 90-302 Test	Lab	NR	NR NR	42 days	NR I	Gericke and Fischer, 1981
Pyridine	46.00	Aqueous Solution	NR.	AFNOR T 90-302 Test	Lab	NR	NR	28 days	NR I	Gericke and Fischer, 1981
Styrene, C3	i >99 i	Petroleum Refinery Waste		Activated Sludge	full	NR	38 mg/l	I NR	NR I	Snider and Manning, 1982
Tetrachloroethane	50.0	Pulp waste	NR NR	Two stage bio.	Full	NR	l NR	12.0 hr	NR I	Leuenberger et al. 1985.
Tetrachloroethane (1,1,2,2-)	99.90	Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	NR	NR	30 min	7	SCS Engineering, 1979
Tetrachloroethylene	>75.0	Domestic Wastewater	4 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	7	NR I	Cormack and Hsu, 1983
Tetrachloroethylene	9.00		1 ' 53/ '	Activated Studge	Pilot	NR	NR	8 hrs	NR I	Kincannon et al, no date
Tetrachloroethylene	91.70	Trickling Filter Effl	NR NR	Secondary Treatment	Full	NR	l NR	l NR	None	McCarty and Reinhard, 1980
Tetrachloroethylene	27.00	Domestic/Ind. Wastewater	NR NR	Secondary Treatment	Full	NR	I NR	NR	None	• • • • • • • • • • • • • • • • • • • •
Tetrachloroethylene	83-98	Industrial Wastewaters	53-57 ug/l	Activated Studge	Full	NR NR	•	i nr		NcCarty and Reinhard, 1980
Toluene	99.10	Dyestuff Manufact Waste	0.8 mg/l	Activated Studge	Full	NR NR	931 mg/l		NR I	Feiler, 1979
Toluene	99.70	Dyestuff Manufact Waste	3.6-4 mg/l				216 g/cu m	NR NR	NR	Keinath, 1984
Toluene	83.10	Dyestuff Manufact Waste	0.16 mg/l	Activated Sludge	Full	NR	850 g/cu m	NR NR	NR I	Keineth, 1984
Toluene	88.10	Dyestuff Manufact Waste			Full	NR	51 g/cum	NR NR	NR I	Keinath, 1984
Toluene	96.20	Dyestuff Manufact Waste	0.16 mg/l	Activated Studge	Full	NR	51 g/ cu m	NR	NR [Keinath, 1984
Toluene	1 51-100	Ind. Wastewater	7.8 mg/l	Activated Sludge	Full	NR	213 g/cu m	NR NR	NR	Keinath, 1984
Toluene	99.90		18-23 ug/l	Activated Sludge	Full	NR	931 mg/l	NR NR	NR	Feiler, 1979
Toluene		Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	MR	140 kg/day	30 min	?	SCS Engineering, 1979
Toluene	>97.4	Domestic Wastewater	14-110 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/L	?	NR I	Cormack and Hsu, 1983
	24.00	Dyestuff Manufact Waste	7.4 mg/l	Activated Sludge	Full	NR	213 g/cu m	NR NR	NR I	Keinath, 1984
Toluene Toluene	99.00	Dyestuff Manufact Waste	0.78 mg/l	Activated Sludge	Full	NR	216 g/cu m	NR NR	NR I	Keinath, 1984
Toluene	>90	Petroleum refinery wastes	l	Activated sludge/AC	Full	NR	38 mg/l) NR	NR	Snider and Manning, 1982

TABLE A-1 (continued)

Chemical	Percent Removal	Waste Stream	Initial Chem Conc	Treatment	Scale	Temp C	Susp Solids Conc	Hydraulic Res. Time	Acclimation	Reference
Toluene	>99	Raw Wastewater	255 ug/l	Activated Sludge	Pilot	NR	2900 mg/l	7.5 hr	NR	Petrasek et al.,1983b
Toluene	97.10		5 ug/l	Activated sludge	Pilot	NR	NR	SRT≈5 days	NR	Bishop, 1982
Toluene	98.00	Coke Plant Effluent	607 ug/l	Activated Sludge	Pilot	NR	45 mg/t	NR	NR	Osantowski and Hendriks, no date
Toxaphene	98.0	Municipal Sewage	150 ug/l	Plug Flow A.S.	Pilot	NR	430 mg/l	7 days	NR	Petrasek et al, 1983
Trichlorethylene	15.0			Activated Sludge	Pilot	NR	NR	8 hrs	NR	Kincannon et al, no date
Trichlorobenzene (1,2,4-)	97.80	Trickling Filter Effl	NR	Secondary Treatment	Full	NR	NR	NR	None	McCarty and Reinhard, 1980
Trichlorobenzene (1,2,4-)	99.90	Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	NR	NR	30 min	7	SCS Engineering, 1979
Trichlorobenzene (1,2,4-)	84.30	Dyestuff Manufact Waste	0.23 ug/l	Activated Sludge	Full	NR	213 g/cu m	NR NR	NR	Keinath, 1984
Trichlorobenzene (1,2,4-)	i >89.00 i	Domestic/Ind. Wastewater	NR	Secondary Treatment	Full	NR	NR	j nr	None	McCarty and Reinhard, 1980
Trichlorobenzene (1,2,4-)	j 99.90 j	Paper/Petrochemical Wastes	28 ug/l	Activated Sludge	Full	NR	NR	NR NR	1 ?	SCS Engineering, 1979
Trichloroethane	i 23.0 i	Pulp waste	NR	Two stage bio.	Full	NR I	NR	12.0 hr	NR I	Leuenberger et al. 1985.
Trichloroethane (1,1,1-)	17.0	Pulp waste	NR	Two stage bio.	Full	i NR i	NR	12.0 hr	i NR İ	Leuenberger et al. 1985.
Trichloroethane (1,1,1-)	59-100	Industrial Wastewaters	17-20 ug/l	Activated Sludge	j Full	NR I	931 mg/l	NR NR	i nr i	Feiler, 1979
Trichloroethane (1.1.1-)	i 99.40 i	NR	50-200 ug/l	Activated Sludge	Pilot	i NR i	NR	i NR	i nr i	Bishop, 1982
Trichloroethane (1,1,1-)	>96.30	Domestic Wastewater	27 ug/l	Bio/Act Carbon	Pilot	NR I	16,300 mg/l	1 ?	i NR I	Cormack and Hsu, 1983
Trichloroethane (1,1,1-)	98.50	Trickling Filter Effl	NR	Secondary Treatment	Full	NR	NR	NR NR	None	McCarty and Reinhard, 1980
Trichloroethane (1,1,1-)	95.00	Domestic/Ind. Wastewater	NR	Secondary Treatment	Full	NR I	NR	i NR	i None i	McCarty and Reinhard, 1980
Trichloroethane (1.1.1-)	>99	Raw Wastewater	132 ug/l	Aeration Basin	Pilot	NR I	2900 mg/l	7.5 hr	i NR İ	Petrasek et al.,1983b
Trichloroethane (1,1,2-)	80.00	Raw Wastewater	133 ug/l	Aeration Basin	Pilot	NR I	2900 mg/t	7.5 hr	I NR I	Petrasek et al., 1983b
Trichloroethane (1,1,2-)	65.60	NR	50-200 ug/l	Activated Sludge	Pilot	NR	NR	NR	I NR I	Bishop, 1982
Trichloroethane (1,1,2-)	99.90	Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	NR	NR	30 min	7	SCS Engineering, 1979
Trichloroethane (1,1,2-)	100.00	Industrial Wastewaters	49-50 ug/l	Activated Sludge	Full	NR	931 mg/l	NR	I NR I	Feiler, 1979
Trichloroethylene	97.80	Trickling Filter Effl	NR NR	Secondary Treatment	Full	NR	NR.	NR	None	McCarty and Reinhard, 1980
Trichloroethylene	23.0	Acid waste	NR	Activated sludge	Pilot	NR I	NR	8.0 hr	NR I	Kincannon et al., no date
Trichloroethylene	65-100	Industrial Wastewaters	24-29 ug/l	Activated Sludge	Full	NR I	931 mg/l	NR	NR I	Feiler, 1979
Trichloroethylene	>95.7	Domestic Wastewater	23 ug/l	Bio/Act Carbon	Pilot	NR	16,300 mg/l	2	NR I	Cormack and Hsu, 1983
Trichloroethylene	97.00	NR	50-200 ug/l	Activated Sludge	Pilot	NR I	NR	NR	NR I	Bishop, 1982
Trichloroethylene	>99	Raw Wastewater	107 ug/l	Aeration Basin	Pilot	NR I	2900 mg/l	7.5 hr	NR I	Petrasek et al.,1983b
Trichloroethylene (2)	99.90	Ind/domestic wastewater	2.2 mg/l	Deep Shaft-Biological	Pilot	NR I	NR NR	30 min	7	SCS Engineering, 1979
Trichlorophenol (2,4,6-)	28.0	Pulp waste	NR	Two stage bio.	Full	NR	NR NR	12.0 hr	NR I	Leuenberger et al. 1985.
Trimethyl Benzene (1.2.4)	>90	Petroleum refinery wastes	1415	Activated sludge/AC	Full	NR I	38 mg/l	NR	NR I	Snider and Manning, 1982
Xylene (p and m)	>90	Petroleum refinery wastes		Activated studge/AC	Full	NR NR	38 mg/l	. NR	HR I	Snider and Manning, 1982
Xylene,m	41.00	Domestic/Ind. Wastewater	NR	Secondary Treatment	Full	NR	NR	NR NR	None	McCarty and Reinhard, 1980
Xylene,m	33.0	DOIRESTICY TIME WESTERBEET	- mx	Activated Studge	Pilot	NR	NR	8 hrs	NR I	Kincannon et al, no date
Xylene.m	52.0	Acid waste	NR	Activated Studge	Pilot	NR NR	NR	1 8.0 hr	NR I	Kincannon et al., no date
Xviene.o	29.00	neid waste	NR	Activated Studge	Pilot	NR I	NR NR	8 hrs	NR NR	Kincannon et al., no date
Xylene,o	9.00	Acid waste	NR	Activated Studge	Pilot	NR I	NR NR	8,0 hr	NR I	Kincannon et al., no date
•	1 >90	Petroleum refinery wastes	, av	Activated studge/AC	Full	NR I	38 mg/l	NR	NR I	Snider and Manning, 1982
Xylene,o		•	NR		Full	I NR	j ∋omg/t INR	NR	1	McCarty and Reinhard, 1980
Xylene,p		Domestic/Ind. Wastewater	ak	Secondary Treatment	1 rucc	, RK	, nk	į nk	None	McCarty and Keinhard, 1900

⁽¹⁾ Name reported in Versar report as bis (2-ethylhexyl) phthalate

⁽²⁾ Name reported in Versar report as trichloroethylene

⁽³⁾ Name reported in Versar report as carbon tetrachloride

⁽⁴⁾ Name reported in Versar report as dichloropropene (trans 1,3)

⁽⁵⁾ Name reported in Versar report as bromodichloromethane

⁽⁶⁾ Name reported in Versar report as methylene chloride

^aExtracted from Estimation of Removal of Organic Chemicals During Wastewater Treatment, Draft Final Report, Versar, Inc. Prepared for US EPA, OTS, Contract No. 68-02-3968.

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The data for Table A-2 were extracted from "Report to Congress on the Discharge of Hazardous Waste to Publicly Owned Treatment Works", U.S. Environmental Protection Agency, EPA/530-SW-86-004, 1986. The following notes apply to this table:

- The data from this table apply only to secondary biological wastewater treatment plants receiving low concentrations (≅ 500 ppb) of the compounds listed. A number of design and operational factors will affect the fate of these compounds in any given treatment plant. These numbers are useful only as rough approximations of pollutant fate.
- All percentages are based on influent loading. The original reference provided removals for volatilization and sludge partitioning as a percentage of overall removal. This data was translated to removals based on influent loading by assuming that all material not volatilized, transferred to sludge, or passed through untreated was biodegraded.
- o (Percent volatilized to air) + (percent partitioned to sludge) +
 (percent biodegraded) + (100 overall percent removal) = 100.
- Percent biodegraded was determined by difference in the preceding equation.
- The percentage which is discharged to receiving waters equals 100 minus the "overall percent removal" (percent discharged to receiving wastes = 100 overall percent removal).
- Percent volatilized to air) + (percent partitioned to sludge) +
 (percent biodegrded) + (percent discharged to receiving waters) =
 100
- "Acclimated" represents those processes which receive a relatively steady amount of the pollutant in question, such that biodegradtion rates stabilize. "Unacclimated, Median and Low" refer to processes which receive unsteady or "slug" loadings of the pollutant in question.

TABLE A-2. FATE OF HAZARDOUS AND/OR TOXIC POLLUTANTS AT LOW CONCENTRATIONS IN SECONDARY, BIOLOGICAL WASTEWATER TREATMENT PLANTS

ſ		OVERALI		T	PERCEN		·	PERCENT	-		T	
		PERCEN			OLATILIZ		·	ARTITION	***********		PERCEN	L
		REMOVA		<u>v</u>	TO AIR	1		OSLUDG	•		DEGRAD	-
		DEIVIOVA		 	IOAIN	 		OSLUDG		DIV	DUEGRAL	
POLLUTANT	ACCUMATED	LINIACCI	INANTED	ACCL MATER	LINIACCI	MAATED	ACCLIMATED	LINIACCI	HAATED	ACCLIMATED	LINIACCI	MAATED
POLLUTANT	ACCLINATED			ACCLIMATED	 	· · · · · · · · · · · · · · · · · · ·	ACCLIMATED			ACCLIMATED	1	
		MEDIAN	 		MEDIAN		 	MEDIAN			MEDIAN	
	%	%	%	%	%	%	%	%	%	%	%	%
0.4.0			50				7			-		
2,4-D	90	60		0	0	0	 	5	4	83	55	46
ACENAPHTHYLENE	95	90	90	19	54	54	9	8	8	67	28	28
ACETALDEHYDE	95	95	95	0	5	5	10	10	10	85	81	81
ACETONE	95	50	30	0	3	2	10	5	3	85	43	26
ACROLEIN	95	95	95	0	5	5	10	10	10	85	81	81
ACRYLAMIDE	90	62	50	0	0	0	9	6	5	81	56	45
ACRYLIC ACID	90	85	80	0	0	0	9	9	8	81	77	72
ACRYLONITRILE	90	75	70	0	4	4	9	8	7	81	64	60
ALDRIN	90	90	90	0	0	0	33	33	33	57	57	57
ANILINE	95	85	80	0	0	0	10	9	8	86	77	72
ANTHRACENE	95	90	90	0	0	0	52	50	50	43	41	41
ANTIMONY	60	60	60	0	0	0	60	60	60	0	0	0
ARSENIC	50	50	50	0	0	0	50	50	50	0	0	0
BARIUM	90	90	90	0	0	0	90	90	90	0	0	0
BENZAL CHLORIDE	90	55	50	0	17	15	7	4	4	83	34	31
BENZENE	95	90	90	24	72	72	2	2	2	69	16	16
BENZOTRICHLORIDE	90	45	40	18	14	12	7	4	3	65	28	25
BENZYL CHLORIDE	90	90	90	23	45	45	7	7	7	60	38	38
BIS-2-CHLOROETHYL ETHER	90	50	30	0	3	2	9	5	3	81.	43	26
BIS-2-ETHYLHEXYL PHTHALATE	90	90	90	0	0	0	66	66	66	24	24	24
BROMOMETHANE	95	95	95	86	90	90	0	0	0	10	5	5
BUTYL BENZYL PHTHALATE	95	90	90	0	0	0	43	41	41	52	50	50
CADMIUM	27	27	27	0	0	0	27	27	27	0	0	0
CAPTAN	90	50	30	0	0	0	7	4	2	83	46	28
CARBON DISULFIDE	95	85	80	76	77	72	1	1	1	18	8	7
CARBON TETRACHLORIDE	90	85	80	72	77	72	12	9	8	6	0	0
CHLORDANE	90	90	90	9	9	9	33	33	33	48	48	48
CHLOROBENZENE	90	90	90	27	45	45	14	14	14	50	32	32
CHLOROBENZILATE	90	60	50	9	6	5	7	5	4	74	49	41
CHLOROETHANE	95	90	90	76	81	81	1	1	1	18	8	8
CHLOROFORM	90	80	80	63	72	72	2	2	2	25	6	6
CHLOROMETHANE	95	90	90	86	86	86	1	1	1	9	4	4

TABLE A-2 (continued)

	<u> </u>	OVERAL	. 1		PERCEN	r I		PERCENT	•	T		
		PERCEN			OLATILIZE		P/	RTITION	ED		PERCEN	Т
		REMOVA			TO AIR		 	OSLUDG		BK	DEGRAD	ED
POLLUTANT	ACCLIMATED	UNACCI	IMATED	ACCLIMATED	UNACCL	MATED	ACCLIMATED	UNACCI	IMATED	ACCLIMATED	UNACCI	IMATED
T OELONA!	7.0027.12.2	MEDIAN	LOW		MEDIAN			MEDIAN			MEDIAN	LOW
	%	%	%	%	%	%	%	%	%	%	%	%
	,9											
2-CHLOROPHENOL	95	65	60	0	0	0	8	5	5	87	60	55
CHROMIUM	70	70	70	0	0	0	70	70	70	0	0	0
CRESOLS	95	50	40	0	0	0	8	4	3	87	46	37
CUMENE	95	95	95	38	57	57	4	4	4	53	34	34
CYANIDE	60	60	60	0	3	3	57	57	57	3	0	0
CYCLOHEXANE	95	95	95	10	86	86	4	4	4	82	6	6
DI-N-BUTYL PHTHALATE	90	90	90	0	0	0	20	20	20	70	70	70
DI-N-OCTYL PHTHALATE	90	90	90	0	0 -	0	7	7	7	83	83	83
DIBROMOMETHANE	85	80	80	43	64	64	13	12	12	30	4	4
1,2-DICHLOROBENZENE	90	87	85	45	78	77	32	9	9	14	0	0
1,3-DICHLOROBENZENE	90	87	85	45	78	77	3	3	3	42	6	6
1,4-DICHLOROBENZENE	90	87	85	45	78	77	23	9	9	23	0	0
1,2-DICHLOROETHANE	90	50	30	45	45	27	5	3	2	41	. 3	2
1,1-DICHLOROETHYLENE	95	90	90	76	81	81	0	0	0	19	9	9
2,4-DICHLOROPHENOL	95	55	50	0	0	0	8	4	4	87	51	46
1,2-DICHLOROPROPANE	90	70	70	45	63	63	0	0	0	45	7	7
DICHLORVOS	- 90	50	30	0	0	0	9	5	3	81	45	27
DICOFOL	90	90	90	45	45	45	8	8	8	37	37	37
DIETHYL PHTHALATE	90	75	70	0	0	0	1	1	1	89	74	69
3,3-DIMETHOXY BENZIDINE	80	30	20	0	0	0	8	3	2	72	27	18
2,4-DIMETHYL PHENOL	95	85	80	0	0	0	8	7	6	87	78	74
DIMETHYL PHTHALATE	95	65	60	0	0	0	0	0	0	95	65	60
2,4-DINITROPHENOL	90	75	70	0	0	0	9	8	7	81	68	63
1,4-DIOXANE	90	50	40	0	0	0	9	5	4	81	45	36
EPICHLOROHYDRIN	87	59	25	0	0	0	9	6	3	78	53	23
ETHYL BENZENE	95	90	90	24	72	72	6	5	5	66	13	13
ETHYLENE OXIDE	90	50	40	0	3	2	9	5	4	81	43	34
ETHYLENE THIOUREA	85	67	60	0	0	0	9	7	6	77	60	54
FORMALDEHYDE	85	85	80	0	4	4	9	9	88	76	72	68
HEXACHLORO-1,3-BUTADIENE	95	90	90	0	5	5	9	8	8	86	77	77
HEXACHLOROETHANE	95	90	90	0	5	5	9	8	8	86	77	77
HYDRAZINE	95	85	80	0	4	4	10	9	8	85	72	68

TABLE A-2 (continued)

		OVERALI		T	PERCEN	f I		PERCENT			ſ.	[
		PERCEN		V	OLATILIZI	D	P/	ARTITION	ED		PERCEN	T
		REMOVA	L		TO AIR		٦	OSLUDG	E	BK	DEGRAD	DED
POLLUTANT	ACCLIMATED	UNACCL	IMATED	ACCLIMATED	UNACCL	IMATED	ACCLIMATED	UNACCI	IMATED	ACCLIMATED	UNACCL	IMATED
		MEDIAN	LOW		MEDIAN	LOW		MEDIAN	LOW		MEDIAN	LOW
	%	%	%	%	%	%	%	% -	%	%	%	%
								,		-		
LEAD	70	70	70	0	0	0	70	70	70	0	0	0
MALEIC HYDRAZIDE	90	75	7.0	- 0	0 -	0	9	8	7	81	68	63
MERCURY	50	50	50	0	3	3	48	48	48	2	0	0 :
METHANOL	100	95	95	1	5	5	10	10	10	90	81	81
METHOXYCHLOR	90	90	90	54	54	54	8	8	8	28	28	28
METHYL ETHYL KETONE	95	50	30	0	3	2	10	5	3	85	43	26
METHYL ISOBUTYL KETONE	90	50	30	- 0	0	0	- 9	5	3	81	45 ·	27
METHYLENE CHLORIDE	95	87	85	38	52	51	13	12	12	44	23	22
N-BUTYL ALCOHOL	95	90	90	0	0	0	10	9	9	86	81	81
N-NITROSODIMETHYL AMINE	90	75	70	- 0	0	0	9	8	7	. 81	68	63
NAPHTHALENE	95	75	70	0	4	4	27	21	20	68	50	47
NICKEL	35	35	35	. 0	0	0	35	35	35	. 0	0	0
NITROBENZENE	90	25	20	0	0	0	9	3	2	81	23	18
2-NITROPROPANE	95	95	95	86	90	90	1	1	1	9	4	4
P-BENZOQUINONE	95	50	. 40	0	0	0	8	4	3	87	46	37
PARATHION	0	55	40	0	0	0	0	. 4	3	0	51	37
PCB	92	92	92	9	9	9	22	22	22	61	61	61
PENTACHLOROPHENOL	95	25	20	0	0	0	17	5	4	78	21	16
PHENOL	95	85	80	0	0	0	14	13	12	81	72	68
PHENYLENE DIAMINE	90	75	70	0	0	0	9	8	. 7	81 ·	68	63
PHOSGENE	100	100	100	1	5	5 :	10	10	10	90	85	85
PHTHALIC ANHYDRIDE	90	90	90	0	0	0	9	- 9	9	81	. 81	81
PYRIDINE	15	15	10	0	1	1	2	2	1	13	13	9
SELENIUM	50	50	50	0	0	0	50	50	50	0	0	0
SILVER	90	90	90	0	0	0	90	90	90	0	0	0
STYRENE	90	90	90	23	- 72	72	14	14	14	54	5	5
1,1,2,2-TETRACHLOROETHANE	90	∞ 2 5	20	36	15	12	4	1	1	50	9	7
TETRACHLOROETHYLENE	90	85	80	45	68	64	3	3	2	42	14	14
THIOUREA	90	75	70	0	0	0	9	8	. 7	81	68	63
TOLUENE	90	90	90	23	72	72	25	18	18	42 -	0	0
TOLUENE DIAMINE	90	75	70	0	0	0	9	8	7	81	68	63
TOXAPHENE	95	90	90	57	72	72	4	4	4	34	-14	14

TABLE A-2 (continued)

		OVERALI		T T	PERCEN	Т		PERCENT				
		PERCEN		V	OLATILIZI	D	P/	ARTITION	ED		PERCEN	Т
		REMOVA			TO AIR		1	OSLUDG	Ε	BK	DEGRAE	DED
POLLUTANT	ACCLIMATED	UNACCI	IMATED	ACCLIMATED	UNACCL	MATED	ACCLIMATED	UNACCL	.IMATED	ACCLIMATED	UNACCL	IMATED
		MEDIAN	LOW		MEDIAN	LOW		MEDIAN	LOW		MEDIAN	LOW
	%	%	%	%	%	%	%	%	%	%	%	%
TRANS-1,2-DICHLOROETHYLENE	90	80	80	63	72	72	27	8	8	0	0	0
TRIBROMOMETHANE	65	35	30	36	21	18	5	3	2	24	11	10
1,2,4-TRICHLOROBENZENE	85	85	85	43	51	51	8	8	8	35	26	26
1,1,1-TRICHLOROETHANE	95	90	85	76	81	77	. 1	1	1	18	8	8
1,1,2-TRICHLOROETHANE	80	25	20	40	20	16	0	0	0	40	5	4
TRICHLOROETHYLENE	95	87	85	67	70	68	6	5	5	23	12	12
2,4,6-TRICHLOROPHENOL	95	55_	50	0	0	0	8	4	4	87	51	46
1,1,2-TC 1,2,2-TF ETHANE	90	85	80	63	68	64	4	3	3	23	14	13
TRIFLURALIN	90	90	90	0	0	0	33	33	33	57	57	57
VINYL CHLORIDE	95	95	95	86	90	90	2	2	2	8	3	3
XYLENES	95	87	85	24	70	68	14	13	13	57	4	4

APPENDIX B

CHEMICAL AND PHYSICAL DATA FOR THE LISTED CHEMICALS

APPENDIX B

The chemical/physical property data in Appendix B was obtained primarily from chemical databases previously compiled by EPA, from computer searches, and from various handbooks. Data was compiled only for those chemicals listed individually by CAS number and not for chemicals reportable by chemical category name. Each property has been referenced, but these references do not appear in the Appendix due to space considerations. Interested persons may obtain a copy of this Appendix with the appropriate reference numbers and a listing of the references from:

Kathleen Franklin USEPA TS-779 401 M St. SW Washington, DC 20460

Data sources used to compile this database and to obtain induvidual references are listed below.

Hansen, S.A., Czarnecki, R.J., Osantowski, R.A. Sept 1987. Radian Corporation. Contents of the USEPA (WERL) Treatability Database. Cincinnati, Ohio: US Environmental Protection Agency, Office of Research and Development, Water Engineering Research Laboratory. Contract No. 68-03-3371.

USEPA. Feb 1985. US Environmental Protection Agency. Physical/Chemical Properties and Categorization of RCRA Wastes According to Volatility. Research Triangle Park, NC: USEPA, Office of Air Quality Planning and Standards. EPA 450/3-85-007.

USEPA. Dec 1985. US Environmental Protection Agency. Chemical Emergency Preparedness Program- Interim Guidance: Chemical Profiles. Washington, DC: USEPA, Office of Toxic Substances, Economics and Technology Division.

USEPA. Oct 1986. US Environmental Protection Agency. Superfund Public Health Evaluation Manual. Washington, DC: USEPA, Office of Emergency and Remedial Response. EPA 540/1-86-060. (OSWER Directive 9285.4-1)

USEPA. 1987. US Environmental Protection Agency. Computer printout of referenced chemical/physical properties of a dataset of chemicals extracted from the Graphical Exposure Modeling System (GEMS). Washington, DC: USEPA, Office of Toxic Substances, Economics and Technology Division.

Verschueren, K. 1977. Handbook of Environmental Data on Organic Chemicals. New York, NY: Van Nostrand Reinhold Company.

Weast, R.C. (ed.) 1981. CRC Handbook of Chemistry and Physics. 62nd edition. Boca Raton, FL: CRC Press, Inc.

Windholz, M. (ed.) 1983. The Merck Index. Tenth edition. Rahway, NJ: Merck and Co., Inc.

Yalkowsky, S. 1987. Arizona Database of Aqueous Solubility. 2nd edition. Tucson, AZ: University of Arizona, College of Pharmacy.

Chemical specific data was also obtained through computer searches of the following databases:

Merck Index
ISHOW
Hazardous Substances Data Base (HSDB) / Toxnet
Heilbron / DIALOG
OHMTADS / Chemical Information System (CIS)
Chemical Hazard Response Information System (CHRIS) / CIS
CHEMFATE / Syracuse Research Corporation

Discrepancies between values obtained from different sources were reconciled where possible by consulting additional data sources. However, the values in this Appendix have not been subject to rigorous review and the reader should exercise good judgement concerning their use.

<u>AMB STATE</u>- physical state of the pure chemical at ambient conditions: room temperature and atmospheric pressure. For chemicals with melting or boiling points close to room temperature (20-30 C), two states are listed with the relevant melting or boiling temperature. For chemicals reportable only as solutions, the ambient state is listed for the liquid solution with the pure chemical state noted. References for ambient state were not compiled.

 $\frac{\text{MOL WT}}{\text{lb/lb-mole.}}$ molecular weight of the pure chemical in g/g-mole or $\frac{\text{molecular}}{\text{lb/lb-mole.}}$ References for molecular weight were not compliled.

SPEC GRAV- Specific gravity is the ratio of the density of the pure chemical in its ambient state (except as noted) at the listed temperature to the density of water at a temperature from 4-25 C. If no temperature is listed, then the chemical density is assumed to be measured at ambient temperature (20-30 C). To obtain the density of the chemical, multiply the specific gravity listed times the density of water (8.33 lb/gallon or 62.4 lb/ft³).

For chemicals which are gases at ambient conditions, the vapor density is listed instead of specific gravity. Vapor density values are noted with an *. Vapor density is the density of the gas as compared to air (Air = 1). To obtain the density of the gas at a specified temperature and pressure, multiply the vapor density value times the density of air at the same temperature and pressure. Density of air at 32 F and 760 mm Hg = 0.0808 lb/ft3

VAPOR PRESSURE- vapor pressure of the pure chemical at the listed temperature. Some of the vapor pressure values in this Appendix, especially those less than 1 mm Hg, are estimated rather than measured values. Since vapor pressure is a function of temperature, the vapor pressures listed should only be used if the chemical is handled at the listed temperature. To estimate the vapor pressure of a chemical at a temperature different than listed, the Claussius-Clapeyron equation can be used.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_V}{R} \frac{(T_2 - T_1)}{T_2}$$

where:

 P_2 = unknown vapor pressure in mm Hg at temperature T_2 P_1 = known vapor pressure in mm Hg at temperature T_1 T_1 , T_2 = temperature in K = C + 273 ΔH_V = heat of vaporization of the chemical (obtained from literature or handbooks) in calorie/g-mole

grams x molecular weight = g-mole
lbs. x molecular weight x 454 = g-mole

 $R = \frac{1.987 \text{ calorie}}{K \text{ g-mole}}$

WATER SOLUBILITY- water solublity is the maximum concentration in milligrams (MG) of chemical that will dissolve in one liter (L) of pure water at neutral pH and a specified temperature. If no temperature is given, assume ambient temperature (20-30 C). Water solubility is also a function of temperature and for most chemicals increases with the temperature of water. Acid or basic water conditions will also affect the solubility of many chemicals. Some chemicals may react or hydrolyze in water, causing them to decompose. For some chemicals, the only information on water solubility was qualitative. Miscible means that the chemical is completely soluble in water and that a minimum value of 1 x 10 6 MG/L can be assumed as the water solubility if a numerical value is needed.

 $1 \text{ MG/L} = 1 \text{ PPM} = \emptyset.0001$ %

TABLE B-1 Chemical/Physical Properties

NAME	CAS NO.	AMBSTATE	MOL WT	SPECGRAV	TEMP.(C)	VAPOR PRESSURE (mm Hg)	TEMP.(C)	WATER SOLUBILITY (mg/l)	TEMP.(C
Formaldehyde (monomeric gas)	50 - 00 - 0	GAS	30.03	1.067*		664	 -22.3	50 E+4	37
Formaldehyde (37% aqueous solution)	50 - 00 - 0	LIQUID	52	1.113	18	1.025	20	37 E+4	37
2,4-Dinitrophenol	51 - 28 - 5	SOLID	184.11	1.683	24	1.49 E-5	20-30	15600	20
Nitrogen Mustard	51 - 75 - 2	LIQUID	156.07	1.118	25	decomp. upon stand		very soluble	-0
Urethane (ethyl carbamate)	51 - 79 - 6	SOLID	89.09	11.1	i	0.315	25	2.0 E+6	25
Trichlorofon	52 - 68 - 6	SOLID	257.45	1.73	20	7.8 E-6	20	154,000	25
2-Acetylaminofluorene	53 - 96 - 3	SOLID	223	i	İ	2.1 E+7	25	6.5	20-30
N-Nitrosodiethylamine	55 - 18 - 5	LIQUID	102.14	0.942	120	1.73	25	408,320	25
Benzamide	55 - 21 - 0	SOLID	121.13	1.341	14	i	i	14000	20
Nitroglycerine	55 - 63 - 0	•	227.09	1.6	i	2.5 E-4	20	1800	20
Carbon tetrachloride	56 - 23 - 5	LIQUID	153.84	1.59	20	1113	25	770	20
Parathion	56 - 38 - 2	LIQUID	291.27	1.26	25	9.7 E-6	20	111.9	120
1,1-Dimethylhydrazine	57 - 14 - 7			0.7914	22	!	25	1.193 E+6	120
Propiolactone, beta-	57 - 57 - 8	LIQUID	72.1	1.14	20			11173 2.0	
Chlordane	57 - 74 - 9	LIQUID	409.80	1.60	25	11 E-5	25	11.9	25
Lindane	58 - 89 - 9	SOLID	290.85	1.85	20		•	6.8	25
N-Nitrosomorpholine	59 - 89 - 2	SOLID	116.11	i	i			MISCIBLE	-
4-Aminoazobenzene	60 - 09 - 3	SOLID	197.23	j	i			SLIGHTLY SOLUBLE	1
4-Dimethylaminoazobenzene	60 - 11 - 7	SOLID	225.30		i	3.3 E-7	20-30	160	20
Methyl hydrazine	60 - 34 - 4	LIQUID		0.874	25			MISCIBLE	120
Acetamide	60 - 35 - 5	SOLID	59.07	1.159	20	•		410,000	25
Aniline	62 - 53 - 3		93.12	1.022	20			37,000	20
Thioacetamide	62 - 55 - 5		75.13	j				163,000	25
Thiourea	62 - 56 - 6	SOLID	76.12	1.405	20			1.72 E+6	20-30
Dichloryos	62 - 73 - 7	LIQUID	220.98		5	0.01	30	10,000	1
N-Nitrosodimethylamine	62 - 75 - 9	LIQUID			18	·	20-30	11 E+6	20-30
Carbaryl	63 - 25 - 2	SOLID	201.22	1.232	20	<u> </u>		40	20
Diethyl sulfate	64 - 67 - 5		154.19		23		47	PRAC.INSOL.DECOMP.	120
Methanol	67 - 56 - 1	LIQUID	32.04	0.796	15		21.2	MISCIBLE	<u> </u>
Isopropyl alcohol (mfgstrong acid processes)	67 - 63 - 0		,		•	:		MISCIBLE	! !
Acetone	67 - 64 - 1					!	20	,	 20-30
Chloroform	67 - 66 - 3		119.39		20	•		7,800	20-30
Hexachloroethane	67 - 72 - 1		236.74		,	ļ ··· ·			20
Triaziquone	68 - 76 - 8	, ,	231.25	_,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		0.50		SPAR. SOLUBLE C.W.	120
n-butyl alcohol				0.810	20	6.5		79,000	20
Benzene	:				20	!			20
1,1,1-Trichloroethane (Methyl chloroform)	71 - 55 - 6								25
Methoxychlor	72 - 43 - 5				25				25 25
Bromoethane (Methyl bromide)	74 - 83 - 9	,		3.27*		1420	•		
Ethylene		, ,		0.978*		•	•	·	20 20

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TABLE B-1 Chemical/Physical Properties

HAME	CAS NO.	AMBSTATE	MOL WT	SPECGRAV	TEMP.(C)	VAPOR PRESSURE (mm Hg)	TEMP.(C)	WATER SOLUBILITY (mg/l)	TEMP.(
Chloromethane (Methyl chloride)	74 - 87 - 3	GAS	51	1.8*		4310	25	4000	25
Hethyl iodide	74 - 88 - 4	LIQUID	141.95	2.279			25		20
Hydrogen cyanide (boiling point = 25.6 C)	74 - 90 - 8	GAS/LIQ	27.03	0.699LIQ		730	25		25
Methylene bromide			173.86	2.495	20	45.8	25	11,700	15
Chloroethane (Ethyl chloride)			64.52	2.23*		1180	20	5,740	20
Vinyl chloride	75 - 01 - 4	GAS		2.15*		2660	25	9,150	20.5
Acetonitrile	75 - 05 - 8	LIQUID	41.05	0.79	20	100	25	2.2 E+6	25
Acetaldehyde	75 - 07 - 0		44.1	1.52*		740	20	INFINITELY SOLUBLE	İ
Dichloromethane (Methylene chloride)	75 - 09 - 2		84.94	1.3255	20	438.0	25	20,000	20
Carbon disulfide	75 - 15 - 0			1 '	20	360	25	2,940	20
Ethylene oxide (boiling point = 11 C)	75 - 21 - 8		44.06	1.582*		1095	20	2.1 E+6	25
Bromoform (Tribromoethane)	• • • • • • • • • • • • • • • • • • • •				20	5.6	25	1,250	25
Dichlorobromomethane	•			1.971	25	,	İ	İ	f
Vinylidene chloride (boiling point = 31.9 C)	75 - 35 - 4		96.94	1.218	20	500	20	2,250	25
Phosgene (boiling point = 8.1 C)	75 - 44 - 5		98.92	3.42*		1215	20	SLIGHTLY SOLUBLE	İ
Propyleneimine				0.80	25	112	20	3.1 E+6	25
Propylene oxide	75 - 56 - 9		58.08	0.859	0	445	20	405,000	20
tert-Butyl alcohol (melting point = 25.6 C)	75 - 65 - 0	•	74.1	0.788	20 (solid)	42	25	SOLUBLE	į .
Freon 113	76 - 13 - 1		187.38	1.56	25	270	20-30		20-30
Heptachlor	76 - 44 - 8	SOLID	373.35	1.58	9	3.0 E-4		0.18	25
Hexachlorocyclopentadiene	77 - 47 - 4	LIQUID	272.77	1.7019	25	8.0 E-2	25	6.4	25
Dimethyl sulfate	77 - 78 - 1	LIQUID	126.14	1.3283	20	0.5	20	28,000	18
Isobutyraldehyde	78 - 84 - 2	LIQUID	72.10	0.7938		170	20	110,000	1
1,2-Dichloropropane	78 - 87 - 5	LIQUID	113	1.16	20	50	25	2,700	20-30
sec-Butyl alcohol	78 - 92 - 2	LIQUID	74.12	0.808	20	10.0	21.7	200,000	20
Methyl ethyl ketone	78 - 93 - 3	LIQUID	72.1	0.805	20	77.5	20		20
1,1,2-Trichloroethane	79 - 00 - 5	LIQUID	133.42	1.44	20	24	25	4500	20
Trichloroethylene	79 - 01 - 6	LIQUID	131.4	1.46	20	75	25	1,100	20
Acrylamide	79 - 06 - 1			1.122	30	0.007	20	2.155 E+6	30
Acrylic acid (melting point 13 C)	79 - 10 - 7	SOL/LIQ	72	1.0511	20 (liq)	4	20-30	1 E+6	20-30
Chloroacetic acid	79 - 11 - 8	SOLID	94.50	1.58	20	6.5 E-2	25	VERY SOLUBLE	1
Peracetic acid	79 - 21 - 0	LIQUID	76.05	1.226	15			VERY SOLUBLE	l
1,1,2,2-Tetrachlorethane	79 - 34 - 5	LIQUID	168.86	1.6	20	4.2	25	2,857	25
Dimethyl carbamyl chloride (boiling point = 167 C)	79 - 44 - 7	LIQUID	108	1	1	2.49	25	1.44 E+7	20-30
2-Nitropropane	79 - 46 - 9	LIQUID		0.992	20	17.5	25	17	25
4,4'-Isopropylidenediphenol (Bisphenol A)	80 - 05 - 7	SOLID	228.28	1.195	ļ	0.20	170	3,400	83
Cumene-hydroperoxide	80 - 15 - 9	LIQUID	152	1.05	25	0.24	20	10,000	25
Methyl methacrylate	80 - 62 - 6	LIQUID		0.936	20	40.0	25.5	15,000	25
Saccharin	81 - 07 - 2	SOLID	183.18	0.828		2.69 E-3	25	448	25
C.I. Food Red 15	81 - 88 - 9	SOLID	479.0	1	1		1	15,000	22

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TABLE B-1 Chemical/Physical Properties

NAME	CAS NO.	AMBSTATE	MOL WT	SPECGRAV	TEMP.(C)	VAPOR PRESSURE (mm Hg)	TEMP.(C)	WATER SOLUBILITY (mg/l)	TEMP-(C
1-Amino-2-methylanthraquinone	82 - 28 - 0	SOLID	237.26					INSOLUBLE	
Quintozene (Pentachloronitrobenzene)	82 - 68 - 8	SOLID	295.34	1.718	25	2.38 E-3	25	0.032	25
Diethyl phthalate	84 - 66 - 2	LIQUID	222.2	1.120	25	8.1 E-3	25	900	20
Dibutyl phthalate	84 - 74 - 2				20	11.4 E-5	20	13	25
Phthalic anhydride	85 - 44 - 9		148.11	•	4	0.0002	20	6,200	26.7
Butyl benzyl phthalate	85 - 68 - 7	LIQUID	312.36		i	0.3	1100	• •	25
N-Nitrosodiphenylamine	86 - 30 - 6			1.23			1.00	SLIGHTLY SOLUBLE	رعا
2,6-Xylidine (2,6-Dimethyaniline)	87 - 62 - 7			•	20	أ 1	44	INSOLUBLE	ł
Hexachloro-1,3-butadiene	87 - 68 - 3	•	261		15.5	2	20-30	•	20-30
Pentachlorophenol (PCP)	i 87 - 86 - 5	•			22	0.0002	20	114	
2,4,6-trichlorophenol	88 - 06 - 2				75	0.12	20-30	!	20
2-Nitrophenol			139.11		20	0.19	25	1	20
Picric acid	:		229.11		-	11.0	1195		20
o-Anisidine				•	20	0.10	30		20
2-Phenylphenol					25	1.0	1100	SLIGHTLY INSOLUBLE	
Michler's ketone	:		268.35	1.213	رے	11.0	1100	PRAC. INSOLUBLE	ļ
Toluene 2,6-diisocyanate	· ·		174.2				ļ	PRAC. INSOLUBLE	ļ
Naphthalene			128.16	1 152		0.232	100	REACTS	ļ
Quinoline			129.15			19.1 E-3	25		25
beta Naphthylamine	•		143.18			9.1 E-3 0.0559	25		20
3,3'-Dichlorobenzidene	91 - 94 - 1		253.13	1.001			25		25
Biphenyl	92 - 52 - 4			0 0440		1.2 E-7	25		25
4-Aminobiphenyl	92 - 67 - 1		169.22		20 20	[]	70.6		25
Benzidine	•					6 E-5	20-30		20-30
4-Nitrobiphenyl	1					1°E-5	25	280	20
Benzoyl peroxide			199.2		20			INSOLUBLE	
Safrole			242.23		25		!	SPAR. SOLUBLE	
2,4-D [Acetic acid,(2,4-dichlorophenoxy)-]				1.1		0.0709	25		20-30
o-Xylene			221			1.59 E-4	25		20
p-Cresol (melting point = 31.1 C)		•		0.88		10			25
1,2-Dichlorobenzene						2.4 E-1	25		20
o-Toluidine	1					1.440	25		25
1,2,4-Trimethylbenzene						0.1	20	16,900	20
• •	:			0.876		2.030	25	57	20
2,4-Diaminotoluene			122.17	ļ		3.8 E-5	20-30	47,700	20-30
2,4,5-Trichlorophenol	•		197.46			0.0496	25		25
Styrene oxide	•			1.05		0.3			20
1,2-Dibromo-3-chloropropane (DBCP)						0.513		: · .	25
lethyl acrylate	96 - 33 - 3			0.958	20 j	70			20
thylene thiourea			102 j	İ	i			: '	25
C.I. Solvent Yellow 3	97 - 56 - 3	SOLID I	225.28 İ	i	i		i	PRAC. INSOLUBLE	

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TABLE B-1 Chemical/Physical Properties

IAHE	CAS NO.	AMBSTATE	HOL WT	SPECGRAV	TEMP.(C)	VAPOR PRESSURE (mm Hg)	TEMP.(C)	WATER SOLUBILITY (mg/l)	TEMP.(
Benzoic trichloride (Benzotrichloride)	98 - 07 - 7	LIQUID	195.48	1.3756	20	0.157	25	360	25
Cumene	98 - 82 - 8	LIQUID	120.19	0.8620	20	3.2	1	50	20
Benzal chloride	98 - 87 - 3	LIQUID	161.03	1.26	14	0.30		410	25
Benzovl chloride	98 - 88 - 4	LIQUID	140.57	1.22	15	0.4		DECOMPOSES	1
Nitrobenzene (melting point = 5.5 C)	98 - 95 - 3	SOL/LIQ	123.11	1.2037	20 (liq)	0.407	25	1,800	25
i-Nitro-o-anisidine	99 - 59 - 2	SOLID	168.16	1.2068			ł	SLIGHTLY SOLUBLE	
-Nitrophenol	100 - 02 - 7	SOLID	139.11		20	0.75	20	1,600	25
rerephthalic acid	100 - 21 - 0	SOLID	166.13				İ	19	25 ⁻
•	100 - 41 - 4	LIQUID	106.17	0.867	20	9.50	25	177	25
Ethylbenzene	100 - 42 - 5	LIQUID	104.14		i 25	5	20	300	25
Styrene Benzyl chloride	100 - 44 - 7	•	126.58	1.100	20	1	22	1,619	25
J-Nitrosopiperidine	100 - 75 - 4	LIQUID	114.15		18.5	0.244	25	284,318	25
-Nitrosopiperiaine ,4'-Methylenebis(2-chloroaniline) (MBOCA)	101 - 14 - 4	SOLID	267	1.44	Ì	6 E-6	25	15	25
4.4'-Methylene bis(N.N-dimethyl) benzenamine	101 - 61 - 1	SOLID	254.36		i	io.1	148.9	INSOLUBLE	
Methylene bis(phenylisocyanate) (MBI) (melt.pt. = 37C)		SOLID	250.26	1.19	50 (liq)	1 E-5	25	2,000 (REACTS)	20
	101 - 77 - 9	SOLID	198.26			İ	i	SLIGHTLY SOLUBLE	İ
4,4'-Methylene dianiline	101 - 80 - 4	SOLID	200.2	i	İ			INSOLUBLE	Ì
4,4'-Diaminodiphenyl ether	103 - 23 - 1	LIQUID	370	0.925	20	2.60	20	90	20
Bis(2-ethylhexyl) adipate	104 - 94 - 9	SOLID	123.15		57		İ	SPAR. SOLUBLE	Ì
o-Anisidine (melting point = 57.2 C) 2,4-Dimethylphenol (melting point = 25.4 C)	105 - 67 - 9	SOL/LIQ		1.036	20 (solid)	io.051	20	7,900	20
	106 - 42 - 3	LIQUID	106.17		20	10	27.3	198	20
p-Xylene	106 - 44 - 5	SOLID		1.0347	20	0.108	j 25	19,000	20
p-Cresol (melting point = 34.8 C) 1,4-Dichlorobenzene (melting point = 53.1 C)	106 - 46 - 7	SOLID	147.00	1.2475	20	0.680	25	69	20
	106 - 50 - 3	•	108.14		-	1.00	98.8	38,000	24
p-Phenylenediamine	106 - 51 - 4	SOLID		1.318	20	0.140	24.6	1,500	25
Quinone	106 - 88 - 7		72.1	0.83	i		İ	82,400	25
1,2-Butylene oxide	106 - 89 - 8	1	92.53	1.801	20	18.8	25	65,800	20
Epichlorohydrin	106 - 93 - 4	•	187.88	2.701	125	1117	25	4,300	25
1,2-Dibromoethane (Ethylene dibromide)	106 - 99 - 0		54.09	1.87*	i	1910	20	740	20
1,3-Butadiene	107 - 02 - 8	!	56.06	0.8389	i20	269.0	25	265,822	20
Acrolein	107 - 05 - 1	LIQUID	76.53	0.94	20	340	20	100	İ
Allyl chloride	107 - 06 - 2	1	199	1.25	20	61	20	8,300	20
1,2-Dichloroethane (Ethylene dichloride)	107 - 13 - 1	:	53.60	0.8004	25	100.0	22.8	74,000	20
Acrylonitrile	107 - 21 - 1	•	62.1	1.113	20	0.120	20	117,000	i
Ethylene glycol		LIQUID	180.52	1.0605	20	214	25	DECOMPOSES	İ
Chloromethyl methyl ether	107 - 30 - 2	!	86.09	0.932	20	83.0	20	20,000	20
Vinyl acetate	108 - 05 - 4		100.2	0.8017	20	7.1	25	19,000	20
Methyl isobutyl ketone	108 - 10 - 1		98.06	0.934	20	0.00005	20	163,000	25
Maleic anhydride	108 - 31 - 6	•	106.16	0.864	20	10	28.3	175	25
m-Xylene	108 - 38 - 3		108.13		20	0.153	25	23,500	20
m-Cresol	100 - 37 - 4	LEIMOID	1,00.12	11.030	120	101.50	1	1	•

TABLE B-1 Chemical/Physical Properties

NAME	CAS NO.	AMBSTATE	MOL WT	SPECGRAV	TEMP.(C)	VAPOR PRESSURE (mm Hg)	TEMP.(C)	WATER SOLUBILITY (mg/l)	TEMP.(C)
Bis(2-chloro-1-methylethyl) ether	•	LIQUID	171.07			0.85	20	1,700 ,	20-30
Melamine	108 - 78 - 1	SOLID	126.13	1.573	16	50	315.	2,700	20
Toluene	108 - 88 - 3	LIQUID	92.14	0.867	20	28.10	25	570	25
Chlorobenzene	108 - 90 - 7	LIQUID	112.56	1.1066	20	10.0	22.2	500	20
Phenol	108 - 95 - 2	SOLID	94.11	1.0722	20	0.20	20	82,000	20 .
2-Methoxyethanol (methyl cellosolve)	109 - 86 - 4	LIQUID	76.1	0.97	20	6.2	20	MISCIBLE	İ
2-Ethoxyethanol	110 - 80 - 5	LIQUID	90.1	0.93	20	5.5	25	MISCIBLE	i
Cyclohexane	110 - 82 - 7	LIQUID	84.16	0.779	20	100.0	25.5	49	20
Pyridine	110 - 86 - 1	LIQUID	79.1	0.982	j	20	25	3 E+8	25
Diethanolamine (melting point = 28 C)	111 - 42 - 2	SOL/LIQ	105.14	1.092	1 30	0.010	20	950,000	1-1
bis (2-chloroethyl) ether	111 - 44 - 4	LIQUID	143.02	1.22	20	0.7	20	10,200	25
Propoxur	114 - 26 - 1	SOLID	209.24	İ	İ	0.010	120	2,000	20
Propylene (Propene)	115 - 07 - 1	GAS	42.08	1.49*	İ	1.0	-131.9	410	20
Dicofol	115 - 32 - 2	SOLID	370.47	İ	İ	1		8 E-4	i
2-Aminoanthraquinone	117 - 79 - 3	SOLID	223.23	i	İ	SUBLIMES		INSOLUBLE	İ
Di(2-ethylhexyl)phthalate (DEHP)	117 - 81 - 7	LIQUID	390.62	0.99	20	0.10	20	1.3	20
n-Dioctyl phthalate	117 - 84 - 0	LIQUID	•	0.9861	i	6.8 E-8	25	0.4	25
Hexachlorbenzene	118 - 74 - 1	SOLID	284.20	2.044	23	1.09 E-5	20-30	4.95 E-3	25
3,3'Dimethoxybenzidene	119 - 90 - 4	SOLID	244	Ì	i	1.9 E-7	25	1,800	25
3,3'-Dimethylbenzidene (o-Tolidine)	119 - 93 - 7	SOLID	212.30	i	i	2.9 E-7	25	146	25
Anthracene	120 - 12 - 7	SOLID	178.22	1.24	i27	1.95 E-4	20-30	4.5 E-2	20-30
p-Cresidine	120 - 71 - 8	SOLID	127.07		j	i		SPAR. SOLUBLE H.W.	
Catechol	120 - 80 - 9	SOLID	110.11	1.371	15	5.0	104	311,000	20
1,2,4-Trichlorobenzene (melting point 17 C)	120 - 82 - 1	LIQUID	181.45	1.574	i 10	0.46	25	30	20
2,4-Dichlorophenol	120 - 83 - 2	SOLID	163.0	1.383	60	0.13	25	4,500	20
2,4-Dinitrotoluene	121 - 14 - 2	SOLID .	182.14	1.521	15	5.1 E-3	20-30	300	22
N.N-Dimethylaniline	121 - 69 - 7	LIQUID	•	0.956	120	11.10	30	INSOLUBLE	i
1,2-Diphenylhydrazine (Hydrazobenzene)	122 - 66 - 7	SOLID	184.23	1.158	16	2.6 E-5	20-30	1,840	20-30
Hydroquinone		SOLID	110.11		15	1.0	132.4	260,000	20
Propionaldehyde		LIQUID		0.807	20	235	20		20
Butyraldehyde	•	LIQUID		0.817	20	71	20	37,000	1
1,4-Dioxane		LIQUID	88.20	1.033	20	40.0	25.2	6 E+6	25
Tris-(2,3-dibromopropyl)phosphate	,	LIQUID	697.93	1		4.80 E-3	65	10,000	20
Chloroprene	126 - 99 - 8	LIQUID	1	0.958	20	200	20	10,000	
Tetrachloroethylene (Perchloroethylene)	1	LIQUID		1.626	20	19	25	145	25
C.I. Vat Yellow 4	128 - 66 - 5	SOLID	332.36	i	i .	1	1	1	i
Dimethyl phthalate		LIQUID		1.196	15.6	<0.01	20	4,300	 25.
Dibenzofuran	•	SOLID	168.11		199		-"	110	25 25
Captan		SOLID	300.59		120	0.10 E-4	20	10.50	20
Chloramben	133 - 90 - 4	1	206.03	! · · · ¬		7 E-3	1100	700	25

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TABLE B-1 Chemical/Physical Properties

HAME	CAS NO.	AMBSTATE	HOL WT	SPECGRAV	TEMP.(C)	VAPOR PRESSURE (mm Hg)	TEMP.(C)	WATER SOLUBILITY (mg/l)	TEMP.(C
o-Anisidine hydrochloride	134 - 29 - 2	SOLID	159.62					SOLUBLE	
alpha-Haphthylamine	134 - 32 - 7	SOLID	143.18	1.131		6.5 E-5	20-30	1,700	20
Cupferron	135 - 20 - 6	SOLID	155.16	i i			İ	FREELY SOLUBLE	İ
Hitrilotriacetic acid	139 - 13 - 9	SOLID	191.14	i i			İ	1,280	22.5
4.4'-Thiodianiline	139 - 65 - 1	SOLID	216.18				İ	SL. SOLUBLE H.W.	İ
Ethyl acrylate	140 - 88 - 5			0.9405	20	39.20	20	20,000	20
Butyl acrylate	141 - 32 - 2	LIQUID	128.2		20	4	20	11,600	20
Ethyleneimine (Aziridine)	151 - 56 - 4			0.8321	20	160	20	2.66 E+6	20-30
p-Nitrosodiphenylamine	156 - 10 - 5	SOLID	198.22					SLIGHTLY SOLUBLE	i
Calcium cyanamide	156 - 62 - 7	•	80.11	2.29	20		i	INSOLUBLE, REACTS	i
Hydrazine	302 - 01 - 2	LIQUID	32.05			14.4	25	3.41 E+8	20-30
Aldrin	309 - 00 - 2					6.0 E-6	25	2.7 E-2	25
Diazomethane		GAS	42.04	11.45*			1	DECOMPOSES	i
Carbonyl sulfide	463 - 58 - 1	IGAS		2.1*			i	1,000	1
C.I. Solvent Yellow 34 (Auramine)	492 - 80 - 8	SOLID	267.38				ì	2.1	i
Mustard gas				1.274	20	0.090	30	680	25
Mustard gas Chlorobenzilate	510 - 15 - 6		325	1		1.2 E-6	20-30	21.9	20-30
2-Chloroacetophenone (melting point = 20-21 C)	532 - 27 - 4		154.59	1 188		0.004	20	PRAC. INSOLUBLE	
	534 - 52 - 1	SOLID	198.13	11.100		1.05 E-6	25	290	20-30
4,6-Dinitro-o-cresol	540 - 59 - 0	•	96.95	1.27		200	25	6,300	25
1,2-Dichloroethylene	541 - 41 - 3	LIQUID	108.53		20	1		DECOMPOSES (INSOL)	•
Ethyl chloroformate	541 - 41 - 3	LIQUID	174.01			2.1	25	1110	20
1,3-Dichlorobenzene	542 - 75 - 6	LIQUID	110.98		25	25	20	2,700	25
1,3-Dichloropropylene	542 - 88 - 1		114.97		20	30	22	DECOMPOSES(22,000)	
Bis(chloromethyl) ether		SOLID	364.95		1	1	155	VERY SOLUBLE	123
C.I. Basic Green 4			174.15	1.2244	 20 (solid)	0 01	20	REACTS	1
Toluene 2,4-diisocyanate (melting point = 21 C)	584 - 84 - 9	1	1	11.493		1058.3	25	KEACIS	-
Vinyl bromide (boiling point = 15.8 C)	593 - 60 - 2	•	106.96	11.493		1.8 E-2	20-30	14 720	20-30
2,6-Dinitrotoluene	606 - 20 - 2	SOLID	182.14		Į.	11.0 6-2	20-30	1,320	120-30
2,4-Diaminoanisole	615 - 05 - 4	SOLID	138.16	•	!		20.70	10,000	20.70
N-Nitrosodi-n-propylamine	621 - 64 - 7		130	0.000		0.4	20-30	9,900	20-30
Methyl isocyanate	624 - 83 - 9	LIQUID	57.05	0.9599	20	348	20	REACTS	20.70
o-Toluidene hydrochloride	636 - 21 - 5	SOLID	143.6	14.07	120	1.19 E-3	25	1.5 E+4	20-30
Hexamethylphosphoramide	680 - 31 - 9	LIQUID	179.20	1.03	20	0.07	30	MISCIBLE	20.30
N-Nitroso-N-methyl urea	684 - 93 - 5	SOLID	103.08	!		33.5	25	6.89 E+8	20-30
N-Nitroso-N-ethyl urea	759 - 73 - 9	SOLID	117	ļ	1	16.3	25	3.31 E+8	20-30
C.I. Solvent Yellow 14	842 - 07 - 9	SOLID	248.28			4.11	25	INSOLUBLE	1
N-Nitroso-di-n-butylamine	924 - 16 - 3		152	0.9009	20			1,100	25
Tetrachlorvinphos	961 - 11 - 5	SOLID	365.95	ļ		4.2 E-8	20	11	22
C.I. Basic Red 1	989 - 38 - 8		479.06	ļ				SOLUBLE	
Propane sultone (melting point = 30 C)	1120 - 71 - 4	SOL/LIQ	122.14	1.51	20 (solid)	6.37 E-4	25	2.3 E+6	25

TABLE B-1 Chemical/Physical Properties

NAME	CAS NO.	AMBSTATE	MOL WT	SPECGRAV	TEMP.(C)	VAPOR PRESSURE (mm Hg)	TEMP.(C)	WATER SOLUBILITY (mg/l)	TEMP.(
Decabromodiphenyl oxide	1163 - 19 - 5	SOLID	959.12				,		
Sodium hydroxide (solution) pure = solid	1310 - 73 - 2	LIQUID	40.01	1.53	(50% soln)		ĺ	MISCIBLE	İ
Molybdenum trioxide	1313 - 27 - 5	SOLID	43.95	4.696	26	1	734	490	28
Thorium dioxide	1314 - 20 - 1	SOLID	264.05	10.0	j		j	INSOLUBLE	İ
Cresol (mixed isomers)	1319 - 77 - 3	LIQUID	108.13	1.03	25	0.24	20-30	31,000	20-30
Xylene (mixed isomers)	1330 - 20 - 7	LIQUID	106.16	0.86		10	27-32	175	25
Asbestos (friable)	1332 - 21 - 4	SOLID	554.2	2.5	İ		İ	İ	j i
Hexachloronaphthalene	1335 - 87 - 1	SOLID	334.85	j			İ	į	į
Polychlorinated biphenyls (PCBs)	1336 - 36 - 3	LIQUID	328	1.38-1.6	25	7.7 E-5	20-30	0.031	20-30
Aluminum oxide	1344 - 28 - 1	SOLID	101.94	4	20	1	2148	PRAC. INSOLUBLE	İ
Diepoxybutane	1464 - 53 - 5	LIQUID	86.10	1.113	18	1.52	25	8.3 E+7	25
Trifluralin	1582 - 09 - 8		•			1.99 E-4	30	24	İ
Methyl tert-butyl ether	1634 - 04 - 4	LIQUID	88.15			245	25	48,000	İ
Nitrofen	•	•				8 E-6	40	j 1	22
Chlorothalonil	1897 - 45 - 6	SOLID	265.89	1.70	25	0.01	İ40	0.6	22
C.I. Direct Black 38	1937 - 37 - 7	SOLID	783.0	į		5 E-5	20	GOOD	i
Fluometuron	2164 - 17 - 2	SOLID	232.21	j i		<1	i	80	25
Octachloronaphthalene	2234 - 13 - 1	SOLID	403.74	2.00	,	<1	İ	INSOLUBLE	j
Diallate	2303 - 16 - 4	LIQUID	270.24	i		6.74 E-3	20-30	14	20-30
C.I. Direct Blue 6	2602 - 46 - 2	SOLID	936.82				j	GOOD	i
C.I. Acid Blue 9, diammonium salt	2650 - 18 - 2	SOLID	783.01	0.65		1 E-7 (est)	25	200,000	20
C.I. Disperse Yellow 3	2832 - 40 - 8	SOLID	269.33	i			j	3.8	60
C.I. Solvent Orange 7	3118 - 97 - 6	SOLID	276.17	j i			İ		
C.I. Food Red 5	3761 - 53 - 3	SOLID	482.4	i				20,000	22
C.I. Acid Blue 9, disodium salt	3844 - 45 - 9	SOLID	792.85	i i		1 E-7 (est)	25	SOLUBLE	i
N-Nitroso methylvinyl amine	4549 - 40 - 0	i	86.02			12.3	20-30	7.6 E+5	20-30
C.I. Acid Green 3	4680 - 78 - 8	•	690.80	i • i		,		SOLUBLE	i
Ammonium nitrate (solution) pure = solid	6484 - 52 - 2	•	80.05	1.725	25 (solid)	11	210	2 E6	i
Aluminum (fume or dust)	7429 - 90 - 5			2.702		1	1284	INSOLUBLE	i .
Lead	7439 - 92 - 1			11.29	20	1 E-5	483	INSOLUBLE	İ
Manganese	7439 - 96 - 5	•	•	7.2		1	1292	DECOMPOSES	i
Mercury	7439 - 97 - 6		200.59		20	1.3 E-3	25		25
Nickel	7440 - 02 - 0	LIQUID	58.71	8.90		1	1810	INSOLUBLE	Ī
Silver	7440 - 22 - 4	SOLID			20		1357	INSOLUBLE	ì
Thallium	7440 - 28 - 0			11.85		1	825	INSOLUBLE	
Antimony	7440 - 36 - 0		121.75		25	1	886	INSOLUBLE	i
Arsenic	7440 - 38 - 2		•			1	372	INSOLUBLE	-
Barium			137.24		20	10	1049	REACTS SLOWLY	i
Beryllium	•	•	•		20	· ·	1	SL.SOL.H.W., DECOMP	i
Cadmium			112.41			1 E-5	148	INSOLUBLE	l

TABLE B-1 Chemical/Physical Properties

NAME	CAS NO.	AMBSTATE	HOL WT	SPECGRAV	TEMP.(C)	VAPOR PRESSURE (mm Hg)	TEMP.(C)	WATER SOLUBILITY (mg/l)	TEMP.(C
Chromium	7440 - 47 - 3	SOLID	52	7.20	28	1 E-5	907	INSOLUBLE	
Cobalt	7440 - 48 - 4	SOLID	58.93	8.9			1	INSOLUBLE	İ
Copper	7440 - 50 - 8	SOLID	63.55	8.92		1	1628	INSOLUBLE	İ
Vanadium (fume or dust)	7440 - 62 - 2	SOLID	50.94	5.96			į	INSOLUBLE	İ
Zinc (fume or dust)	7440 - 66 - 6	SOLID	65.38	7.14		1	487	INSOLUBLE	İ
Titanium tetrachloride	7550 - 45 - 0	LIQUID	189.73	1.726		10	21.3	SOLUBLE	ĺ
Hydrochloric acid	7647 - 01 - 0	IGAS	36.46	1.268*	İ	30400	17.8	673,000	30
Phosphoric acid (melting point = 42.4 C)	7664 - 38 - 2	SOL/LIQ.	98.00	1.8741	25 (liq)		İ	1 E+6	İ
Hydrogen fluoride (boiling point = 49.2 C)	7664 - 39 - 3	GAS/LIQ	20.01	0.991	19.5 (liq)	800	25	200,000	25
Ammonia	7664 - 41 - 7	LIQUID	17.03	0.6*		7600	25.7	440,000	28
Ammonia water (28% in water)	•	LIQUID	17.03	0.90			İ	İ	İ
Sulfuric acid	7664 - 93 - 9	LIQUID	98.08	1.841	25	10	31	SOLUBLE	İ
Nitric acid	7697 - 37 - 2	LIQUID	63.01	1.5027	20	47.8	20	SOLUBLE	İ
Phosphorus (yellow or white)	7723 - 14 - 0	SOLID	30.97	1.8	į	0.026	20	0.33	j
Sodium sulfate (solution) pure = solid	7757 - 82 - 6	LIQUID	142.06	2.7	solid		Ì	330,000	33
Selenium (amorphous form)	7782 - 49 - 2	SOLID	78.96	4.28	İ	1	356	INSOLUBLE	199
Selenium (crystalline or red form)	7782 - 49 - 2	SOLID	78.96	4.26 RED	j	أ 1	356	INSOLUBLE	199
Selenium (gray or metallic form)	7782 - 49 - 2	SOLID	78.96	4.81	20	 1	356	INSOLUBLE	137
Chlorine	7782 - 50 - 5	GAS	70.91	2.5*	-34.6	7600	30	5,700	30
Ammonium sulfate (solution) pure = solid	7783 - 20 - 2	LIQUID	132.14	İ	İ		İ	434,700	25
Toxaphene	8001 - 35 - 2	SOLID	414	1.65	 25	0.4	25	3	22
Hydrazine sulfate	10034 - 93 - 2	SOLID	130.12	2.016	7	į	İ	29,000	İ
Chlorine dioxide (boiling point = 11 C)	10049 - 04 - 4	GAS	67.46	1.642	0	760	11.1	İ	İ
Zineb	12122 - 67 - 7	SOLID	275.75	į	ĺ	NEGLIGIBLE	İ	j<1	25
Maneb	12427 - 38 - 2	SOLID	265.29	1.92	Ĭ	7.5 E-8	20	40	Ì
Titanium dioxide (rutile form)	13463 - 67 - 7	SOLID	79.90	4.23	İ	į	İ	INSOLUBLE	
Titanium dioxide (anatase form)	13463 - 67 - 7	SOLID	79.90	3.90	İ		į	INSOLUBLE	i
Titanium dioxide (brookite form)	13463 - 67 - 7	SOLID	79.90	4.13	İ	İ	İ	INSOLUBLE	Ì
C.I. Direct Brown 95	16071 - 86 - 6	SOLID	762.15	į	İ	ĺ	İ	G000	
N-Nitrosonornicotine	16543 - 55 - 8	LIQUID	177.08	İ	İ	İ	İ		İ
Osmium tetroxide	20816 - 12 - 0	SOLID	254.20	4.906	22	j 11	27	62,300	25
Dichlorobenzene (mixed isomers)	25321 - 22 - 6	LIQUID	174.0	1.2884	20	0.68-2.1	25	140	25
Diaminotoluene (mixed isomers)	25376 - 45 - 8	SOLID	122.17	i	İ	İ	İ	SOLUBLE	i
2,4-Diaminoanisole sulfate	39156 - 41 - 7	•	236.08	i	i	i	i	SOLUBLE	i

7 1 10

APPENDIX C

ESTIMATING ATMOSPHERIC RELEASES FROM STORAGE OF ORGANIC LIQUIDS

(From "Compilation of Air Pollutant Emission Factors" Volume 1, EPA Publication AP-42 4th Edition September 1985)

4.3 STORAGE OF ORGANIC LIQUIDS

4.3.1 Process Description

Storage vessels containing organic liquids can be found in many industries, including (1) petroleum producing and refining, (2) petrochemical and chemical manufacturing, (3) bulk storage and transfer operations, and (4) other industries consuming or producing organic liquids. Organic liquids in the petroleum industry, usually called petroleum liquids, generally are mixtures of hydrocarbons having dissimilar true vapor pressures (for example, gasoline and crude oil). Organic liquids in the chemical industry, usually called volatile organic liquids, are composed of pure chemicals or mixtures of chemicals with similar true vapor pressures (for example, benzene or a mixture of isopropyl and butyl alcohols).

Five basic tank designs are used for organic liquid storage vessels, fixed roof, external floating roof, internal floating roof, variable vapor space, and pressure (low and high).

Fixed Roof Tanks - A typical fixed roof tank is shown in Figure 4.3-1. This type of tank consists of a cylindrical steel shell with a permanently affixed roof, which may vary in design from cone or dome shaped to flat.

Fixed roof tanks are commonly equipped with a pressure/vacuum vent that allows them to operate at a slight internal pressure or vacuum to prevent the release of vapors during very small changes in temperature, pressure or liquid level. Of current tank designs, the fixed roof tank is the least expensive to construct and is generally considered the minimum acceptable equipment for storage of organic liquids.

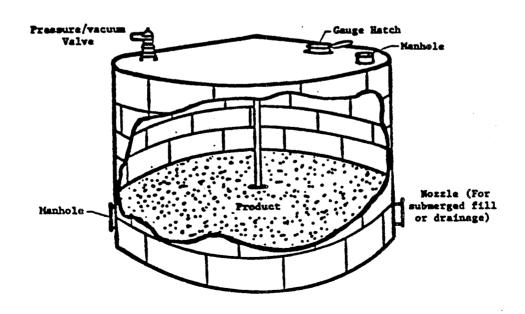


Figure 4.3-1. Typical fixed roof tank. 1

External Floating Roof Tanks - A typical external floating roof tank is shown in Figure 4.3-2. This type of tank consists of a cylindrical steel shell equipped with a roof which floats on the surface of the stored liquid, rising and falling with the liquid level. The liquid surface is completely covered by the floating roof, except at the small annular space between the roof and the tank wall. A seal (or seal system) attached to the roof contacts the tank wall (with small gaps, in some cases) and covers the annular space. The seal slides against the tank wall as the roof is raised or lowered. The purpose of the floating roof and the seal (or seal system) is to reduce the evaporation loss of the stored liquid.

Internal Floating Roof Tanks - An internal floating roof tank has both a permanent fixed roof and a deck inside. The deck rises and falls with the liquid level and either floats directly on the liquid surface (contact deck) or rests on pontoons several inches above the liquid surface (noncontact deck). The terms "deck" and "floating roof" can be used interchangeably in reference to the structure floating on the liquid inside the tank. There are two basic types of internal floating roof tanks, tanks in which the fixed roof is supported by vertical columns within the tank, and tanks with a self-supporting fixed roof and no internal support columns. Fixed roof tanks that have been retrofitted to employ a floating deck are typically of the first type, while external floating roof tanks typically have a self-supporting roof when converted to an internal floating roof tank. Tanks initially constructed with both a fixed roof and a floating deck may be of either type.

The deck serves to restrict evaporation of the organic liquid stock. Evaporation losses from decks may come from deck fittings, nonwelded deck seams, and the annular space between the deck and tank wall. Typical contact deck and noncontact deck internal floating roof tanks are shown in

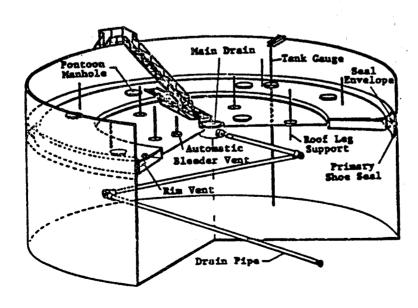


Figure 4.3-2. External floating roof tank. 1

Figure 4.3-3. Contact decks can be aluminum sandwich panels with a honeycomb aluminum core floating in contact with the liquid, or pan steel decks floating in contact with the liquid, with or without pontoons. Typical noncontact decks have an aluminum deck or an aluminum grid framework supported above the liquid surface by tubular aluminum pontoons or other bouyant structures. Both types of deck incorporate rim seals, which slide against the tank wall as the deck moves up and down. In addition, these tanks are freely vented by circulation vents at the top of the fixed roof. The vents minimize the possibility of organic vapor accumulation in concentrations approaching the flammable range. An internal floating roof tank not freely vented is considered a pressure tank.

Pressure Tanks - There are two classes of pressure tanks in general use, low pressure (2.5 to 15 psig) and high pressure (higher than 15 psig). Pressure tanks generally are used for storage of organic liquids and gases with high vapor pressures and are found in many sizes and shapes, depending on the operating pressure of the tank. Pressure tanks are equipped with a pressure/vacuum vent that is set to prevent venting loss from boiling and breathing loss from daily temperature or barometric pressure changes. High pressure storage tanks can be operated so that virtually no evaporative or working losses occur. In low pressure tanks, working losses can occur with atmospheric venting of the tank during filling operations.

Variable Vapor Space Tanks - Variable vapor space tanks are equipped with expandable vapor reservoirs to accommodate vapor volume fluctuations attributable to temperature and barometric pressure changes. Although variable vapor space tanks are sometimes used independently, they are normally connected to the vapor spaces of one or more fixed roof tanks. The two most common types of variable vapor space tanks are lifter roof tanks and flexible diaphragm tanks.

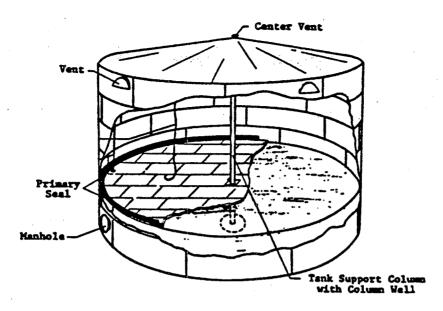
Lifter roof tanks have a telescoping roof that fits loosely around the outside of the main tank wall. The space between the roof and the wall is closed by either a wet seal, which is a trough filled with liquid, or a dry seal, which uses a flexible coated fabric.

Flexible diaphragm tanks use flexible membranes to provide expandable volume. They may be either separate gasholder units or integral units mounted atop fixed roof tanks.

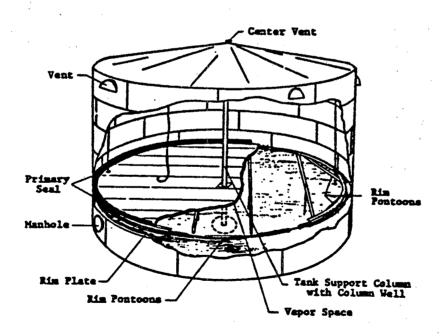
4.3.2 Emissions And Controls

Emission sources from organic liquids in storage depend upon the tank type. Fixed roof tank emission sources are breathing loss and working loss. External or internal floating roof tank emission sources are standing storage loss and withdrawal loss. Standing storage loss includes rim seal loss, deck fitting loss and deck seam loss. Pressure tanks and variable vapor space tanks are also emission sources.

Fixed Roof Tanks - Two significant types of emissions from fixed roof tanks are breathing loss and working loss. Breathing loss is the expulsion of vapor from a tank through vapor expansion and contraction, which are the results of changes in temperature and barometric pressure. This loss occurs without any liquic level change in the tank.



Contact Deck Type



Noncontact Deck Type

Figure 4.3-3. Internal floating roof tanks. EMISSION FACTORS

The combined loss from filling and emptying is called working loss. Filling loss comes with an increase of the liquid level in the tank, when the pressure inside the tank exceeds the relief pressure and vapors are expelled from the tank. Emptying loss occurs when air drawn into the tank during liquid removal becomes saturated with organic vapor and expands, thus exceeding the capacity of the vapor space.

The following equations, provided to estimate emissions, are applicable to tanks with vertical cylindrical shells and fixed roofs. These tanks must be substantially liquid and vapor tight and must operate approximately at atmospheric pressure. Fixed roof tank breathing losses can be estimated from²:

$$L_{B} = 2.26 \times 10^{-2} M_{V} \left(\frac{P}{P_{A} - P} \right)^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_{P} CK_{C}$$
 (1)

where:

 L_R = fixed roof breathing loss (lb/yr)

M_V = molecular weight of vapor in storage tank (lb/lb mole), see
Note 1

 P_A = average atmospheric pressure at tank location (psia)

P = true vapor pressure at bulk liquid conditions (psia), see Note 2

D = tank diameter (ft)

H = average vapor space height, including roof volume correction
 (ft), see Note 3

 ΔT = average ambient diurnal temperature change (°F)

 F_p = paint factor (dimensionless), see Table 4.3-1

C = adjustment factor for small diameter tanks (dimensionless), see Figure 4.3-4

 $K_C =$ product factor (dimensionless), see Note 4

Notes: (1) The molecular weight of the vapor, M_V, can be determined by Table 4.3-2 for selected petroleum liquids and volatile organic liquids or by analysis of vapor samples. Where mixtures of organic liquids are stored in a tank, M_V can be estimated from the liquid composition. As an example of the latter calculation, consider a liquid known to be composed of components A and B with mole fractions in the liquid X and X_h, respectively. Given the vapor pressures of the pure

4.3-5

TABLE 4.3-1. PAINT FACTORS FOR FIXED ROOF TANKS^a

,		Paint fa	ctors (F _P)	
Tank col	Paint condition			
Roof	Shell	Good	Poor	
White	White	1.00	1.15	
Aluminum (specular)	White	1.04	1.18	
White	Aluminum (specular)	1.16	1.24	
Aluminum (specular)	Aluminum (specular)	1.20	1.29	
White	Aluminum (diffuse)	1.30	1.38	
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46	
White	Gray	1.30	1.38	
Light gray	Light gray	1.33	1.44 ^b	
Medium gray	Medium gray	1.40	1.58 ^b	

Reference 2. bEstimated from the ratios of the seven preceding paint factors.

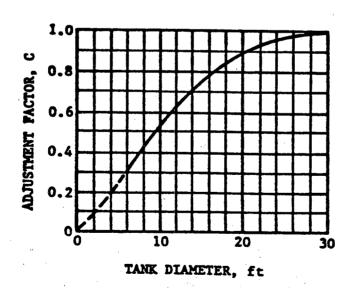


Figure 4.3-4. Adjustment factor (C) for small diameter tanks.²

TABLE 4.3-2. PHYSICAL PROPERTIES OF TYPICAL ORGANIC LIQUIDS^a

	Vapor molecular	Product density (d),	Condensed vapor density (w),		•	True vapor	pressure	in psia at	:	
Organic liquid ^b	weight 0 60°F	lb/gal @ 60°F	lb/gal @ 60°F	40°F	50°F	60°F	70°F	80°F	90°F	100°F
Petroleum Liquids ^C										
Gasoline RVP 13	62	5.6	4.9	4.7	5.7	6.9	8.3	9.9	11.7	13.8
Gasoline RVP 10	66	5.6	5.1	3.4	4.2	5.2	6.2	7.4	8.8	10.5
Gasoline RVP 7	68	5.6	5.2	2.3	2.9	3.5	4.3	5.2	6.2	7.4
Crude oil RVP 5	50	7.1	4.5	1.8	2.3	2.8	3.4	4.0	4.8	5.7
Jet naphtha (JP-4)	80	6.4	5.4	0.8	1.0	1.3	1.6	1.9	2.4	2.7
Jet kerosene	130	7.0	6.1	0.0041	0.0060	0.0085	0.011	0.015	0.021	0.029
Distillate fuel no. 2	130	7.1	6.1	0.0031	0.0045	0.0074	0.0090	0.012	0.016	0.022
Residual oil no. 6	190	7.9	6.4	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.0001
Volatile Organic Liquids										
Acetone	58	6.6	6.6	1.7	2.2	2.9	3.7	4.7	5.9	7.3
Acrylonitrile	53	6.8	6.8	0.8	1.0	1.4	1.8	2.4	3.1	4.0
Benzene	78	7.4	7.4	0.6	0.9	1.2	1.5	2.0	2.6	3.3
Carbon disulfide	76	10.6	10.6	3.0	3.9	4.8	6.0	7.4	9.2	11.2
Carbon tetrachloride	154	13.4	13.4	0.8	1.1	1.4	1.8	2.3	3.0	3.8
Chloroform	119	12.5	12.5	1.5	1.9	2.5	3.2	4.1	5.2	6.3
Cyclohexane	84	6.5	6.5	0.7	0.9	1.2	1.6	2.1	2.6	3.2
1,2-Dichloroethane	99	10.5	10.5	0.6	0.8	1.0	1.4	1.7	2.2	2.8
Ethylacetate	88	7.6	7.6	0.6	0.8	1.1	1.5	1.9	2.5	3.2
Ethyl alcohol	46	6.6	6.6	0.2	0.4	0.6	0.9	1.2	1.7	2.3
Isopropyl alcohol	60	6.6	6.6	0.2	0.3	0.6	0.7	0.9	1.3	1.8
Methyl alcohol	32	6.6	6.6	0.7	1.0	1.4	2.0	2.6	3.5	4.5
Methylene chloride	85	11.1	11.1	3.1	4.3	5.4	6.8	8.7	10.3	13.3
Methylethyl ketone	72	6.7	6.7	0.7	0.9	1.2	1.5	2.1	2.7	3.3
Methylmethacrylate	100	7.9	7.9	0.1	0.2	0.3	0.6	0.8	1.1	1.4
1,1,1-Trichloroethane	133	11.2	11.2	0.9	1.2	1.6	2.0	2.6	3.3	4.2
Trichloroethylene	131	12.3	12.3	0.5	0.7	0.9	1.2	1.5	2.0	2.0
Toluene	92	7.3	7.3	0.2	0.2	0.3	0.4	0.6	0.8	1.0
Vinylacetate	86	7.8	7.8	0.7	1.0	1.3	1.7	2.3	3.1	4.0

References 3-4.

Brown a more comprehensive listing of volatile organic liquids, see Reference 3.

RVP = Reid vapor pressure in psis.

components, P and P , and the molecular weights of the pure components, M a and M b, M is calculated:

$$M_{V} = M_{a} \left(\frac{P_{a}X_{a}}{P_{t}} \right) + M_{b} \left(\frac{P_{b}X_{b}}{P_{t}} \right)$$

where: P_t , by Raoult's law, is: $P_t = P_a X_a + P_b X_b$

- (2) True vapor pressures for organic liquids can be determined from Figures 4.3-5 or 4.3-6, or Table 4.3-2. In order to use Figures 4.3-5 or 4.3-6, the stored liquid temperature, T_S, must be determined in degrees Fahrenheit. T_S is determined from Table 4.3-3, given the average annual ambient temperature, T_A, in degrees Fahrenheit. True vapor pressure is the equilibrium partial pressure exerted by a volatile organic liquid, as defined by ASTM-D-2879 or as obtained from standard reference texts. Reid vapor pressure is the absolute vapor pressure of volatile crude oil and volatile nonviscous petroleum liquids, except liquified petroleum gases, as determined by ASTM-D-323.
- (3) The vapor space in a cone roof is equal in volume to a cylinder, which has the same base diameter as the cone and is one third the height of the cone. If information is not available, assume H equals one half tank height.
- (4) For crude oil, $K_C = 0.65$. For all other organic liquids, $K_C = 1.0$.

Fixed roof tank working losses can be estimated from²:

$$L_W = 2.40 \times 10^{-5} M_V PVNK_N K_C$$
 (2)

where:

L_u = fixed roof working loss (lb/year)

 M_V = molecular weight of vapor in storage tank (lb/lb mole), see Note 1 to Equation 1

P = true vapor pressure at bulk liquid temperature (psia), see Note 2 to Equation 1

V = tank capacity (gal)

S = number of turnovers per year (dimensionless)

 $S = \frac{\text{Total throughput per year (gal)}}{\text{Tank capacity, V (gal)}}$

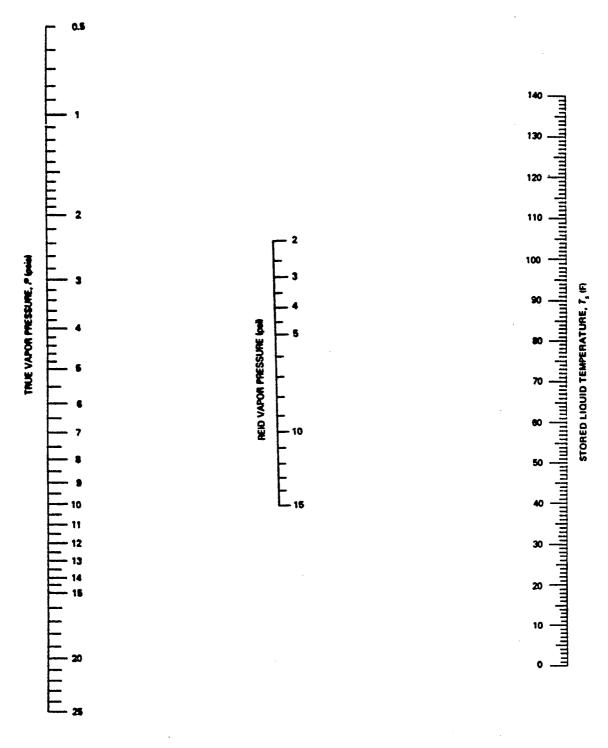
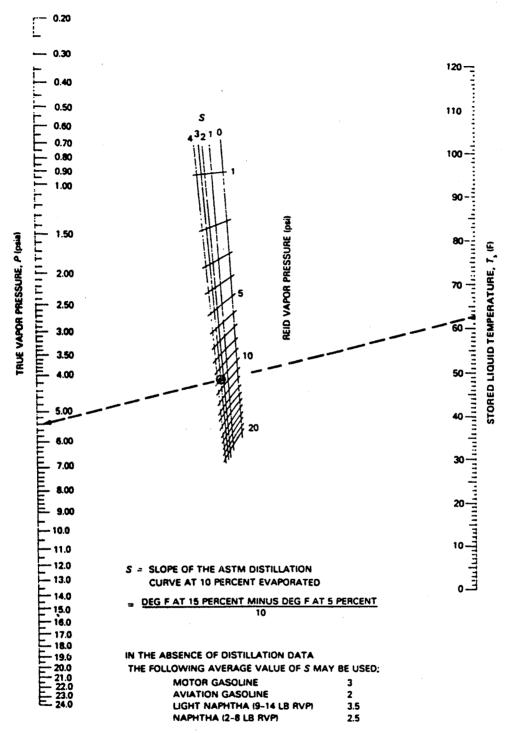


Figure 4.3-5. True vapor pressure (P) of crude oils (2-15 psi RVP).6



Note: Dashed line illustrates sample problem for RVP = 10 pounds per square inch, gasoline (S = 3), and $T_c = 62.5$ F SOURCE: Nomograph drawn from the data of the National Bureau of Standards.

Figure 4.3-6. True vapor presure (P) of refined petroleum liquids like gasoline and napththas (1-20 psi RVP).6

 K_N = turnover factor (dimensionless), see Figure 4.3-7

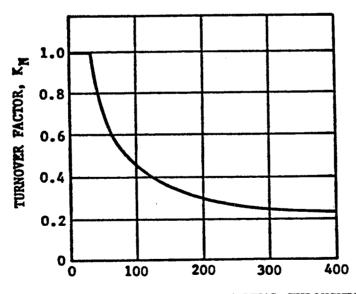
 $K_C = product factor (dimensionless), see Note 1$

Note: (1) For crude oil, $K_C = 0.84$. For all other organic liquids, $K_C = 1.0$.

TABLE 4.3-3. AVERAGE STORAGE TEMPERATURE (T_S) AS A FUNCTION OF TANK PAINT COLOR

	Average storage temperature,
Tank color	T _S
White	T _A ^b + 0
Aluminum	T _A + 2.5
Gray	T _A + 3.5
Black	T _A + 5.0

^aReference 5. ^bT_A is the average annual ambient temperature in degrees Fahrenheit.



TURNOVERS PER YEAR = ANNUAL THROUGHPUT TANK CAPACITY

Hote: For 36 turnovers per year or less, $K_N = 1.0$

Figure 4.3-7. Turnover factor (KN) for fixed roof tanks.

Several methods are used to control emissions from fixed roof tanks. Emissions from fixed roof tanks can be controlled by the installation of an internal floating roof and seals to minimize evaporation of the product being stored. The control efficiency of this method ranges from 60 to 99 percent, depending on the type of roof and seals installed and on the type of organic liquid stored.

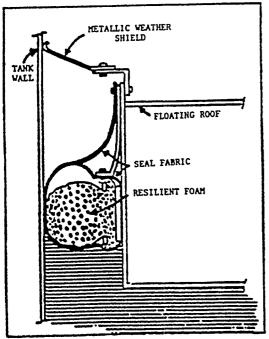
The vapor recovery system collects emissions from storage vessels and converts them to liquid product. Several vapor recovery procedures may be used, including vapor/liquid absorption, vapor compression, vapor cooling, vapor/solid adsorption, or a combination of these. The overall control efficiencies of vapor recovery systems are as high as 90 to 98 percent, depending on the method used, the design of the unit, the composition of vapors recovered, and the mechanical condition of the system.

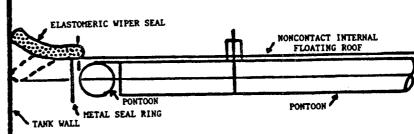
Another method of emission control on fixed roof tanks is thermal oxidation. In a typical thermal oxidation system, the air/vapor mixture is injected through a burner manifold into the combustion area of an incinerator. Control efficiencies for this system can range from 96 to 99 percent.

External And Internal Floating Roof Tanks - Total emissions from floating roof tanks are the sum of standing storage losses and withdrawal losses. Standing storage loss from internal floating roof tanks includes rim seal, deck fitting, and deck seam losses. Standing storage loss from external floating roof tanks, as discussed here, includes only rim seal loss, since deck fitting loss equations have not been developed. There is no deck seam loss, because the decks have welded sections.

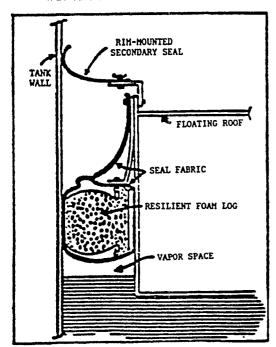
Standing storage loss from external floating roof tanks, the major element of evaporative loss, results from wind induced mechanisms as air flows across the top of an external floating roof tank. These mechanisms may vary, depending upon the type of seals used to close the annular vapor space between the floating roof and the tank wall. Standing storage emissions from external floating roof tanks are controlled by one or two separate seals. The first seal is called the primary seal, and the other, mounted above the primary seal, is called the secondary seal. There are three basic types of primary seals used on external floating roofs, mechanical (metallic shoe), resilient (nonmetallic), and flexible wiper. The resilient seal can be mounted to eliminate the vapor space between the seal and liquid surface (liquid mounted), or to allow a vapor space between the seal and liquid surface (vapor mounted). A primary seal serves as a vapor conservation device by closing the annular space between the edge of the floating roof and the tank wall. Some primary seals are protected by a metallic weather shield. Additional evaporative loss may be controlled by a secondary seal. Secondary seals can be either flexible wiper seals or resilient filled seals. Two configurations of secondary seal are currently available, shoe mounted and rim mounted. Although there are other seal system designs, the systems described here compose the majority in use today. See Figure 4.3-8 for examples of primary and secondary seal configurations.

Typical internal floating roofs generally incorporate two types of primary seals, resilient foam filled seals and wipers. Similar in design

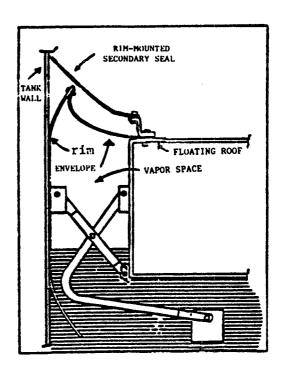




a. Liquid mounted seal with weather shield.



c. Vapor mounted seal with rim mounted secondary seal. b. Elastomeric wiper seal.



d. Metallic shoe seal with shoe mounted secondary seal.

Figure 4.3-8. Primary and secondary seal configurations. 1

to those in external floating roof tanks, these seals close the annular vapor space between the edge of the floating roof and the tank wall. Secondary seals are not commonly used with internal floating roof tanks.

Deck fitting loss emissions from internal floating roof tanks result from penetrations in the roof by deck fittings, fixed roof column supports or other openings. There are no procedures for estimating emissions from external roof tank deck fittings. The most common fittings with relevance to controllable vapor losses are described as follows:

- 1. Access Hatch. An access hatch is an opening in the deck with a peripheral vertical well that is large enough to provide passage of workers and materials through the deck for construction or servicing. Attached to the opening is a removable cover which may be bolted and/or gasketed to reduce evaporative loss. On noncontact decks, the well should extend down into the liquid to seal off the vapor space below the deck.
- 2. Automatic Gauge Float Well. A gauge float is used to indicate the level of liquid within the tank. The float rests on the liquid surface, inside a well that is closed by a cover. The cover may be bolted and/or gasketed to reduce evaporation loss. As with other similar deck penetrations, the well extends fixed into the liquid on noncontact decks.
- 3. Column Well. For fixed roofs that are column-supported, the columns pass through deck openings with peripheral vertical wells. On noncontact decks, the well should extend down into the liquid. The wells are equipped with closure devices to reduce evaporative loss and may be gasketed or ungasketed to further reduce the loss. Closure devices are typically sliding covers or flexible fabric sleeve seals.
- 4. Ladder Well. Some tanks are equipped with internal ladders that extend from a manhole in the fixed roof to the tank bottom. The deck opening through which the ladder passes has a peripheral vertical well. On noncontact decks, the well should extend down into the liquid. The wells are typically covered with a gasketed or ungasketed sliding cover.
- 5. Roof Leg or Hanger Well. To prevent damage to fittings underneath the deck and to allow for tank cleaning or repair, supports are provided to hold the deck a predetermined distance off the tank bottom. These supports consist of adjustable or fixed legs attached to the floating deck or hangers suspended from the fixed roof. For adjustable legs or hangers, the load-carrying element passes through a well or sleeve into the deck. With noncontact decks, the well should extend into the liquid.
- 6. Sample Pipe or Well. A funnel-shaped sample well may be provided to allow for sampling of the liquid with a sample thief. A closure is typically located at the lower end of the funnel and frequently consists of a horizontal piece of fabric slit radially to allow thief entry. The well should extend into the liquid on noncontact decks. Alternatively, a sample well may consist of a slottled pipe extending into the liquid, equipped with a gasketed or ungasketed sliding cover.

7. Vacuum Breaker. A vacuum breaker equalizes the pressure of the vapor space across the deck as the deck is either being landed on or floated off its legs. The vacuum breaker consists of a well with a cover. Attached to the underside of the cover is a guided leg of such length that it contacts the tank bottom as the internal floating deck approaches. When in contact with the tank bottom, the guided leg mechanically opens the breaker by lifting the cover off the well; otherwise, the cover closes the well. The closure may be gasketed or ungasketed. Because the purpose of the vacuum breaker is to allow the free exchange of air and/or vapor, the well does not extend appreciably below the deck.

The decks of internal floating roofs typically are made by joining several sections of deck material, resulting in seams in the deck. To the extent that these seams are not completely vapor tight, they become a source of emissions. It should be noted that external floating roof tanks and welded internal floating roofs do not have deck seam losses.

Withdrawal loss is another source of emissions from floating roof tanks. This loss is the vaporization of liquid that clings to the tank wall and is exposed to the atmosphere when a floating roof is lowered by withdrawal of liquid. There is also clingage of liquid to columns in internal floating roof tanks which have a column supported fixed roof.

Total Losses From Floating Roof Tanks - Total floating roof tank emissions are the sum of rim seal, withdrawal, deck fitting, and deck seam losses. It should be noted that external floating roof tanks and welded internal floating roofs do not have deck seam losses. Also, there are no procedures for estimating emissions from external floating roof tank deck fittings. The equations provided in this Section are applicable only to freely vented internal floating roof tanks or external floating roof tanks. The equations are not intended to be used in the following applications: to estimate losses from closed internal floating roof tanks (tanks vented only through a pressure-vacuum vent); to estimate losses from unstabilized or boiling stocks or from mixtures of hydrocarbons or petrochemicals for which the vapor pressure is not known or cannot be readily predicted; or to estimate losses from tanks in which the materials used in the seal system and/or deck construction are either deteriorated or significantly permeated by the stored liquid. Total losses may be written as:

$$L_{T} = L_{R} + L_{W} + L_{F} + L_{D}$$
 (3)

where:

 $L_{T} = total loss (lb/yr)$

 $L_p = rim seal loss (see Equation 4)$

 L_{ω} = withdrawal loss (see Equation 5)

 $L_F = deck fitting loss (see Equation 6)$

 $L_{D} = deck seam loss (see Equation 7)$

Rim Seal Loss - Rim seal loss from floating roof tanks can be estimated by the following equation 5-6:

$$L_{R} = K_{S} V^{n} P * D M_{V} K_{C}$$
 (4)

where:

 $L_{R} = rim seal loss (lb/yr)$

 $K_S = \text{seal factor (lb-mole/(ft (mi/hr)}^n \text{ yr)), see Table 4.3-4}$

V = average wind speed at tank site (mi/hr), see Note 1

n = seal related wind speed exponent (dimensionless), see Table 4.3-4

P* = vapor pressure function (dimensionless), see Note 2

$$P^* = \frac{\frac{P}{P_A}}{\left[1 + \left(1 - \frac{P}{P_A}\right)^{0.5}\right]^2}$$

where:

P = true vapor pressure at average actual liquid storage temperature (psia), see Note 2 to Equation 1

P_A = average atmospheric pressure at tank location (psia)

D = tank diameter (ft)

M_V = average vapor molecular weight (lb/lb-mole), see Note 1 to Equation 1

K_C = product factor (dimensionless), see Note 3

Notes: (1) If the wind speed at the tank site is not available, wind speed data from the nearest local weather station may be used as an approximation.

- (2) P* can be calculated or read directly from Figure 4.3-9.
- (3) For all organic liquids except crude oil, $K_C = 1.0$. For crude oil, $K_C = 0.4$.

Withdrawal Loss - The withdrawal loss from floating roof storage tanks can be estimated using Equation 5.5-6

$$L_{W} = \frac{(0.943)QCW_{L}}{D} \left[1 + \left(\frac{N_{C}F_{C}}{D} \right) \right]$$
 (5)

TABLE 4.3-4. SEAL RELATED FACTORS FOR FLOATING ROOF TANKS

	Welded	Tank	Riveted	Tank
Tank and seal type	K _S	n	KS	n
External floating roof tanks b				
Metallic shoe seal				
Primary seal only	1.2	1.5	1.3	1.5
With shoe mounted secondary seal	0.8	1.2	1.4	1.2
With rim mounted secondary seal	~ 0.2	1.0	0.2	1.6
Liquid mounted resilient seal		_	C	27.4
Primary seal only	1.1	1.0	NAC	NA
With weather shield	0.8	0.9	NA	NA
With rim mounted secondary seal	0.7	0.4	NA	NA
Vapor mounted resilient seal				374
Primary seal only	1.2	2.3	NA	NA
With weather shield	0.9	2.2	NA	NA
With rim mounted secondary seal	0.2	2.6	NA	NA
Internal floating roof tanks ^d				
Liquid mounted resilient seal				37.
Deimany coal only	3.0	0	NA	N/
With rim mounted secondary seal	1.6	0	NA	N
Vapor mounted resilient seal			27.4	27
Primary seal only	6.7	0	NA	N.
With rim mounted secondary seal	2.5	0	NA	N.

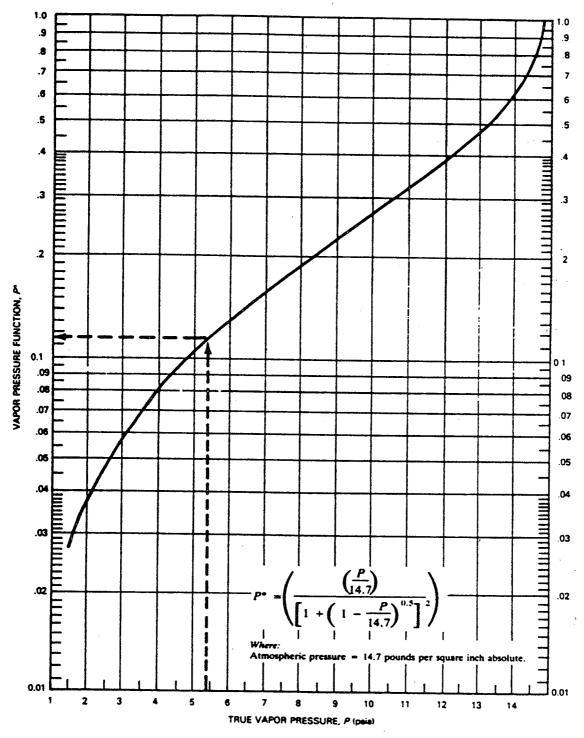
^aBased on emissions from tank seal systems in reasonably good working condition, no visible holes, tears, or unusually large gaps between the seals and the tank wall. The applicability of K decreases in cases where the actual gaps exceed the gaps assumed during development of the correlation.

Reference 5.

CNA = Not Applicable.

Reference 6.

endership enders seal on an internal floating roof tank, then assume only a primary seal is present.



NOTE: Dashed line illustrates sample problem for P=5.4 pounds per square inch absolute.

Figure 4.3-9. Vapor pressure function $(P^{*}).5$

4.3-18

EMISSION FACTORS

9/85

where:

L, = withdrawal loss (lb/yr)

Q = throughput (bbl/year) (tank capacity [bbl] times annual turnover rate)

C = shell clingage factor (bbl/1,000 ft2), see Table 4.3-5

 W_r = average organic liquid density (lb/gal), see Note 1

D = tank diameter (ft)

 $N_C = \text{number of columns (dimensionless)}$, see Note 3

 $F_C = \text{effective column diameter (ft) [column perimeter (ft)/<math>\pi$], see

Notes: (1) If W_L is not known, an average value of 5.6 lb/gallon can be assumed for gasoline. An average value cannot be assumed for crude oil, since densities are highly variable.

- (2) The constant, 0.943, has dimensions of (1,000 ft³ \times gal/bbl²).
- (3) For self-supporting fixed roof or an external floating roof tank:

$$N_C = 0$$
.

For column supported fixed roof:

 N_C = use tank specific information, or see Table 4.3-6.

(4) Use tank specific effective column diameter; or

F_C = 1.1 for 9 inch by 7 inch builtup columns, 0.7 for 8 inch diameter pipe columns, and 1.0 if column construction details are not known.

Deck Fitting Loss - Deck fitting loss estimation procedures for external floating roof tanks are not available. Therefore, the following procedure applies only to internal floating roof tanks.

Fitting losses from internal floating roof tanks can be estimated by the following equation⁶:

$$L_{F} = F_{F} P * M_{V} K_{C}$$
 (6)

TABLE 4.3-5. AVERAGE CLINGAGE FACTORS (C) (bb1/1,000 ft2)a

	Shell condition		
Liquid 	Light rust ^b	Dense rust	Gunite lined
Gasoline	0.0015	0.0075	0.15
Single component stocks	0.0015	0.0075	0.15
Crude oil	0.0060	0.030	0.60

aReference 5.

TABLE 4.3-6. TYPICAL NUMBER OF COLUMNS AS A FUNCTION OF TANK DIAMETER FOR INTERNAL FLOATING ROOF TANKS WITH COLUMN SUPPORTED FIXED ROOFS^a

Tank diameter range D (ft)	Typical number of columns, N _C
0 < D ≤ 85	1
85 < D ≦ 100	6
$100 < D \le 120$	7
120 < D ≤ 135	8
135 < D ≤ 150	9
150 < D ≦ 170	16
$170 < D \le 190$	19
190 < D ≦ 220	22
220 < D ≤ 235	31
235 < D ≦ 270	37
270 < D ≤ 275	43
275 < D ≤ 290	49
290 < D ≤ 330	61
330 < D ≦ 360	71
$360 < D \le 400$	81

Reference 1. This table was derived from a survey of users and manufacturers. The actual number of columns in a particular tank may vary greatly with age, fixed roof style, loading specifications, and manufacturing perogatives. Data in this table should not supersede information on actual tanks.

If no specific information is available, these values can be assumed to represent the most common condition of tanks currently in use.

where:

L = the fitting loss in pounds per year

F_r = total deck fitting loss factor (lb-mole/yr)

=
$$[(N_{F_1} K_{F_1}) + N_{F_2} K_{F_2}) + ... + (N_{F_n} K_{F_n})]$$

where:

 N_{F} = number of deck fittings of a particular type (i = 0,1,2,...,n) (dimensionsless)

 $K_{\hat{F}_{i}} = \text{deck fitting loss factor for a particular type fitting}$ (i = 0,1,2,...,n) (lb-mole/yr)

n = total number of different types of fittings
 (dimensionless)

 P^* , M_V , K_C = as defined for Equation 4

The value of F_F may be calculated by using actual tank specific data for the number of each fitting type (N_F) and then multiplying by the fitting loss factor for each fitting (K_F) . Values of fitting loss factors and typical number of fittings are presented in Table 4.3-7. Where tank specific data for the number and kind of deck fittings are unavailable, then F_F can be approximated according to tank diameter. Figures 4.3-10 and 4.3-11 present F_F plotted against tank diameter for column supported fixed roofs and self-supporting fixed roofs, respectively.

<u>Deck Seam Loss</u> - Deck seam loss applies only to internal floating roof tanks with bolted decks. External floating roofs have welded decks and, therefore, no deck seam loss. Deck seam loss can be estimated by the following equation:

$$L_{D} = K_{D}S_{D}D^{2}P*M_{V}K_{C}$$
 (7)

where

 $L_{\rm p} = {\rm deck \ seam \ losses \ (lb/yr)}$

K_D = deck seam loss per unit seam length factor (lb-mole/ft yr)

= 0.0 for welded deck and external floating roof tanks, 0.34 for bolted deck

 $S_D = \text{deck seam length factor (ft/ft}^2)$ $= \frac{L_{\text{seam}}}{L_{\text{seam}}}$

TABLE 4.3-7. SUMMARY OF INTERNAL FLOATING DECK FITTING LOSS FACTORS (K_F) AND TYPICAL NUMBER OF FITTINGS (N_F)

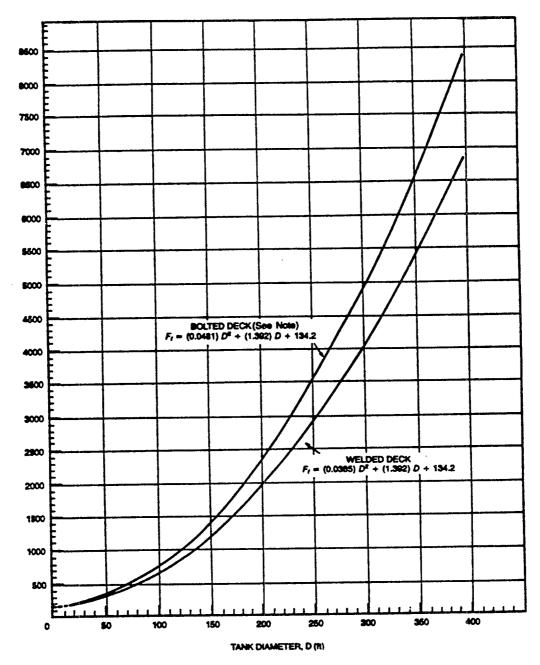
Deck fitting type	Deck fitting loss factor, K _F (lb-mole/yr)	Typical number of fittings, ^N F
Access hatch Bolted cover, gasketed Unbolted cover, gasketed Unbolted cover, ungasketed	1.6 11 _b 25	1
Automatic gauge float well Bolted cover, gasketed Unbolted cover, gasketed Unbolted cover, ungasketed	5.1 15 28 ^b	1
Column well Builtup column-sliding cover, gasketed Builtup column-sliding cover, ungasketed Pipe column-flexible fabric sleeve seal Pipe column-sliding cover, gasketed Pipe column-sliding cover, ungasketed	33 _b 47 ^b 10 19 32	(see Table 4.3-6)
Ladder well Sliding cover, gasketed Sliding cover, ungasketed	56 _b 76	1
Roof leg or hanger well Adjustable Fixed	7.9 ^b 0	$(5 + \frac{D}{10} + \frac{D^2}{600})^c$
Sample pipe or well Slotted pipe-sliding cover, gasketed Slotted pipe-sliding cover, ungasketed Sample well-slit fabric seal, 10% open area	44 57 _b 12 ^b	1
Stub drain, 1 inch diameter ^d	1.2	$\left(\frac{D^2}{125}\right)^c$
Vacuum breaker Weighted mechanical actuation, gasketed Weighted mechanical actuation, ungaskete	0.7 ^b d 0.9	. 1

Reference 1.

If no specific information is available, this value can be assumed to represent the most common/typical deck fittings currently used.

CD = tank diameter (ft).

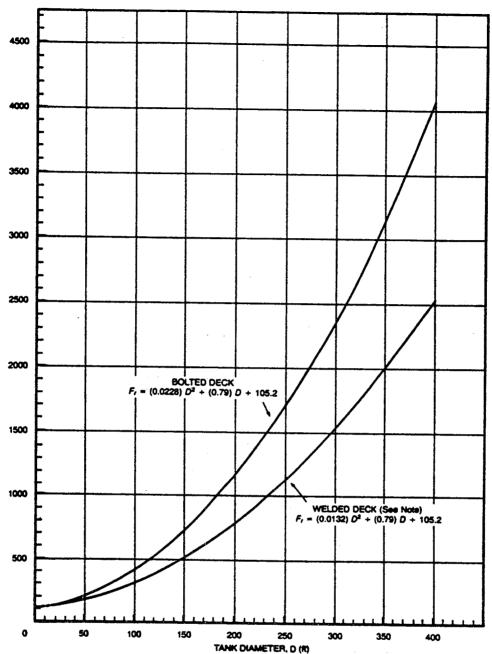
Not used on welded contact internal floating decks.



Basis: Fittings include: (1) access hatch, with ungasketed, unboked cover; (2) built-up column wells, with ungasketed, sliding cover; (3) adjustable deck legs; (4) gauge float well, with ungasketed, unboked cover; (5) ladder well, with ungasketed sliding cover; (6) sample well, with slit fabric seal (10 percent open area); (7) 1-inch diameter stub drains (only on boked deck); and (8) vacuum breaker, with gasketed weighted mechanical actuation. This basis was derived from a survey of users and manufacturers. Other fittings may be typically used within particular companies or organizations to reflect standards and/or specifications of that group. This figure should not supersede information based on actual tank data.

Note: If no specific information is available, assume bolted decks are the most common/typical type currently in use in tanks with column-supported fixed roofs.

Figure 4.3-10. Approximated total deck fitting loss factors (F_f) for typical fittings in tanks with column supported fixed roofs and either a bolted deck or a welded deck.⁶ This figure is to be used only when tank specific data on the number and kind of deck fittings are unavailable.



BASIS: Fittings include: (1) access hatch, with ungasketed, unbolted cover; (2) adjustable deck legs; (3) gauge float well, with ungasketed, unbolted cover; (4) sample well, with slit fabric seal (10 percent open area); (5) linch diameter stub drains (only on bolted deck); and (6) vacuum breaker, with gasketed weighted mechanical actuation. This basis was derived from a survey of users and manufacturers. Other fittings may be typically used within particular companies or organizations to reflect standards and/or specifications of that group. This figure should not supersede information based on actual tank data.

Notes: If no specific information is available, assume welded decks are the most common/typical type currently in use in tanks with self-supporting fixed roofs.

Figure 4.3-11. Approximated total deck fitting loss factors (F₎ for typical deck fittings in tanks with self-supporting fixed roofs and either a bolted deck or a welded deck. This figure is to be used only when tank specific data on the number and kind of deck fittings are unavailable.

4.3-24

where:

L_{seam} = total length of deck seams (ft)

 A_{deck} = area of deck (ft²) = π D²/4

D, P*, M_V , K_C = as defined for Equation 4

If the total length of the deck seam is not known, Table 4.3-8 can be used to determine S_D . Where tank specific data concerning width of deck sheets or size of deck panels are unavailable, a default value for S_D can be assigned. A value of 0.20 (ft/ft²) can be assumed to represent the most common bolted decks currently in use.

TABLE 4.3-8. DECK SEAM LENGTH FACTORS (S_D) FOR TYPICAL DECK CONSTRUCTIONS FOR INTERNAL FLOATING ROOF TANKS^a

Deck construction	Typical deck seam length factor, S _D (ft/ft ²)
Continuous sheet construction b	
5 ft wide	0.20 ^C
6 ft wide	0.17
7 ft wide	0.14
Panel construction ^d	
5 x 7.5 ft rectangular	0.33
5 x 12 ft rectangular	0.28

^aReference 6. Deck seam loss applies to bolted decks only.

$$^{b}S_{D} = \frac{1}{W}$$
, where W = sheet width (ft)

^CIf no specific information is available, these factors can be assumed to represent the most common bolted decks currently in use.

 ${}^{d}S_{D} = \frac{(L+W)}{LW}$, where W = panel width (ft) and L = panel length (ft)

Pressure Tanks - Losses occur during withdrawal and filling operations in low pressure (2.5 to 15 psig) tanks when atmospheric venting occurs. High pressure tanks are considered closed systems, with virtually no emissions. Vapor recovery systems are often found on low pressure tanks. Fugitive losses are also associated with pressure tanks and their equipment, but

with proper system maintenance, these losses are considered insignificant. No appropriate correlations are available to estimate vapor losses from pressure tanks.

<u>Variable Vapor Space Tanks</u> - Variable vapor space filling losses result when vapor is displaced by liquid during filling operations. Since the variable vapor space tank has an expandable vapor storage capacity, this loss is not as large as the filling loss associated with fixed roof tanks. Loss of vapor occurs only when the tank's vapor storage capacity is exceeded.

Variable vapor space system filling losses can be estimated from: 3-7

$$L_V = (2.40 \times 10^{-2}) \frac{M_V P}{V_1} ((V_1) - (0.25 V_2 N_2))$$
 (8)

where:

 L_V = variable vapor space filling loss (lb/10³ gal throughput)

M_V = molecular weight of vapor in storage tank (lb/lb-mole), see Note 1 to Equation 1

P = true vapor pressure at bulk liquid conditions (psia), see Note 2 to Equation 1

 V_1 = volume of liquid pumped into system, throughput (bbl)

 V_2 = volume expansion capacity of system (bbl), see Note 1

 N_2 = number of transfers into system (dimensionless), see Note 2

Notes: (1) V₂ is the volume expansion capacity of the variable vapor space achieved by roof lifting or diaphragm flexing.

(2) N_2 is the number of transfers into the system during the time period that corresponds to a throughput of V_1 .

The accuracy of Equation 8 is not documented. Special tank operating conditions may result in actual losses significantly different from the estimates provided by Equation 8. It should also be noted that, although not developed for use with heavier petroleum liquids such as kerosenes and fuel oils, the equation is recommended for use with heavier petroleum liquids in the absence of better data.

4.3.3 Sample Calculations

Three sample calculations to estimate emission losses are provided, fixed roof tank, external floating roof tank, and internal floating roof

tank. Note that the same tank size, tank painting, stored product, and ambient conditions are employed in each sample calculation. Only the type of roof varies.

Problem I - Estimate the total loss from a fixed roof tank for 3 months based on data observed during the months of March, April and May and given the following information:

Tank description: Fixed roof tank; 100 ft diameter; 40 ft height;

tank shell and roof painted specular aluminum

color.

Stored product: Motor gasoline (petroleum liquid); Reid vapor

pressure (RVP), 10 psia; 6.1 lb/gal liquid density; no vapor or liquid composition given;

375,000 bbl throughput for the 3 months.

Ambient conditions: 60°F average ambient temperature for the 3 months;

10 mi/hr average wind speed at the tank site for the 3 months; assume 14.7 psia atmospheric pressure; average maximum daily temperature, 68°F;

average minimum daily temperature, 47°F.

Calculation: Total loss = breathing loss + working loss.

(a) Breathing Loss - Calculate using Equation 1.

$$L_{B} = 2.26 \times 10^{-2} M_{V} \left(\frac{P}{P_{A}-P}\right)^{0.68} D^{1.73}H^{0.51}\Delta T^{0.50}F_{P}CK_{C}$$
 (1)

where:

L_B = breathing loss (lb/yr)

 $M_{V} = 66 \text{ lb/lb-mole (from Table 4.3-2 and RVP 10 gasoline)}$

 $T_A = 60^{\circ}F \text{ (given)}$

 $T_S = 62.5$ °F (from Table 4.3-3, for an aluminum color tank in good condition and $T_A = 60$ °F)

RVP = 10 psia (given)

 $P_A = 14.7 \text{ psia (assumed)}$

 $P = 5.4 \text{ psia (from Figure 4.3-6, for 10 psia Reid vapor pressure gasoline and } T_S = 62.5°F)$

D = 100 ft (given)

H = 20 ft (assumed H = 1/2 tank height)

ΔT = 21°F (average daily maximum, 68°F, minus average daily minimum, 47°F)

 $F_p = 1.20$ (from Table 4.3-1 and given specular aluminum tank color)

C = 1.0 (tank diameter is larger than 30 ft)

 $K_C = 1.0$ (value appropriate for all organic liquids except crude oil)

 L_{R} (lb/yr) =

$$(2.26 \times 10^{-2})(66) \left(\frac{5.4}{14.7-5.4}\right)^{0.68} (100)^{1.73} (20)^{0.51} (21)^{0.50} (1.20)(1.0)(1.0) =$$

$$75,323 \text{ lb/yr}$$

For the 3 months, $L_{B} = \frac{75,323}{4} = 18,831 \text{ lb}$

(b) Working Loss - Calculate using Equation 2.

$$L_W = 2.40 \times 10^{-5} M_V PVNK_N K_C$$
 (2)

where:

 $L_W = working loss (lb/yr)$

 M_{V} = 66 lb/lb-mole (from Table 4.3-1 and RVP 10 gasoline)

P = 5.4 psia (calculated for breathing loss above)

V = 2,350,000 gal

where: V (cubic feet) = $\frac{\pi D^2 h}{4}$

 $\pi = 3.141$

D = 100 ft

h = 40 ft

$$V = \frac{3.141(100)^2(40)}{4}$$

= 314,100 cubic ft

$$V (gal) = (7.48 gal/ft^3) V (ft^3)$$

V (gal) = 7.48 (314,100) = 2,349,468 gal, round to 2,350,000 gal

 $N = \frac{\text{throughput/year}}{\text{tank volume}}$

$$= \frac{(375,000 \text{ bbl})(4)(42 \text{ gal/bbl})}{2,350,000 \text{ gal}} = 26.8$$

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EMISSION FACTORS

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 $K_{N} = 1.0$ (from Figure 4.3-7 and N = 26.8)

 $K_C = 1.0$ (value appropriate for all organic liquids except crude oil)

$$L_W$$
 (lb/yr) =

 2.40×10^{-5} (66)(5.4)(2.35×10⁶)(26.8)(1.0)(1.0) = 538,705 lb/yr

For the 3 months, $L_W = \frac{538,705}{4} = 134,676$ lb

(c) Total Loss for the 3 months -

$$L_{T} = L_{B} + L_{W}$$
= 18,831 + 134,676
= 153,507 lb

Problem II - Estimate the total loss from an external floating roof tank for 3 months, based on data observed during the months of March, April and May and given the following information:

Tank description: External floating roof tank with a mechanical

(metallic) shoe primary seal in good condition; 100 ft diameter; welded tank; shell and roof

painted aluminum color.

Stored product: Motor gasoline (petroleum liquid); Reid vapor

pressure, 10 psia; 6.1 lb/gal liquid density; no vapor or liquid composition given; 375,000 bbl

throughput for the 3 months.

Ambient conditions: 60°F average ambient temperature for the 3 months;

10 mi/hr average wind speed at tank site for the 3 months; assume 14.7 psia atmospheric pressure.

Calculation: Total loss = rim seal loss + withdrawal loss +

deck fitting loss + deck seam loss.

(a) Rim Seal Loss - Calculate the yearly rim seal loss from Equation 4.

$$L_{R} = K_{S} V^{n} P * DM_{V} K_{C}$$
 (4)

where:

 $L_{R} = rim seal loss (lb/yr)$

K_S = 1.2 (from Table 4.3-4, for a welded tank with a mechanical shoe primary seal; note that external floating roofs have welded decks only)

n = 1.5 (from Table 4.3-4, for a welded tank with a mechanical shoe
 primary seal)

V = 10 mi/hr (given)

 $T_{\Lambda} = 60^{\circ} F \text{ (given)}$

 $T_S = 62.5$ °F (from Table 4.3-3, for an aluminum color tank in good condition and $T_A = 60$ °F)

RVP = 10 psia (given)

P = 5.4 psia (from Figure 4.3-6, for 10 psia Reid vapor pressure gasoline and $T_S = 62.5$ °F)

 $P_{\Delta} = 14.7 \text{ psia (assumed)}$

$$P^* = \frac{\left(\frac{5.4}{14.7}\right)}{\left(1 + \left(1 - \frac{5.4}{14.7}\right)^{0.5}\right)^2} = 0.114$$

(can also be determined from Figure 4.3-9 for P = 5.4 psia)

D = 100 ft (given)

 $M_{V} = 66 \text{ lb/lb-mole (from Table 4.3-2 and RVP 10 gasoline)}$

 $K_{C} = 1.0$ (value appropriate for all organic liquids except crude oil)

To calculate yearly rim seal loss based on the 3 month data, multiply the K $_{\rm S}$, K $_{\rm C}$, P*, D, M $_{\rm V}$, and V values, as in Equation 4.

$$L_{R} = (1.2)(10)^{1.5}(0.114)(100)(66)(1.0)$$

= 28,551 lb/yr

For the 3 months, $L_R = \frac{(28,551)}{4} = 7,138$ lb

(b) Withdrawal Loss - Calculate the withdrawal loss from Equation 5.

$$L_{W} = (0.943) \frac{QCW_{L}}{D} \left[1 + \left(\frac{N_{C}F_{C}}{D} \right) \right]$$
 (5)

where:

 L_{w} = withdrawal loss (lb/yr)

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EMISSION FACTORS

 $0 = 3.75 \times 10^5$ bbl for 3 months = 1.5 x 10^6 bbl/yr (given)

C = 0.0015 bb1/1,000 ft² (from Table 4.3-5, for gasoline in a steel tank with light rust assumed for tank in good condition as given)

 $W_{\tau} = 6.1 \text{ lb/gal (given)}$

D = 100 ft (given)

 $N_C = 0$ (value for external floating roof tanks)

F_C = 1.0 (default value when column diameter is unknown; however, there are no columns in this tank, and an F_c value is used only for calculation purposes)

To calculate yearly withdrawal loss, use Equation 5.

$$L_W (1b/yr) = \frac{(0.943)(1.5 \times 10^6)(0.0015)(6.1)}{100} + \frac{(0.0)(1.0)}{100}$$
$$= 129 \text{ lb/yr}$$

To calculate withdrawal loss for 3 months, divide by 4.

For the 3 months, $L_W = 129/4 = 32 \text{ lb}$

- (c) <u>Deck Fitting Loss</u> As stated, deck fitting loss estimation procedures for external floating roof tanks are not available. The deck fitting loss for the 3-month period is unknown and will be assumed to 0.
- (d) <u>Deck Seam Loss</u> External floating roof tanks have welded decks; therefore, there are no deck seam losses.
- (e) Total Loss for the 3 months Calculate the total loss using Equation 3.

$$L_{T} = L_{R} + L_{W} + L_{F} + L_{D}$$
 (3)

where:

 $L_T = total loss (1b/3 mo)$

 $L_p = 7,138 \text{ lb/3 mo}$

 $L_{w} = 32 \text{ lb/3 mo}$

 $L_F = 0$ (assumed)

 $r^{D} = 0$

$$L_T = 7,138 + 32 + 0 + 0$$

= 7,170 lb/3 mo

Problem III - Estimate the total loss for 3 months from an internal floating roof tank based on data observed during the months of March, April and May and given the following information:

Tank description: Freely vented internal floating roof tank;

contact deck made of welded 5 ft wide continuous sheets, with vapor mounted resilient seal; the fixed roof is supported by 6 pipe columns; tank shell and roof painted aluminum; 100 ft diameter.

Stored product: Motor gasoline (petroleum liquid); Reid vapor

pressure of 10 psia; 6.1 lb/gal liquid density; no vapor or liquid composition given; 375,000 bbl

throughput for the 3 months.

Ambient conditions: 60°F average ambient temperature for the 3 months;

10 mi/hr average wind speed at the tank site for

the 3 months; assume 14.7 psia atmospheric

pressure.

Calculation: Total loss = rim seal loss + withdrawal loss +

deck fitting loss + deck seam loss.

(a) Rim Seal Loss - Calculate yearly rim seal loss using Equation 4.

$$L_{R} = K_{S} V^{n} P^{*} D M_{V} K_{C}$$
 (4)

where:

 $L_R = rim seal loss (lb/yr)$

K_S = 6.7 (from Table 4.3-4; for a welded tank with a vapor mounted resilient seal and no secondary seal)

V = 10 mi/hr (given)

n = 0 (from Table 4.3-4 for a welded tank with a vapor mounted resilient seal and no secondary seal)

P* = 0.114 (calculated in Problem II)

D = 100 ft (given)

 $M_V = 66 \text{ lb/lb-mole (from Table 4.3-2 and RVP 10 gasoline)}$

 $K_{C} = 1.0$ (value appropriate for all organic liquids except crude oil)

$$L_{R} = 6.7(10)^{0}(0.114)(100)(66)(1.0)$$

= 5,041 lb/yr

For the 3 months, $L_R = \frac{5,041}{4} = 1,260 \text{ lb}$

(b) Withdrawal Loss - Calculate using Equation 5.

$$L_{W} = (0.943) \frac{QCW_{L}}{D} \left[1 + \left(\frac{N_{C}F_{C}}{D} \right) \right]$$
 (5)

where:

L_t = withdrawal loss (lb/yr)

 $Q = 1.5 \times 10^6$ bbl/yr (calculated in Problem II)

 $C = 0.0015 \text{ bbl/1,000 ft}^2 \text{ (from Table 4.3-5, light rust)}$

 $W_{T} = 6.1 \text{ lb/gal (given)}$

D = 100 ft (given)

 $N_C = 6$ (given)

 $F_{C} = 1.0$ (default value since column construction details are unknown)

$$L_{W} = \frac{(0.943)(1.5\times10^{6})(0.0015)(6.1)}{100} \left[1 + \left(\frac{(6)(1.0)}{100}\right)\right]$$
= 137 lb/yr

For the 3 months, $L_W = \frac{137}{4} = 34 \text{ lb}$

(c) Deck Fitting Loss - Calculate using Equation 6.

$$L_{F} = F_{F}P*M_{V}K_{C}$$
 (6)

where:

 $L_r =$ deck fitting loss (lb/yr)

 $F_F = 700 \text{ lb-mole/yr (interpreted from Figure 4.3-10, given tank diameter of 100 ft)}$

P* = 0.114 (calculated in Problem II)

 $M_V = 66 \text{ lb/lb-mole}$ (from Table 4.3-2 and RVP 10 gasoline)

 $K_C = 1.0$ (value appropriate for all liquid organics except crude oil)

$$L_F = 700(0.114)(66)(1.0)$$

= 5.267 lb/yr

For the 3 months, $L_F = \frac{5,267}{4} = 1,317$ lb

Evaporation Loss Sources

4.3-33

(d) Deck Seam Loss - Calculate using Equation 7.

$$L_{D} = K_{D}S_{D}^{D2}P * M_{V}K_{C}$$
 (7)

where:

 $L_{D} = deck seam loss (lb/yr)$

K_D = 0 for welded seam deck, therefore

 $L_D = 0$

(e) Total Loss for 3 months - Calculate from Equation 3.

$$L_{T} = L_{R} + L_{W} + L_{F} + L_{D}$$
 (3)

where:

 $L_T = total loss (lb/yr)$

 $L_{p} = 1,260 \text{ lb/3 mo}$

 $L_{w} = 34 \text{ lb/3 mo}$

 $L_{\rm F} = 1,317 \text{ lb/3 mo}$

 $L_{n} = 0$

$$L_T = 1,260 + 34 + 1,317 + 0$$

For the 3 months, $L_T = 2,611 \text{ lb}$

References for Section 4.3 -

- VOC Emissions From Volatile Organic Liquid Storage Tanks Background <u>Information for Proposed Standards</u>, EPA-450/3-81-003a, U. S. Environ-mental Protection Agency, Research Triangle Park, NC, July 1984.
- 2. Background Documentation for Storage of Organic Liquids, EPA Contract No. 68-02-3174, TRW Environmental, Inc., Research Triangle Park, NC, May 1981.
- 3. Petrochemical Evaporation Loss From Storage Tanks, Bulletin No. 2523, American Petroleum Institute, New York, NY, 1969.
- 4. Henry C. Barnett, et al., Properties of Aircraft Fuels, NACA-TN 3276, Lewis Flight Propulsion Laboratory, Cleveland, OH, August 1956.
- 5. Evaporation Loss From External Floating Roof Tanks, Second Edition, Bulletin No. 2517, American Petroleum Institute, Washington, D. C., 1980.

- 6. Evaporation Loss From Internal Floating Roof Tanks, Third Edition, Bulletin No. 2519, American Petroleum Institute, Washington, D. C., 1983.
- 7. Use of Variable Vapor Space Systems To Reduce Evaporation Loss, Bulletin No. 2520, American Petroleum Institute, New York, NY, 1964.

APPENDIX D

TABLE OF UNCONTROLLED FUGITIVE EMISSION FACTORS FOR THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY

TABLE D-1. AVERAGE FUGITIVE EMISSION FACTORS FOR THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY (SOCMI)^a

Fugitive-emission source	Emission factor (lb/h)
Pump seals	
Light liquids Heavy liquids	0.11 0.047
Valves (in-line)	
Gas Light liquid Heavy liquid	0.012 0.016 0.00051
Gas safety-relief valves	0.23
Open-ended lines	0.0037
Flanges	0.0018
Sampling connections	0.033
Compressor seals	0.50

Emission Factors for Equipment Leaks of VOC and HAP, EPA-450/3-86-002, January 1986, Table 3-4. These factors take into account a leak frequency determined from field studies in the synthetic organic chemicals manufacturing industry. Light liquids have a vapor pressure greater than 0.1 psia at 100°F.

TABLE D-2. LEAKING AND NONLEAKING AVERAGE FUGITIVE EMISSION FACTORS FOR THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY (SOCMI)

Fugitive- emission source	Leaking (>10,000 ppm) emission factor (1b/h)	Nonleaking (<10,000 ppm) emission factor (1b/h)
Pump seals		
Light liquids Heavy liquids	0.96 0.85	0.026 0.030
Valves (in-line)		
Gas Light liquid Heavy liquid	0.099 0.19 0.00051	0.0011 0.0038 0.00051
Gas safety-relief valves	3.72	0.098
Open-ended lines	0.0263	0.0033
Flanges	0.083	0.00013
Sampling connections	•	
Compressor seals	3.54	0.20

Emission Factors for Equipment Leaks of VOC and HAP, EPA-450/3-86-002, January 1986, Table 3-3. These factors take into account a leak frequency determined from field studies in the synthetic organic chemicals manufacturing industry. Light liquids have a vapor pressure greater than 0.1 psia at 100°F.

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APPENDIX E

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"Compilation of Air Pollutant Emission Factors"

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APPENDIX F

UNIT CONVERSION FACTORS

(FROM U.S. COAST GUARD COMMANDANT INSTRUCTION M.16465.12A

CONVERSION FACTORS

To Convert	То	Multiply by
Length		
inches	millimeters	25.4*
inches	feet	0.0833
feet	inches	12*
feet	meters	0.3048*
feet	yards	0.3333
feet	miles (U.S. statute)	0.0001894 3*
yards	feet	0.0005682
yards	miles (U.S. statute)	5280°
miles (U.S. statute)	feet	1760*
miles (U.S. statute)	yards meters	1609
miles (U.S. statute)	nautical miles	0.868
miles (U.S. statute)	feet	3.281
meters meters	vards	1.094
meters	miles (U.S. statute)	0.0006214
nautical miles	miles (U.S. statute)	1.152
naucai mies		
Area		6.452
square inches	square centimeters	0.006944
square inches	square feet square inches	144*
square feet	square meters	0.09290
square feet	square feet	10.76
square meters square miles	square yards	3,097,600*
square yards	square feet	9*
aquate yarus	0422.0	-
Volume		16.39
cubic inches	cubic centimeters	
cubic inches	cubic feet	0.0005787 1728*
cubic feet	cubic inches	0.02832
cubic feet	cubic meters	7.481
cubic feet	U.S. gallons cubic feet	35.31
cubic meters	quarts (U.S. liquid)	1.057
liters	liters	0.9463
quarts (U.S. liquid)	barreis (petroleum)	0.02381
U.S. gallons	cubic feet	0.1337
U.S. galions U.S. galions	Imperial gallons	0.8327
barrels (petroleum)	U.S. gallons	42*
Imperial gallons	U.S. gallons	1.201
milliliters	cubic centimeters	1*
Time seconds	minutes	0.01667
seconds	hours	0.0002778
seconds	days	0.00001157
minutes	seconds	60*
minutes	hours	0.01667
minutes	days	0.0006944
hours	seconds	3600*
hours	minutes	60*
hours	days	0.04167
	· · · · · · · · · · · · · · · · · · ·	

^{*}Exact value

(Continued)

To Convert	То	Multiply by
Mass or Weight		
pounds	kilograms	0.4536
pounds	short tons	0.0005*
pounds	long tons	0.0004464
pounds	metric tons	0.0004536
tons (short)	pounds	2000*
tons (metic)	pounds	2205
tons (long)	pounds	2240°
kilograms	pounds	2.205
tonnes (metic tons)	kilograms	1000*
Energy		in the second se
calories	Btu	0.003968
calories	joules	4.187
Btu (British thermal units)	calories	252.0
Btu	joules	1055
joules	calories	0.2388
joules	Btu	0.0009479
Velocity		· · · · · ;
feet per second	meters per second	0.2040
feet per second	miles per hour	0.3048 0.6818
feet per second	knots	
meters per second	feet per second	0.5921
meters per second	miles per hour	3.281
miles per hour	meters per second	2.237
miles per hour	feet per second	0.4470
knots	•	1.467
knots	meters per second	0.5148
knots	miles per hour	1.151
RIIOIS	feet per second	1.689
	ensity	*** · ·
pounds per cubic foot	grams per cubic centimerter	0.01600
grams per cubic centimeter	pounds per cubic foot	0.01602 62.42
grams per cubic centimeter	kilograms per cubic meter	1000*
kilograms per cubic meter	grams per cubic centimeter	0.001
Pressure		0.001
pounds per square inch (absolute)	kilonoudono nos equas	
(psia)	kilonewtons per square meter (kN/m²)	6.895
psia	atmospheres	0.0680
psia	inches of water	27.67
psia	millimeters of mercury (torr)	51.72
pounds per square inch (gauge)	psia	add 14.70
(psig)		14.70
millimeters of mercury (torr)	psia	0.01934
millimeters of mercury (torr)	kN/m²	0.1333
inches of water	psia	0.03614
kilograms per square centimeter	millimeters of mercury (torr)	735.6
inches of water	kN/m²	0.2491
kilograms per square centimeter	atmospheres	0.9678
atmospheres	kN/m²	101.3
kilograms per square centimeter	psia	14.22
atmospheres	psia	14.70
bars	kN/m²	100*
kilonewtons per square meter (kN/	psia	0.1450
m²)		
bars	atmospheres	0.9869
kilonewtons per square meter (kN/	atmospheres	0.009869
m³)		0.009669
bars	kilograms per square centimeter	1.020
Viscosity		,
Viscosity centipoises	moundo mon forth	
pounds per foot per second	pounds per foot per second	0.0006720
positios per toot per second	centipoises	1488

^{*}Exact value

(Continued)

To Convert	То	Multiply by
centipoises	poises	0.01*
centipoises	newton seconds per square meter	0.001*
poises	grams per centimeter per second	1*
grams per centimeter per second	poises	1*
newton seconds per square meter	centipoises	1000*
Thermal Conductivity		
Btu per hour per foot per *F	watts per meter-kelvin	1.731
Btu per hour per foot per *F	kilocalories per hour per meter per °C	1.488
watts per meter-kelvin	Btu per hour per foot per *F	0.5778
kilocalories per hour per meter per	watts per meter-kelvin	1.163
*C	Watto por motor motor.	
kilocalories per hour per meter per *C	Btu per hour per foot per *F	0.6720
Heat Capacity		
Btu per pound per *F	calories per gram per °C	1*
Btu per pound per *F	joules per kilogram-kelvin	4187
joules per kilogram-kelvin	Btu per pound per *F	0.0002388
calories per gram per °C	Btu per pound per *F	1*
Concentration (in water solution)		
parts per millon (ppm)	milligrams per liter	1*
milligrams per liter	ppm	1*
milligrams per cubic meter	grams per cubic centimeter	1X10-*
grams per cubic centimeter	milligrams per cubic meter	1X10°
grams per cubic centimeter	pounds per cubic foot	62.42
pounds per cubic foot	grams per cubic centimeter	0.01602
Temperature		
degrees Kelvin (*K)	degrees Rankine (*R)	1.8*
degrees Rankine (*R)	degrees Kelvin (*K)	0.5556
degrees centigrade (°C)	degrees Fahrenheit (*F)	first multiply by 1.8, then add 32
degrees Fahrenheit (*F)	degrees centigrade (°C)	first subtract 32, then multiply by 0.5556
degrees centigrade (°C)	degrees Kelvin (*K)	add 273.2
degrees Fahrenheit (°F)	degrees Rankine (*R)	add 459.7
Flow		
cubic feet per second	U.S. gallons per minute	448.9
U.S. gallons per minute	cubic feet per second	0.002228
Universal Gas Constant (R)		•
8.314 joules per gram mole- kelvin		
1.987 calories per gram mole- kelvin		
1.987 Btu per pound mole per		
10.73 psia-cubic feet per pound mole per *F		
82.057 atm-cubic centimeters		
62.361 millimeters mercury liter per gram mole-kelvin		•