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HYDROCARBON POLLUTANTS FROM STATIONARY SOURCES

by

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Contract No. 68-02-1319
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16. ABSTRACT The report gives results of a study of hydrocarbon pollutants from stationary sources. Early in the study, readily available information was assembled on stationary sources of hydrocarbon emissions and effluents. Information was also obtained on process descriptions, operating parameters, current controls, and control problems. As the data base was assembled, the data was divided into major categories for subsequent evaluation. Pollutants from process streams were evaluated along with fugitive emissions associated with equipment leaks (e.g., from pumps, valves, and flanges). Emissions were also included from open sources (e.g., forest fires) and from natural sources (e.g., pine forests). Information in each category was divided into logical classes and grouped for further assessment of emissions and effluents from processes and operations. A list of the emission and effluent rates from the processes and operations studied is in the Appendix. Major emission and effluent sources in each category were identified and assessed as to source controllability. Specific processes and operations representing the greatest potential for the reduction of hydrocarbon emissions and effluents by the application of central technology were selected for further study.

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Emission	Fugitive Emissions	
Effluents	Open Sources	
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1.0 INTRODUCTION

The purpose of this report is to provide the Environmental Protection Agency with an identification and quantification of the important multi-media organic emissions, effluents, and wastes from stationary sources on a nationwide basis.

This report divides the major pollutant sources into thirteen categories. The organic emissions and effluents from these categories are quantified and the major sources are identified within the categories. The sources with the largest potential for reduction of organic emissions and effluents are identified and the controls required to achieve the reductions are discussed. Because all but a few of the numbers in this report are estimates of indeterminate accuracy, errors of 10% and, in some cases, 15% are to be expected.

1.1 Objectives

The objective of this program is to describe the relative importance of existing multi-media organic emissions and effluents from domestic stationary sources. The quantity and control potential of the discharges are addressed. The stationary sources considered are grouped in thirteen major categories. These categories are as follows:

Category	Description
I	Fossil fuel extraction (gas wells, oil wells, oil/gas wells, coal mines, etc.)
II	Fossil fuel processing (natural gasoline plants, sulfur recovery, coal preparation, etc.
III	Fossil fuel transportation, storage, and distribution (pipelines, gasoline transfer, etc.)

Category	Description
IV	Fossil fuel refining (petroleum refineries, coke ovens, etc.)
V	Fossil fuel combustion (commercial, industrial, utility, etc.)
VI	Fossil fuel feedstock chemical processing (all processes which start with feedstock derived from fossil fuels and produce intermediate or end products)
VII	Non-combustion organic chemical utilization (industrial/commercial, printing, dry cleaning, etc.)
VIII	Agricultural and forest products (corn oil, turpentine, food processing, etc.)
IX	Open sources (agricultural burning, etc.)
X	Natural sources (pine forests, etc.)
XI	Solid waste disposal (solid waste incineration, landfilling, etc.)
XII	Municipal wastewater treatment
XIII	Other sources (forest fires, etc.)

1.2 Approach

In the initial phase of the program, readily available information on stationary sources of organic emissions and effluents was assembled. Information concerning process descriptions,

operating parameters, current organic chemical controls, and control problems were also obtained. The information sources include previous and current EPA studies, new source performance standard studies, known emission factors, Radian files, and other published or unpublished information.

As the data base was assembled, the data was divided into the major categories for subsequent evaluation. Pollutants resulting from process streams were evaluated along with "fugitive" type emissions associated with equipment leaks such as those from pumps, valves, and flanges. Emissions resulting from "open" sources such as forest fires and from natural sources such as pine forests are also included.

The information collected for each category was divided into logical classes and grouped for further assessment of emissions and effluents from processes and operations. A complete list of the emission and effluent rates from the processes and operations studied is presented in Section 2. An attempt was made to identify the major sources of emissions and effluents from each category.

The controllability of the source was assessed. Then, specific processes and operations that represented the greatest potential for the reduction of organic emissions and effluents by the application of control technology were selected for further study.

The selected processes and operations are described in detail in Section 3. The descriptions give considerable attention to the specific nature and source of the organic emissions and effluents. Also discussed in detail are the control technologies required for reduction of the emission and effluent rate, and the potential reduction in organic pollutants resulting from the application of that control technology.

1.3 Methodology

Procedures were established for assessing the emission and effluent rates for the various sources and for determining the control of these sources. The procedures apply to all the categories studied.

The quantification of the organic pollutants was accomplished by assembling readily available information. Occasionally, sources gave conflicting information on pollutant quantities. In these instances, several approaches were used to select the source which provided the most accurate information. These approaches are discussed below.

1) Frequently, information sources provide an evaluation of the quality of the data used to estimate the pollutant rates. This evaluation was particularly valuable in the fossil fuel feed stock chemical processing (FFFCP) category. The definitions of the data quality and an example of the distribution of the quality in the FFFCP category is summarized as follows:

Quality	Meaning	Percent of Total Data
A	Adequate data of reasonable accuracy.	1%
B	Partially estimated data of indeterminate accuracy.	55%
C	Totally estimated data of indeterminate accuracy.	36%
D	No data; estimates based on generalized loss factor.	8%

When conflicting data were encountered and the data quality was rated, the best quality data were used.

2) Occasionally, data of the same estimated quality gave conflicting pollutant rates or conflicting data had no estimated quality. In these instances, the reports were assessed and references were checked when necessary to evaluate the data and procedures used. Then, the best data were selected on that basis.

3) Finally, if none of the above information was provided, engineering judgement was used to select the best data. The engineering judgement was based on a knowledge of the process operation and pollutant rates from similar processes.

Specific examples of poor quality data or a lack of data are discussed in Section 3.

1.4 Definitions

Three terms are used throughout this report. The term emissions is used to describe pollutants emitted to the atmosphere. Effluents refers to pollutants emitted to bodies of water. Wastes refers to solid waste emissions. These terms and some other terms are defined further in the following paragraphs.

Atmospheric Pollutants

The atmospheric pollutants are separated into volatile organics and organic particulates. Each emission type is analyzed

and discussed separately since the two types have different effects on the ambient air quality. Also, the control technologies for the two types are significantly different and the potentials for emission reduction must be assessed separately.

Special emphasis was given to the quantification and control of the volatile organics. The organic particulate emissions were determined by estimating the fraction of organics present in the total particulate emissions. Where possible, the emissions were quantified by assuming the current degree of control practiced today. Reduction potentials were determined by estimating emissions to be fully controlled by currently available technology.

Water Effluents

In general, current estimates of organic water effluents are lacking. However, EPA publications of development documents for effluent limitations guidelines are available for a large segment of industry. The guidelines provide information sources relating to effluent limitations for 1977 (Best Practicable Control Technology Currently Available, BPCTCA) and 1983 (Best Available Technology Economically Achievable, BATEA). Consequently, this report assumes 1977 effluent limits as "current" control levels and the 1983 effluent limits as the control technology providing potential effluent reductions. This assumption may provide higher rates and reductions than actually anticipated since the 30-day limitations were used and these are usually higher than the average yearly effluent. However, the assumption is generally consistent within the report and consequently, the effluent and reduction comparisons should be realistic.

The organic content of water effluents was selected as the parameter to assess the organic effluent quantity from the processes and operations studied. Organic content refers to the actual quantity of organics present in effluent water streams. This parameter was selected in the study as the best measure of organics actually introduced into the environment. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) are more commonly used parameters associated with water quality studies; however, these parameters do not estimate the actual mass rate of organic effluents. For example, BOD is the most commonly reported parameter in the literature, but many organic compounds are not biologically degradable and their presence is not indicated by BOD measurements.

The organic content of water effluents is estimated from information on biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC). The organic content of effluents was estimated by several methods which are listed in decreasing order of preference:

1) from the literature, determine correlations between BOD, COD, or TOC and organic content,

2) from TOC information, calculate the organic content by assuming the composition and average molecular weight of the organic,

3) from BOD:TOC correlations in literature for similar processes, calculate the organic content as in 2), or

4) from COD information, estimate the carbon present assuming complete oxidation of the organic and calculate the organic content as in 2).

There are inaccuracies associated with the above methods for estimating organic content of water effluents. The first method should be reasonably accurate. The basic assumption associated with the other methods is that, since TOC is directly related to the organic content, the organic composition of the effluent can be represented by one typical compound. The typical compound is selected as the major product from a process or operation. For special cases, such as polymerization, the monomer is selected, or for refineries, a typical or average hydrocarbon is selected. This selection is based on the assumption that feed material to processes and by-products from processes which can contribute to effluent rates are similar to the products of the process. The accuracy of this assumption decreases for processes having organic effluents that are not similar to the product, such as diluent streams, lubricants, solvent refining, and inhibitors.

Other organic water effluent parameters examined are oil and grease (O/G) effluents and suspended solids (SS). Suspended solids from the processes studied here usually contain some organic matter. However, information on the organic content of SS is very limited. Consequently, the total SS rate is reported with no breakdown of organic content. For this report, greatest emphasis in assessing importance of waste water effluents is placed on organic content of the water calculated from BOD, COD, and TOC.

Solid Wastes

The solid wastes produced are not listed by category since adequate information was not available. Most operations and processes dispose of solid waste on site by incineration, landfill, or other means, or they retain contractors to properly dispose of solid wastes off site. The solid waste that is

properly disposed of is not considered a pollutant. However, the solid waste category does examine the environmental impact of disposal techniques for municipal facilities handling solid wastes. In this manner, the environmental impacts of solid wastes are assessed and compared with atmospheric emissions and water effluents from other categories, since solid wastes ultimately result in atmospheric emissions by decomposition or incineration and water effluents by leaching.

Stationary Sources

Most organic pollutant sources involve fossil fuels. These fossil fuel operations involve extraction, various processing and handling steps, and utilization. Other sources not related to fossil fuels include agricultural and forest products, open and natural sources, solid waste disposal and municipal sewage.

Some sources not related to fossil fuels are also not point sources. An example of this is the natural source category. This category examines organic emissions from such natural sources as living plants, decomposition of organic material and enteric fermentation in animals. Evaluation of emissions from natural sources allows comparisons between them and the fossil fuels categories. These comparisons are made so that the results of pollution controls can be determined realistically on a mass basis.

Hydrocarbons

In general, organic compounds are composed primarily of carbon and other elements such as hydrogen, oxygen, nitrogen and halogens. Hydrocarbons refer to a specific class of organics composed solely of carbon and hydrogen. For the purposes of this report, the term "hydrocarbons" sometimes refers to other organic materials also.

Organic Chemical Control Technology

The reduction in organic emissions and effluents from the major categories and individual processes and operations is determined from current control technol gy. Where possible, the controls for pollutants from specific sources are those commonly used. In some cases, commonly used specific control information was not available. Engineering judgement was then used to determine a specific control or typical control efficiency for the class or type of emission to determine a reduction potential. As an example: it is beyond the scope of this report to determine the most desirable control for a process vent stream if controls are not used in the industry. However, most process vents can be controlled by adsorption, absorption, condensation or incineration. These controls have typical operating efficiencies and control potentials can be estimated. The selection of a specific control as the most desirable in actual applications will require an indepth study and may differ for the same process from one location to the next.

1.5 Summary of Results

1. Total volatile organic emissions are about an order of magnitude higher than the organic particulate emissions and the organic water effluents. Total non-methane volatile organic emissions are two-to-three times as high as either the organic particulate emissions or the organic water effluents.

2. Forty-eight percent of the non-methane volatile organic emissions and 75% of the organic particulate emissions are controllable. About half of these controllable volatile emissions

and one-third of the controllable particulate emissions are from open burning sources which usually occur in remote areas and contribute little to photochemical smog. These open sources account for over 20% of the total non-methane organic emissions.

3. Thirty-five percent of the particulate emissions are from the plywood and veneer industry and grain and feed processors, all of which are controllable.

4. Effluents from natural sources were not considered because a natural BOD is inherent in the aquatic ecosystem. Thirty-five percent of the remaining effluents are considered controllable. Twenty-nine percent could be controlled with tertiary control of municipal waste water treatment facilities.

5. Process emissions should be considered foremost because they tend to be in populated areas and are amenable to control technology. Also, most toxic emissions are from these sources.

6. Fifty percent of the process volatile non-methane emissions are from non-combustion organic chemical utilization and chemical processing. Another 45% are from fossil fuel refining and transportation. There is no single large controllable emission source.

7. Agricultural and forest products account for 90% of the process organic particulate emissions.

Seventy-five percent of these emissions are from the plywood and veneer industry and from grain and feed processors.

8) Fifty percent of the process organic effluents are from agricultural and forest products; 47% are from chemical processing. These is no single large controllable effluent source.

1.6 Conclusions and Recommendations

This report incorporates several unique features that distinguish it from previous studies concerning organic chemical pollutants from stationary sources. These features are as follow:

- It is the first report to assess multi-media impacts together for comparison.

- While it does not generate new data, it pulls previous studies together into one package to compare the impacts of important processes and operations on a mass emission basis.

- It is the first report to break atmospheric emissions of organics down into volatiles and particulates for comparison.

- It is the first in depth look at major emission and effluent sources from organic chemical processing.

- It is the first attempt to address the quantities of controllable emissions and effluents from a broad cross section of sources and to assess and compare the data.

Conclusions

These unique features and the methodology of the report allow the data to be processed to make the following conclusions:

1) The organic emissions and effluents are a reasonably complete assessment of the major organic pollutants from the respective industries.

2) As a result of the time allocated to assess the major categories, the data for process type categories are reasonably firm while the data for the other categories (especially natural sources, open sources and "other" sources) are not as firm.

3) Other factors, such as geographical location of sites, reactivity, toxicity of pollutants, cost of controls, and meteorological characteristics, must be considered in addition to mass pollutant rates to develop a control strategy in the U.S. Pollutant sources should be considered on an area-wide basis. These factors and the contribution of all significant point sources within these areas should also be considered.

4) The quantities of organic atmospheric emissions are greater than organics in water effluents; however, the air emissions are dispersed in a larger medium.

5) Open sources, which usually occur in remote areas, are the largest source of non-methane organic emissions. Other sources of volatile organic emissions are varied; none is significantly large.

6) About half of the non-methane volatile emissions, most from fossil fuel-related industries, are controllable.

7) Control of grain and feed processors and the plywood and veneer industry could reduce particulate organic emissions by one third.

8) Natural sources of organic effluents were not considered. Tertiary control of municipal waste water treatment facilities would greatly reduce organic effluents. The pulp and paper industry is the only other contributor of any consequence.

Recommendations

The evaluation of organic pollutants from stationary sources and their control potential leads to the identification of several areas for further consideration. There are:

1) Specific problem areas relating to organic pollutants should be identified and assessed on a source-by-source basis.

2) Additional field work and sampling should be conducted to verify emission and effluent rates and identify components.

3) The processes in particular problem areas with the greatest degree of control should receive special attention.

4) The chemical processing industry is so complex and diverse that it requires special attention. The mass emission and effluent rates should be verified and expanded to improve the quality of available data. The pollutants should be characterized by monitoring. Specific geographical sites and complexes should be considered.

5) Additional work is needed to identify BOD/COD/TOC/Total Organic relationships.

6) Information should be generated on the quantity, composition and ultimate fate of solid wastes.

7) Additional data is needed regarding the fate of pollutants in the environment and their long-term effects.

8) More work is needed to assess the toxicity and health effects of the pollutants with

proper consideration for composition changes and their ultimate fate.

9) The cost effectiveness of various control strategies should be considered so that relationships between control potentials and control costs can be optimized to reduce pollutants to required levels.

2.0 RESULTS

The organic emissions and effluents from the major categories are examined in this section so that the impact of emission controls may be assessed. A listing of the emissions and effluents from the selected processes is presented in Table 2.0-1. Reduction potentials are presented in Table 2.0-2. A summary of these two is presented in Table 2.0-3. A more complete listing of all the emissions and effluents considered in the fossil fuel feedstock chemical processing category is presented in the Appendix.

The areas representing the greatest potential for reduction are discussed in the following sections.

2.1 Overall Organic Emissions and Effluents

The emissions and effluents and their control potentials from all the categories are discussed in this section. The effect of controls for the various categories and processes are assessed.

The total volatile organic emissions are about an order of magnitude higher than the organic particulate emissions and the water effluents. Non-methane volatile organics alone are only three times the organic particulates and twice the organic water effluents. The controllable volatile emissions are also only 2-3 times the controllable organic particulates and controllable organic water effluents.

2.1.1 Atmospheric Emissions

The atmospheric emissions are divided into volatiles and particulates. Both types of emissions are discussed.

TABLE 2.0-1

ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emissions: Volatile Organics (MT/yr)	Atmospheric Emissions: Organic Particulates (MT/yr)	Water Effluents (MT/yr)
I. Fossil Fuel Extraction	*2,510,000	--	
Major Sources:			Major Sources:
Coal Production	•1,610,000	--	Crude Oil and Associated Gas Production 29,000
Crude Oil and Associated Gas Production	* 630,000	--	
Natural Gas Extraction	* 270,000	--	--
II. Fossil Fuel Processing	•1,716,400	7,300	--
Major Sources:			
Natural Gasoline Plants	•1,714,000	--	--
Coal Preparation Plants	2,400	7,300	--
III. Fossil Fuel Transportation, Storage, and Distribution	2,071,000	77,300	--
Major Sources:			
Crude Oil Storage	526,000	--	--
Gasoline Service Station Automobile Filling	467,000	--	--
Gasoline Service Station Underground Tank Filling	399,000	--	--
Gasoline Bulk Station Storage	109,000	--	--

TABLE 2.0-1 (Continued)

ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

	Category	Atmospheric Emissions: Volatile Organics (MT/yr)	Atmospheric Emissions: Organic Particulates (MT/yr)		Water Effluents (MT/yr)
IV.	Fossil Fuel Refining	2,173,500	269,000		34,700
	Major Sources:			Major Sources:	
	Storage, Petroleum Refineries	965,000	--	Petroleum Refineries	23,600
				Coke Manufacturing	11,100
	Blowdown, Petroleum Refining	328,000			
	Process Drains and Waste Water Separators, Petroleum Refineries	216,000			
	Fluid Catalytic Cracker Unit, Petroleum Refineries	147,000			
	Vacuum Jets, Petroleum Refineries	117,000			
V.	Fossil Fuel Combustion	724,000	--		--
	Major Sources:				
	Industrial Internal Combustion Gas	*237,000	--		--
	Utilities - coal fired	105,000	--		--
	Industrial - natural gas	* 76,400	--		--
	Industrial Internal Combustion-Oil	68,200	--		--
	Industrial/Commercial Fuel Oil	56,400	--		--

TABLE 2.0-1 (Continued)

ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emissions: Volatile Organics (MT/yr)	Atmospheric Emissions: Organic Particulates (MT/yr)		Water Effluents (MT/yr)
VI. Fossil Fuel Feedstock Chemical Processing	1,400,000	45,800		460,000
Major Sources:			Major Sources:	
Ammonia	* 323,000	--	Dyes and Pigments	60,800
Carbon Black	96,700	3,674	Polyvinyl Chloride	32,300
Acrylonitrile	83,000	--	Methyl Methacrylate	30,900
Ethylene Dichloride	56,300	--		
Toluene	51,000	--		
Carbon Tetrachloride	43,400	--		
VII. Noncombustion Organic Chemical Utilization	3,529,000	--		100
Major Sources:			Major Sources:	
Rubber and Plastics Processing	1,280,000	--		100
Paper and Paperboard Coating	475,000	--		
Sheet, Strip and Coil Coating	469,000	--		
Miscellaneous Surface Coating	385,000	--		
Dry Cleaning	367,000	--		
Fabric Treatment	210,000	--		
Graphic Arts-Gravure	107,000	--		

TABLE 2.0-1 (Continued)

ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emissions: Volatile Organics (MT/yr)	Atmospheric Emissions: Organic Particulates (MT/yr)		Water Effluents (MT/yr)
VII. Noncombustion Organic Chemical Utilization				
Major Sources: cont.				
Cast Iron Foundry Core Ovens	102,000	--		--
Auto and Truck Coating	100,000	--		--
VIII. Agricultural and Forest Products	508,000	3,324,000		488,000
Major Sources:			Major Sources:	
Pulp and Paper	143,000	--	Pulp & Paper	208,000
Wood Waste Combustion	137,000	--	Processed Fruits & vegetables	92,200
Beer Brewing	67,800	108,000	Beer Brewing	73,800
Fruit and Vegetables Processing	47,700	--		
Tobacco	39,710	--		
IX. Open Sources	3,010,000	973,000		--
Major Sources:			Major Sources:	
Agricultural Field Burning of Land Clearance	2,540,000	821,000		--
Prescribed Forest Burning	472,000	152,000		--

TABLE 2.0-1 (Continued)

ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emissions: Volatile Organics (MT/yr)	Atmospheric Emissions: Organic Particulates (MT/yr)	Water Effluents (MT/yr)	
X. Natural Sources	*85,300,000	1,500,000	N/A	
Major Sources:			Major Sources:	
Decomposition of Organic Material	*71,700,000	--	N/A	
Living Plants	9,100,000	1,500,000		
Enteric Fermenation in Animals	* 4,500,000	--	N/A	
XI. Solid Waste Disposal	2,690,000	640,000	736,000	
Major Sources:			Major Sources:	
Open Burning of Refuse	1,660,000	378,000	Leachate From Open Dumps	293,000
Open Burning of Uncollected Urban Refuse	345,000	80,000	Leachate From Burning Dumps	245,000
Open Burning of Rural Refuse	322,000	74,000	Leachate From Landfills	171,000
Methane from Decomposition in Dumps and Landfills	*247,000	0	Leachate From Sanitary Landfills	25,350
Municipal Incineration	51,500	65,400		
XII. Municipal Sewage Disposal	--	--	9,980,000	
Major Sources:			Major Sources:	
			Septic Tanks	5,700,000
			Primary Treatment	1,370,000
			None or Minor Treatment	1,020,000

N/A - Not applicable natural sources of organics in surface waters are not considered.

TABLE 2.0-1 (Continued)

ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emissions: Volatile Organics (MT/yr)	Atmospheric Emissions: Organic Particulates (MT/yr)	Water Effluents (MT/yr)
XIII. Other Sources	917,000	234,000	--
Major Sources:			
Forest Wildfires	791,000	213,000	--
Structural Fires	64,800	20,900	--
Coal Refuse Fires	61,200		--

*Indicates emissions consisting mostly of methane.
N/A - not available.

TABLE 2.0-2

POTENTIAL REDUCTIONS OF ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

	Category	Atmospheric Emission Reductions: Volatile Organics (MT/yr)	Atmospheric Emission Reductions: Organic Particulates (MT/yr)		Water Effluents (MT/yr)
I.	Fossil Fuel Extraction	*1,830,000	--		29,000
	Major Sources:			Major Sources:	
	Coal Extraction	*1,290,000	--	Crude Oil & Associated Gas Production	29,000
	Crude Oil & Associated Gas Production	* 380,000	--		
	Natural Gas Extraction	* 162,000	--		--
II.	Fossil Fuel Processing	1,030,000	3,650		--
	Major Sources:			Major Sources:	
	Natural Gasoline Plants	1,030,000	--		--
	Coal Preparation Plants	--	3,650		--
III.	Fossil Fuel Transportation, Storage, and Distribution	1,363,000	69,600		--
	Major Sources:			Major Sources:	
	Service Station Auto Filling	420,000	--		--
	Service Station Underground Tank Filling	383,000	--		--
	Crude Transportation - Storage	246,000	--		--
	Gasoline Bulk Station - Storage	104,000	--		--
	Gasoline Bulk Station - Loading	91,600	--		--

TABLE 2.0-2 (Continued)

POTENTIAL REDUCTIONS OF ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emission Reductions: Volatile Organics (MT/yr)	Atmospheric Emission Reductions: Organic Particulates (MT/yr)		Water Effluents (MT/yr)
IV. Fossil Fuel Refining	1,400,000	243,600		26,360
Major Sources:			Major Sources:	
Petroleum Refining - Storage	452,000	--	Petroleum Refining	16,700
Petroleum Refining - Blowdown	318,000	--	Coke Manufacturing	9,680
Petroleum - Process Drains and Waste Water Separators	195,000	--	--	--
Petroleum Refineries-FCCU	147,000	--		--
Petroleum Vacuum Jets	117,000	--		--
V. Fossil Fuel Combustion	*314,000	--		--
Major Sources:			Major Sources:	
Industrial Internal Combustion - Gas	234,600	--		
Utility Internal Combustion - Oil	67,500	--		--
VI. Fossil Feedstock Chemical Processing	1,270,000	40,900		400,000
Major Sources:			Major Sources:	
Ammonia	319,500	--	Dyes and Pigments	52,900
Carbon Black	96,700	--	Polyvinyl Chloride and Copolymers	28,100

TABLE 2.0-2 (Continued)

POTENTIAL REDUCTIONS OF ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emission Reductions: Volatile Organics (MT/yr)	Atmospheric Emission Reductions: Organic Particulates (MT/yr)		Water Effluents (MT/yr)
VI. Fossil Feedstock Chemical Processing, (Cont'd)				
Major Sources: (Cont'd)			Major Sources:	
Acrylonitrile	82,000	--	Methyl Methacrylate	26,900
Ethylene Dichloride	55,000	--		
Toluene	43,800	--		
Carbon Tetrachloride	41,700	--		
Soap and Detergent Manufacture	--	17,900		
VII. Noncombustion Organic Chemical Utilization	2,868,000	--		--
Major Sources:			Major Sources:	
Rubber and Plastic Processing	1,150,000	--		--
Surface Coating	989,100	--		--
Graphic Arts	337,500	--		--
Dry Cleaning	202,000	--		--

TABLE 2.0-2 (Continued)

POTENTIAL REDUCTIONS OF ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emission Reductions: Volatile Organics (MT/yr)	Atmospheric Emission Reductions: Organic Particulates (MT/yr)	Water Effluents (MT/yr)
VIII. Agricultural and Forest Products	504,000	3,300,000	317,000
Major Sources:			Major Sources:
Pulp and Paper	142,000	--	Pulp and Paper 104,000
Wood Waste Combustion	137,000	47,400	Processed Fruits and Vegetables 69,900
Beer Brewing	67,100	103,000	Beer Brewing 55,530
Processed Fruits and Vegetables	47,200	--	
Tobacco	39,300	--	
Grain and Feed Milling and Storage	--	1,300,000	
IX. Open Sources	3,010,000	973,000	--
Major Sources:			Major Sources:
Agriculture Field Burning	2,540,000	820,000	--
Prescribed Forest Burning	472,000	152,000	--
X. Natural Sources	--	--	--
XI. Solid Waste Disposal	2,210,000	607,000	70,900
Major Sources:			Major Sources:
Open Burning Dumps and Open Dumps Replaced by Landfills	1,656,000	378,000	Open Burning Dumps and Open Dumps Replaced by Landfills 48,900

TABLE 2.0-2 (Continued)

POTENTIAL REDUCTIONS OF ORGANIC EMISSIONS AND EFFLUENTS FROM MAJOR CATEGORIES

Category	Atmospheric Emission Reductions: Volatile Organics (MT/yr)	Atmospheric Emission Reductions: Organic Particulates (MT/yr)		Water Effluents (MT/yr)
XI. Solid Waste Disposal, (Cont'd)				
Major Sources: (Cont'd)			Major Sources:	
Replace Open Burning of Uncollected Refuse with Landfills	604,000	154,000		--
XII. Municipal Wastewater	--	--		
Major Sources:			Major Sources:	
	--	--	Upgrade all Municipal Water Treatment to Secondary Biological Facilities	2,080,000
	--	--	Upgrade all Municipal Water Treatment Facilities to Tertiary Control (Include Secondary Control)	1,050,000
XIII. Other Sources	--	--		--

*Indicates emissions consisting mostly of methane.

TABLE 2.0-3

SUMMARY OF EMISSIONS AND EFFLUENTS FROM CATEGORIES, MT/yr

CATEGORY	VOLATILE ORGANICS						PARTICULATE ORGANICS				WATER EFFLUENTS			
	Total Emissions	Total Controllable Emissions	Total Nonmethane Emission	Controllable Nonmethane Emissions	Total Nonmethane Emissions from Controllable Sources	Controllable Nonmethane Emissions from Controllable Sources	Total Emissions	Total Controllable Emissions	Total Emissions from Controllable Sources	Controllable Emissions from Controllable Sources	Total Effluents	Total Controllable Effluents	Total Effluents from Controllable Sources	Controllable Effluents from Controllable Sources
I. Fossil Fuel Extraction	2,510,000	1,830,000									29,000	29,000		
II. Fossil Fuel Processing	1,716,400	1,030,000					7,300	3,650						
III. Fossil Fuel Transportation, Storage & Distribution	2,071,000	1,363,000	2,071,000	1,363,000	2,071,000	1,363,000	77,300	69,600	77,300	69,600				
IV. Fossil Fuel Refining	2,173,500	1,400,000	2,173,500	1,400,000	2,173,500	1,400,000	269,000	243,600	269,000	243,600	34,700	26,400	34,700	26,400
V. Fossil Fuel Combustion	724,000	314,000	383,900	67,500										
VI. Fossil Fuel Feedstock Chemical Processing	1,400,000	1,270,000	1,077,000	953,000	1,077,000	953,000	45,800	40,900	45,800	40,900	460,000	400,000	460,000	400,000
VII. Noncombustion Organic Chemical Utilization	3,529,000	2,868,000	3,529,000	2,868,000	3,529,000	2,868,000								
VIII. Agricultural and Forest Products	508,000	504,000	508,000	504,000	508,000	504,000	3,324,000	3,300,000	3,324,000	3,300,000	488,000	317,000	488,000	317,000
IX. Open Sources	3,010,000	3,010,000	3,010,000	3,010,000			973,000	973,000						
X. Natural Sources	85,300,000	9,100,000					1,500,000							
XI. Solid Waste Disposal	2,690,000	2,210,000	2,443,000	2,219,000			640,000	607,000			746,000	70,900		
XII. Municipal Sewage Disposal											9,980,000	3,420,000		
XIII. Other Sources	917,000	917,000					234,000							

2.1.1.1 Volatile Organic Emissions

The volatile organic emissions are presented in Table 2.1-1. Non-methane emissions are also identified and the controllable non-methane emissions are presented by category. The processes and operations representing the greatest potential for emission reduction are presented. Processes which can potentially reduce the total non-methane emissions by less than 1 percent are considered too small for the purpose of reduction of emissions on a mass basis. These relationships are shown graphically in Figures 2.1-1 and 2.1-2.

Approximately 49% of the total non-methane volatile organic emissions are controllable. This total may be subdivided as follows: agricultural and prescribed forest burning, 12%; open burning of refuse, 9%; petroleum refining and plastics processing industries, 10%; gasoline marketing and surface coating, 8%; graphic arts and dry cleaning, 2%; all other pollutant sources, 8%.

2.1.1.2 Organic Particulate Emissions

The organic particulate emissions are presented in Table 2.1-2. The controllable particulate emissions are also presented along with operations and processes representing the largest emission reduction potential. These relationships are presented graphically in Figures 2.1-3 and 2.1-4.

Approximately 74% of the total organic particulate emissions are controllable. This total is distributed as follows: grain and feed milling and storage, 18%; plywood and veneer, 17%; agricultural and forest prescribed burning, 14%; open refuse burning, 9%; coal rail transportation and beehive coke ovens, 3%; all other sources, 13%.

TABLE 2.1-1

AIR - VOLATILE ORGANIC EMISSIONS

	Category	Total Organic MT/yr	Non-Methane MT/yr; Percent*		Controllable Non-Methane Emissions (MT/yr); Percent*		Largest Non-Methane Reductions From Operations MT/yr; Percent*; Operation		
I	Fossil Fuel Extraction	2,510,000							
II	Fossil Fuel Processing	1,716,400							
III	Fossil Fuel Transportation	2,071,000	2,071,000	8%	1,363,000	5%	1,013,000	4%	Gasoline Marketing
							67,900	<1%	Diesel & Distillate
IV	Fossil Fuel Refining	2,173,500	2,173,500	9%	1,400,000	6%	1,229,000	5%	Petroleum Refining
V	Fossil Fuel Combustion	724,000	383,900	1%	67,500	<1%			
VI	Fossil Fuel Feedstock Chemical Processing	1,400,000	1,077,000	4%	953,000	4%	96,700	<1%	Carbon Black
VII	Fossil Fuel Product Utilization	3,529,000	3,529,000	14%	2,868,000	11%	1,150,000	5%	Rubber&Plastic Processing
							989,100	4%	Surface Coating
							338,000	1%	Graphic Arts
							202,000	1%	Dry Cleaning
							189,000	<1%	Fabric Treatment
VIII	Agriculture and Forest Products	508,000	508,000	2%	504,000	2%	142,000	<1%	Pulp and Paper
IX	Open Sources	3,010,000	3,010,000	12%	3,010,000	12%	3,010,000	12%	Agricultural and Prescribed Forest Burning
X	Natural Sources	85,300,000	9,100,000	36%	—	-	--	-	
XI	Solid Waste Disposal	2,690,000	2,443,000	10%	2,219,000	9%	2,210,000	9%	Open Burning of Refuse
XII	Municipal Waste Water	--	--	-	--	-	--	-	
XIII	Other Sources	917,000	917,000	4%	--	-	--	-	
	TOTAL	106,548,900	25,212,400	100%	12,384,500	49%	10,636,700	41%	

*Percent of Total Non-Methane Emissions, which are 25,212,400 MT/yr.)

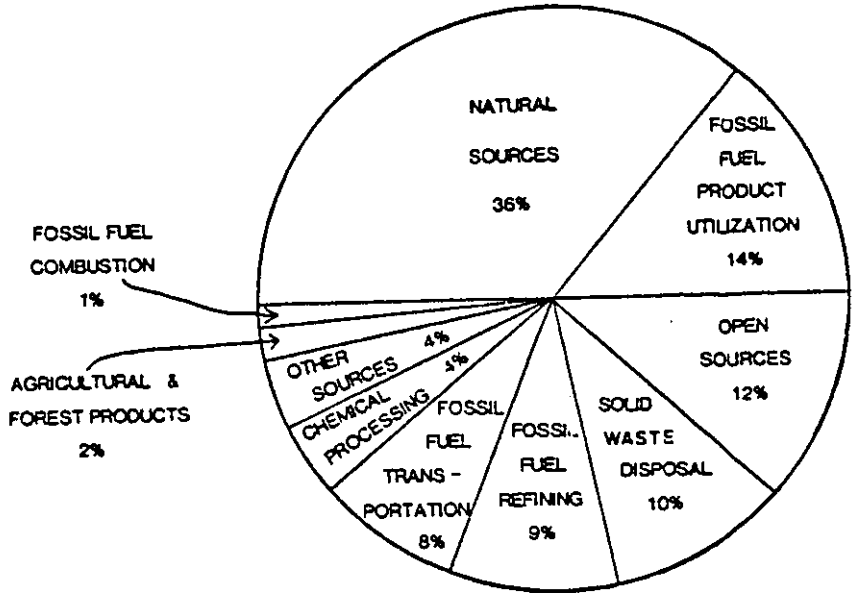


FIGURE 2.1-1 DISTRIBUTION OF TOTAL VOLATILE NON-METHANE EMISSIONS

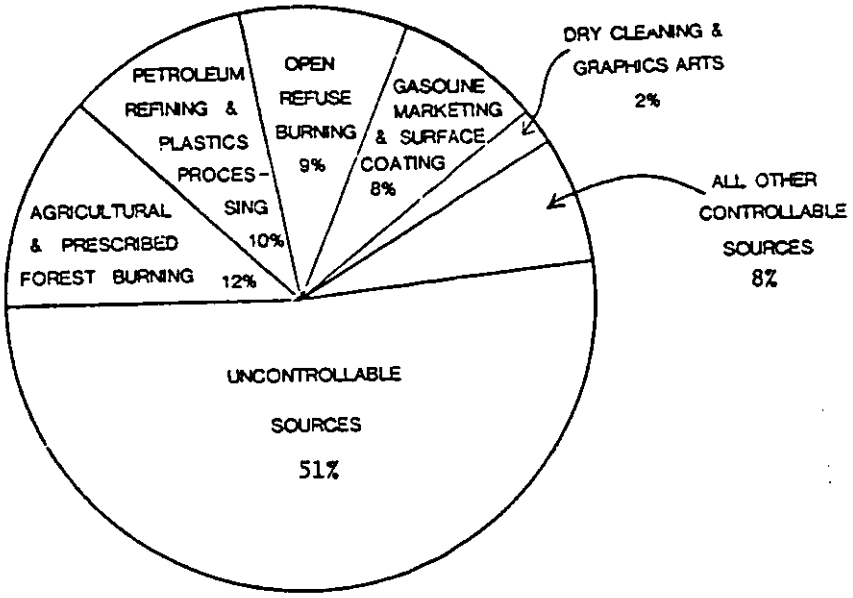


FIGURE 2.1-2 DISTRIBUTION OF CONTROLLABLE VOLATILE NON-METHANE EMISSIONS

TABLE 2.1-2

AIR - PARTICULATE ORGANICS

	Category	Total Particulates MT/yr	Percent Total	Controllable MT/yr	Percent Total	Largest Reductions From Operations MT/yr	Percent Total	Operation
I	Fossil Fuel Extraction	--	-	--	-	--	-	--
II	Fossil Fuel Processing	7,300	<1%	3,650	<1%	3,650	<1%	Coal Processing
III	Fossil Fuel Transportation	77,300	1%	69,600	1%	69,600	1%	Coal Rail Transportation
IV	Fossil Fuel Refining	269,000	4%	243,600	3%	126,000	2%	Beehive Coke Ovens
V	Fossil Fuel Combustion	--	-	--	-	--	-	--
VI	Fossil Fuel Feedstock Chemical Processing	45,800	1%	40,900	<1%	17,900	<1%	Soap and Detergent
VII	Fossil Fuel Product Utilization	--	-	--	-	--	-	--
VIII	Agricultural & Forest Products	3,324,000	47%	3,300,000	47%	1,300,000	18%	Grain & Feed Milling and Storage
						1,196,000	17%	Plywood and Veneer
IX	Open Sources	973,000	14%	973,000	14%	973,000	14%	Agriculture and Forest Prescribed Burning
X	Natural Sources	1,500,000	21%	--	-	--	-	--
XI	Solid Waste Disposal	640,000	9%	606,500	9%	606,500	9%	Open Burning of Refuse
XII	Municipal Wastewater	--	-	--	-	--	-	--
XIII	Other Sources	234,000	3%	--	-	--	-	--
	Total	7,040,400	100%	5,237,250	74%	4,292,650	61%	

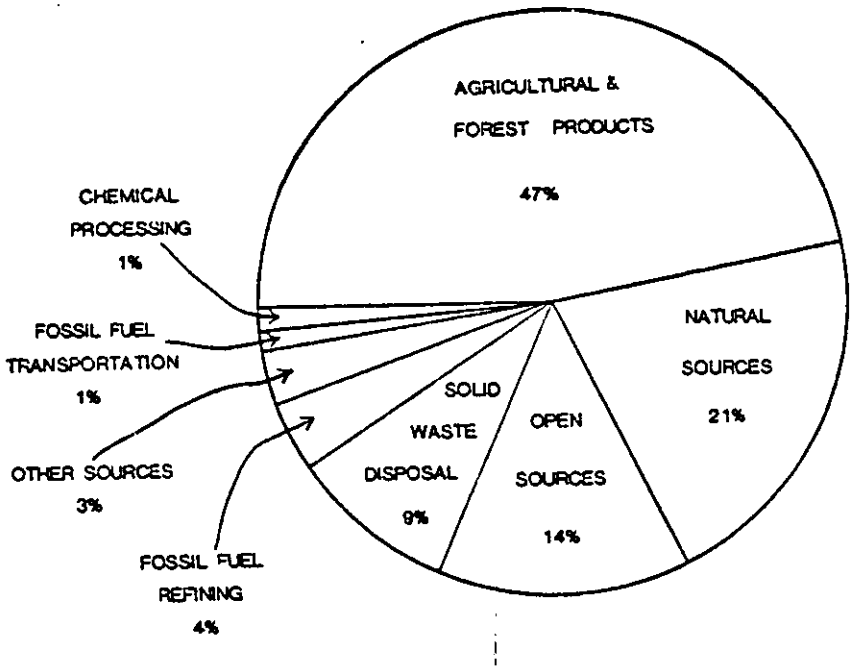


FIGURE 2.1-3 DISTRIBUTION OF TOTAL ORGANIC PARTICULATE EMISSIONS

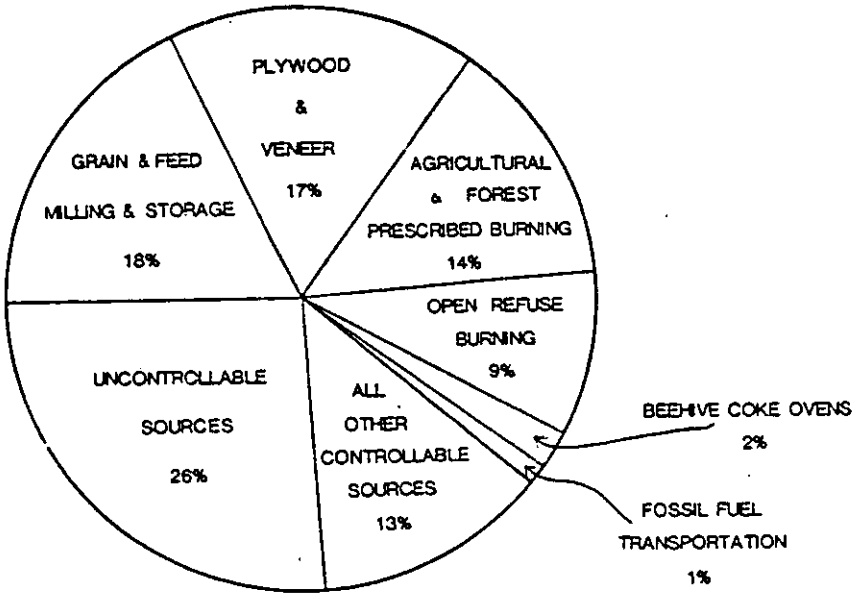


FIGURE 2.1-4 DISTRIBUTION OF CONTROLLABLE ORGANIC PARTICULATE EMISSIONS

2.1.2 Water Effluents

The organic water effluents from the major categories are presented in Table 2.1-3 along with the controllable organic effluents and the processes and operations representing the greatest potential for organic effluent reduction. Processes which reduce the total organic effluents by less than 1 percent were not included as potential methods for pollutant reduction. Effluents from natural sources were not quantified. A natural BOD is inherent in the aquatic ecosystem. Figure 2.1-5 represents the distribution of the total organic water effluent.

Upgrading of municipal wastewater systems to tertiary control accounts for a reduction of 29 percent out of the total 35 percent potentially controllable effluents. The pulp and paper industry is the only other process or operation that represents a reduction potential of 1 percent or more. This distribution is presented graphically in Figure 2.1-6.

2.2 Process Organic Emissions and Effluents

The data from the thirteen major categories presented in Section 2.1 indicate that a few large emission and effluent sources dominate the organic emission and effluent picture in the U.S. This is especially true for the volatile atmospheric emissions and water effluents. Therefore, other considerations are important when assessing reduction potentials for organic emissions and effluents. These other considerations include site-specific problems relating to geographical areas, pollutant toxicities, meteorological and dispersion characteristics, cost effectiveness of controls, photochemical reactivity, health effects, and other effects such as odor and plant ecology.

TABLE 2.1-3

WATER EFFLUENTS

	Category	Total Organic MT/Yr;	Total Organic Percent Total	Controllable Organic MT/Yr;	Controllable Organic Percent Total	Largest Reduction from Operations MT/Yr;	Largest Reduction from Operations Percent Total;	Operation
I	Fossil Fuel Extraction	29,000	<1%	29,030	<1%	29,000	<1%	On Shore Crude Production
II	Fossil Fuel Processing	--	-	--	-	--	-	--
III	Fossil Fuel Transportation	--	-	--	-	--	-	--
IV	Fossil Fuel Refining	34,700	<1%	26,400	<1%	16,700	<1%	Petroleum Refining
V	Fossil Fuel Combustion	--	-	--	-	--	-	--
VI	Fossil Fuel Feedstock Chemical Processing	460,000	4%	384,000	3%	52,900	<1%	Organic Dyes and Pigments
VII	Fossil Fuel Product Utilization	100	<1%	--	-	--	-	--
VIII	Agricultural and Forest Products	488,000	5%	317,000	3%	104,000 69,900	1% <1%	Pulp and Paper Processed Fruits and Vegetables
IX	Open Sources	--	-	--	-	--	-	--
X	Natural Sources*	--	-	--	-	--	-	--
XI	Solid Waste Disposal	736,000	6%	70,900	<1%	48,900	<1%	Leachate From Open Dumps
XII	Municipal Wastewater	9,980,000	85%	3,420,000	29%	3,420,000	29%	Upgrade Existing Facilities to Tertiary Control
XIII	Other Sources	--	-	--	-	--	-	--
	TOTAL	11,727,800	100%	4,263,330	35%	3,741,400	30%	

*The contribution of total organics to waterways from Natural Sources is not estimated.

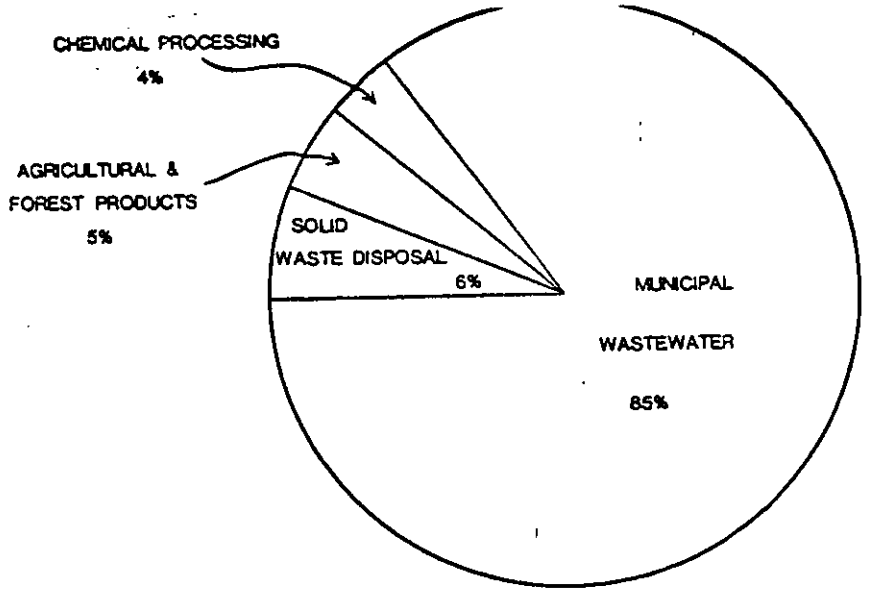


FIGURE 2.1-5 DISTRIBUTION OF TOTAL ORGANIC WATER EFFLUENTS

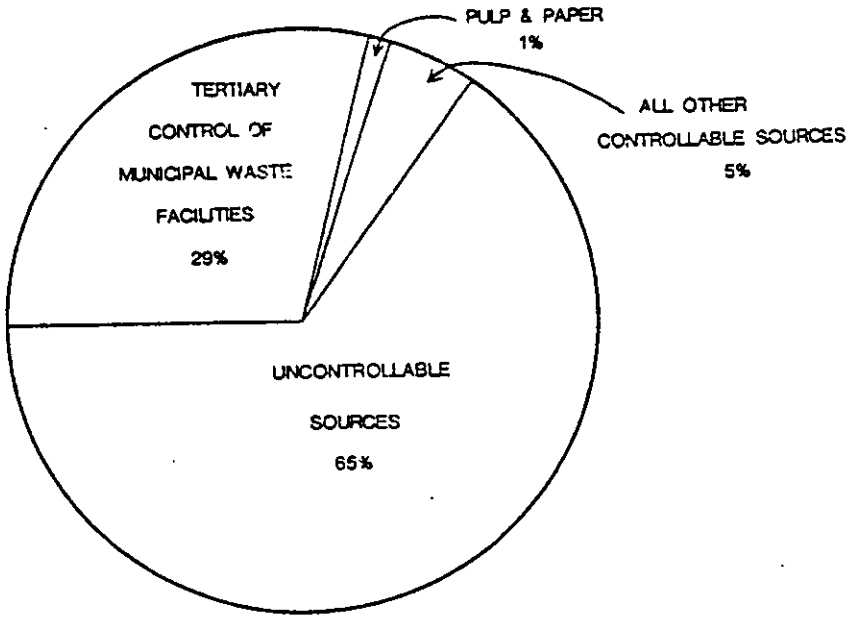


FIGURE 2.1-6 DISTRIBUTION OF CONTROLLABLE ORGANIC WATER EFFLUENTS

A detailed assessment of these considerations is beyond the scope of this report. However, certain general assumptions can be made to provide insight into the impact of some of these considerations:

1) Methane emissions are of secondary importance because of their negligible health effects and photochemical reactivity. Therefore, the methane emitters are not considered as important as the others in this report.

2) Natural emissions are of secondary importance since they occur over a large geographical area and are, therefore, relatively dilute. Natural emissions also occur in remote locations with minimal effect on large population centers. Since NO_x emissions are concentrated in heavily populated areas, the photochemical smog effects from natural organic emissions are not as important. Finally, natural sources are essentially uncontrollable.

3) Other categories excluded from consideration for similar reasons are "open" sources and "other" sources. "Other" sources are usually uncontrollable and occur most often in remote areas. "Open" sources, though mostly controllable, also tend to occur in remote areas.

Therefore, consideration of the process emission categories is logical when benefits from organic emission reductions are assessed. These categories include fossil fuel transportation, refining, combustion, feedstock chemical processing,

organic chemical utilization and agricultural and forest products. In general, these process operations are located mostly in populated areas where health effects are very important and where high NO_x concentrations combine with the emissions to create photochemical smog problems. Also, process emissions usually are amenable to existing control technology (although the economics still remain a question for many specific processes). Finally, most of the toxic emissions result from these categories.

Consequently, these assumptions allow the process emission categories to be assessed separately by the impact of their reduction potentials as a class.

Similarly, process water effluents are completely dominated by the municipal wastewater category. Overall, the effluents from septic tanks are the most serious problem but septic tanks are considered uncontrollable effluents from rural or remote sources. Municipal sewage is considered to be a minor problem after controls are implemented. Therefore, the impact of the process effluents can be considered.

The non-methane volatile organic emissions from the process categories are over twice as large as the organic particulate emissions and an order of magnitude higher than the organic water effluents. Similarly, controllable non-methane volatile organic emissions from the process categories are more than twice as large as controllable organic particulate emissions and an order of magnitude higher than the controllable water effluents.

2.2.1 Process Atmospheric Emissions

Atmospheric emissions from fossil fuel transportation, refining, feedstock chemical processing, non-combustion organic chemical utilization, and agricultural and forest products categories are considered in this section.

2.2.1.1 Volatile Organic Emissions

The volatile organic emissions from the process categories are presented in Table 2.2-1. The processes selected for study in this project are also presented. These processes are generally the largest emitters in their category and have the largest reduction potential.

The non-combustion organic chemical utilization category accounts for 38% of the total volatile organics from process categories. Next are fossil fuel refining and transportation with 23.2% and 22.1% of the total, respectively. Fossil fuel chemical feedstock processing is next with 11.5% of the total followed by agricultural and forest products which account for 5.4% of the total process type emissions.

Table 2.2-1 also presents the estimated total controllable emissions for each category. The organic chemical utilization category has the highest reduction potential with 30.6% of the total emissions estimated to be controllable from this category. Next are the refining, transportation and chemical processing categories with reduction potentials of 15%, 14.6% and 10.2%, respectively. The smallest reduction potential is from the agricultural and forest products category with 5.4%. Therefore, a reduction potential of approximately 75.8% exists for all the process type categories.

TABLE 2.2-1

VOLATILE NON-METHANE ORGANIC EMISSIONS FROM CONTROLLABLE PROCESSES

	Category	Total Non-Methane Emissions* MT/yr	Percent Total	Controllable Non-Methane Emissions MT/yr	Percent Total	Largest Non-Methane Reductions From Operations MT/yr	Percent Total	Operation
III	Fossil Fuel Transportation	2,071,000	22.1%	1,363,000	14.6%	420,000	4.5%	Service Station - Automobile Filling
						383,000	4.1%	Service Station - Underground Tank Filling
						146,000	1.6%	Crude Transportation - Storage
						106,000	1.1%	Gasoline Bulk Station - Storage
						91,400	1.0%	Gasoline Bulk Station - Loading
	Subtotal					1,244,400	13.3%	
IV	Fossil Fuel Refining	2,173,500	23.2%	1,400,000	15.0%	454,000	4.8%	Petroleum Refining - Storage
						318,000	3.4%	Petroleum Refining - Blowdown
						195,000	2.1%	Petroleum Refining - Process Drains and Wastewater Separator
						147,000	1.6%	Petroleum Refining Fluid Catalytic Cracking Units
						117,000	1.2%	Petroleum Refining - Vacuum Jets
	Subtotal					1,229,000	13.1%	
VI	Fossil Fuel Feedstock Chemical Processing	1,077,090	11.5%	953,000	10.2%	98,700	1.0%	Carbon Black
						80,900	0.9%	Acrylonitrile
						55,000	0.6%	Ethylene Dichloride
						43,800	0.5%	Toluene
						41,700	0.4%	Carbon Tetrachloride
	Subtotal					317,100	3.4%	
VII	Noncombustion Organic Chemical Utilization	3,529,500	37.8%	2,868,000	30.6%	1,150,000	12.3%	Rubber and Plastic Processing
						428,000	4.5%	Paper and Paperboard Coating
						422,000	4.5%	Sheet, Strip, and Coil Coating
						338,000	3.6%	Graphic Arts
						202,000	2.2%	Dry Cleaning
						189,000	2.0%	Fabric Treatment
						139,000	1.5%	Miscellaneous Surface Coating
	Subtotal					2,868,000	30.6%	
VIII	Agricultural and Forest Products	508,000	5.4%	506,000	5.4%	142,000	1.5%	Pulp and Paper
						137,000	1.5%	Waste Wood Combustion
						47,100	0.5%	Beer Brewing
						47,200	0.5%	Processed Fruits and Vegetables
						39,300	0.4%	Tobacco
	Subtotal					432,600	4.6%	
	Total	9,358,500	100.0%	7,358,000	78.6%	6,091,300	65.0%	

*Estimated

The processes studied in this report account for 65.0% of the total estimated reduction potential of 74.2%. The processes studied account for all but 1% of the estimated reduction potential in each category except chemical processing and fossil fuel transportation. The chemical processing and hydrocarbon utilization categories in particular have many more emission sources than do the other categories. The chemical processing category emissions result from many smaller operations grouped into chemical complexes which can have a significant emission rate at processing sites.

The above relationships are presented graphically in Figure 2.2-1 and Figure 2.2-2.

2.2.1.2 Particulate Organic Emissions

Emphasis is placed on the quantification and control of volatile organic air emissions rather than particulate organic emission. Consequently, the processes selected for further study are usually chosen on the basis of the control potential for the volatile organics. The control potential for the organic particulates is usually assessed only when a large volatile organic reduction is also achievable. However, large particulate organic emitters are occasionally selected when they have a large impact on a category such as soap and detergent production in the fossil fuel feedstock chemical processing category and grain and feed mills and elevators in the agricultural and forest products category.

The particulate organic emissions from the process categories are presented in Table 2.2-2. The processes selected for further study in this project are also presented. These processes are generally the largest emitters in their category

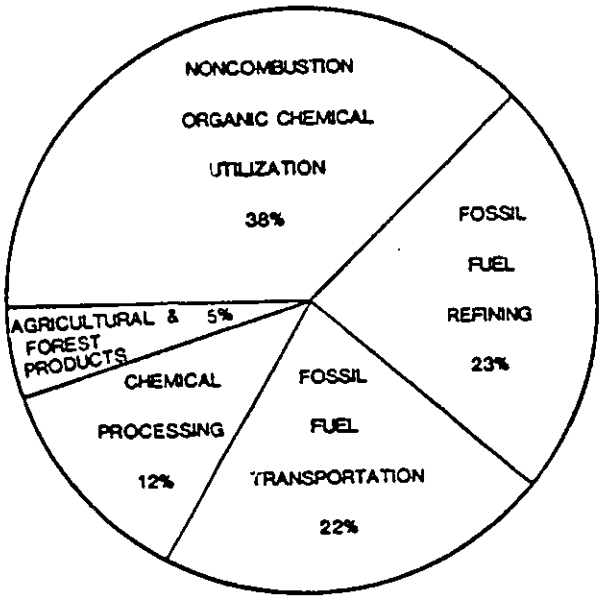


FIGURE 2.2-1 DISTRIBUTION OF VOLATILE NON-METHANE EMISSIONS FROM CONTROL-LABLE PROCESSES

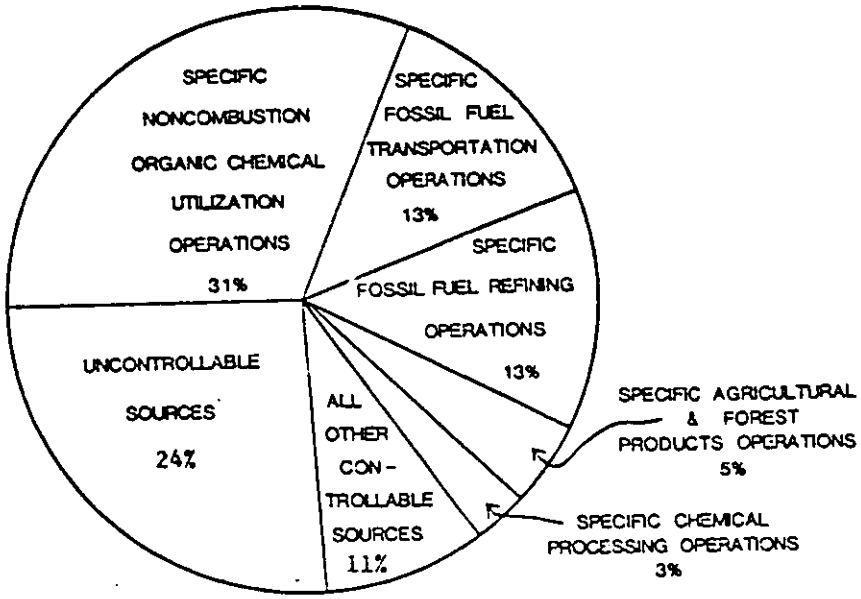


FIGURE 2.2-2 DISTRIBUTION OF CONTROLLABLE VOLATILE NON-METHANE EMISSIONS FROM CONTROLLABLE PROCESSES

TABLE 2.2-2

AIR - PARTICULATE ORGANIC EMISSIONS FROM CONTROLLABLE PROCESSES

	Total Emissions		*Controllable Emissions		Largest Reductions From Operations		
	MT/yr	Percent Total	MT/yr	Percent Total	MT/yr	Percent Total	Operation
III. Fossil Fuel Transportation Storage and Distribution	77,300	2%	69,600	2%	69,600	2%	Coal Rail Transportation
IV. Fossil Fuel Refining	269,000	7%	243,600	7%	126,000	3%	Beehive Ovens, Coke Production
VI. Fossil Fuel Feedstock Chemical Processing	45,800	1%	40,900	1%	17,900	< 1%	Soap and Detergent
VIII. Agricultural and Forest	3,324,000	96%	3,300,000	89%	1,580,000	43%	Grain and Feed Mills & Elevators
Products					*1,200,000	32%	Plywood & Veneer
Subtotal					2,780,000	75%	
Total	3,716,100	100%	3,654,100	98%	2,993,500	80%	

* Estimated

and have the largest reduction potential. Some organic particulate emitters are not listed in this table but were assessed for reduction potentials that are too small for further consideration.

The agricultural and forest products category is by far the largest emitter of organic particulates from the process type categories with 90% of the total emissions. Next is fossil fuel refining with 7% of the total followed by fossil fuel transportation, storage, and distribution and by feedstock chemical processing with 2% and 1%, respectively.

Table 2.2-2 also presents the estimated total controllable emissions for each category. The agricultural and forest products category has the highest potential for reduction with 89% of the total estimated controllable emissions. Next are the refining, transportation, and chemical processing categories with 7%, 2%, and 1%, respectively. Therefore, approximately 98% of the total emissions from the process type categories are controllable.

The fossil fuel, grain and feed mills, and elevators categories account for a reduction potential of 48%. When an estimated reduction potential of 32% for plywood and veneer is added (this process was not selected for study) the reduction potential for 5 processes is 80% of the emission total. Therefore, the difference between the reduction potentials for the listed processes and the total reduction potentials of the process categories is 18%. Most of this difference is in the agricultural and forest categories. Several other large sources of particulates (see the Appendix) have reduction potentials. These relationships are shown graphically in Figures 2.2-3 and 2.2-4.

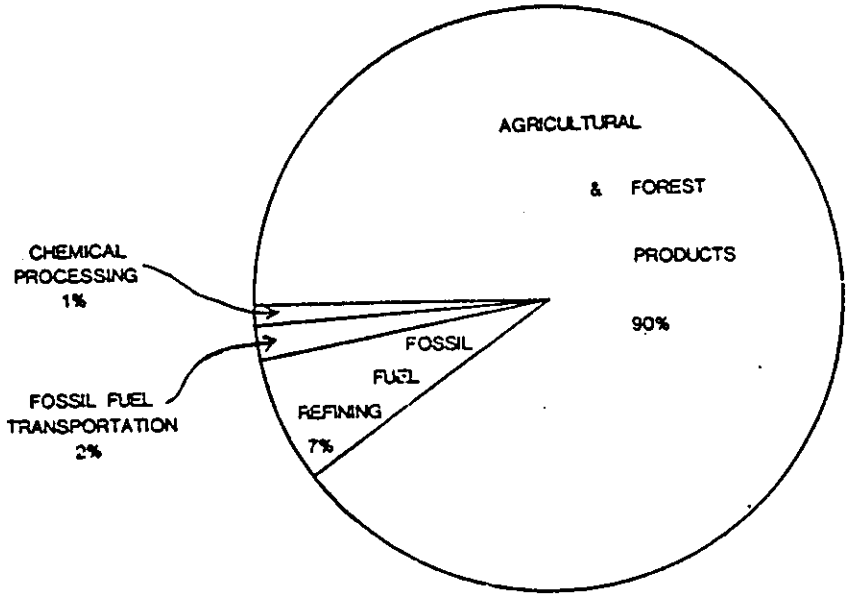


FIGURE 2.2-3 DISTRIBUTION OF TOTAL PARTICULATE ORGANIC EMISSIONS FROM CONTROLLABLE PROCESSES

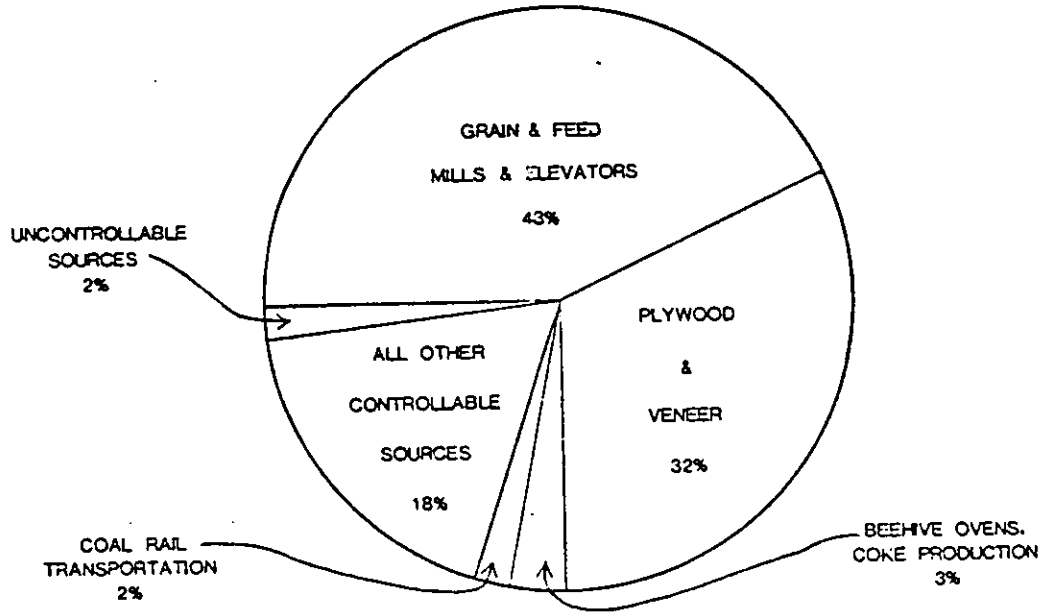


FIGURE 2.2-4 DISTRIBUTION OF CONTROLLABLE PARTICULATE ORGANIC EMISSIONS FROM CONTROLLABLE PROCESSES

Although this analysis does not account for secondary particulate generation, it does illustrate the impact that geographical considerations can have on emission reduction potentials of organic particulates in the U.S.

2.2.2 Process Water Effluents

Water effluents from fossil fuel refining, feedstock chemical processing, and agricultural and forest products categories are considered in this section. Water effluents from organic chemical utilization and fossil fuel transportation are considered to be too small for this discussion.

The organics present in water effluents from the process categories are presented in Table 2.2-3. The processes selected for study in this project are generally the largest sources of organic effluents in their category and have the largest reduction potential.

The fossil fuel chemical processing and agricultural and forest products categories are the largest sources of organic water effluents with 46.8% and 49.7% of the total, respectively. The fossil fuel refining category accounts for 3.5% of the total organic water effluents.

Table 2.2-3 also presents the estimated total controllable organic water effluents for the categories. The chemical processing category has the largest potential for reduction with 40.7% of the total effluents estimated to be controllable from this category. The agricultural and forest products category follows with 32.3% and last is the refining category with 2.7%. Therefore, a reduction potential of about 75.7% exists for all the process type categories.

TABLE 2.2-3

WATER - ORGANIC EFFLUENTS FROM CONTROLLABLE PROCESS

Category	Total Effluents Mt/yr	Total Effluents Percent Total	*Controllable Effluents Mt/yr	*Controllable Effluents Percent Total	Largest Reductions From Operations Mt/yr	Largest Reductions From Operations Percent Total	Operation
IV. Fossil Fuel Refining	34,700	3.5%	26,400	2.7%	16,700	1.7%	Petroleum Refining
					9,700	1.0%	By-Products Coke Ovens
Subtotal					26,400	2.7%	
VI. Fossil Fuel Feedstock Chemical Processing	460,000	46.8%	400,000	40.7%	52,900	5.4%	Dyes and Pigments
					28,100	2.9%	Polyvinyl Chloride and Copolymers
					26,900	2.7%	Methyl Methacrylate
Subtotal					107,900	11.0%	
VIII. Agricultural and Forest Products	488,000	49.7%	317,000	32.3%	104,000	10.6%	Pulp and Paper
					69,900	7.1%	Processed Fruits and Vegetables
					55,500	5.6%	Beer Brewing
Subtotal					229,400	23.3%	
Total	982,700	100%	743,400	75.7%	363,700	37.0%	

* estimated

The processes studied in this report have a combined reduction potential of only 37.0% of the total 75.7% controllable organic water effluents. In the refining category, the two operations studied account for all the emissions from this category. However, for the agricultural and forest products category a 9% difference exists between the reduction potential of the processes studied and that of the category total. For the chemical processing category the difference between the reduction potential of selected processes and that of the category total is 29.7%. Many processes in the agricultural and forest products category are water effluent sources; the chemical processing category has even more water effluent sources, none of which are extremely large. However, chemical processes tend to be grouped together in chemical complexes, causing a significant organic water effluent rate at processing sites. These relationships are shown graphically in Figures 2.2-5 and 2.2-6.

The analysis of the organic water effluents again illustrates the impact that geographical considerations can have on organic water effluent reduction potentials overall in the U.S.

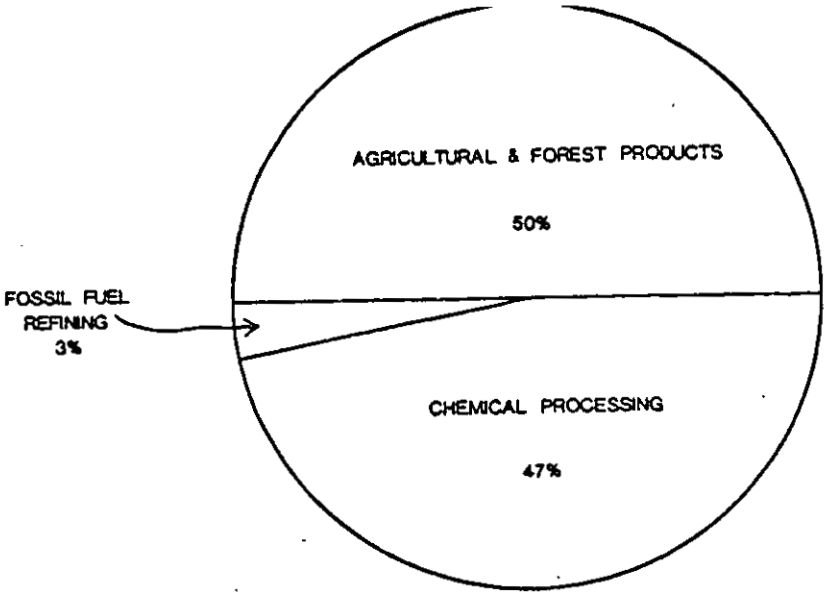


FIGURE 2.2-5 DISTRIBUTION OF TOTAL ORGANIC EFFLUENTS FROM CONTROLLABLE PROCESSES

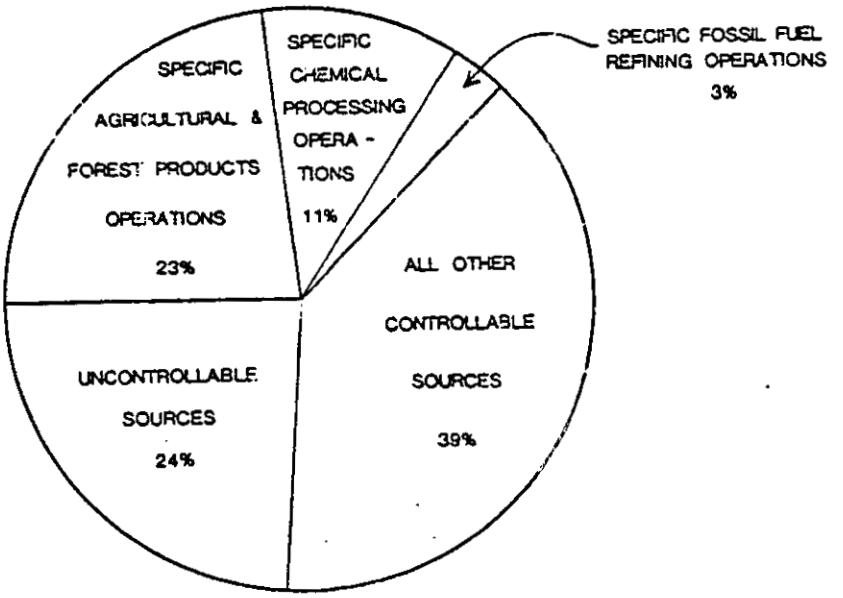


FIGURE 2.2-6 DISTRIBUTION OF CONTROLLABLE ORGANIC EFFLUENTS FROM CONTROLLABLE PROCESSES

3.0 REDUCTION POTENTIALS OF ORGANIC EMISSIONS AND EFFLUENTS FROM THIRTEEN MAJOR CATEGORIES

This section of the report describes the industrial processes employed in each category and discusses in detail the emissions and effluents from the processes selected for further study, the control methods available for effluent and emission reduction from each process, and an estimate of the potential reduction of organics in metric tons (MT) per year.

3.1 Fossil Fuel Extraction

The fossil fuel extraction category encompasses the crude oil, natural gas, and coal production industries. Almost all of the organic emissions associated with extraction of fossil fuels result from fugitive sources.

A summary of the atmospheric emissions from the industries in this cateogry is presented in Table 3.1-1.

Organic water effluents from fossil fuel extraction are also considered in ths section. Enough data was available that the organic effluents could be estimated from crude oil production. Table 3.1-2 contains these estimates. However, organic emissions due to oil spills from crude production into surface waters are not quantified in this report. The impact on the environment is difficult to assess, since limited information is available on the parameters involved. Data such as amount of organic recovered after the spill, amount of organic reaching the atmosphere by evaporation, amount of organic reaching surface waters. and amount of organic soluble in surface waters are generally unavailable. Waterborne effluents are produced only from crude production. The generation of solid wastes from fossil fuel extraction is assumed to be negligible.

TABLE 3.1-1. FOSSIL FUEL EXTRACTION - VOLATILE EMISSIONS

	Year	Emissions of Volatile Organics	Ref.
Fossil Fuel Extraction			
Crude Oil	1975	630,000	1
Natural Gas	1975	270,000	1
Coal	1973	1,610,000	2
Total:		2,510,000	

Source: 1. MO-201
2. IR-011

TABLE 3.1-2. FOSSIL FUEL EXTRACTION - ORGANIC EFFLUENTS

	Effluents (MT/year)				
	Total Organics	BOD	COD	SS	O/G
Fossil Fuel Extraction					
Crude Oil					
Onshore	29,000	41,000	56,000	8,000	12,000
Offshore	30	N/A	N/A	N/A	12
Total:	29,030				

Sources: EN-154

3.1.1 Crude Oil Production

Process Description

In an onshore producing oil well, three methods are used for bringing the oil to the surface: natural flow, gas lifting (injection of gas into the flowing column), and pumping. Most producing wells are operated by mechanical lifting methods using either plunger or centrifugal type subsurface pumps.

The production from each well is then sent to a complex gathering system which consists of pipes, valves, and fittings necessary for combining all of the production or for separating the individual well productions in the case of varying qualities. There are, in addition, test separators and tanks for testing the oil quality.

Because the crude oil is produced in association with gases and water (usually brine), the crude must be separated. The water can be removed by one of several means: (1) heat, (2) chemical destabilization, (3) electrical coalescence, and (4) gravitational settling. The associated hydrocarbon gases are separated by one of two methods. The two-phase method is used for separating oil and gas while the three-phase method is used when gas, oil, and water are being separated.

Following water and gas separation, the crude oil is usually sorted in tanks prior to shipment to the refinery. The recovered liquids produced with the crude are handled in horizontal cylinders or spheres. The associated gas separated from the crude is usually sent to processing plants for upgrading. Occasionally, the recovered gases are vented or flared if their quantity does not warrant the expense of shipment for processing and sales and/or the well is located in a remote area.

Offshore production operations are very similar to onshore operations with the added complications of space limitations and the generally hostile environment. As with onshore wells, offshore oil is brought to the surface by natural flow, gas life, or pumping with subsurface pumps.

The crude is commonly sent to a central production platform via pipeline for processing. Delivery to shore for processing is also a possibility, but the usual practice is the separation of gas and water from the oil on offshore platforms.

Offshore production is generally transported to land via pipelines minimize the storage of crude on the offshore structures. However, as development proceeds farther from shore, more offshore storage will be utilized. The oily water that has been separated from the crude may be delivered onshore for treatment at a conventional cleaning and dehydrating plant before release to the ocean. Alternatively, it may be reinjected to the reservoir to help maintain pressure. Reinjection is widespread in offshore California operations. The separated gases are either collected and processed for market or they are vented and flared.

Atmospheric Emissions and Control

The atmospheric emissions from domestic offshore and onshore crude production result primarily from fugitive sources: wastewater separators, pump seals, compressor seals, relief valves, pipeline valves, and flanges. Other sources include the storage tanks which emit light hydrocarbons not removed in the gas separation units and the gases which are vented from remote production facilities. Monsanto Research Corporation estimates that 630,000 metric tons per year of volatile organics are

emitted to the atmosphere from petroleum extraction (MO-201). These losses are almost entirely low molecular weight saturated gases such as methane and ethane. These types of hydrocarbons are among the least photochemically reactive volatile organics.

In brief, the existing control technology for petroleum production of hydrocarbon emissions consists of the following:

Storage Facilities:

- Floating roof tanks or internal floating covers
- Vapor recovery units

Wastewater Separators:

- Seal from atmosphere
- Vent to vapor recovery
- Floating covers

Pump and Compressor Seals:

- Convert packed seals to mechanical seals
- Install double seals

Relief Valves:

- Upstream rupture discs
- Vent to vapor recovery or flare

Pipeline Valves:

- Regular maintenance of stuffing boxes

Heaters and Compressor Engines:

- Carburetion adjustments

Remote Location Vents:

- Incineration

Miscellaneous Losses:

- Regular maintenance
- Good housekeeping

The potential for reduction of the organic emissions from petroleum production is difficult to assess due to the scarcity of data on the degree of organic emission control currently practiced by the industry. Assuming the use of the above controls on petroleum production facilities, the organic emissions could be reduced 60 percent. This results in a reduction of 378,000 MT/year.

Water Effluents and Control

Waterborne organic effluents from the crude oil production industry result from one of two sources: the disposed oily brine produced along with the crude, and the accidental spills resulting from the production activities and equipment.

On the average, two to three cubic meters of water are produced per cubic meter of oil produced onshore. Thus, approximately 4.0 million cubic meters (1.05×10^9 gallons) of oily saltwater are produced daily in the United States. Approximately four percent of this total is discharged to rivers. The bulk of the remaining water is injected in underground formations, used for secondary recovery, or disposed of in such a way that the oily water does not reach United States waterways.

Based on average pollutant concentration figures reported for produced formation water in the EPA's Effluent Guidelines Document for the Offshore Segment of the Oil and Gas Extraction Point Source Category, estimates for the amount of BOD, COD, TOC, suspended solids, and oil and grease emitted can be calculated (EN-376). These calculations reveal that roughly 41,000 MT/year of BOD; 24,000 MT/year of TOC; 56,000 MT/year of COD; 8,000 MT/year of suspended solids; and 12,000 MT/year of oil and grease are discharged to water from onshore petroleum production. Assuming an organic compound to carbon molecular weight ratio of 1.2 for the discharged organic compounds, the total organic emission level is calculated to be 29,000 MT/year for onshore production.

Crude oil spills from production activities represent another potential for water pollution. Estimates for the yearly quantity of oil spilled from production systems have been calculated from data presented by EPA in its Petroleum Systems Reliability Analysis document (RI-107). Calculations show that approximately 260,000 MT/year of oil is lost from onshore production systems primarily from leaking pipes and valves. All of this oil does not reach the waterways; much is recovered, some volatilizes, and some biodegrades on the land. However, data on the disposition of spilled oil is not available, so for

the purpose of this report, spilled oil is not quantified for air and water pollution. An estimate of 40,000 MT/year for offshore petroleum spills was obtained from data on offshore production systems. Again, much of this oil is recovered, but some volatilizes so that the disposition of the spilled oil is unknown. The major sources are leaking pipes, valves, pumps, malfunctioning level sensors causing system overloads, relief valves, and rupture discs.

The offshore production of petroleum produces roughly one barrel of brine water per barrel of oil (EK-376). In 1973, 0.253 hm^3/day (1.59×10^6 barrels/day) of oil was produced from offshore wells. Therefore, approximately the same amount of brine water was also produced. Assuming the offshore segment of the oil and gas extraction industry will meet the EPA regulations established for its water effluents for 1977, the discharge of organics from offshore production of oil can be estimated. That regulation states that 48 mg of oil and grease per liter of water discharged is the maximum allowable rate. This amounts to a total organic discharge of 30 metric tons per year from offshore crude production, based on the same assumptions made concerning onshore production effluent wastes.

A wide range of control and treatment technologies have been developed to deal with petroleum production wastes. Local factors, discharge criteria, availability of space, waste characteristics, and other factors influence the method of treatment. Techniques used to separate oil from the produced formation water include: (1) gas flotation, (2) parallel plate coalescers, (3) filters, (4) gravity separation, and (5) chemical treatment. Two "zero discharge" techniques commonly used to dispose of oily wastewater are: (1) discharge of the water to pits, ponds, or reservoirs for evaporation, and (2) reinjection to acceptable underground formations.

The control techniques involved in reducing crude oil production spills include the application of regular inspection and maintenance practices especially for spill-prone equipment such as level sensors, relief valves, pump gaskets, seals, packing, saltwater dump valves, and rupture discs. Another control measure includes the piping of relief valve and rupture disc overflow to a sump or secondary containment. The use of corrosion preventing techniques such as chemical inhibitors, sacrificial cathodes, galvanizing, or increased use of plastic, glass reinforced or similar pipe materials in limited low pressure areas of the gathering subsystem are several other methods which help prevent the spillage of crude oil or oily water from production systems.

The reduction potential for the oil spillage from crude production systems appears rather high since many field operations have eliminated spill problems with preventive programs. Data is lacking for the calculation of an organic emission reduction percentage, but proven spill control measures are available. The reduction potential is difficult to determine for oil spills to waterways.

The best available control technology achievable for treating produced formation water has been identified by the EPA as evaporation ponds or holding pits and reinjection (EN-376). Thus, the potential for reduction of this source of organic effluent is assumed to be 100 percent. This amounts to a reduction of 29,030 MT/year of organic effluents from offshore and onshore oil production.

3.1.2 Natural Gas Extraction

Process Description

Natural gas produced in facilities separate from crude oil production comprises 80 percent of the total amount of gas marketed in the United States. Gas produced from underground reservoirs not containing crude oil varies considerably in composition. The basic production equipment for onshore and offshore wells is practically the same. However, the gas-conditioning equipment located at the well site or at some nearby central location usually varies depending upon the gas composition.

The basic equipment at the wellhead includes various valves and fittings commonly referred to as a christmas tree. The wellhead equipment regulates the high pressure natural flow of the gas from the reservoir. After the wellhead, the gas is treated according to its composition. The conditioning equipment may include separators which remove liquid hydrocarbons and condensed water from the gas stream, heaters, dehydrators, and compressors. Should the natural gas contain corrosive elements such as H_2S, the gas may be treated by chemical injection for inhibition of corrosive attach on the flow system equipment. In some cases removal of the corrosive compound or compounds is economical.

Offshore gas wells are similar in many respects to their onshore counterparts. However, space limitations usually prohibit processing of the produced gas. Therefore, this gas is usually sent to shore for conditioning. Safety precautions and regulations ordinarily necessitate better maintenance practices offshore than for onshore operations.

Atmospheric Emissions and Control

Volatile organic emissions from natural gas extraction result primarily from fugitive sources. The valves, pipe flanges, corroded pipelines, compressor seals, separators, and dehydrators are all potential sources of fugitive emissions. Monsanto Research Corporation (MO-201) estimates that 270,000 metric tons of volatile organics are emitted from natural gas extraction to the atmosphere yearly. These volatile organics are composed primarily of the light saturated hydrocarbons commonly found in natural gas with methane being the primary component of the emissions.

The control of organic emissions from natural gas production relies heavily upon regular maintenance of equipment and good housekeeping at the well site. Equipment changes can offer some help in reducing the organic emissions. For example, the substitution of mechanical seals for packed seals on centrifugal compressors and the installation of dual packed seals on reciprocating compressors are control methods used to reduce emissions from compressors.

Pressure relief valves are occasional sources of organic emissions, especially during system upsets. Their emissions may be controlled by manifolding to a vapor control device or a blowdown system. For relief valves where discharge into a closed system is not desirable because of convenience or safety, fragile blanks called rupture discs can be installed before the valve. Rupture discs prevent the pressure relief valve from leaking and protect the valve seat from corrosive environments (WA-086). The organic emissions from relief valves controlled by rupture discs or blowdown systems are negligible.

Organic emissions originating from product leaks at valves and flanges can only be controlled by regular inspection and prompt maintenance of valve packing boxes and flange gaskets. The emissions reduction from control of valves and flanges is undefinable because of its dependence on the corrosiveness of the gas handled, the degree of maintenance, and the characteristics of the equipment.

As with crude oil production, insufficient data exists for a reliable estimate of the reduction potential for the mass emissions of atmospheric hydrocarbons from natural gas extraction. Because the primary source of atmospheric emissions of organics from gas production is fugitive emission sources, as is that for oil production, the reduction potential is assumed to be the same--60 percent. This amounts to a mass emission reduction potential of 162,000 MT/year of volatile organics from natural gas production.

3.1.3 Coal Production

Process Description

Coal mines are classified by the methods used to extract the coal. The actual ethod selected, whether surface mining or underground mining, is based upon a number of physical and economic factors. However, only underground coal mines have reported organic chemical emissions to the atmosphere (IR-011). For this reason only underground mining will be discussed.

Underground mines are developed by driving entryways into a coal seam and are classified according to the manner in which the seam is entered. The three common methods of entry

to the coal seam are: (1) drift mines, (2) slope mines, and (3) shaft mines.

The mining techniques used in the mines are not dependent on the type of entryway in use. The majority of the coal mines in the United States use the room and pillar extraction technique. Room and pillar extraction begins with the driving of main tunnels, or headings, from the points of entry to the seam. From these main headings, perpendicular secondary headings are driven. Blocks of coal are then extracted in a systematic pattern, forming rooms along both sides of the headings. Pillars of intact coal are left between the mined areas to support the roof and prevent surface subsidence above the mine. Initial development in an underground mine may leave as much as 60 percent of the coal in pillars. Following development, some of those pillars may be safely mined and removed as the machinery retreats from an area of the mine. This may significantly increase the coal recovery.

Atmospheric Emissions and Control

All coal beds contain hydrocarbon gases. These gases (98 percent methane) are contained in the fine pore structure in the beds and migrate into active mine workings when the bed's equilibrium conditions are upset. However, the deeper coal beds, accessible only by underground mining techniques, are the only ones which contain significant amounts of methane.

The Bureau of Mines estimated for 1973 that over 6.5 hm^3 of methane are emitted daily (229.7×10^6 ft^3/day) from underground coal mines (IR-011). This amounts to approximately 1,608,000 metric tons of methane emitted yearly from coal extraction. This estimation is a conservative one. The Bureau of

Mines included in their study only those mines which produced methane in excess of 2,830 m^3/day (100,000 ft^3/day).

A promising control method for reducing the emissions of methane from underground coal mines is the drilling of vertical boreholes from the surface into the coal seam at selected spots and recovering the methane as natural gas. This control technique offers the advantage of recovering a marketable product which could be sold if produced in enough quantity. The Bureau of Mines reports several mines which emit around 280,000 m^3/day (10×10^6 ft^3/day) of methane. Other promising control methods available include (ZA-044): the use of horizontal holes in a coal seam to infuse an active face area with water, thus diverting the flow of methane away from the mining area; the use of long horizontal holes to degasify a section prior to mining; and hydraulic fracturing of the bed to increase its permeability, thus aiding methane flows through the coal to a vertical or horizontal degasification hole.

The procedures mentioned above have been found effective for removing 20 to 50 percent of the methane that would ordinarily be ventilated to the atmosphere (ZA-044). Based on these efficiencies, a reasonable estimate is that the reduction potential for hydrocarbon emissions from coal extraction is rather high and the percent reduction could be up to 80 percent. This results in a reduction potential of 1,290,000 MT/year.

3.2 Fossil Fuel Processing

Organic emissions from the natural gas processing and coal processing industries, and their control, are examined here. The primary source of atmospheric emissions from gas processing is fugitive leaks in equipment. Most volatile organic emissions from coal processing are from process vents and stacks such as thermal driers.

A summary of the atmospheric emissions from the industries in this category is presented in Table 3.2-1.

TABLE 3.2-1

FOSSIL FUEL PROCESSING - ATMOSPHERIC EMISSIONS

		Emissions (MT/yr)	
	Year	Volatile Organics	Particulate Organics
Fossil Fuel Processing			
Natural Gas	1975	1,714,000	--
Coal	1975	2,400	7,300
Total		1,716,400	7,300

Reference: MO-201

No information was found concerning the water or solid wastes from natural gas and coal processing. For the purposes of this study, solid wastes processed on site by landfill, spoil pile, or other means were not assumed to be an environmental problem. Organic solid waste emissions and organic water effluents are assumed to be negligible for this category.

3.2.1 Natural Gas Processing

Process Description

The gas treatment facilities normally encountered in the field are designed to condition the natural gas to make it marketable. The operations may include the removal of impurities such as H_2S and CO_2, dehydration, product recovery, and the control of delivery pressure through the use of pressure reducing regulators or compressors.

Gas-processing plants, on the other hand, are usually operated to recover valuable products which may be left in the gas following field processing. These products may include natural gasoline, butane, propane, ethane, and even pure methane at some plants. To accomplish this, the processing plant includes many of the functions performed by gas-conditioning equipment such as dehydration and acid gas removal. For this reason a gas plant may be considered as another gas-conditioning facility. These facilities, often referred to as natural gasoline plants, usually provide fractionating equipment for separating the recovered liquid hydrocarbons into pure products or predetermined mixtures. Where H_2S is removed from the gas, a plant may include facilities to recover elemental sulfur.

The units found in gas-plant operations are similar to those found in the field; the primary difference is the size and perhaps the mechanical design of the units. The typical types of equipment found in natural gasoline plants are absorbers, strippers, fractionators, heat exchangers, and air coolers or cooling towers.

Atmospheric Emissions and Control

The primary sources of atmospheric organic emissions from natural gas processing operations are fugitive losses and natural gas venting. The fugitive losses occur from sources such as pipeline valves, flanges, gaskets, and compressor seals. Venting losses occur primarily during processing system upsets or from the faulty operation of pressure relief valves. An estimated 1.714×10^6 metric tons per year of hydrocarbons are emitted from natural gas processing (MO-201). These emissions are composed primarily of methane with lesser quantities of ethane, propane, butane, and other low-molecular weight saturated hydrocarbons.

The control of these emissions from natural gas processing relies heavily upon regular maintenance of equipment and good housekeeping at the processing site. Equipment changes can offer some help in reducing the emissions of hydrocarbons. For example, substituting mechanical seals for packed seals on centrifugal compressors and installing dual packed seals on reciprocating compressors are control measures which reduce the quantity of hydrocarbons emitted.

The controls used to reduce the loss of hydrocarbons from relief valves include the installation of manifolding to a vapor control device or a blowdown system. For relief valves where discharge into a closed system is not desirable, fragile rupture discs prevent the relief valve from leaking and protect the valve seat from corrosive environments (WA-086). These controls effectively reduce the emissions from relief valves to negligible quantities.

The emissions from product leaks at valves and flanges can only be controlled by regular inspection and prompt maintenance of valve packing boxes and flange gaskets. The emissions reduction from proper maintenance of valves and flanges is difficult to determine because it is dependent on the corrosiveness of the gas handled, the degree of maintenance, and the characteristics of the environment. However, because the primary source of atmospheric hydrocarbon emissions from gas processing is fugitive leaks, the reduction potential is assumed to be the same as that for crude oil and natural gas processing, 60 percent. This means a mass emission reduction potential of 1,030,000 MT/yr of hydrocarbons to the atmosphere.

3.2.2 Coal Processing

Process Description

Coal processing consists of the operations used by the industry to upgrade the quality of raw coal prior to its sale. The physical character and chemical composition of the raw coal and the customer specifications on the product determine the extent and type of processing.

Three types of processing plants are used to prepare the various types of product coal demanded by the market: 1) "complete processing", 2) "partial processing", in which only coarse coal is cleaned; and 3) "coal crushing", in which the coal is merely crushed to a specified maximum size. Because the complete preparation plant includes all processing operations, it is the only one described.

At the preparation plant, coal from the mine is broken and screened to remove oversized material, then stored until the

batch processing in the plant begins. From storage the coal is classified according to size by screening and then routed to various cleaning process equipment. In general, this cleaning process may be wet, dry, or a combination of both.

Wet cleaning systems utilize centrifugal or gravity separation of heavier impurities from the coal. The wet cleaning itself does not emit organics; however, the auxiliary processes of handling and drying can be major sources. After the cleaning, the coal is mechanically dried by dewatering screens and centrifugal driers. Should the customer desire low surface moisture coal, secondary drying is required. Low moisture levels are best accomplished by thermal drying. A survey of the industry indicates that new coal preparation plants installing thermal driers will use a fluidized-bed type. In this drying technique, hot flue gases from a coal-fired furnace pass up through a moving bed of fine wet coal. The coal is dried as the coal particles come into intimate contact with the hot gases during fluidization. Particulate organic emissions occur in the form of ultrafine coal particles entrained and carried from the drier by the combustion gases. The dried coal is stored prior to shipment.

All coal cleaning systems installed since 1966 have used pulsating air columns to separate coal from its impurities (EN-220). The particulate organic chemical emissions from these operations are negligible.

Atmospheric Emissions and Control

Potential particulate organic emissions for fluidized-bed driers upstream of control equipment are in the range of 115 to 460 grams per normal cubic meter. The emissions measured downstream of cyclones, which are an integral part of the coal

cleaning process, range from 1.6 to 32 grams per normal cubic meter (EN-220).

The products of combustion from the coal burned in the drier to generate the hot gases contain measurable quantities of gaseous organics. Particulate emissions from thermal driers amount to about 7.3×10^3 metric tons per year while the gaseous organic emissions are 2.4×10^3 metric tons per year (MO-201).

Single cyclone collectors and multiple cyclones for product recovery have efficiencies of 70 and 85%, respectively. Water sprays following cyclones have an efficiency of 95% (EN-071), and wet scrubbers following cyclones have efficiencies of from 99 to 99.9%.

The reduction potential for particulate organic emissions from coal processing is fairly high because of the limited number of processing plants and the extent of the development of applicable control technology. However, the reduction potential for gaseous hydrocarbon emissions from thermal drying is very low. Only combustion modifications could reduce the gaseous emissions, and only limited control is available from this method. The percent reduction estimated for particulate emissions from thermal driers is a little less than 50 percent (EN-071, EN-220). This results in a reduction potential of 3650 MT/yr of organic particulates.

3.3 Fossil Fuel Transportation, Storage, and Distribution

This category includes emissions from the distribution network for the transportation of fossil fuels and their products. The emissions associated with the distribution network result from storage at distribution facilities and loading and unloading at distribution points.

The category is divided into subgroups by the type of material transported. The major subgroups are gasoline marketing, jet fuel marketing, distillate and diesel fuel marketing, residual fuels marketing and crude transport. These major subgroups are characterized by emissions from storage facilities, pipelines, and loading operations. Loading operations include both marine loading and rail and truck loading.

A summary of the atmospheric emissions from the processes in this category is presented in Table 3.3-1.

The total emissions from the transportation category are over 2.0×10^6 MT/yr. The potential reduction in emissions from storage operations is nearly 0.5×10^6 MT/yr and from loading operations is almost 0.9×10^6 MT/yr. These potential reductions are estimated by assuming that current use of controls is extended to complete application of controls. These controls are generally assumed to be floating-roof tanks for the storage facilities and bottom loading or submerged fill along with vapor recovery and vapor balance for loading operations.

Water effluents and solid wastes are negligible in this category. Contamination of surface waters from spills during distribution is a source of water pollution. However, the impact on the environment depends on a knowledge of the amount of organic

TABLE 3.3-1

FOSSIL FUEL TRANSPORTATION, STORAGE, AND DISTRIBUTION ATMOSPHERIC EMISSIONS

	Emissions (MT/yr)				
	Year	Volatile Organics	Ref.	Particulate Organic	Ref.
Crude Oil Storage	1973	526,000	1	-	-
Gasoline Service Station Automobile Filling	1973	467,000	1	-	-
Gasoline Service Station Underground Tank Filling	1973	399,000	1	-	-
Gasoline Bulk Terminal Loading	1973	189,000	1	-	-
Gasoline Bulk Station Storage	1973	109,000	1	-	-
Gasoline Bulk Station Loading	1973	94,700	1	-	-
Diesel & Distillate Storage	1973	79,100	1	-	-
Refinery Loading, Products	1973	65,600	1	-	-
Petroleum Gathering and Distribution, Pipeline	1970/71	63,200	2	-	-
Gasoline Bulk Station Pump Seals	1973	52,300	1	-	-
Gasoline Service Station Storage	1973	42,400	1	-	-
Gasoline Bulk Terminal Storage	1973	33,400	1	-	-
Crude Oil Transportation, Marine Loading	1973	17,600	1	-	-
Gasoline Bulk Terminal Pump Seals	1973	10,700	1	-	-
Gasoline Marketing, Marine Loading	1973	9,030	1	-	-
Jet Kerosine Marketing, Storage	1973	8,940	1	-	-
Jet Naphtha Marketing, Storage	1973	6,950	1	-	-
Crude Oil Transportation, Rail & Truck Loading	1973	6,620	1	-	-
Diesel & Distillate Marketing, Rail & Truck Loading	1973	4,970	1	-	-
Aviation Gasoline Marketing, Storage	1973	4,640	1	-	-
Aviation Gasoline Marketing, Loading	1973	3,870	1	-	-
Jet Naphtha Marketing, Rail & Truck Loading	1973	1,990	1	-	-
Gasoline Bulk Station Valves	1973	1,960	1	-	-
Jet Kerosine Marketing, Rail & Truck Loading	1973	662	1	-	-
Diesel & Distillate Marketing, Marine Loading	1973	662	1	-	-
Gasoline Bulk Station Valves	1973	410	1	-	-
Jet Kerosine Marketing, Marine Loading	1973	331	1	-	-
Coal Rail Transportation, Unloading	1973	-	-	77,300	3
SUBTOTAL, LOADING		1,195,435		77,300	
STORAGE		810,430			
FUGITIVE		65,370			
TOTAL		2,071,235			

REFERENCES:
1. BU-185
2. RI-107
3. CA-246

recovered after the spill, the amount of organic reaching the atmosphere by evaporation, the amount of organic reaching surface waters, and the amount of organic soluble in surface waters. Little information is available on these factors. In addition, the overall quantity of organics spilled is small when compared to total emissions from the transportation category. The potential for reduction of these spills is not as large as for many other emission sources. For these reasons, spills during transportation operations will not be quantified in this report.

The important processes which emit organic chemicals in the fossil fuel transportation, storage, and distribution category are identified in this section. These processes are examined to determine the point of organic emissions from the processes. Emissions from process effluent streams and from fugitive sources are considered. The current level of control of organic emissions from the processes or operations is assessed when possible.

3.3.1 Gasoline Marketing

The gasoline marketing industry includes all transfer and storage operations that occur when gasoline products are transported from petroleum refineries to the consumer. Figure 3.3-1 shows flow patterns for motor gasoline from refinery storage to the vehicle refueling stations in the U.S. marketing network. Gasoline is transported from refinery storage to terminals by pipelines, tankers and barges, or rail tank cars.

3.3.1.1 Bulk Terminals

The primary distribution facility in the gasoline marketing network is the bulk terminal. Gasoline products arrive

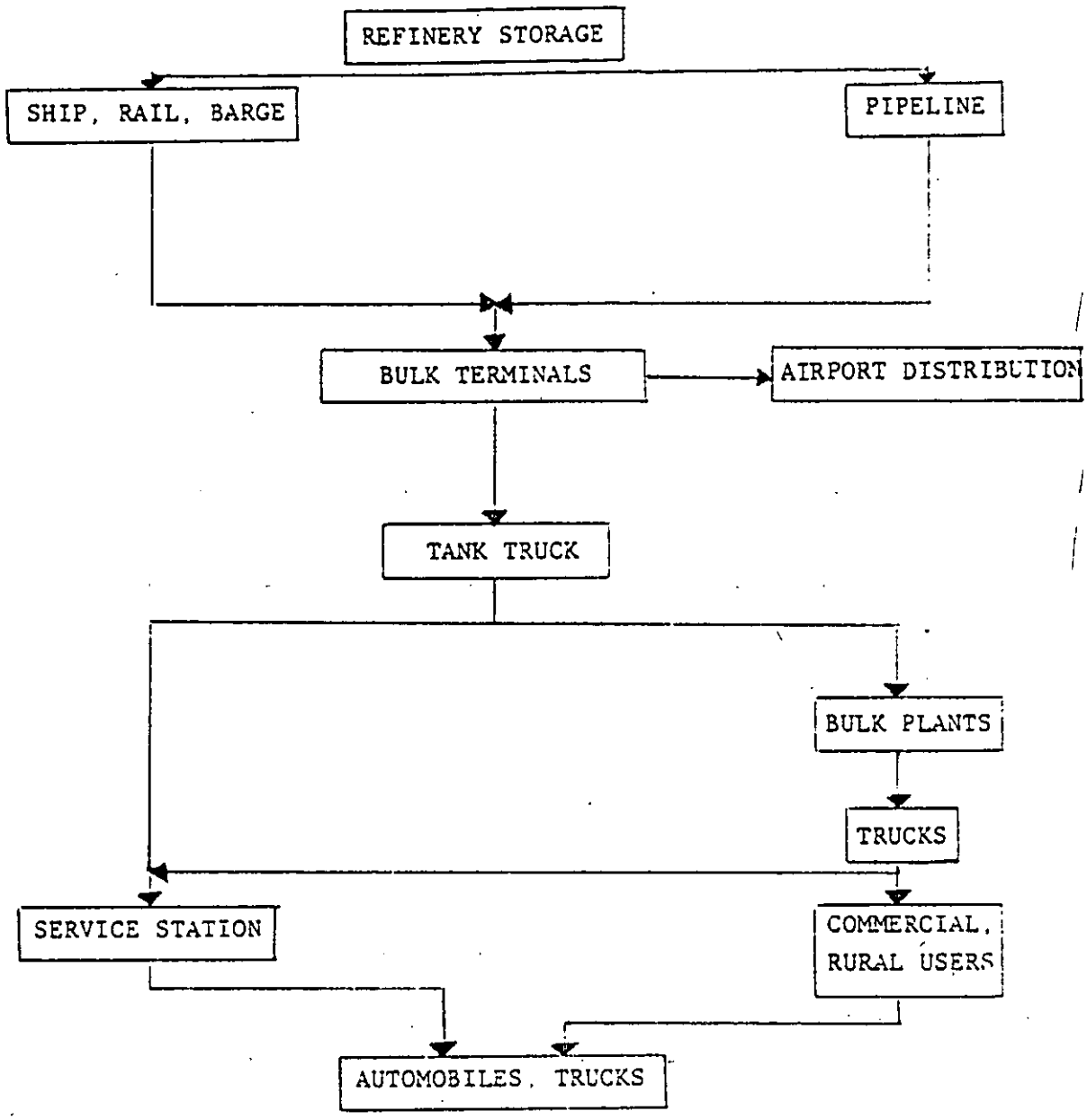


FIGURE 3.2-1

The Gasoline Marketing Distribution System In The United States

at the bulk terminal by pipeline and are stored in large above-ground tanks. From these storage tanks the gasoline is loaded into tank trucks and transported to smaller bulk loading stations and to service stations.

Statistics from the 1967 Census of Business show 2701 terminals in that year. Total national liquid storage capacity of motor gasoline at terminals was 23 hm^3 (6.2 billion gallons) with an average capacity of 8700 m^3 (2.3 million gallons) per terminal (US-031). Table 3.3-2 contains a compilation of the nation's bulk storage capacities as a function of tank size. By 1973, gasoline consumption had increased to 401 hm^3 (106 billion gallons). Sales volume at bulk terminals had presumably increased at a rate commensurate with the increase in gasoline consumption while the number of bulk terminals remained unchanged.

Generally, the gasoline storage tanks are subject to regulations requiring that they be equipped with floating roofs. Organic chemical emissions from tanks of this design are limited to vapors escaping past the wall seals and to gasoline evaporating from the wetted walls as the liquid level is lowered. These minor organic chemical emissions are generally less than 0.3 gallons/1000 gallons handled (DU-001).

Organic chemical emissions from the tank truck loading racks are potentially much greater than those from the storage tanks at bulk terminals. As the empty tank trucks are filled, the organic chemicals in the vapor space are displaced to the atmosphere unless vapor collection facilities have been provided. The quantity of organic chemicals contained in the displaced vapors is dependent on the Reid Vapor Pressure, temperature, method of tank filling, and the conditions under which the truck was previously loaded.

TABLE 3.3-2

U. S. BULK STORAGE CAPACITY BY TANK SIZE

Tank Size	Storage Capacity hm^3 (10^3 gal)	
Less than 42,000 gallons	0.36	(95,975)
42,000 - 62,000 gallons	0.92	(242,837)
63,000 - 83,000 gallons	0.94	(249,542)
84,000 - 104,000 gallons	0.52	(137,078)
105,000 - 209,000 gallons	0.81	(214,148)
210,000 - 1,049,000 gallons	0.71	(186,960)
1,050,000 - 2,099,000 gallons	0.84	(221,792)
2,100,000 - 6,299,000 gallons	5.25	(1,386,821)
6,300,000 - 20,999,000 gallons	8.92	(2,357,165)
Greater than 21,000,000 gallons	8.03	(2,120,770)

Source: US-031

3.3.1.2 Bulk Stations

Bulk loading stations are secondary distribution facilities which receive gasoline from bulk terminals by large tank trucks, store the gasoline in somewhat smaller aboveground storage tanks, and subsequently dispense the gasoline via smaller tank trucks to local farms, businesses, and service stations. In 1967 there were 26,338 bulk stations. Liquid storage capacity of gasoline at bulk stations was 4 hm^3 (1.0 billion gallons) with an average capacity of 151 m^3 (40,000 gallons) per bulk station (US-031).

There were fewer bulk stations and terminals in 1972 than in 1967. Oil company officials and industry representatives confirm this assessment. They indicate that this reduction, primarily in the number of bulk stations, is for economic reasons. More gasoline deliveries will be made directly from terminals with large tank trucks. Storage volumes at terminals will be increased. The decrease in number of bulk stations will not necessarily have a major impact on overall marketing operations.

The combined sales volume at bulk stations and terminals is presumed to have increased at a rate commensurate with the steady increase in gasoline consumption.

Atmospheric Emissions and Control

Significant organic emissions from storage tanks are generated at bulk stations. Because the storage tanks are often horizontal and cannot be fitted with floating roofs, or because roof regulations do not apply to such small tanks, the storage tanks at bulk loading stations are generally uncontrolled and are thus a significant source of organic emissions.

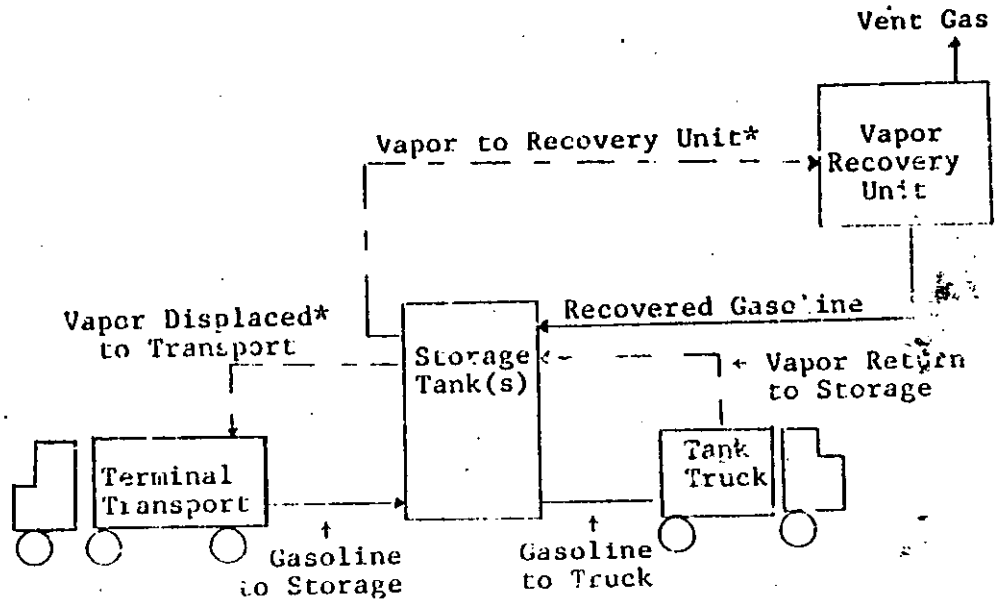
Organic emissions from bulk stations can be controlled with the installation of a vapor recovery system, since control with floating roof tanks may not be feasible. A vapor recovery system designed for a bulk station may be designed to recover emissions from both storage and tank truck loading operations. Figure 3.3-2 is a schematic drawing of the vapor and liquid flow at a typical bulk station with controls.

The organic emission reduction potential for bulk station storage operations is 95%. This will amount to a reduction in emissions of 104,000 MT/yr of hydrocarbons from the present emission rate of 109,000 MT/yr.

The other significant emission source from gasoline bulk stations results from tank truck loading operations. During the loading operation, vapor in the transport truck is displaced to the atmosphere as it is being filled from bulk station storage. The amount of emissions generated is dependent primarily on the type of loading operation.

Top loading and bottom loading are the two basic methods of filling transport tanks. The top loading procedure can be done with splash fill or submerged fill. With splash loading, gasoline is discharged into the upper part of the tank compartment through a short spout which never dips below the surface of the space liquid. The free fall of the gasoline droplets promotes evaporation and may even result in liquid entrainment of some gasoline droplets in the expelled vapors.

With subsurface or submerged loading, gasoline is discharged into the tank compartment below the surface of liquid in the tank. This is accomplished for top loading operations by the use of a long spout or fixed pipe extending internally from



*Vapor emissions from bulk plants may potentially be controlled by vapor displacement, in which case the recovery unit would be eliminated.

FIGURE 3.3-2

Vapor and Liquid Flow in a Typical Bulk Station With Recovery of Displaced Vapors

the top tank entry to the bottom of the compartment. With direct bottom loading, transfer piping is connected directly to the tank bottom. This method achieves the same effect as submerged top loading while providing other advantages such as ease of loading operations and safety. Consequently, many bulk stations have already been converted to bottom loading.

Organic emission levels from loading operations are partly influenced by the transport's previous operation. If low volatility products were transported previously or the transport was purged of organic vapor prior to loading, the organic emissions from gasoline loading may be significantly lower. The potential reduction in emissions from loading operations using vapor recovery systems is estimated to be 95%. This would result in a reduction of organic emissions of 91,600 MT/yr from a present level of 94,700 MT/yr.

3.3.1.3 Service Stations

In 1973 there were 218,000 service stations (NA-168). A gasoline service station is defined by the U.S. Department of Commerce as a retail outlet with more than 50% of its dollar volume coming from the sale and service of petroleum products. The total number of gasoline service stations is undergoing rapid change. A survey conducted in May and June 1974 by Audits and Surveys, Inc., a New York firm, reveals that in 1974 there were 196,000 U.S. service stations, 9.1% less than their 1973 survey figure of 216,000 (AU-020).

Detailed breakdowns of service station sizes as functions of sales volumes are difficult to obtain due to the reluctance of oil companies to make this information public. In 1973, average monthly service station throughput was 117 m^3

(30,800 gallons) per month according to an estimate by Lundberg Survey, Inc. (LU-044).

An EPA analysis of service station sales statistics from the 1967 Census of Business reveals the totals shown in Table 3.3-3 for the number of stations in various size categories (MA-314).

Service stations are the final facility in the gasoline marketing network. At the stations, gasoline is received by tank truck, stored in underground tanks, and dispensed to automobile fuel tanks.

Figure 3.3-3 is a schematic drawing of vapor and liquid flow through a typical service station.

Atmospheric Emissions and Control

Volatile organics in the storage tank vapor space are displaced as the tank is filled with gasoline from the tank truck. The quantity of these emissions is dependent on filling rate, filling method, Reid Vapor Pressure, and the system temperature. An analogous situation occurs when a partially empty vehicle tank is filled.

Breathing losses from the underground gasoline storage tanks are another source of organic emissions. Because the tanks are underground, breathing losses due to diurnal temperature effects are minimized.

Emissions resulting from underground tank filling vary with the method of tank loading, *i.e.*, splash or submerged loading. Use of splash loads results in large emissions of

TABLE 3.3-3

U.S. GASOLINE SERVICE STATION

SALES VOLUME DISTRIBUTION

Service Station Sales Volume (Gallons/Year)	Number of Stations in 1967
Less than 150,000	54,100
150,000-200,000	17,100
200,000-250,000	21,200
250,000-300,000	25,500
Larger than 300,000	98,100
	216,000

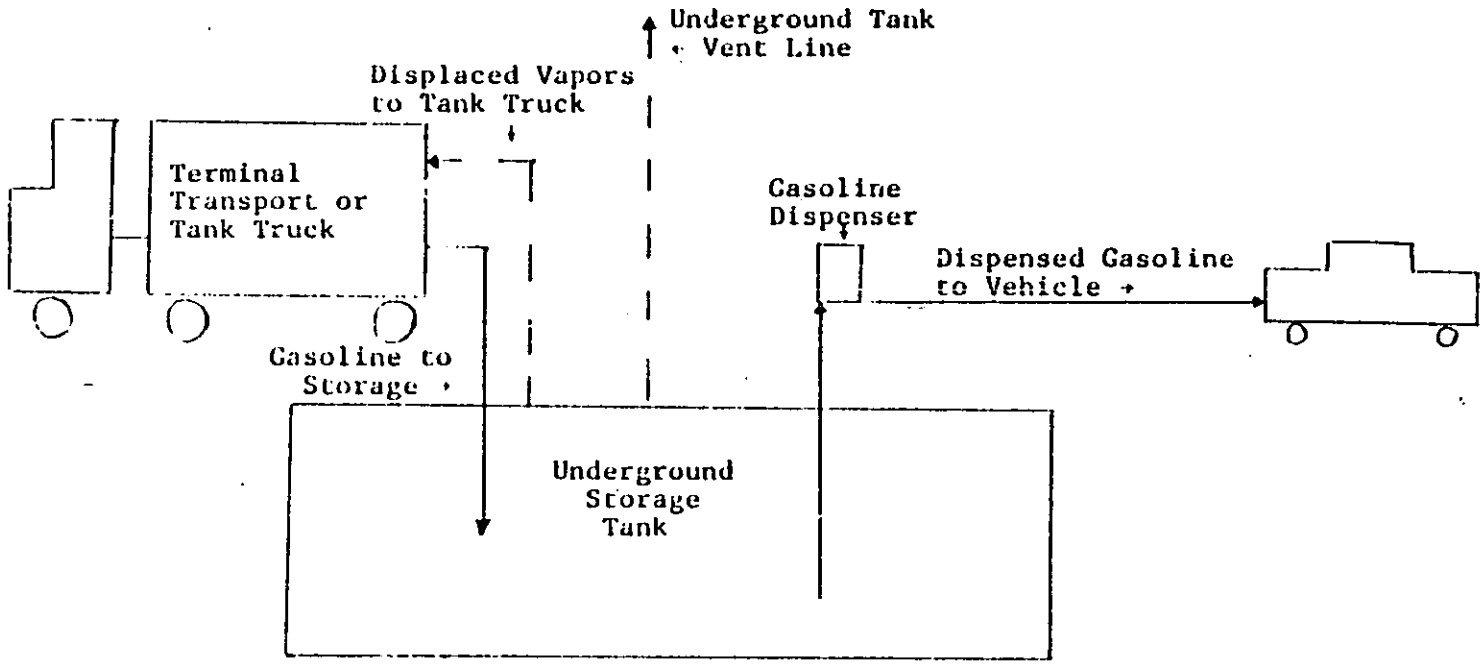


FIGURE 3.3-3

Vapor and Liquid Flow in a Typical Service Station

organics. Submerged loading reduces the vapors generated. In addition, test data indicate that 95% of the displaced vapor can be recovered by returning the displaced vapors to the tank truck. This data indicates that a well-designed vapor balance or displacement system will provide efficient control of underground tank refilling vapors with the use of emission control technology and equipment commercially available today.

The estimated potential reduction of volatile organics emitted from service station underground tank filling is 95%. This provides a reduction in volatile organic emissions of 383,000 MT/yr from 399,000 MT/yr.

There are two basic types of emission control systems for vehicle refueling: vapor displacement and vacuum assist. There is some disagreement on the relative effectiveness of these two systems. The vapor displacement, or vapor balance, system operates by simply transferring vapors from the vehicle fuel tank to the underground tank where they are stored until final transfer to a tank truck. Vacuum assist systems employ a blower or a vacuum pump and a secondary recovery device. The vacuum pump creates a negative pressure in the vehicle fillneck which "pulls" hydrocarbon vapor to a secondary recovery unit.

The estimated potential reduction in organic emissions from refueling operations by using vapor balance or vacuum assist systems is 90%. This reduces the current emission rate of 467,000 MT/yr by 420,000 MT/yr.

3.3.2 Jet Fuel Marketing

Jet fuel is essentially kerosene-boiling-range material with critical freeze point, flash point, and smoke point specifications. The flash point is controlled by the amount of naphtha

blended into the jet fuel. Naphtha tends to lower the pour point and in most instances maximum naphtha (up to flash point restrictions) is used. Hydrocrackers can be used to produce high-quality kerosene blend stocks by isomerizing the paraffins. This isomerization lowers the freeze point and raises the smoke point by saturating the aromatics (DO-070).

Data for 1973 shows that approximately 95% of all jet fuel consumed in the U.S. was for airline or military use. The demand for kerosene-type jet fuel for 1973 was 48 hm^3 (303 million barrels), while the demand for naphtha-type jet fuel was 13 hm^3 (80 million barrels). These figures show an increase in the demand for kerosene-type fuel and a decrease in the demand for naphtha-type fuel when compared to 1972 figures, 46.6 hm^3 (293 million barrels) and 14 hm^3 (88 million barrels), respectively.

Of the 60.5 hm^3 (381 million barrels) of jet fuel consumed in the U.S. in 1972, 7.6 hm^3 (48 million barrels) were transported by barge and tanker (AM-099), while 36.4 hm^3 (229 million barrels) were transported by pipeline (US-144). According to this data, 15 hm^3 (95 million barrels) of jet fuel were transported by some other means, such as railroad tank car or tank truck, with some 1.4 hm^3 (9 million barrels) left unaccounted (AM-099).

Nonrefinery storage capacities for jet fuels in 1968 with a refinery throughput of 55.5 hm^3 (349 million barrels) was 2.76 hm^3 (17.4 million barrels) (MS-001). Since the 1973 throughput exceeds the 1968 figure by 10%, storage capacities are assumed to have also increased, although 1973 capacities are unavailable. Within the marketing system, jet fuels are stored at bulk stations and bulk terminals. Petroleum bulk

stations are defined generally as those having capacities less than 8 dam^3 (2 million gallons) and receiving their supply by truck or rail transport. Bulk terminals generally handle large throughputs and are supplied primarily by pipeline, tanker, or barge.

Storage capacities for naphtha-type jet fuels amounted to 1 hm^3 (6.1 million barrels) in 1968, while those for kerosene-type jet fuels amounted to 1.79 hm^3 (11.3 million barrels) (MS-001).

Organic emission sources in the jet fuels marketing industry are very similar to the emission sources in the gasoline marketing industry. In brief, storage losses can be controlled by converting to floating-roof tanks or by venting excess vapor from fixed-roof tanks to a vapor recovery system. Loading and unloading emissions can be controlled by venting the displaced vapors to a vapor recovery unit.

3.3.3 Distillate and Diesel Fuel Marketing

Distillate fuel oil refers to petroleum products which boil in the 176 to 343°C (350 to 650°F) range. This includes Numbers 1, 2, and 4 fuel oils. Diesel fuels are also included in this fraction. Grade No. 2 fuel oil is the designation given to the heating or furnace oil most commonly used for domestic and small commercial space heating and is the fuel oil generally referred to as distillate fuel. Domestic heating oil is generally a clean product with a low sulfur and ash content and no asphaltic matter. As a result, distillate fuels form no sediment in storage and have less tendency to form ash or carbon deposits when burned. These properties, combined with viscosities much lower than residual fuels, make clean and trouble-free combustion easier to achieve.

Diesel fuel is similar to distillate fuel. Diesel fuel is often referred to by ASTM grade numbers 1-D and 2-D, since it is marketed as burner fuel and grades 1 and 2. Some typical specifications for fuel oil and diesel fuels are listed in Table 3.3-4 (DO-070).

Diesel fuel is burned in the compression ignition engine rather than in a fuel burner. As a result, ignition quality becomes an important characteristic. This ignition quality is expressed as a cetane number which may be improved (raised) by the removal of aromatics or by the inclusion of additives to initiate the combustion processes. Paraffinic fuels are better suited for diesel use because of lower self-ignition temperatures.

Forty-eight percent of the 174 hm^3 (1.1 billion barrels) of distillate fuel oil consumed in the U.S. in 1973 was used as heating oil. Twenty-four percent of the total was used as diesel fuel. Table 3.3-5 shows a breakdown of distillate fuel oil demand by uses in 1973.

Transportation data for 1972 show that of the 168 hm^3 (1.06 billion barrels) of distillate fuel oil used in the U.S., 21.9 hm^3 (138 million barrels) were moved by tanker and barge (AM-099) and 104 hm^3 (657 million barrels) were moved by pipeline (US-144). The remaining 42.5 hm^3 (268 million barrels) were transported by means of railroad tank car and tank truck. Pipeline movement figures are not available for 1973, but of the 174 hm^3 (1.1 billion barrels) consumed, 17.2 hm^3 (108 million barrels) were moved by tanker and barge (AM-099).

Storage capacities for distillate fuel oil in the marketing system in 1968 (with a throughput of 138 hm^3 (872 million barrels) amounted to 26.8 hm^3 (169 million barrels) (MS-001).

TABLE 3.3-4

PROPERTIES OF DISTILLATE FUELS

Property	No. 2. Fuel Oil	Diesel Fuel
Flash, min., °C(°F)	60(140)	62.7to68.3(145to155)
Pour Point, max., °C(°F)	-20(- 5)	-23 to-12 (-10to+10)
Sulfur, max. wt%	0.5	0.5
Cetane Number, min.	40.0	52.0

TABLE 3.3-5

U.S. DISTILLATE FUEL OIL DOMESTIC DEMAND BY USES

(Daily averages in dam^3 (10^3 42 gallon barrels)

	1973
Heating Oils:	
No. 1	
Automatic Burners	14 (91)
Other Heating	6 (40)
No. 2	194 (1,222)
No. 4	18 (115)
Total	233 (1,468)
Industrial	29 (184)
Oil Company Fuel	7 (41)
Electric Utility Company	34 (214)[1]
Railroads	45 (282)
Vessel Bunkering	12 (73)
Military Use	9 (54)
Diesel Type	
On Highway	94 (594)
Off Highway	25 (155)
Total	119 (749)
All Other	2 (15)
TOTAL	489 (3,080)[1]

[1] Includes 11 dam^3/day (68,000 barrels per day) of distillate fuel used by steam electric plants. Also included are 3 dam^3/day (17,000 barrels per day) of kerosene-type jet fuel used by electric-utility companies.

In 1973 throughput exceeded the 1968 figure by 29 percent. Storage capacities have also been increased accordingly.

Organic emissions from the marketing of distillate and diesel fuels primarily originate from storage tank evaporation and from tank truck and railcar loading.

Emission controls have not been applied to diesel and distillate fuels marketing because of their relatively low volatility and organic emission rate.

3.3.4 Residual Fuels Marketing

Residual fuel oils are generally defined as crude oil distillation residues having a boiling point of 343°C(650°F) or greater. In addition to these "straight-run" oils, fuels of the residual type are produced from the various refinery cracking processes. Residual oil is not considered a choice energy source among the fossil fuels. It is composed of the heaviest parts of the crude and contains asphaltic matter, asphaltenes, sulfur, and small amounts of metals. Typically, residual fuels are used to provide steam and heat for industry and large buildings, generate electricity, and power ships.

Residual fuel oils can be defined as Number 5 and Number 6 heating (burner) oils, heavy diesel, heavy industrial, and heavy marine (Bunker "C") fuel oils. Fuel oil terminology is not sharply defined. For example, Bunker C fuel is a heavy fuel oil that generally corresponds to Grade 6 fuel oil. The terms heating oils and burner fuel oils are often used synonymously.

The steady increase in the use of catalytic cracking refineries following World War II had the effect of decreasing

the percentage yield of residual fuels as well as changing their makeup. As more high-boiling materials were charged to catalytic cracking, the remaining oil sold as residual fuel became heavier and heavier. Previous common industry practice was to blend these heavy stocks with lighter distillates to reduce their viscosities to a salable fuel level. After the war, refining processes in the United States began to produce the more profitable products more efficiently. Residual fuel oils account for 7.6 percent of average national petroleum production and refining yields (EN-043). In 1973, 0.15 hm^3/day (971 thousand barrels per day) of residual oils were produced in domestic refineries while another 0.29 hm^3/day (1827 thousand barrels per day) were imported (AM-099). U.S. refineries have continued to reduce the yield of residual fuels; however, if the current residual shortages and higher prices prevail, this trend could be slowed or even reversed.

Fixed-roof tanks operated at atmospheric pressure are predominantly used in the storage of residual fuel oils. These fuels have low volatilities; and evaporation, breathing, and working losses are minimal. Residual fuels are heated throughout storage and transportation operations to maintain manageable viscosities.

Residual fuel oil can be transported by tanker, barge, pipeline, tank truck, or railroad tank car. Of the 0.4 hm^3/day (2.8 million barrels per day) of residual oil consumed in the U.S. in 1973, 0.25 hm^3/day (1.8 million) were imported; thus, the majority of residual fuels are handled by tanker and barge. Furthermore, in 1973, 7 dam^3/day (44,000 barrels per day) of residual oils were transported by tanker and barge from the Gulf Coast to the East Coast and 4 dam^3 (24,000 barrels per day) were transported from the Gulf Coast to the Midwest via the Mississippi River (AM-099).

The possibility of substantial atmospheric hydrocarbon emissions from residual fuel oils during storage or transportation is minimal. Number 6 residual fuel oil has a negligible vapor pressure, i.e., less than 690 Pa(0.1 psia), and as a result, hydrocarbon emissions from marketing this fuel are negligible.

3.3.5 Crude Oil Transport

The most important mode of transporting petroleum overland is the pipeline. The basic function of trunk pipelines in domestic oil fields is that of transporting crude oil from field storage to refinery storage. In 1973 a daily average of 1.3 hm^3 (8.0 million barrels) of domestic crude was moved to refineries through pipelines. This figure represented 87 percent of domestic production for that year (AM-099).

Before the pipelines are buried, they are wrapped with a protective coating to prevent corrosion of the pipe exterior. The pipe may also be equipped with cathode protection. Internal corrosion is a problem only in those lines carrying crudes containing sulfides.

Nearly all of the existing pipelines are laid below grade. Subsurface installation protects them from weather and from accidental damage by earth-moving equipment. Offshore pipelines are laid in trenches on the floor of the sea to guard against damage by wave action, storms, and shipping accidents.

Although the U.S. pipeline system is extensive, it is sometimes necessary and economical to transport crude by barge or tanker to refineries in certain parts of the country. Many refineries are located on navigable waters and operate docks for receiving or shipping oil by tanker or barge. Tankers of many

sizes transport crude oil and products in coastal traffic and over inland waterways. The United States has 20,000 km(12,000 miles) (EN-045) of coastline and 40,000 km(25,000 miles) (AM-155) of navigable inland waterways and therefore offers a large potential for domestic traffic by water.

Tanker and barge movements of crude oil for several recent years are shown in Table 3.3-6 in daily averages of dam^3 (thousands of barrels). Crude transported by water is usually moved by pipeline from the point of production to the point of water shipment. The barges used for transport of crude oil are called tank barges. They are designed to carry liquid products in bulk and are powered by towboats or tugboats. Other forms of crude transport are railway tank cars and tank trucks. These are less commonly used methods, but they are necessities in some areas. The daily average of crude transported to the refineries by tank car and tank truck in 1973 was 2.42 dam^3(159,000 barrels), or about 2 percent of the domestic production.

Imports of crude oil for 1973 averaged 0.5 hm^3(3.2 million barrels per day). This figure constituted a 46 percent increase of crude imports over 1972 figures. Table 3.3-7 provides an illustration of the rate of growth of crude imports over the past years.

TABLE 3.3-6

TANKER AND BARGE MOVEMENTS OF CRUDE OIL

dam^3/day (10^3 barrels/day)

	1971	1972	1973
Gulf Coast to East Coast	89.7 (565)	46.4 (292)	24.6 (155)
Gulf Coast to Mid-West	7.9 (50)	7.9 (50)	4.4 (28)
Gulf Coast to West Coast	--	0.3 (2)	--

Source: AM-099

TABLE 3.3-7

CRUDE OIL IMPORTS

in dam^3 (10^3 barrels/day)

1968	1969	1970	1971	1972	1973	1974*	1975**
205	224	210	267	352	515	556	609
(1290)	(1409)	(1324)	(1680)	(2216)	(3244)	(3500)	(3830)

* Preliminary
** January

Source: AM-099

A large percentage of the imports must be transported over the ocean in marine tankers. Since more and more oil has been transported from the lesser developed countries to the highly industrialized nations, the world tanker fleet has grown in numbers and in capacity. In 1950 tankers totaled 25.7 Gg (25.3 million deadweight tons (DWT)). By 1972 tanker tonnage was 186.1 Gg(183.2 million DWT). The average size tanker increased in the same time period from 12 Mg(12,000 DWT) to 60 Mg(58,000 DWT). The largest tanker in use in 1950 was under 25 Mg(25,000 DWT), but in 1972 the largest tanker in use was in excess of 305 Mg(300,000 DWT), and vessels of 548 Mg(540,000 DWT) were under construction (PR-074). The increasing emphasis on large carriers results from the favorable economics of carrying large loads on long trips.

The existing United States ports are unable to accomodate the large "supertankers". This fact has necessitated loading and unloading at offshore anchorages. The oil may be loaded and unloaded via submarine pipeline to the shore. It may also be handled in an offshore storage facility and later transported to shore by smaller tankers and barges.

Crude oil is handled in a system closed except for points of transfer. Crude is supplied to refineries through a transportation system which includes tank farms, bulk terminals, and other storage points connected by overland and water transportation systems. Figure 3.3-4 illustrates the relative sizes of systems involved in transporting crude oil to refineries.

Atmospheric Emissions and Control

The organic chemicals emitted in transferring crude to the refinery are mostly low molecular weight saturated hydrocarbons. If the oil transportation system is open to the atmosphere at any point, dissolved light gases will be lost. As in every other phase of production, storage tanks are potential sources of emission.

Pipelines are subject to losses caused by corrosion damage or accidents. Spills account for only a small percentage of the quantity of products carried, but the volume of products carried is very large. Other emissions sources in pipeline systems are valves, pumps, flanges, and other fittings. Even small leaks in the many fittings and pumping equipment may result in sizable emissions because of the large volumes transported through the pipeline network.

Most emissions from tank cars, tank trucks and marine facilities occur during loading operations. Most tank cars and trucks are filled from the top by subsurface loading and marine tankers are filled from the bottom through fill pipes which are integral parts of the carriers. These methods of loading create the least amount of turbulence and result in the least amount of vaporization when compared to splash loading methods.

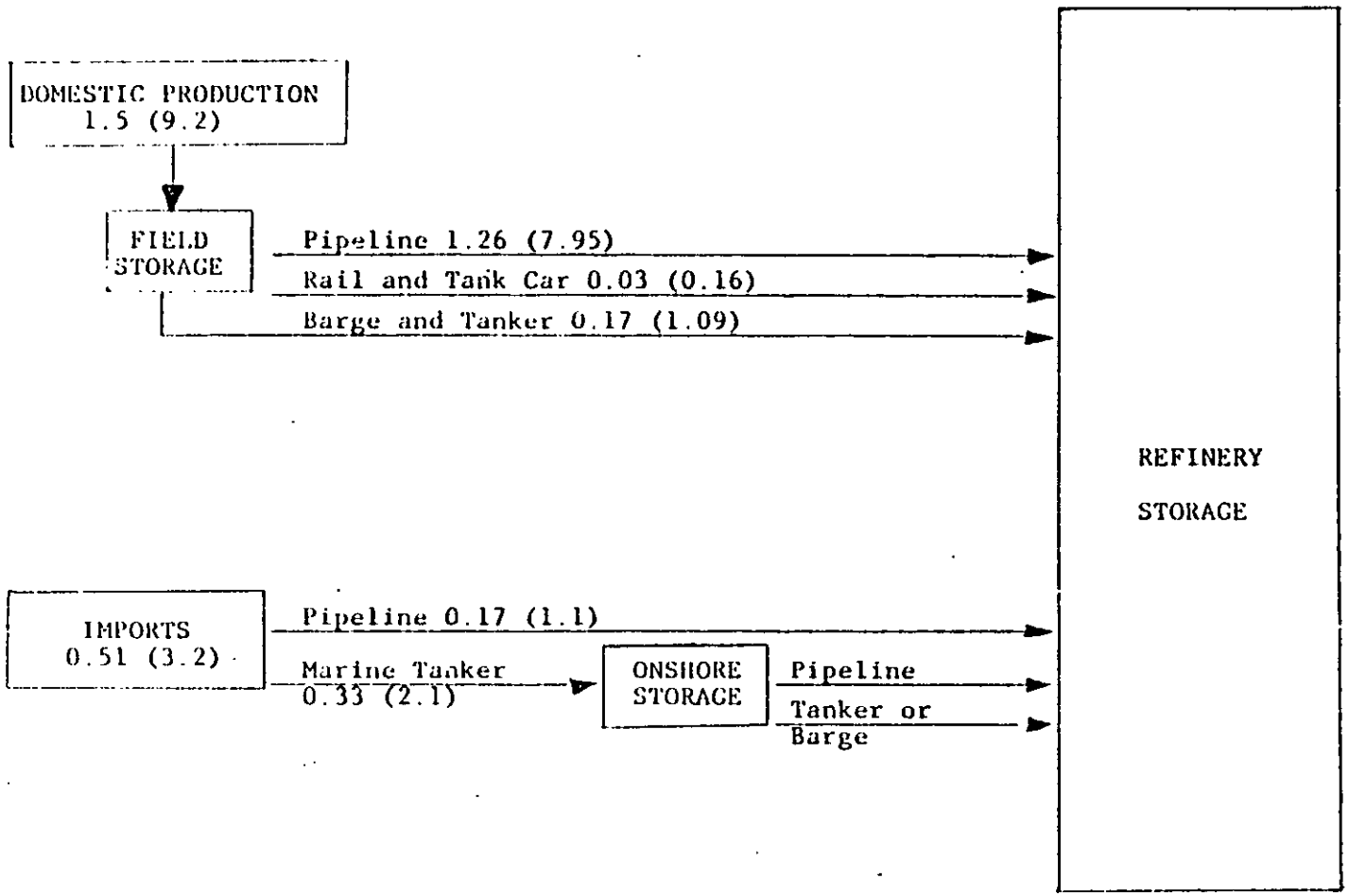


FIGURE 3.3-4

Transportation of Crude Oil, 1973

Rates in hm^3/day (10^6barrels/day

Storage tanks are another significant source of organic emissions. Light hydrocarbon gases which have remained with the crude may be discharged to the atmosphere from a storage tank or during filling operations as a result of ambient temperature changes. In 1968, approximately 75% of the storage tanks at refineries were equipped with floating-roof tanks. It is assumed that storage facilities in the crude transportation system are similarly equipped. The reduction in organic emissions resulting from the application of floating-roof tanks to the remaining storage tanks is 246,000 MT/yr from the total emission rate of 526,000 MT/yr. The actual emission rate and, thus, the reduction potential for organic emissions from storage tanks in the crude transportation system may be considerably less, since it is likely that floating roofs have been employed in many of the tanks that were uncontrolled in 1968.

3.4 Fossil Fuel Refining

Organics produced by the fossil fuel refining category include air emissions and water effluents resulting from the refining of petroleum and coal. Emissions resulting from natural gas processing and natural gasoline plant operation are discussed in Section 3.2, Fossil Fuel Processing.

The emissions and effluents associated with petroleum refining result from the processing steps that make up today's complex petroleum refinery. Coal coking operations are the major source of organic emission and effluents from coal refining in the U.S. Other coal processing and refining operations such as coal gasification and liquefaction are not yet conducted on a large enough scale to impact overall U.S. organic emission rates.

The petroleum refining and coal coking operations are further divided into subgroups relating to processing steps or operations contributing to atmospheric emissions. A summary of the atmospheric emissions from the processes and operations in this category is presented in Table 3.4-1. Water effluents resulting from petroleum refining and coal coking are also examined. For this study organics from solid waste processed by industry on site by incineration, landfill, or other means were not quantified. However, the environmental impact of any industrial solid waste disposed of by municipalities is considered in Section 3.12. Section 3.12 also contains an evaluation of the impact of organic emissions resulting from solid waste disposal.

The important organic emission sources in the fossil fuel refining category are identified in this section and are examined to determine the point of organic emission. Emission from process effluent streams and from fugitive sources are

TABLE 3.4-1
FOSSIL FUEL REFINING EMISSIONS

	Year	Volatile Organics (MT/yr.)	Ref	Particulate Organics (MT/yr.)	Ref
Fossil Fuel Refining					
Storage, Petroleum Refining	1973	965,000	1		
Blowdown, Petroleum Refining	1973	328,000	1		
Process Drains & Waste Water Separators, Petroleum Refining	1973	216,000	1		
FCC Unit, Petroleum Refining	1973	147,000	1		
Vacuum Jets, Petroleum Refining	1973	117,000	1		
Charging, By-Product Coke Oven	1974	102,000	2	61,200	2
Coking Cycle, By-Product Coke Oven	1974	61,200	2	4,080	2
Pipeline Valves and Flanges, Petroleum Refining	1973	57,600	1		
Pump Seals, Petroleum Refining	1973	34,800	1		
Compressor Engines, Petroleum Refining	1973	32,800	1		
Pressure Relief Valves, Petroleum Refining	1973	22,500	1		
Boilers & Heaters, Petroleum Refining	1973	20,500	1		
Cooling Tower, Petroleum Refining	1973	20,500	1		
Compressor Seals, Petroleum Refining	1973	10,300	1		
Discharging, By-Product Coke Oven	1974	8,170	2	24,500	2

TABLE 3.4-1 (Continued)
FOSSIL FUEL REFINING EMISSIONS

	Year	Volatile Organics (MT/yr.)	Ref	Particulate Organics (MT/yr.)	Ref
TCC Unit, Petroleum Refining	1973	5,470	1		
Beehive Ovens, Coke Products	1974	5,040	2	126,000	2
Sampling, Petroleum Refining	1973	4,830	1		
Blind Changing, Petroleum Refining	1973	610	1		
Misc. Fugitive, Petroleum Refining	1973	14,200	1		
Quenching, By-Product Coke Oven	1973	---	-	36,700	2
Unloading, By-Product Coke Oven	1974	---	-	16,300	2
Subtotal, Petroleum Refineries,		1,997,110			
Coke Manufacture		176,410			
TOTAL		2,173,520		268,780	

Sources: 1 BU-185
2 EN-071

considered. The process vent and storage losses are the largest volatile emissions and also have the greatest potential for reduction.

The specific operations which represent the largest potential for reduction of volatile organic emissions result mainly from the petroleum refining industry. The coke manufacturing industry has potential for organic emission reduction but these reductions are smaller and less defined than those in the petroleum industry (BA-283).

The total volatile organic emission rate from the refining category is nearly 2.2×10^6 MT/yr. The potential reduction in emissions is about 0.9×10^6 MT/yr from process vents and is nearly 0.5×10^6 MT/yr from storage operations. The potential reduction for fugitive emissions in only 0.02×10^6 MT/yr. Where possible, the potential reductions are estimated by assuming the degree of application of current controls and extending the use of the controls across the industry.

Development documents for proposed effluent limitations guidelines and new source performance standards in fossil fuel refining industries provided the most recent and comprehensive assessment of organic effluents and their control. For this reason, the anticipated petroleum refining and coking effluent rates reflect the BPCTCA for industries to achieve by July 1, 1977. Many facilities have already converted to meet BPCTCA effluent rates and many more are in the process of converting.

The potential for reduction of organic water effluents is assumed from effluent guideline documents to be the July 1, 1983 effluent limitation or Best Available Technology Economically

Achievable (BATEA). The reduction of organic effluents from the BPCTCA level to the BATEA level is the potential organic water effluent reduction.

A significant reduction is achievable in both the petroleum refining and by-product coking industries. No potential reduction for beehive ovens is achievable from BPCTCA to BATEA since BPCTCA results in no effluents from this operation.

3.4.1 Petroleum Refining

3.4.1.1 Process Description

Petroleum refining is the third largest industry in the United States and represents a potential organic emission problem because of the large quantities of petroleum liquids refined and the intricacy of the refining process.

Generally, each petroleum refinery is a unique hybrid whose design is determined by the local market demands and the characteristics of the crude being processed. However, refineries normally can be classified into one of the following five basic refinery types.

The diverse range of products and manufacturing processes in petroleum refineries suggests that subcategories for different segments of the industry be developed. A process oriented subcategorization of the industry has been developed. Subcategories are based on raw waste load characterisitcs and are related to the complexity of refinery operations.

The American Petroleum Institute (API) has developed a classification system which uses this technology breakdown. The U.S. refineries have been divided into five classifications

with varying degrees of processing complexity and a characteristic distribution of products. The API classification system is presented below (EN-407):

- Topping - Primary operation is separation of crude into its major fractions but may include some hydrotreating.

- Topping and Cracking - Operations include separation, conversion, and cracking processes for maximization of gasoline product.

- Topping, Cracking and Petrochemical - Some petrochemical processing is performed in addition to cracking, conversion, and topping operations.

- Integrated - Lube oil, wax, and asphalt processing are integrated into topping, cracking and conversion processing.

- Integrated and Petrochemical - Petrochemical manufacturing is combined with the refining operations of an integrated refinery.

Approximately 28 percent of the refineries in the U.S. are topping and cracking refineries; 20 percent are topping, cracking, and petrochemical refineries; and 20 percent are integrated refineries.

As of January 1, 1974, were 247 petroleum refineries were operating in the U.S. with a total crude capacity of 2.26 hm^3 (14,200,000 barrels per day) (AN-089). Individual refinery

capacities range from 159 m^3 (1,000 barrels per day) to 70 dam^3 (445,000 barrels per day). The ten largest refineries comprise over 25 percent of the nation's capacity (EN-043). Table 3.4-2 presents a distribution of the refinery sizes for 1971 (EN-043). There is a trend toward larger and fewer refineries.

Characterization of the refining processes applied to a so-called "typical" refinery is difficult because of the wide variety of refining schemes and processes available to the refiner. Because of the emphasis today on gasoline, a fully integrated gasoline refinery will be used in the example of a typical refinery.

The commonly used refinery process units are:

- atmospheric and vacuum distillation;
- gas treating and light ends recovery;
- conversion processes - alkylation, reforming, isomerization;
- hydrodesulfurization;
- cracking;
- alternative vacuum residual processing, such as solvent deasphalting, coking, and asphalt distillation; and
- lube processing.

TABLE 3.4-2

REFINERY SIZE DISTRIBUTION - 1971

Refinery Capacity	% of Total Refineries	% of Total Refining Capacity
1 dam^3 (<70,000 b/cd)	75.9	28.4
1-3.2 dam^3 (70,000-200,000 b/cd)	19.0	41.6
>3.2 dam^3 (>200,000 b/cd)	5.1	30.0

In addition, there are several important auxiliary processes, such as:

- crude desalting,
- sulfur recovery and tail gas treatment,
- hydrogen production,
- blending and storage,
- sour water stripping,
- wastewater stripping,
- wastewater treatment, and
- utility steam boilers.

Organic emissions vary greatly from one petroleum refinery to another depending on such factors as capacity, age, crude type, processing complexity, application of control measures, and degree of maintenance (EN-043).

Because refineries are a complex collection of integrated processing units, the pinpointing of individual organic emission sources would be an extensive task. This section attempts to characterize and, where possible, to quantify the organic emissions from major sources within a typical refinery.

3.4.1.2 Atmospheric Emissions and Control

These emission sources are grouped into combustion sources, tankage and loading sources, process sources, and fugitive sources.

3.4.1.2.1 Combustion Sources

A typical petroleum refinery has several major combustion sources which include process heaters, boilers and compressor engines. Organics are emitted from these sources because of incomplete fuel combustion.

3.4.1.2.2 Storage and Loading Sources

The high volatility of feedstocks, intermediates, and products stored and loaded in refinery tank farms makes storage and loading losses one of the largest potential volatile organic emission sources in the refining industry. Because most products and feedstocks are transported by pipeline, storage losses are greater than loading losses.

Fixed-roof, floating-roof, and internal floating cover tanks are the most common tanks in refinery service. These tanks range in size from 3 to 25 dam^3 (20,000 to 160,000 barrels) and average 11 dam^3 (70,000 barrels) (MS-001). The major sources of organic emissions from fixed-roof tanks are breathing and filling losses, while the major source of emissions from floating roofs and internal floating covers is standing storage losses.

In 1968 approximately 75 percent of the storage tanks at refineries were equipped with floating roofs. The reduction in organic emissions resulting from the application of floating roofs to the remaining storage tanks is 452,000 MT/yr. The actual emission rate and, thus, the reduction potential for

organic emissions from storage tanks in refineries may be considerably less today since floating roofs have probably been employed in many of the tanks that were uncontrolled in 1968.

The greatest determinant in the total emissions generated in product loading is the method of dispensing. In splash loading the liquid is discharged by a short spout into the upper part of the tank. The resultant free fall not only increases evaporation but may result in a fine mist of liquid droplets. In submerged surface and bottom loading, the product is discharged within a few inches of the tank bottom. Turbulence decreases markedly, therefore, losses by evaporation and entrained droplets are correspondingly reduced.

3.4.1.2.3 Process Sources

A substantial portion of the volatile organic emissions from petroleum refineries can be attributed to individual refining processes or to individual auxiliary processes. These sources include catalyst regenerators, barometric condensers, blowdown systems, wastewater separators, air blowing, and cooling towers. Because process emission sources are identifiable, their emissions are more accurately quantified and more easily controlled.

Catalytic Cracker Catalyst Regenerators

An integral part of a catalytic cracking unit is the catalyst regenerator (Figures 3.4-1 and 3.4-2) where coke that is formed on the catalyst surface during cracking is burned off. Catalytic cracker regenerators operate continuously. Because the combustion rate is controlled by limiting the air to the regenerator, there is only partial oxidation, leaving many unburned hydrocarbons in the regenerator flue gas.

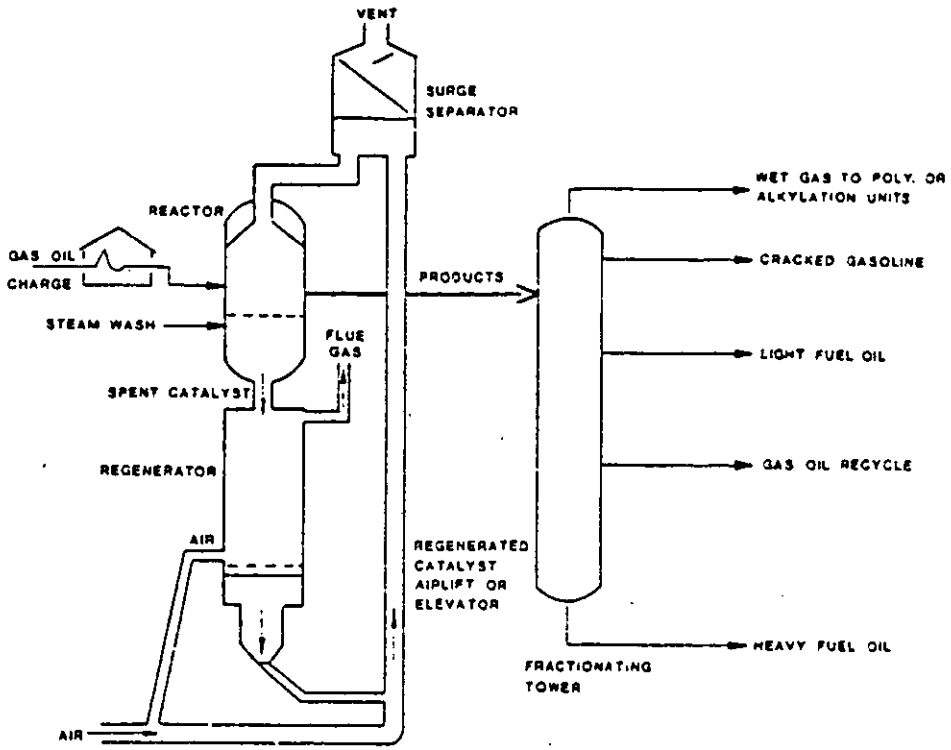


FIGURE 3.4-1 TYPICAL MOVING-BED CATALYTIC CRACKING UNIT

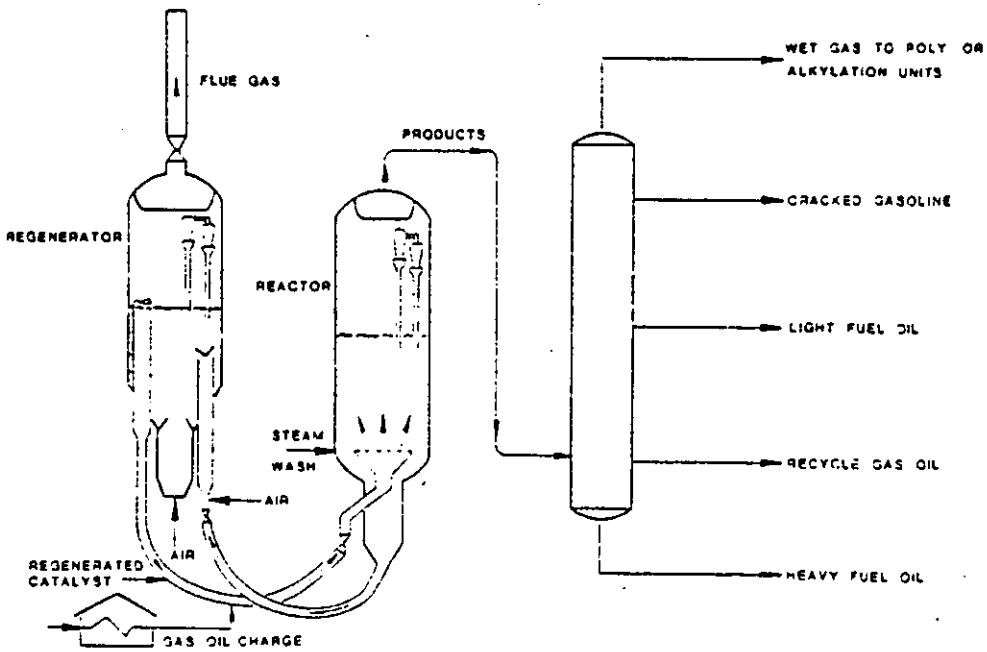


FIGURE 3.4-2 TYPICAL FLUIDIZED BED CATALYTIC CRACKING UNIT

The main control method for the reduction of volatile organic emissions in this flue gas is incineration in a carbon monoxide waste heat boiler. The emissions can be almost completely eliminated and valuable thermal energy can be recovered from the flue gas.

Although CO boilers are not extensively used today, they are becoming standard equipment in new refineries and expansions of existing units. This is a result of both energy conservation and increased concern for air quality.

The reduction potential for volatile organic emissions from catalytic cracking units, assuming fuel addition for complete combustion of hydrocarbons, is 147,000 MT/yr (BU-185). This is the result of controlling essentially 100 percent of the volatile organics from catalytic cracking units.

Vacuum Jet-Barometric Condensers

Most refineries operate some processing equipment below atmospheric pressure. The vacuum distillation column is the most common of the processes operating at a vacuum. Steam driven vacuum jets or ejectors coupled with a barometric condenser are frequently used in refineries to produce and maintain vacuums (Figure 3.4-3). Light hydrocarbons which do not condense in the barometric condenser are discharged to the atmosphere.

Volatile organic hydrocarbon emissions from barometric condensers on vacuum jets are attributable to both the venting of non-condensable hydrocarbons as well as to the evaporation of hydrocarbons from the oily barometric condensates.

Three measures for minimizing oily condensate generation are mechanical vacuum pumps, lean oil absorption, and surface

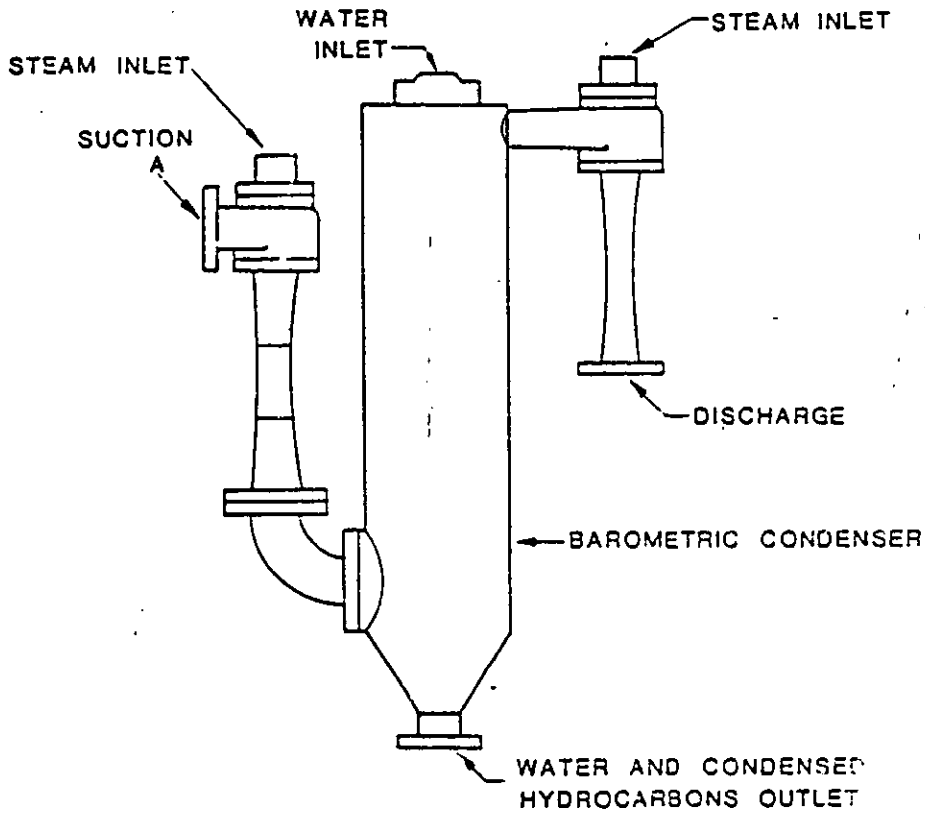


FIGURE 3.4-3 TYPICAL STEAM EJECTOR-BAROMETRIC CONDENSER

condensers. While mechanical vacuum pumps have little effect on the quantity of non-condensable hydrocarbons generated, they do eliminate the generation of oily steam condensate. The insertion of a lean oil absorption unit between the vacuum tower and the first stage vacuum jet helps to minimize the quantities of both non-condensables and oily condensate (AM-055). The rich oil effluent is reused as charge stock and not regenerated. Surface condensers in place of barometric condensers minimize oily condensates but have little effect on the quantity of non-condensables (AT-040).

Because generation of non-condensable vapors cannot be completely eliminated from vacuum pumps or steam ejectors, these emissions must be controlled by either vapor incinerators or vapor recovery units. Vapor incinerators combust the vapors by catalytic or direct flame methods. Vapor recovery units on the other hand recover the hydrocarbon vapors and return them to processing streams.

The reduction potential for organic chemical emissions from vacuum jets in the petroleum refining industry is 117,000 MT/yr.

Blowdown Systems

Periodic maintenance and repair of equipment are essential to refinery operation.

Blowdown emissions resulting from the purging of organics from equipment can be effectively controlled by venting into an integrated vapor-liquid recovery system. All units and equipment subject to shutdowns, upsets, emergency venting, and purging are manifolded into a multi-pressure collection system.

Discharges into the collection system are segregated according to their operating pressures. A series of flash drums and condensers arranged in descending pressures separates the blowdown into vapor pressure cuts. These recovered gaseous and liquid cuts can be flared and/or re-refined.

Fully integrated recovery systems can reduce refinery blowdown emissions and have a reduction potential of 318,000 MT/yr of organics (BU-185). This reduction potential assumes that most refineries are currently applying some degree of blowdown system control.

Air Blowing

Air blowing of petroleum products is today confined largely to the manufacture of asphalt, although air is occasionally blown through heavier petroleum products to remove moisture. Figure 3.4-4 depicts a typical asphalt air-blowing process. The use of air blowing for agitation, formerly quite common, is today practically non-existent.

Prosess Drains and Waste Water Separators

Some equipment and a number of operations in oil refineries including blind changing, sampling, turnarounds, leaks, and spills, allow organic chemicals to reach drains and eventually the wastewater separators. In addition, much of the water routed to the drains, including water from processing, pump seal cooling, and flushing, is already contaminated with hydrocarbons. Drains generally flow to an API separator for gravity separation of the oil and water prior to treatment in the wastewater treatment plant. If the drains and wastewater separator are uncovered, organics can evaporate to the atmosphere.

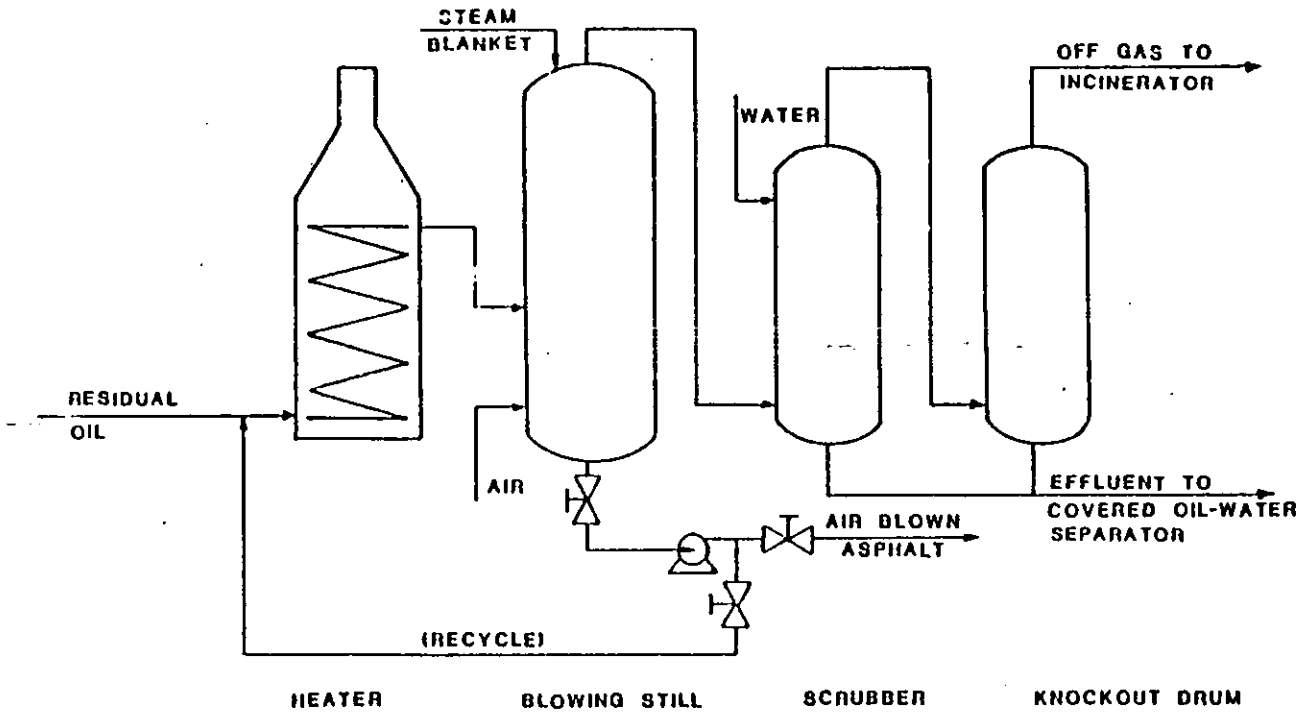


FIGURE 3.4-4 FLOW DIAGRAM OF ASPHALT BLOWING PROCESS

Control measures for reducing the evaporative emissions from process drains and wastewater separators center around (1) reducing the quantity of organics evaporated and (2) enclosing the wastewater systems.

The quantity of organic chemicals evaporated can first be reduced by minimizing through good housekeeping the volume of oil leaked to the wastewater systems. Lowering the temperature of the wastewater will also reduce organic chemical evaporation (AM-055).

Measures for enclosing the wastewater systems include manhole covers, catch basin liquid seals, and fixed or floating roofs for API separators. The potential also exists for some form of vapor disposal or vapor recovery device in conjunction with fixed roofs on API separators (EL-033).

The potential for reduction of volatile organic emissions, accounting for the existing degree of control, is 195,000 MT/yr (BU-185).

Cooling Tower

Petroleum refineries use large quantities of water for cooling. Before the water can be reused, the heat absorbed in passing through process heat exchangers must be removed. This cooling is usually accomplished by allowing the water to cascade through a cooling tower where evaporation removes the sensible heat from the water. Organic chemicals are leaked into the cooling water system by heat exchangers. Organic emissions are generated at the cooling towers when these organics evaporate to the surface.

3.4.1.2.4 Fugitive Sources

One of the largest, yet hardest to control, categories of volatile organic emissions from petroleum refineries is fugitive sources. Fugitive emissions are not solely attributed to a particular type of refining processes or auxiliary processes but occur throughout the refinery. Fugitive losses from individual sources are generally small, but they become significant because of their prevalence. Fugitive sources include pump seals, relief valves, pipeline valves, sampling, and blind changing.

Pump and Compressor Seals

Pumps and compressors can leak at the point of contact between the moving shaft and the stationary casing. If volatile, the leaked product will evaporate to the atmosphere. The two types of seals commonly used in the petroleum industry are packed seals and mechanical seals.

Pressure Relief Valves

For safety and equipment protection, high pressure vessels are commonly equipped with relief valves to vent excessive pressures. Corrosion may cause pressure relief valves to reseat improperly after blowoff, creating a potential source for volatile organic leaks and emissions.

Pipeline Blind Changing

Refinery operations frequently require that a pipeline be used for more than one product. To prevent leakage and contamination of a particular product, other product-connecting or product-feeding lines are customarily "blinded off". "Blinding" a line involves inserting a flat solid plate between two flanges

of a pipe connection. In inserting or withdrawing a blind, spillage of the product in the pipeline can occur. The magnitude of volatile organic emissions from the spillage is a function of the spilled liquid's vapor pressure, type of ground surface, distance to nearest drain, and amount of liquid spilled.

Purging Sampling Lines

The operation of process units is constantly checked throughout the refinery by routine analysis of feedstocks and products. To obtain representative samples for these analysis, sampling lines must be purged, resulting in possible organic vapor emissions.

Others

Every refinery has several unaccountable volatile organic emission sources plus sources not common to all refineries, such as asphalt blowing, coke processing, and lube processing. This category of emissions amounts to about 20 kg of organics/ dam^3 (7 lbs of organics/10^3 barrels) of refinery feed (AT-040).

3.4.1.3 Water Effluents and Control

Considerable information is available for making meaningful qualitative interpretations of organic effluent loadings from refinery processes. A summary of this information is presented in Table 3.4-3. The pollutant parameters describing organic effluents are BOD, COD, TOC, oil and grease, and suspended solids. Phenol is another common parameter, but phenol values are much smaller than on a mass emission rate basis. The organic effluent parameters and associated rates are listed in Table 3.4-4. The potential reductions are estimated as the difference between BPCTCA levels and BATEA levels.

TABLE 3.4-3

QUALITATIVE EVALUATION OF WASTEWATER FLOW AND CHARACTERISTICS

BY FUNDAMENTAL REFINERY PROCESSES

Production Processes	Flow	BOD	COD	Phenol	Oil	Emulsified Oil	Susp. Solids	Process Complexity
Crude Oil and Product Storage	XX	X	XXX	X	XXX	XX	XX	A,B,C,D,E
Crude Desalting	XX	XX	XX	X	X	XXX	XXX	A,B,C,D,E
Crude Distillation	XXX	X	X	XX	XX	XXX	X	A,B,C,D,E
Thermal Cracking	X	X	X	X	X		X	B,C,D,E
Catalytic Cracking	XXX	XX	XX	XXX	X	X	X	B,C,D,E
Hydrocracking	X			XX				B,C,D,E
Polymerization	X	X	X	O	X	O	X	B,C,D,E
Alkylation	XX	X	X	O	X	O	XX	B,C,D,E
Isomerization	X							B,C,D,E
Reforming	X	O	O	X	X	O	O	B,C,D,E
Solvent Refining	X		X	X		X		D,E
Asphalt Blowing	XXX	XXX	XXX	X	XXX			D,E
Dewaxing	X	XXX	XXX	X	X	O		D,E
Hydrotreating	X	X	X			O	O	B,C,D,E
Drying and Sweetening	XXX	XXX	X	XX	O	X	XX	A,B,C,D,E

XXX - Major Contribution, XX - Moderate Contribution, X - Minor Contribution, O - No Problem - No Data

Source: EN-407

TABLE 3.4-4. PETROLEUM REFINERY ORGANIC EFFLUENTS

Effluent Parameter by Class	RWL[2] (MT/yr)	BPCTCA (MT/yr)		BATEA (MT/yr)
BOD -A	772	412		70
-B	23,200	2,810		511
-C	27,500	1,720		350
-D	32,500	2,390		559
-E	18,600	1,620		401
Totals	102,572	8,952		1,891
Potential Reduction (MT/yr)[1]			7,061	
COD -A	2,140	2,180		290
-B	69,000	21,700		3,070
-C	73,200	10,800		1,720
-D	81,300	17,500		3,020
-E	31,100	[illegible],900		2,270
Totals	256,740	64,080		10,370
Potential Reduction (MT/yr)[1]			53,710	
Oil and Grease -A	476	191		15
-B	9,910	1,250		109
-C	8,370	812		72
-D	18,000	1,130		107
-E	7,070	803		81
Totals	43,826	4,186		384
Potential Reduction (MT/yr)[1]			3,802	
Suspended Solids -A	673	557		70
-B	5,690	3,770		511
-C	7,590	2,260		350
-D	10,700	3,330		559
-E	5,450	[illegible],100		401
Totals	30,103	[illegible]2,017		1,891
Potential Reduction (MT/yr)[1]			10,126	
TOC -A	-	906		215
-B	-	6,190		1,600
-C	-	3,780		1,080
-D	-	5,250		1,630
-E	-	3,570		1,240
Totals	-	19,696		5,765
Potential Reduction (MT/yr)[1]			13,931	

Source: EN-407

[1] Potential reduction of organic from BPCTCA controls to BATEA controls.

[2] RWL - Raw Waste Load

The potential reduction in organic effluents from petroleum refineries is estimated to be 16,700 MT/yr of organics. This reduction is estimated from the difference between BPCTCA levels and BATEA levels for TOC. The TOC reduction is increased by a factor of 1.2 to calculate the organic effluent reduction. The 1.2 factor is the ratio of organic carbon molecular weights obtained by assuming most of the organics are C_5 hydrocarbons with an average molecular weight of 72.

The actual potential organic reduction may be less than that estimated from BPCTCA and BATEA since these values represent 30-day maximums rather than yearly averages. However, the potential reduction for the refining industry should be consistent with the other categories since the method of calculation is similar.

The BPCTCA is based on both in-plant and end-of-pipe controls. The in-plant technology includes the following (EN-407):

- installation of sour water strippers to reduce sulfide and ammonia loads entering the wastewater treatment plant,

- elimination of once-through barometric condenser water by using surface condensers or recycle systems with oily water cooling towers,

- segregation of unpolluted storm runoff and once-through cooling waters from normally treated process waters, and

- better monitoring and maintenance of surface condensers or use of wet and dry recycle

- systems to eliminate pollution of once-through cooling water.

The BPCTCA end-of-pipe treatment consists of (EN-407):

- equalization and storm diversion,
- initial oil and solids removal (API separators or baffle plate separators),
- further oil and solids removal (clarifiers, dissolved air flotation, or filters),
- carbonaceous waste removal (activated sludge, aerated lagoons, oxidation ponds, trickling filter, activated carbon, or combinations of these), and
- filters (sand, dual media, or multi-media) following biological treatment methods.

The BATEA results from further reduction of water flows in-plant and the addition of activated carbon treatment to the end-of-pipe controls.

Required treatment to achieve BPCTCA and BATEA is dependent upon the needs and operations of the individual refinery and requires specific studies.

Crude Oil and Product Storage

During storage, water and suspended solids in crude oil separate; the water layer accumulates below the oil and is drawn off. Finished product storage is also a source of

separated water layers. Tank cleaning can contribute large amounts of water streams high in organic content.

Ballast waters from tankers are often discharged into ballast water tanks or holding ponds at refineries.

Crude Desalting

Two common methods are used for crude oil desalting: chemical desalting and electrostatic desalting. Both methods employ process water to remove impurities, resulting in a wastewater stream.

Crude Distillation

Several processes can be used to fractionate crude. These are atmospheric distillation, vacuum distillation, vacuum flashing, and three-stage crude distillation. There are two sources of wastewater from crude oil fractionation:

- wastewater from overhead accumulators, and
- wastewater from barometric condensers.

Organic wastewater loading can also be increased during sampling when oil sampling lines are discharged to the sewer.

Cracking

The major source of wastewater in cracking is from the steam strippers and overhead accumulators on the fractionators.

Polymerization

Most of the wastewater comes from the pretreatment of feedstock to the reactor by caustic washing.

Alkylation

The major discharge from sulfuric acid alkylation is the spent caustic wash from the neutralization of hydrocarbon streams leaving the sulfuric acid alkylation reactor. Water also is drawn off the overhead accumulators.

Hydrofluoric acid alkylation does not have spent acid or caustic waste streams. The major sources of wastewater are the overhead accumulators on the fractionator.

Iosmerization

Isomerization wastewaters present no major pollutant discharge problems (EN-407).

Reforming

A small volume of wastewater containing a low concentration of oil is produced by the reformer overhead accumulator (EN-407).

Solvent Refining

The major solvent refining processes are solvent deasphalting, dewaxing, lube oil solvent refining, aromatic extraction, and butadiene extraction. The major potential pollutants from the various solvent refining processes are the solvents themselves. The main source of wastewater is from the bottom of fractionation towers. Some solvent enters the sewer from pump seals, flange leaks and other sources.

Hydrotreating

The principle hydrotreating processes are pretreatment of catalytic reformer feedstock, naphtha desulfurization, lube oil polishing, pretreatment of catalytic cracking feedstock, heavy gas-oil and residual desulfurization, and naphtha saturation. The organic loading and quantity of wastewater generated by hydrotreating depends on the process used and the feedstock.

Asphalt Blowing

Wastewaters from asphalt blowing contain high concentrations of oils and have a high oxygen demand (EN-407).

Drying and Sweetening

The most common waste stream from drying and sweetening operations is spent caustic which has high BOD_5 and COD. Other waste streams from the process result from water washing of the treated product and regeneration of the treating solution.

3.4.2 Coke Manufacturing

The majority of coke manufacturing in the United States is performed to supply coke to the steel industry. In an integrated steel mill, coke is a basic raw material for the blast furnace. This section describes the coking industry and sources of organic emissions associated with coking processes.

The beehive and the by-product processes are used for coke manufacture in the United States today. Beehive ovens are not widely used because of economic and environmental disadvantages. Volatile organic emissions in the beehive process are high because they are not recovered, but organic effluents are low.

Today the by-product process, which recovers the volatile organics, produces about 99 percent of the metallurgical coke (EN-395).

Coke production in 1974 decreased from previous years because of a strike. In 1973, probably a more representative year, 61.7 x 10^6 MT of coke was produced from by-product processes and 0.8 x 10^6 MT of coke was produced from the beehive process.

3.4.2.1 By-Product Coking

3.4.2.1.1 Process Description

Coke manufacturing by the by-product process is accomplished in ovens in which bituminous coal is heated to drive off the volatile components. Air is excluded from the ovens. The residue remaining in the ovens is coke, and the volatiles are recovered in the by-product plant to produce tar, light oils, coke oven gas, and other potentially valuable materials. The coking is done in narrow, rectangular, silica brick ovens arranged side by side in groups called batteries. Each oven is typically 45 centimeters wide, 4.5 meters high, and 12 meters long. Heat is supplied by burning gas in flues between the walls of the adjacent ovens. Typically forty percent of the coke oven gas produced is used to heat the ovens. Usually, the remaining gas is used as fuel in other steel mill operations (EN-395).

Coal is charged through ports located on the top of an oven and then heated. At the end of the coking period, the coke is pushed out of the oven with a ram into an open railway car. The coke is transported to a tower for water quenching and then transferred to a sizing plant.

3.4.2.1.2 Atmospheric Emissions

Volatile organic emissions can occur during the following coking steps: charging, coking cycle, and discharging. In addition, organic particulate emissions can occur during the following coking steps: unloading, charging, coking cycle, discharging, and quenching.

Unloading

Organic particulates in the form of coal are emitted as the coal is unloaded at the coking site and stockpiled for future use.

Charging

The coal is charged into the coke ovens by a mobile machine called a larry car, traveling on rails on top of the coke ovens. A leveler bar is inserted into the oven to level the coal. Lids which seal the charging holes in the oven roof are then set in place. The emissions during charging result from the displacement of about 90 percent of the free space in the oven by the coal charge. Heating of the coal during charging produces volatiles. As a result, steam, gas, and displaced air blow out of the oven ports carrying volatile organics and organic particulates.

Coking Cycle

After charging, coal is heated in the ovens. During the heating cycle, the oven is sealed and usually maintained at a slight positive pressure to prevent air infiltration. Gases can evolve from the coke ovens around seals at the charging ports and doors.

Discharging

After the coking cycle, a pushing machine removes the oven door on the pushing end of the oven and aligns a ram inside the door jams. On the coke side, a machine removes the door and positions a coke guide against the door jams. The pushing machine then pushes the slab of hot coke out of the oven and into a quench car positioned below the coke guide.

The emissions during the discharging cycle are smoke from imcompletely coked coals and dust from thermal drafting of particles of abraded coke.

Quenching

The quench car containing the discharged coke is moved to a semi-enclosed tower where water is sprayed on the hot coke. After the coke has been quenched and cooled, the quench car moves to a coke wharf where the coke is dumped onto a conveyor belt moving to the coke handling area.

Fine coke breeze formed during the push and settling in the quench car is raised into the plume of quenching steam by the draft from the steam formation.

3.4.2.1.3 Water Effluents and Control

A variety of methods, usually by-product recovery techniques, has been used through the years. These methods have changed due to changing economic factors, effluent quality restrictions and treatment technology capabilities.

As in petroleum refineries, the significant pollution parameters relating to organic effluents are BOD, TOC, oil and

grease, and suspended solids. Estimates of COD levels are not available. The organic effluent parameters and associated rates for coke manufacture are presented in Table 3.4-5. The potential reductions are estimated as the difference between BPCTCA levels and BATEA levels (EN-395).

The potential reduction in organic effluents from coke manufacture is estimated to be 9680 MT/yr of organics. This reduction is estimated as the difference between BPCTCA levels and BATEA levels. The TOC for BPCTCA is estimated to be similar to petroleum refineries and, therefore, a factor of 2.2 higher than BOD_5. The TOC for BATEA is estimated by assuming an 87% reduction in TOC from BPCTCA levels. Experimental data in the organic chemicals industry indicates 87% removal from a cross-section of processes with similar wastewater treatment (EN-384).

To obtain the potential organic reduction, the TOC reduction is increased by a factor of 1.2 which assumes that most of the organics present are hydrocarbons with an average molecular weight of 72.

As mentioned earlier, the actual potential organic reduction may be less than that estimated from BPCTCA and BATEA since these values represent 30-day maximums rather than yearly averages. However, the potential reduction for the coke manufacturing industry should be consistent with the other categories.

The base level of treatment in Table 3.4-5 is an estimate of the effluents with a level of treatment in existence for practically all plants within the industry (EN-395).

The BPCTCA is based on the employment of the following technologies (EN-395):

TABLE 3.4-5

COKE MANUFACTURE ORGANIC EFFLUENTS

Effluent Parameters	Base Line[1] (MT/yr)	BPCTCA (MT/yr)	BATEA (MT/yr)	Potential Reduction (MT/yr)
By-Product Ovens				
BOD	12,700	4,220	482	3,738
Oil and Grease	844	422	241	181
Suspended Solids	2,110	2,110	241	1,869
TOC[2]	-	9,280	1,210	8,070
Beehive Ovens	No effluents for BPCTCA and BATEA			

[1]Base Line - Minimum level of treatment in existence for practically all plants within the industry.

[2]TOC for BPCTCA is estimated to be 2.2 x BOD. The TOC for BATEA is estimated assuming 87% removal from BPCTCA levels (EN-384).

Source: EN-395

- weak ammonia liquor equalization and storage,
- free and fixed leg ammonia still operation with lime addition,
- dephenolization,
- sedimentation,
- final cooler blowdown to dephenolizer,
- benzol wastes blowdown to dephenolizer,
- once-through crystallizer effluent to sedimentation, and
- pH neutralization.

The BATEA results, from controls established in addition to BPCTCA, are as follows (EN-395):

- recycle crystallizer effluent to final cooler recycle system,
- clarification,
- multi-stage biological oxidation with methanol addition, and
- pressure filtration.

The most significant water wastes resulting from the by-product coke plant are excess ammonia liquor, final cooling water overflow, light oil recovery wastes, and indirect cooling

water (EN-395). In addition, small volumes of water may result from wharf drainage, quench water overflow and coal pile runoff.

Ammonia Liquor

In the reduction of coal to coke, the coal volatiles are collected and cooled by spraying with water. This cooling condenses a large portion of tar in the gas and the mixture flows to a decanter tank. The partially cooled gas passes through primary coolers where the temperature is further reduced. The water and tar resulting from this operation are also pumped to the decanter tank. Moisture in the coal accounts for the net production of water from these cooling steps. The excess liquid is the ammonia liquor and is the major single source of contaminated water from coke making.

Final Cooling Water Overflow

Direct contact of the gas in the final cooler with sprays of water absorbs remaining soluble gas components and removes condensed or solidified organics. This water is usually recirculated. When a closed system is not used, this wastewater may exceed the ammonia liquor as the major source of high contamination loads (EN-395).

Light Oil Recovery Wastes

The light oil recovery system produces contaminated wastewater from the stripping operations. Cooling water is also discharged to the sewer.

Indirect Cooling Water

Indirect cooling water is not usually considered waste, but leaks in coils and tubes may contribute significantly to the organic loading of this stream (EN-395).

Miscellaneous Effluents

Coke wharf drainage and stock pile runoff are minor sources of effluents. These areas are usually trenched and the wastewaters do not enter a receiving stream.

3.4.2.2 Beehive Coking

In the beehive process, air is admitted to the coking chamber in controlled amounts to burn the volatile products distilled from the coal and to generate heat for further distillation. The beehive oven produces only coke and no successful attempts have been made to recover the products of distillation.

The oven is charged from above and coking proceeds from the top of the coal. At the end of the coking cycle the coke is quenched in the oven with water and then the coke is drawn from the oven. The process is very dirty and generates smoke which discharges to the atmosphere when the brickwork door is removed. Water is used only for coke quenching. The use of recycle in the beehive process can greatly reduce the the volume of wastewater. A properly controlled beehive oven will have very little water discharge.

3.5 Fossil Fuel Combustion

The fossil fuel combustion category examines the organic emissions from external combustion stationary sources as well as internal combustion stationary sources. External combustion sources include steam-electric generating plants, industrial boilers and furnaces, commercial and institutional boilers, and commercial and residential space heating units. Internal combustion stationary source include internal combustion engines used to generate electricity and engines used to pump gas and other fluids.

Volatile organics from fossil fuel combustion are discharged with the flue gases from the combustion unit. The organics result from the incomplete combustion of the fuel. Table 3.5-1 summarizes atmospheric organic emissions from fossil fuel combustion in stationary sources. The organic water effluents and solid wastes from fossil fuel combustion are negligible. The magnitude of an overall reduction potential for this category could not be determined from the available literature. Assuming that catalytic converters could be adapted to industrial internal combustion engines, a reduction in that subgroup's emissions has been calculated. This is discussed in Section 3.5.2.

3.5.1 External Combustion Stationary Sources

The external combustion sources are organized according to the type of fuel burned in the unit. Coal, fuel oil, and natural gas are the primary fuels used in stationary external

TABLE 3.5-1

FOSSIL FUEL COMBUSTION - ATMOSPHERIC EMISSIONS

	Emissions (MT/yr)		
	Year	Volatile Organics	Ref
Fossil Fuel Combustion			
Coal Combustion			
Utility	1975	105,000	1
Industrial	1975	55,400	1
Residential	1975	11,700	1
Commercial	1975	8,900	2
Fuel Oil Combustion			
Industrial/Commercial	1975	56,400	1
Residential	1975	24,300	2
Utility	1975	20,800	1
Natural Gas Combustion			
Industrial	1972	76,400	3
Residential	1975	12,400	2
Commercial	1975	1,800	1
Utility	1975	1,700	1
Wood Combustion			
Industrial	1972	28,000	3
Residential	1972	4,300	3

TABLE 3.5-1 (Cont'd.)

FOSSIL FUEL COMBUSTION - ATMOSPHERIC EMISSIONS

	Emissions (MT/yr)		
	Year	Volatile Organics	Ref
Internal Combustion			
Natural Gas - Industrial	1975	237,000	4
Fuel Oil - Utili:	1975	68,200	4
Natural Gas - Industrial	1975	11,800	4
TOTAL		724,000	

References:
1. PU-036
2. MO-201
3. EN-226
4. AE-014

combustion units. Wood is used in some instances and is a significant source of atmospheric organic emissions. The following sections discuss coal, oil, natural gas, and wood combustion in externally fired units.

3.5.1.1 Coal Combustion

Coal is the most abundant fossil fuel in the United States. It is burned to produce heat and steam in a wide variety of furnaces ranging in size from small hand-fired units with capacities of 4.5 to 9 kilograms (10 to 20 pounds) of coal per hour to large pulverized-coal-fired units which may burn 275 to 360 MT (300 to 400 tons) of coal per hour. Approximately 480 x 10^6 MT (530 x 10^6 tons) of coal were consumed in 1972 to supply thermal energy in the United States (US-205).

Atmospheric Emissions and Control

The combustion of coal in externally fired equipment results in the emission of hydrocarbons and other organic material if combustion is not complete. Due to variations in combustion efficiency, organic emissions depend on the particular size and type of combustion unit. Also, considerable variation in organic emissions can occur depending on the operation of an individual unit. Atmospheric organic emissions from coal combustion in externally fired units are presented in Table 3.5-2.

Organic emissions from stationary combustion of coal can be reduced by improved operating practices and improved equipment design. Good operating practice is the most practical technique available for controlling atmospheric organic emissions from coal combustion. The combustion units should always be operated within their design limits and according to

the specifications recommended by the manufacturer to achieve a high degree of combustion efficiency. Combustion units and equipment should be kept in good repair to meet design specifications. Flue gas monitoring equipment is helpful in detecting changes in the performance of the unit and thus is useful in keeping organic emissions at a minimum.

The organic emissions from coal combustion may also be controlled by improved equipment design. Improved design can reduce emissions by reducing the quantity of fuel required for a given energy output.

These organic emission controls provide some potential for a reduction of emissions; however, no information is available concerning the percent reduction that can be expected. The reduction potential is not anticipated to be large, however, especially for the smaller units such as those found in commercial and residential applications. Smaller units do not have air-fuel mixing ability comparable to larger units. They operate at somewhat lower temperatures and therefore have lower average combustion efficiencies.

TABLE 3.5-2
ATMOSPHERIC ORGANIC EMISSIONS
FROM COAL COMBUSTION

Source	Refs	Emissions (MT/yr)
Utility	1	105.0×10^3
Industrial	1	55.4×10^3
Residential	2	11.7×10^3
Commercial	1	8.9×10^3

Source: 1. PU-036
2. MO-201

3.5.1.2 Fuel Oil Combustion

The two major types of fuel oil are residual and distillate. Distillate fuel is primarily a domestic fuel, but it is used in some commercial and industrial applications where a high-quality oil is required. The primary differences between residual oil and distillate oil are the higher ash and sulfur content of residual oil and the fact that residual oil is much more viscous and therefore harder to burn properly.

Atmospheric Emissions and Control

Organic emissions from fuel oil combustion are dependent on type and size of equipment, method of firing, and maintenance practices. Table 3.5-3 presents the estimates for the yearly atmospheric emission rates of organics from fuel oil combustion in externally fired units.

TABLE 3.5-3
ATMOSPHERIC ORGANIC EMISSIONS
FROM FUEL OIL COMBUSTION

Source	Refs	Emissions (MT/yr)
Industrial/Commercial	1	56.4×10^3
Residential	2	24.3×10^3
Utility	1	20.8×10^3

Sources: 1. PU-306
2. MO-201

These emissions can be reduced by good operating practice and improved equipment design. No information was found concerning the expected percent reduction of emissions

through the application of these control methods. However, the potential is not estimated to be very large.

3.5.1.3 Natural Gas Combustion

Natural gas has become one of the major fuels used in the U.S. It is used primarily in power plants, industrial heating, and domestic and commercial space heating. Marketed production of natural gas in the United States in 1974 totaled almost 600 billion cubic meters (22 trillion ft^3) according to the U.S. Bureau of Mines (US-474). The majority of this total was used as fuel with most of the remainder going to feedstock for chemical plants.

Atmospheric Emissions and Control

Natural gas is considered to be a relatively clean fuel. However, some organic emissions do occur from its combustion. When insufficient air is supplied to the combustion unit, large amounts of volatile organic chemicals may be emitted to the atmosphere. The emission from natural gas combustion varies according to the type and size of equipment and attention given to maintenance. Table 3.5-4 presents estimates for the yearly atmospheric organic emission rates from natural gas combustion in externally fired units.

The control of these emissions is accomplished in the same manner as are the organic emissions from coal and oil combustion. Proper operating practices and improved equipment design allow for more efficient combustion of the gas/air mixture and therefore reduce the quantity of hydrocarbons (and carbon monoxide) emitted. No information was found which discussed the percent reduction of emissions following application of these

control methods. However, assuming most natural gas combustion units operate in a reasonably efficient manner the reduction potential is not expected to be very large.

TABLE 3.5-4
ATMOSPHERIC ORGANIC EMISSIONS
FROM NATURAL GAS COMBUSTION

Source	Refs	Emissions (MT/yr)
Industrial	1	76.4×10^3
Residential	2	12.4×10^3
Commercial	3	1.8×10^3
Utility	3	1.7×10^3

Sources: 1. EN-226
2. MO-201
3. PU-036

3.5.1.4 Wood Combustion

Wood is no longer a major energy source for industrial heat or power generation. However, it is used as a domestic heat source and to some extent in those industries which generate considerable quantities of wood wastes. This section is concerned with the combustion of wood in furnaces and residential fireplaces for process or space heating purposes. It is not concerned with the burning of wood wastes as a means of solid waste disposal.

Atmospheric Emissions and Control

Atmospheric organic emissions resulting from the burning of wood in furnaces and fireplaces are due mostly to

inefficient combustion. As with coal, oil, and gas combustion, the size of the furnace and degree of maintenance affect the quantity of hydrocarbons emitted. Another major factor is the water content of the fuel. Moisture increases the atmospheric organic emissions. Table 3.5-5 presents the yearly organic atmospheric emissions from the external combustion of wood (EN-226).

TABLE 3.5-5
ATMOSPHERIC ORGANIC EMISSIONS
FROM WOOD COMBUSTION

Source	Emissions (MT/yr)
Industrial	28.0 x 10
Residential	4.3 x 10

Source: EN-226

The control of organic emissions from wood-fired furnaces is best accomplished through the proper maintenance of the combustion equipment. No information was found regarding the percent reduction of emissions from applying proper maintenance practices. The reduction potential for these emissions may be moderate assuming that most wood-fueled furnaces are not subject to regular maintenance. However, the percent reduction cannot be determined from available literature.

3.5.2 Internal Combustion Stationary Sources

In general, sources included in this category are internal combustion engines used in applications similar to those associated with external combustion sources. This category includes gas turbines and large, heavy-duty, general

utility reciprocating engines. Most stationary internal combustion engines are used to generate electric power, to pump gas or other fluids, and to compress air for pneumatic machinery.

Atmospheric Emissions and Control

The organic emissions from stationary internal combustion sources result from incomplete combustion of the fuel and subsequent discharge of the unburned hydrocarbons in the exhaust. The organics emitted may contain components present in the fuel as well as organics formed from the partial combustion and thermal cracking of the fuel (aldehydes and low molecular weight saturated and unsaturated hydrocarbons).

Table 3.5-6 presents estimates of the quantities of organics emitted yearly to the atmosphere from fuel oil and gas combustion in stationary internal combustion engines (AE-014).

TABLE 3.5-6
ATMOSPHERIC ORGANIC EMISSIONS
FROM STATIONARY INTERNAL COMBUSTION SOURCES

Source	Emissions (MT/yr)
Industrial - Gas	237.0×10^3
Utility - Oil	68.2×10^3
Utility - Gas	11.8×10^3

Source: AE-014

The quantity of organics emitted from these sources may be minimized by proper operating practices and good maintenance. The organic emissions could be essentially eliminated through the application of catalytic converters to the engine exhaust. For this reason, the percent reduction of these emissions is assumed to be 99 percent. This results in a reduction potential of nearly 314,000 MT organics/yr.

3.6 Organic Chemical Processing

The organic chemical processing industries (OCPI) convert hydrocarbons obtained mainly from petroleum, coal and natural gas into synthetic intermediates and products. The major products of these industries are synthetic organic chemicals which include solvents, pesticides, plastics and resins, surface active agents, elastomers, explosives, fibers, plasticizers, and dyes and pigments. Processes normally considered as operations of petroleum refining and natural gas and coal processing are excluded from the OCPI. Figure 3.6-1 shows the relationships between the industries and examples of organic chemicals processed in the industries (RA-222).

3.6.1 Atmospheric Emissions

Organic pollutants may be emitted to the atmosphere from organic chemical processing in various ways. Vented gases from various process operations may contain organic compounds. Vents are required for pressure control and removal of by-products or inerts, and venting may be necessitated by upset conditions in the plant. Other sources of organic pollutants considered fugitive emissions include evaporation from storage tanks, loading facilities, sampling, spillage, processing equipment leakage, barometric condensors, cooling towers, and miscellaneous sources.

The quantity of volatile organics and organic particulate emissions from significant processes and groups of processes included in the OCPI has been estimated. Estimates for 140 operations which produce basic petrochemicals, synthetic organic chemicals, or industrial organic chemical products are summarized in Table A-1 in the Appendix. The 140 products included in Table A-1 were selected on the basis of production volume data and descriptions of processing from the literature (RA-222),

BASIC PETROCHEMICALS INDUSTRY → INDUSTRIAL ORGANIC CHEMICALS INDUSTRY → DOWNSTREAM PROCESSING INDUSTRIES

Produces Products From Natural Gas and Petroleum Refinery Streams:

- Benzene
- Toluene
- Xylenes
- Naphthalene
- Cresols
- Ethylene
- Propylene
- Butylenes
- Butadiene
- Paraffins

Produces Some 400 Synthetic Organic Intermediates From Basic Petrochemicals

Major Examples:

- Acetic Acid
- Cumene
- Cyclohexane
- Ethylbenzene
- Ethylene Dichloride
- Ethylene Glycol
- Ethylene Oxide
- Methanol
- Phenol
- Styrene
- Terephthalic Acid
- Toluene
- Urea
- Vinyl Chloride

Produce Industrial Organic Chemical Products From Synthetic Intermediates

Industry Examples:

- Pesticides
- Organic Dyes and Pigments
- Surfactants
- Plastics and Resins
- Elastomers
- Synthetic Fibers
- Explosives
- Plasticizers

FIGURE 3.6-1

ORGANIC CHEMICAL PROCESSING INDUSTRIES

ER-030, MO-201, EN-68). Generally, organic chemical intermediates were included if their production volume exceeded 23,000 MT (50×10^5 pounds) (RA-222) or if published emission rates were greater than 1000 MT/yr. Table A-1 gives production volumes and the products are listed in order of decreasing quantities of volatile organic emissions. The total estimated atmospheric emissions from these industries are 1,400,000 MT/yr volatile organics and 45,800 MT/yr organic particulates.

The best emission data was selected from estimates in the literature (ER-030, PE-160, MO-201, EI-017, SH-241, HO-244, PR-115, PR-116). Large discrepancies were found in the emission estimates obtained from various sources; therefore, the quality of each estimate was considered. Estimates were ranked by the following index of uncertainty levels based on the quality of the data used in making the estimate. Uncertainty levels are given for each estimate in Table A-1.

Level	Meaning
A	Adequate data of reasonable accuracy
B	Partially estimated data of indeterminate accuracy
C	Totally estimated data of indeterminate accuracy
D	No data; estimates based on generalized loss factor

Quantitative data on fugitive emissions from chemical processes are extremely scarce. The available information is generally based totally on estimated data and is not substantiated by actual field tests. In some cases, fugitive emission estimates have been based on "unexplained" losses appearing in material balances around processing units. Estimates based on this type of data are probably inaccurate, since the "unexplained" losses represent small differences between large numbers subject to metering and analytical inaccuracies.

Calculations of fugitive organic emissions from a 227,000 MT (500 x 10^8 pound) per year ethylene plant were done in 1967 by Mencher (ME-136) using emission factors found in Public Health Service Publication No. 763 for a plant practicing stringent control. Organic losses from valves, pumps, compressors, cooling water, relief valves, storage tanks, and other miscellaneous losses were estimated to be equal to 0.21 percent of throughput for the plant. Mencher stated that most calculations of this sort show that the total emissions of hydrocarbons from hydrocarbon processing plants range from 0.1 to 0.6 percent of total plant throughput. The low value of 0.21 percent determined for the ethylene plant is applicable to plants where stringent control is practiced.

Fugitive emissions from petrochemical processing plants were addressed by Pervier, et al. (PE-160) in a recent survey of atmospheric emissions from the petrochemical industry. In these survey reports, operators within the industry estimated that fugitive emissions from their plants ranged from 0.01 to 2.0 percent of throughput with an average of about 0.5 percent of throughput.

It has been concluded from the above information that fugitive emissions from fossil fuel chemical processing plants average about 0.5 percent of throughput and that process emissions

average about 0.73 percent of throughput. The summation of these emission factors gives the industry-wide total organics emission factor of 1.23 percent of throughput.

Several investigations have concluded that emissions during the production, conversion and handling of organic chemicals range from about 0.5 to 2.0 percent of total production (ER-030). The results of this study indicate that emissions from the OCPI average 1.23 percent of total production, which is approximately equal to the median value of the previous studies. This type of emission factor is not necessarily applicable to individual processes since emissions vary greatly with plant design, maintenance and operational procedures, feedstocks, products, and other factors, but the factor appears to be applicable to the industry as a whole.

Process emissions normally emanate from vents within a plant. The volatile organics in these vent streams can be controlled by conventional methods of controlling organic atmospheric pollutants from stationary sources, i.e., combustion, condensation, adsorption, absorption, and process changes. These controls can be used to achieve almost a 100 percent removal efficiency. A removal efficiency of 99 percent of volatile organics will be assumed as feasible for vent streams in the OCPI in determining reduction potentials. In most cases, further study will be required to determine the economically feasible reduction potentials for the various processes.

Organic particulate emissions in vent streams can be reduced by conventional methods of particulate removal, i.e., mechanical collectors, electrostatic precipitators, scrubbers, and filters. The removal efficiency of these devices varies depending on design, operation, and particle size.

Fugitive emissions can be minimized by various methods including (ME-136):

1) Good housekeeping and maintenance practices.

2) Installation of floating roof tanks to control evaporation of light hydrocarbons.

3) Installation of vapor recovery lines to vents of vessels that are continually filled and emptied.

4) Manifolding of purge lines used for startups and shutdowns to vapor recovery or flare systems.

5) Venting of vacuum jet exhaust lines to suitable recovery positions or replacement of vacuum jets with vacuum pumps.

6) Shipment of products by pipeline rather than by railcar or trucks.

7) Covering of wastewater separators.

8) Discharging of relief valves to a flare manifold.

In calculating the reduction potential associated with fugitive emissions, stringent control practices will be assumed capable of maintaining fugitive emissions at 0.21 percent of throughput and that the industry's current, average emissions from fugitive sources are equal to 0.50 percent of throughput. These values indicate that a 58 percent reduction of fugitive emissions is achievable by the application of stringent controls.

Industry-wide reduction of volatile organic process emissions by 99 percent and fugitive emissions by 58 percent would result in the reduction of an estimated 1,270,000 MT per year of volatile organic emissions. Descriptions of the processes, emissions, and control techniques for the seven major sources of volatile organic emissions and organic particulates within the OCPI are given in Sections 3.6.1.1 through 3.6.2.3. The reduction potential for each of the specific processes discussed is given in Table 3.6-1.

In general, the seven processes discussed, approximately 45 percent of the volatile organics emitted from the volatile organics emitted from the industry, are large volume processes which require major purge streams. These types of process emissions are amenable to conventional hydrocarbon control techniques for stationary sources and represent the greatest potentials for reduction within the industry.

3.6.1.1 Ammonia Production

Process Description

Ammonia is manufactured by the catalytic reaction of hydrogen and nitrogen at high temperatures and pressures. In a typical plant a hydrocarbon feed stream is desulfurized, mixed with steam, and catalytically reformed to carbon monoxide and hydrogen. Air is supplied to the secondary reformer to provide oxygen and a nitrogen to hydrogen ratio of 1 to 3. The gases enter a two-stage shaft converter where the carbon monoxide reacts with steam to form carbon dioxide and hydrogen. The gas stream is scrubbed to yield a gas containing less than 1 percent CO_2. A methanator may be used to convert unreacted CO to inert CH_4 before the gases are compressed and fed to the converter.

TABLE 3.6-1

CONTROL OF ATMOSPHERIC EMISSIONS IN THE FOSSIL FUEL CHEMICAL PROCESSING INDUSTRY

SUBCATEGORY	AIR EMISSIONS (MT/YR) VOLATILE ORGANICS (ORGANIC PARTICULATES)	REDUCTION POTENTIAL (%)	CONTROL METHODS
Ammonia	322,700	99	*
Carbon Black	96,700	99	*
	(3,670)	nil	Fabric filters commonly used, represent best control.
Acrylonitrile	83,000	99	*
Ethylene Dichloride	56,300	96	*
Toluene	51,000	86	*
Carbon Tetrachloride	43,400	96	*
Soap and Detergent	(18,400)	97	†

*Volatile organic emissions can be controlled by conventional methods including incineration adsorption, absorption, condensation, and various methods for reducing fugitive emissions. Individual processes must be studied to determine best application of control devices.

†Particulate emissions can be controlled by conventional methods including settling chambers, cyclones, electrostatic precipitators, scrubbers, and baghouses. Individual study of processes is required to determine best application.

Alternatively, the gases leaving the CO_2 scrubber may pass through a CO scrubber and then to the converter. The synthesis gases are converted to ammonia in the converter.

Atmospheric Emissions and Controls

The converted ammonia gases are partially recycled, and the balance is cooled and compressed to liquefy the ammonia. The noncondensable portion of the gas stream, consisting of unreacted nitrogen, hydrogen, and traces of inert gases such as methane, carbon monoxide, and argon, is largely recycled to the converter. To prevent the accumulation of these inert gases some of the noncondensable gases must be purged from the system. Atmospheric emissions of purge gas produce 45 kg organics per MT of ammonia (EN-071). The purge gas is sometimes scrubbed with water to reduce atmospheric emissions of ammonia, but other organics are not reduced by this control method. Fugitive organic emissions from ammonia processes have not been estimated, but they are probably negligible when compared to purge gas emissions.

The organic compounds in the purge gas stream can be almost completely eliminated (approximately 99 percent removal) by conventional methods of controlling organic emissions from stationary sources. This reduction potential applied to the total organic emissions from the ammonia process, 322,700 MT per year (MO-201), would result in a reduction of 319,500 MT organics per year. These emissions are considered to be essentially methane.

3.6.1.2 Carbon Black Production

Process Description

Carbon black is produced by the reaction of oil and/or gas with a limited supply of air at temperatures of 1,370 to

1,650°C. Three basic processes for producing carbon black currently exist in the United States. They are the furnace process, accounting for about 89 percent of production; the older channel process, which accounts for less than 2 percent of production; and the thermal process (SC-312).

The channel process has the greatest potential for atmospheric pollution; however, this process is unlikely to be incorporated into any future plant designs and the single remaining plant in the United States may soon be phased out (RA-222). Usage of the thermal process is expected to achieve only limited growth. Effluent gases are recycled in this process; therefore, there are essentially no atmospheric emissions (SC-312). For these reasons, the channel and thermal processes do not warrant further consideration in this report.

The furnace process employs either gas or oil as the primary source of the carbon black. In either process, the fuel is injected into a reactor with a limited supply of combustion air. The processes are similar, but the furnace designs are different.

The flue gases, largely carbon monoxide, hydrogen, nitrogen, and water vapor, carry the carbon from the furnace to a cooling tower where water sprays reduce the temperature to about 260°C. Agglomeration of the fine black particles occurs in either an electrostatic precipitator or cyclone collector. The electrostatic precipitator, when used, is generally followed by cyclone collectors and bag filters. The gases are discharged through the stack of the final collector directly to the atmosphere.

The recovered carbon black is transported to the finishing area by screw or pneumatic conveyors where it is passed through

a pulverizer to break up lumps. The carbon black is then converted to pellets or beads by a wet procedure. The wet product is then sent to driers, screened, bagged, and sent to storage.

Atmospheric Emissions and Controls

An extensive engineering and cost study of air pollution control for carbon black manufacture by the furnace process has been published (SC-312) and was the basis for this discussion.

The main process vent gas consists of the gross reactor effluent plus quench water after recovery of carbon black. This gas represents the main source of emissions from the carbon black plant. For a "typical" 40,800 MT/yr (90 million lb/yr) furnace oil carbon black process, the vent stream emits about 318 kg of hydrocarbons (methane and acetylene) and 11 kg of particulate carbon black per hour (SC-312).

In carbon black plants where pneumatic conveyors are used for moving products to the finishing area, the carrier gas may be vented after recovery of entrained carbon black. Data indicates that this stream can emit from 0.06 to 0.3 kg of carbon black particulates per MT of production (SC-312). Some plants use a closed loop system and eliminate this venting.

In most plants much of the hot gas used in the drying operation does not come in direct contact with the carbon black but is used as an indirect heat source and, therefore, contains no entrained carbon black. The remainder of the hot gas, 35 to 70 percent, is charged directly to the drier interior for removal of water vapor. This purge gas entrains carbon particles and is usually vented after passing through a filter or water scrubber for particulate removal. This vent stream typically contains about 2 kg of carbon black particles per MT of product (SC-312).

Carbon black content of this baggage and storage area vent stream varies depending upon the operations being performed in the storage area. The storage and bagging areas are usually within a building and a vacuum clean-up system which ejects filtered air is typically included. No estimates of the quantity of carbon black emitted from this vent were available.

Some plants vent the furnace reactors directly to the atmosphere during reactor warm-up. This venting occurs only when a new reactor is put into service to meet increased production requirements. Reactor warm-up is accomplished by burning natural gas before the reactor is put on line feeding only oil. Therefore, essentially no carbon black or hydrocarbons are emitted during this venting operation.

Particulate emissions can occur from a number of miscellaneous sources including:

1. inadvertent spillages when drawing samples from production line,

2. unplugging production line stoppages,

3. cleaning of process equipment and hopper cars,

4. leaks in process equipment,

5. bagging operation of hopper cars, and

6. bags torn during stacking in warehouses or loading and unloading of box cars or trucks.

Miscellaneous carbon black losses equal about 0.1 kg/MT of product (SC-312). No fugitive emissions of volatile organics were reported in the literature.

Based upon observations and economics, the best feasible air pollution control system for existing carbon black plants would include bag filters for recovery of product from combustion process vent gas, entrained carbon black from driers, and product finishing vent gas streams. In addition, a plume burner or flare system, depending upon the off-gas heating value, should be used to combust burnable material in the effluent of the process vent gas filter. The drier vent should also be burned if it contains combustible material. The best control systems for new plants would include the above equipment plus a waste heat boiler and steam driven process equipment. The implementation of these controls would essentially eliminate the emissions of volatile organics from the furnace carbon black process and result in a reduction of approximately 96,700 MT hydrocarbons per year. Bag filters are commonly used for product recovery in furnace carbon black plants (SC-132); since this represents the best control method, the reduction potential for particulates is considered negligible.

3.6.1.3 Acrylonitrile Production

Process Description

Acrylonitrile is produced in the U.S. by the Sohio version of the ammoxidation of propylene. In this vapor-phase catalytic process, approximately stoichiometric proportions of air, ammonia, and propylene are fed to a fluid bed reactor at 400-510°C. Prior to 1972, an antimony-uranium oxide system (Catalyst 21) was used as a reaction catalyst. Since that time,

a new catalyst (Catalyst 41) has been introduced which increases the yield of acrylonitrile and hydrogen cyanide and produces 35 percent less hydrocarbon emissions. Catalyst 41 is gradually replacing the older catalyst.

The reaction is exothermic and heat removal is required. The reaction heat is usually used to generate steam, and the cooled effluent is then sent to a water quench tower where unconverted ammonia is neutralized. The stream is then fed to a water absorber-stripper system where reaction products are recovered and inert gases are rejected. The reaction product stream contains acetonitrile, acrylonitrile, and hydrogen cyanide. This stream is usually fractionated to remove HCN and then acetonitrile is separated from the tower bottoms by extractive distillation using water as the extraction solvent. The final two steps involve drying of the acrylonitrile stream and distillation to remove heavy ends.

Atmospheric Emissions and Controls

An extensive engineering and cost study of air pollution control for acrylonitrile manufacture has been published and was the basis for this discussion (SC-287).

The main process gas vent from the absorber is the chief source of air emissions from the process. The composition and flow rate of the vent gas vary somewhat depending on the type of catalyst and reactor conditions. In a 90,700 MT per year plant, the vent gas flow averages about 9,220 moles per hour if Catalyst 21 is used and about 7,180 moles per hour if Catalyst 41 is used. The organic content of the vent gas is normally 0.4-1.7 mole percent using Catalyst 21 and 0.8 mole percent with Catalyst 41. The volatile organics consist primarily of propylene, propane, and acetonitrile. All plants use a mist

eliminator on this stream to remove entrained water. However, no additional air pollution control devices are currently used on this stream.

The product fractionation vent is a small vent stream which varies greatly in composition depending upon the type of product recovery system used. Normally the vent streams from the fractionation system are combined and sent to an incinerator or flare.

The production of acetonitrile and hydrogen cyanide by-products usually exceeds demand and the excess production is sent to an incinerator. The composition of this material would be expected to result in emissions of volatile organics and other pollutants.

A plant start-up usually occurs every one or two years. During this operation, the reactor effluent may be directly vented to the atmosphere. A start-up normally requires less than one hour. Vent streams resulting from plant upsets or other emergencies are diverted to the flare stack or by-product incinerator. Therefore, emissions resulting from these occurrences are minimal.

Fugitive emissions result from vents on acrylonitrile and acetonitrile storage tanks which are directly vented to the atmosphere. In some cases, conservation type vents are employed on these tanks. Hydrogen cyanide is stored under a positive pressure and vapors are normally cooled to recover hydrogen cyanide and then sent to incinerators. No quantitative estimates of organic emissions from these or other fugitive emissions sources were made.

The use of Catalyst 41 instead of Catalyst 21 reduces hydrocarbon emissions from the process by approximately 35 percent.

The most feasible control method for future reductions of organic air emissions would be to provide a thermal incinerator on the absorber vent. Plants using Catalyst 21 and thermal incineration of the absorber vent stream would emit approximately 0.5 kg of hydrocarbons per MT of production, or less than 1 percent of the 165 kg per MT of hydrocarbons emitted by a typical plant using Catalyst 21 without an incinerator. The application of these control methods to acrylonitrile plants would result in an estimated reduction of 82,000 MT per year of volatile organic emissions.

3.6.1.4 Ethylene Dichloride Production

Ethylene dichloride (EDC) is produced from ethylene by either a direct or oxychlorination process. Most EDC plants are based on a balanced combination of these two processes. About 58 percent of the EDC is produced by direct chlorination and the remaining portion by oxychlorination (SC-316). Both of these processes have significant environmental impacts and will be discussed.

3.6.1.4.1 Process Descriptions

Direct Chlorination

Stoichiometric quantities of chlorine and ethylene are fed to the bottom of a tower-type reactor filled with liquid EDC and a ferric chloride catalyst. The reactor operates at about 43°C and 2 kg per cm^2 (PE-160). The top of the column is a fractionator. The vapors exiting the column pass condensers and then absorbers to remove EDC, hydrogen chloride, and chlorine. The crude EDC is washed with a dilute caustic solution and then dried. In some plants the EDC undergoes a final distillation to remove heavy ends.

Oxychlorination

Approximately stoichiometric amounts of ethylene, anhydrous hydrogen chloride, and air (or oxygen) are fed to a catalytic reactor operating at 200-300°C (SC-316). The reactor effluent is initially cooled by either a direct water quench or indirect heat exchange. After further cooling, the partially condensed effluent is sent to a phase separator. Noncondensable gases, primarily nitrogen, are vented to the atmosphere. Usually the gases are contacted with either water or an aromatic solvent for removal of hydrogen chloride and EDC recovery. The crude EDC from the separator undergoes the same final processing steps as in the direct process.

3.6.1.4.2 Atmospheric Emissions

Engineering and cost studies of air pollution control for EDC manufacture have been published (PE-160, SC-316). These reports provide the basis for the discussion of emissions and controls.

Direct Process

The scrubbing column vent is the major source of air emissions from the direct chlorination process. The stream contains small amounts of ethylene, ethylene dichloride, vinyl chloride, ethyl chloride, and inert impurities in the feed. About 4.7 kg of organic compounds are emitted from this source per MT of EDC produced.

Fugitive emissions from leaks, spills, and miscellaneous causes are estimated to be 0.71 kg per MT of EDC produced. EDC storage tanks are usually vented directly to the atmosphere. Emissions are reduced in some cases by nitrogen padding. Storage losses are equal to about 0.6 kg per MT of EDC produced.

Oxychlorination Process

The main process vent gas stream usually is vented from a scrubber and is the primary air emission source in the process. The stream consists of the gross reactor effluent after quenching and trim cooling to recover EDC. The vent stream flow averages about 36 MT per hour (2740 moles per hour) in a typical 318,000 MT per year (700 million pounds per year) EDC plant. The organic fraction of the stream normally ranges from 0.27 to 11.2 mole percent consisting primarily of ethylene, ethane, EDC, ethyl chloride, and methane (if present in the feed). The quantity and composition of the stream vary depending on factors such as feed purity, catalyst activity, reactor operating conditions, and the specific processing scheme employed.

The product fractionation vent is a small stream which varies greatly in composition, depending upon the type of fractionation system used and the final product purity. Fugitive emissions are reported to be "minor". EDC storage tanks are vented directly to the atmosphere and losses are estimated to be about 0.6 kg per MT of EDC produced.

3.6.1.4.3 Control of Emissions

The organic emissions from vent streams in both processes can be eliminated by thermal incineration of the streams. Emissions from the fractionation area can be controlled by vent condensers. An incinerator should be followed by an absorber to remove any hydrogen chloride produced in the incinerator. Fugitive emissions can be reduced by stringent application of controls such as good housekeeping and maintenance practices and installation of floating roof tanks. The reduction potential which could be achieved by the application of these control methods is estimated to be 55,400 MT of volatile organics per year.

3.6.1.5 Toluene Production

Process Description

Approximately 85 percent of the recovered toluene is isolated from petroleum refinery catalytic reformate, approximately 12 percent is obtained from pyrolysis gasoline (a by-product of olefin manufacture), and the remainder comes from coke-oven light oil and as a by-product of styrene manufacture (HE-154).

Several methods are used for extracting aromatics from reformate. These methods include extractive distillation, liquid/liquid extraction, and adsorption on silica gel. The favored method is solvent extraction using sulfonane (CA-303)

In the extraction process, feed is introduced to the center of a continuous countercurrent-extraction column. The rich solvent is charged to a stripper. A fraction is removed overhead and the partially stripped extract is further distilled to recover the aromatics. The raffinate and extract are water washed to recover small amounts of entrained solvents.

In obtaining aromatics from pyrolysis gasoline, the feed must first be stabilized by hydrotreating prior to the recovery of aromatics by solvent extraction. The feedstock and recycled hydrogen are preheated and passed through a series of hydrotreating reactors containing a platinum catalyst. The reactor effluent is cooled and discharged into a separator. The gas stream taken overhead is scrubbed with caustic solution and recycled to the reactor. The liquid phase from the separator is passed through a coaleser where water is used to trap coke particles and a stabilizer where light hydrocarbons are removed. The stabilized liquid is then extracted with a solvent to recover

aromatics in a process similar to that discussed above for recovering aromatics from catalytic reformate.

Atmospheric Emissions and Control

No data is available concerning atmospheric emissions from these processes for producing toluene. The total emissions from the processes are estimated to be 1.5 percent of the product (ER-030). This estimate was based on the normal range of emissions occurring from the production, conversion, and handling of organic chemicals (0.5 - 2.0 percent) and was adjusted for the volatility and solubility of toluene. It is also estimated that the fugitive emissions from the processes are equal to one-third of the total emissions (0.5 percent) based on the industry average (PE-160, ME-136).

Process (vent) emissions can be almost completely eliminated (approximately 99 percent reduction) by conventional methods, i.e., condensation, incineration, adsorption, etc. The fugitive emissions can be reduced to about 0.21 percent (ME-136) of throughput by stringent maintenance. Based on these reduction potentials and the emissions estimates, the annual volatile organic emissions from toluene manufacturing processes could be reduced by about 43,800 MT per year.

3.6.1.6 Carbon Tetrachloride Production

3.6.1.6.1 Process Descriptions

Carbon tetrachloride is made by the following three industrial processes:

(1) thermal chlorination of methane,

(2) thermal chlorination of propane, and

(3) chlorination of carbon disulfide.

In 1970, approximately 40 percent of the carbon tetrachloride was produced by the first process, about 35 percent by the second process, and the remainder by the third process (PR-116).

Chlorination of Methane

This process involves four main steps: (1) reaction, (2) hydrogen chloride recovery, (3) chlorides recovery, and (4) chlorides refining. High purity methane, recycle methane, and chlorine are mixed and fed to the reactor operating at 400° to 500°C. The reactor effluent is cooled and fed to the HCl recovery system. This system consists of two columns; in the first, the hydrogen chloride is absorbed in water and the second column strips anhydrous HCl.

The HCl-free gases from the absorber are scrubbed with caustic soda to remove final traces of HCl and are fed to chlorides recovery. Compression, cooling, and distillation are used to separate the carbon tetrachloride and by-products. Unreacted methane is separated, dryed with sulfuric acid in the dehydrator column, and recycled.

Thermal Chlorination of Propane

Chlorine and propane feeds are introduced to a vaporizor where they are mixed with recycled chlorides. The gases are fed to an adiabatic reactor which operates at atmospheric pressure and 550° to 700°C. The reactor effluent is essentially free of unreacted hydrocarbon and consists mainly of carbon tetrachloride, perchloroethylene, HCl and excess chlorine. The effluent is

rapidly quenched by contact with a liquid which is largely perchloroethylene. The cooled effluent is fed to a column which separates perchloroethylene as a bottoms stream. Carbon tetrachloride is withdrawn from the condenser as a liquid, and hydrogen chloride, chlorine, and traces of hydrocarbon gases and removed overhead. The vapor stream is scrubbed with water to remove hydrogen chloride, dried with concentrated sulfuric acid, and recycled to feed. A portion of the dried gas is purged to remove inerts.

Carbon Disulfide Chlorination

Both direct and indirect chlorination of carbon disulfide are employed industrially. In the direct process, a recycled mixture of carbon tetrachloride, carbon disulfide and sulfur chlorides is contacted with excess chlorine over an iron catalyst at approximatley 30°C. Distillation of the reactor effluent yields an overhead product of relatively pure carbon tetrachloride. This material may be treated with a base, to remove sulfur chlorides, and then dried.

The indirect process is similar. Fresh carbon disulfide feed is reacted with sulfur monochloride. A direct-chlorination polishing reactor is used to convert residual carbon disulfide and to facilitate the subsequent distillation, where crude carbon tetrachloride is removed overhead and molten sulfur containing some sulfur monochloride is the bottoms product. The crude carbon tetrachloride may be purified as in the direct chlorination process.

3.6.1.6.2 Atmospheric Emissions and Control

Processes for the thermal chlorination of both methane and propane require continuous purging of recycled vapor for

inerts removal. The methane process is vented at the dehydrator column. The streams contain both raw materials and chlorinated materials. One estimate of the quantities of the organic compounds emitted from the methane based process is shown below (PR-116).

Compound	Quantity Emitted (kg/MT Product)
CH_3Cl	13
CH_2Cl_2	2
CH_4	1
CCl_4	1
CCl_3H	1

The dry chlorine recycle in the propane process is purged. Chlorine is the major pollutant in this stream, but trace quantities of chlorocarbons are expected to be present. No estimates of the quantities of these organic compounds in the purge stream were available. Reportedly, no organic control devices are utilized on these purge streams.

The vent from the neutralizer in the carbon disulfide process contains an estimated 2 kg CS_2 and 14 kg CCl_4 per MT of product (PR-116).

No estimates of fugitive emissions from the carbon tetrachloride manufacturing processes were available. However, unexplained (fugitive) losses were included in the total emissions estimate, 43,398 MT of organics from the methane and carbon disulfide processes, in 1973 (MO-201)*. These losses were determined by material balances, conversion, and yield data for the processes.

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*This estimate indicates that the total emissions from the process are equal to approximately 9.4 percent of the weight of the total tetrachloride production. This base factor seems abnormally high.

Approximately 99 percent of the organic compounds in the process vent streams can be eliminated by conventional control methods, i.e. condensation, incineration, adsorption, etc. If incineration is used for vent stream control, the incinerator or afterburner should be followed by a scrubber to remove HCl formed by the combustion of the chlorocarbons. Fugitive emissions and storage losses can be reduced from the estimated industry average of about 0.5 percent of throughput to about 0.21 percent of throughput by stringent maintenance (ME-136).

Application of these potential reductions to the estimated total emissions from carbon tetrachloride manufacture indicates a reduction potential of about 41,700 MT/yr.

3.6.1.7 Soap and Detergent Manufacture

Process Description

Soap is manufactured by the catalytic hydrolysis of various fats or oils to produce fatty oils which are then neutralized or "saponified" with sodium or potassium hydroxide to form the soap. Glycerin may be generated as a by-product of fatty acid manufacture or as a by-product from saponification of the fatty acid in the kettle-boil process. The glycerin is concentrated to 80 percent and refined by distillation.

Detergent manufacture generally begins with sulfuration by sulfuric acid of a fatty alcohol or linear alkylate. The sulfurated compound is neutralized, and various dyes, perfumes, and other compounds are added. The resulting paste or slurry is then sprayed into a vertical drying tower where it is dried with a stream of hot air. The dried product is cooled and packaged.

Atmospheric Emissions and Control

The major air pollutants in the manufacture of soap and detergent are odor and particulates. Odors may be controlled by scrubbing all exhaust fumes and, if necessary, incinerating the remaining compounds. Uncontrolled particulate emissions are about 45 kg per MT of dried detergent and 7.5 kg per MT of soap produced (EN-071, HO-244). Application of the best particulate control system (combinations of cyclones, scrubbers, etc.) can reduce the particulate emissions to approximately 0.22 kg per MT of dried detergent and 0.013 kg per MT of soap produced (HO-244). The reduction of particulate emissions to these levels would result in the reduction of an estimated 17,900 MT per year of organic particulates.

3.6.2 Water Effluents

Wastewater sources within the organic chemical processing industry can be divided into the following five general categories (JE-027):

1. wastes containing raw material or product resulting from the stripping of the product from solution;

2. by-products;

3. spills, slab washdowns, vessel cleanouts, sample overflows, etc;

4. cooling tower and boiler blowdown, steam condensate, water-treatment wastes, and general washing water; and

5. storm run-off.

The large variety of compounds produced by the organic chemical processing industry makes characterization and treatment of wastewaters difficult and complex. Wastewaters from plants manufacturing similar or even the same products usually have dissimilar characteristics. These differences can be ascribed to the use of different manufacturing processes, operating procedures and by-product disposal practices. The wastes are, however, related to the method of water usage associated with the various manufacturing processes. The organic chemicals industry has been subcategorized (EN-153) by the type of process water usage in the processes. Process water is defined as all water coming in contact with chemicals within the process and includes:

1. water required or produced in the chemical reaction;

2. water used as a solvent or as an aqueous reaction medium;

3. water entering the process with a reactant or which is used as a diluent;

4. water associated with a catalyst system, either during the reaction or during catalyst regeneration;

5. water used as an absorbent or as a scrubbing medium for separation purposes;

6. steam used in steam stripping operations;

7. water used to wash, remove, or separate chemicals from the reaction mixture;

8. water associated with mechanical devices such as steam jet ejectors;

9. water used as a quench or direct contact coolant;

10. water used to clean or purge equipment; and

11. runoff or wash water associated with the process area.

Four process-oriented subcategories describing mode of water usage have been established for the organic chemicals industry. Subcategories A, B, and C relate to continuous processes, while subcategory D relates to batch processes. These subcategories were further described by waste loads from processes within the subcategories. The subcategories are described as follows (EN-153):

A. Nonaqueous Processes

Minimal contact occurs between water and reactants or products within the process. Water is not required as a reactant or diluent and is not a reaction product. The only water usage stems from periodic washes of working fluids or catalyst hydration.

B. Processes with Process Water Contact as Steam Diluent or Absorbent

Process water usage is in the form of diluent steam, a direct contact quench, or as an absorbent for reactor effluent gases. Reactions are all vapor phase and occur over solid catalysts. Most processes have an absorber coupled with steam

stripping of chemicals for purification and recycle. Steam is also used for catalyst de-coking.

C. Continuous Liquid-Phase Reaction Systems

Process water usage involves liquid-phase reactions where the catalyst is in an aqueous medium. Additional water may be required for final purification or neutralization of products.

D. Batch and Semicontinuous Processes

Processes are carried out in reaction kettles. Many reactions are liquid-phase with aqueous catalyst systems. Filter presses and centrifuges are commonly used to separate solid products from liquid.

Raw waste load (RWL) data were obtained in field surveys of representative processes for the four subcategories (EN-157). These data are summarized in Table 3.6-2. The RWL's associated with the continuous processes are based on contact process water only. Most continuous processes achieve segregation and do not include noncontact cooling water or steam. Subcategory D includes all wastewater associated with the process.

The RWL's for the various processes of the OCPI were estimated from data generated in the above study and similar studies made for various segments of organic chemical industry (EN-385, EN-160, EN-154, EN-162, EN-384). The RWL's were derived from data on the specific processes whenever possible. When data was unavailable for a process, its RWL was estimated by using the average RWL of the subcategory to which it was assigned.

TABLE 3.6-2

MAJOR RWL's OF POLLUTANTS BASED ON PROCESS WASTEWATER USE

Category	Flow RWL gal./1,000 lb	BOD_5 RWL kg/MT(mg/ℓ)	COD RWL kg/MT(mg/ℓ)	TOC RW kg/MT(mg/ℓ)
A	0.25 - 2,000	0.1 - 0.13	0.3 - 3.7	0.034 - 0.9
Conc. Range		(400 - 1,000)	(200 - 10,000)	(50 - 2,000)
B	50 - 3,000	0.09 - 7.0	0.47 - 21.5	0.2 - 40
Conc. Range		(50 - 500)	(200 - 5,000)	(100 - 2,000)
C	30 - 3,000	1.3 - 125	1.9 - 385	1.5 - 150
Conc. Range		(3,000 - 10,000)	(10,000 - 50,000)	(3,000 - 15,000)
D	10,000 - 100,000	52 - 220	180 - 4,800	60 - 1,600
Conc. Range		(100 - 3,000)	(1,000 - 10,000)	(200 - 2,000)

Three different levels of treatment to reduce the discharge of aqueous pollutants have been designated. These levels of treatment are listed below; the first two are applicable to existing plants and the third to new plants.

Best Practicable Control Technology Currently Available (BPCTCA) (by 7-1-77)

Best Available Technology Economically Achievable (BATEA) (by 7-1-83)

Best Available Demonstrated Control Technology (BADCT) (new sources)

Effluent limitation guidelines have been defined for the various processes in the previously mentioned development documents. Many alternate systems of end-of-pipe wastewater treatment and in-process modification and pollution control equipment exist. Individual manufacturers select specific combinations of pollution control measures best suited for complying with the published limitations and standards.

BPCTCA and Current Effluent Estimates

BPCTCA for the organic chemicals industry includes both in-process controls and end-of-process treatment technologies. These technologies are exemplary of those for the entire OCPI.

Waste characterization studies indicate which contaminated contact process water streams can be segregated from non-contaminated streams to reduce the waste volume to be treated in a centralized waste treatment plant. In addition, process water streams can be characterized by the ease with which certain constituents can be recovered or difficulty of ultimately treating the wastes.

BPCTCA process modifications include the substitution of nonaqueous media for carrying out the reaction or purifying the products. Changes in the reactants, reactant purity, or catalyst systems can sometimes eliminate aqueous waste by-products. Reuse of water within the process also should be investigated. Equipment for separation of an organic phase from aqueous phase are provided with backup coalescers or polishing filters for the aqueous phase. Direct vacuum-jet condensers replace indirect condensers or vacuum pumps.

In addition to waste reductions through the above practices, recovery of products and by-products can be combined with wastewater purification. Chemical recovery from the wastewaters includes physical separation of the chemicals from the wastewater as well as subjecting the wastewaters to additional chemical reactions that will render them more amenable to recovery and purification.

End-of-process treatment technologies commensurate with BPCTCA are based on the utilization of biological oxidation systems including activated sludge, extended aeration, aerated lagoons, trickling filters, and anaerobic and floculative lagoons. These systems include additional treatment operations such as equalization, neutralization, primary clarifications with oil removal, nutrient addition, and effluent polishing steps such as coagulation, sedimentation, and filtration. Effluent suspended solids (primarily biological solids) are expected to be maintained below 60 mg/liter for the maximum 30-day average (EN-153). The waste reduction factors shown in Table 3.6-3 are consistent with BPCTCA (SI-105):

TABLE 3.6-3

WASTE REDUCTION FACTORS ACHIEVABLE THROUGH USE OF BPCTCA LEVEL OF WATER TREATMENT

Process Water Use Subcategory	BPCTCA Reduction of RWL Median Values (%)	
	BOD_5	COD[1]
A	90	75
B-1	90	75
B-2	98	75
C-1	95	75
C-2	99	75
D	95	75

[1]COD effluent limitations have not been specified for BPCTCA.

For quantifying emissions in this report, current effluents from the various processes are assumed at the levels achievable by application of BPCTCA required in 1977. The total quantity of pollutants was estimated using production data from the most recent available year along with COD, BOD_5, SS, and TOC emissions based on BPCTCA. The quantity of pollutants emitted after application of BPCTCA was estimated by either applying reduction factors for BPCTCA to the estimated RWL's or by utilization of the published effluent limitations (maximum average of daily values for any period of 30 consecutive days). The first method was normally used to estimate effluent COD, since BPCTCA effluent limitations for most segments of the industry do not include COD values. The latter method was usually used to estimate effluent BOD_5 and SS. The 30-day maximum average limitation allows for normal variations of exemplary designed and operated waste treatment systems; therefore, this method probably gives a somewhat high estimate of effluent concentrations.

The estimated current emissions from the processes within the organic chemical processing industries are presented in Table A-2 in the Appendix. The accuracy of these estimates is questionable due to the assumptions involved in making the estimates and the differences noted previously between processes which produce similar or even the same products.

BATEA and Reduction Potential

The BATEA is based upon the most exemplary combination of in-process and end-of-process treatment and control technologies. The following in-process controls are included:

1. the substitution of noncontact heat exchangers for direct contact water cooling;

2. the use of nonaqueous quench media where direct contact quench is required;

3. the recycle and reuse (after treatment) of water where possible;

4. the use of process water to produce low pressure steam by noncontact heat exchangers in reflux condensers of distillation columns;

5. the recovery of spent acids or caustic solutions for reuse;

6. the recovery and reuse of spent catalyst solutions; and

7. the use of nonaqueous solvents for extraction of products.

The model end-of-process treatment system was determined to be biological treatment followed by filtration and additional activated carbon treatment.

This model system or equivalent combinations can provide 90 percent BOD_5 and 69 percent COD reductions below BPCTCA effluents. The SS BATEA effluent limitations average approximately 45 percent of BPCTCA limitations. The TOC BATEA levels average about 87 percent reduction below BPCTCA.

The reduction potentials for organic water pollutants in the organic chemical processing industry were calculated from the difference between effluents with BPCTCA systems and BATEA systems. These differences were usually estimated by one of three methods: (1) application of the reduction factors for BATEA to the estimated effluents with BPCTCA; (2) use of the difference between the published effluent limitations (maximum 30-day averages) for BPCTCA and BATEA; or (3) reductions below BPCTCA effluent levels by control methods applicable to a specific process. The specific processes found to be the largest sources of organic water pollutants within the industry are discussed in detail in the following section. The BOD_5, COD, TOC, and total organics in effluents from these processes and their reduction potentials are shown in Table 3.6-4.

The concentration of total organics in the effluents was estimated from the TOC values for BPCTCA and BATEA. The TOC values were assumed to result from the major product of the process or, for processes such as polymers, the major feedstock of the process. This assumes that the by-products are similar to the feedstock or product. This assumption does not consider other materials that can add to the waste load such as organic diluents, inhibiters, or lubricants. To calculate total organics, the TOC values were multiplied by the ratio of molecular

TABLE 3.6-4

MAJOR WATER EFFLUENTS FROM THE ORGANIC CHEMICAL PROCESSING INDUSTRY

Effluent Parameters	RWL (MT/yr)	BPCTCA (MT/yr)	BATEA (MT/yr)	Reduction Potential[1] (MT/yr)
Dyes and Pigments				
BOD_5	63,300	8,230	905	7,325
COD	262,000	73,300	22,700	50,600
TOC	72,300	30,400	3,950	26,450
Total Organics	144,600	60,800	7,900	52,900
Polyvinyl Chloride and Copolymers				
BOD_5	11,800	1,532	168	1,364
COD	51,700	14,500	4,490	10,010
TOC	29,700	12,500	1,620	10,880
Total Organic	76,600	32,300	4,180	28,120
Methyl Methacrylate				
BOD_5	13,000	1,690	186	1,504
COD	112,000	31,300	9,720	21,580
TOC	44,100	18,500	2,410	16,090
Total Organics	73,600	30,900	4,020	26,880

[1]Reduction Potential calculated from the difference between BPCTCA and BATEA.

weights shown in equation 1, where MW product is the molecular weight of the process product or feedstock.

$$\frac{(MW_{product})}{(MW_{carbon})} \times (TOC) = \text{Total Organics}$$

3.6.2.1 Dyes and Pigment Production

Process Description

The organic dyes and pigments industry converts intermediate organic chemicals into more complex materials and ultimately into dyes and pigments. The industry is extremely complex due to the diversity of the products. The organic dyes and pigments industry in the United States sells more than 1000 different products.

Because of the large number of compounds that are produced, most dyes and pigments are produced in small batches. A total of forty-eight processes summarize the operations carried out in manufacturing dyes and pigments (RA-222). Detailed discussions of these operations will not be included in this report; however, the great majority of dyes and pigments are manufactured by processes similar to a typical azo dye manufacturing process (EN-153).

Raw materials (including aromatic hydrocarbons, intermediates, various acids and alkalies, and solvents) are fed into the reactor which normally operates at atmospheric pressure. The reactions are exothermic and temperature control is accomplished primarily by direct addition of ice to the reactor. Jacket cooling is also commonly practiced.

The dye particles precipitate from the reaction mixture. The vent gases from the reactor are scrubbed with water before being discharged into the atmosphere. The liquid effluent from the reactor is treated in a plate-and-frame filter press where the dye particles are separated from the mother liquor. The mother liquor is either directly discharged into sewers or treated to recover some of the metal salts. The moist cake is discharged into shallow trays which are placed in a circulating air dryer. Vacuum dryers and drum dryers may also be used. The dried dye is ground and mixed with a diluent, such as salt, to make it uniform in color strength.

Water Effluents and Control

The major water pollution sources from the azo dye process are the mother liquor from the filter press, intermittant reactor clean-up waters, the draw-off from the vent gas scrubber, and general cleaning waters. Because of the frequent changing of feed materials and products, large amounts of water and cleaning aids are required to clean reactors and filter presses.

Plant wastewater surveys have been conducted at dye and pigment plants (EN-385). The RWL's were found to vary greatly, due to the batch nature of the processes. The high organic loading in the wastewater is due primarily to incomplete crystallization and separation of the products from the mother liquor. Organic losses and cleaning aids also contribute to the organic loading.

Noncontact cooling water is discharged into sewers to dilute the wastewaters to be treated. Reuse or recycle of the wastewater from this type of process is considered unfeasible because the wastewater is contaminated with salts, metal ions, and a high color intensity (EN-153).

The application of BATEA will reduce effluents of BOD_5, COD, and SS by approximately 90, 69, and 55 percent, respectively, below effluent with BPCTCA (EN-153). By utilizing these reduction factors, annual effluents from dye and pigment plants could be reduced by about 52,900 MT of organic/yr. The BOD_5, COD, TOC and organic loads are presented in Table 3.6-2.

3.6.2.2 Polyvinyl Chloride Production

Process Description

Polyvinyl chloride (PVC) is produced by a free radical polymerization of vinyl chloride. All vinyl chloride polymerizations are conducted in batch operations at low temperature and pressure. PVC is primarily made by suspension polymerization, but it may also be made by bulk polymerization or emulsion polymerization (HE-154).

In emulsion and suspension polymerization the vinyl chloride monomer is dispersed in an aqueous phase during the reaction. Some technical differences between emulsion and suspension systems pertain to the polymerization reaction itself, but these do not have a bearing on the potential aqueous pollution problem (EN-160). Therefore, both processes will be discussed together.

Jacketed, stirred batch reactors for PVC polymerization vary in size from 8 to 40 m^3 (2000 to 10,000 gallons). The batch cycle consists of the introduction of a water-monomer emulsion to the stirred reactor. The heat of reaction is removed by circulating cooling water through the reactor jacket. The reactor is vented through a condenser for monomer recovery and the condensate, including any water, is returned directly to the vessel.

On completion of the batch a short "soaking" time is allowed for completion of the reaction. The wastewater load depends on the final processing steps including coagulation, steam stripping, washing, and drying.

Water Effluents and Control

The major wastewater stream from PVC production by emulsion or suspension polymerization processes is the water separated from the emulsion or suspension after the batch reactor (EN-160). The major wastewater flow from the bulk polymerization process is decanted condensate from the condenser at the vacuum stripper which removes untreated monomer, contaminants and by-products from the reactor (EN-160).

The potential reduction of organic waste in effluents from PVC production resulting from application of BATEA to BPCTCA is 28,100 MT organic/yr. The reduction is estimated by determining the difference in BPCTCA and BATEA TOC levels (EN-160) and multiplying by the ratio of the molecular weight of vinyl chloride to carbon. This assumes that most of the organic load is vinyl chloride monomer or an organic by-product of similar composition. The BOD_5, TOC, COD and organic loads are presented in Table 3.6-2.

3.6.2.3 Methyl Methacrylate Production

Process Description

Methyl methacrylate is produced commercially in the U.S. by the acetone cyanohydrin process. First, acetone cyanohydrin is made by reacting hydrogen cyanide and acetone in a cooled reactor with an alkaline catalyst. The excess catalyst is neutralized and crude acetone cyanohydrin is stored in holding tanks. The salt formed by neutralization is filtered and the crude acetone

cyanohydrin is fed to a two-stage distillation unit. Water and acetone are removed and recycled in the first column, and the remainder of the water is removed at high vacuum from the second column.

Acetone cyanohydrin and concentrated sulfuric acid react in a cooled hydrolysis kettle to make methacrylamide sulfate. Methacrylamide sulfate reacts continuously with methanol in an esterification kettle. Inhibitors are added at various points to prevent polymerization. The esterified stream is pumped to the acid stripping column from which the acid residue (10% wt. organic substances) can be sent to a spent acid recovery unit (SAR). The recovered sulfuric acid is recycled to the hydrolysis reactor.

The acid stripping column overhead stream is distilled to remove methyl methacrylate and unreacted methanol. The methanol is recycled. The remaining traces of methanol in the methyl methacrylate are removed by water extraction, after which the monomer is purified in a rerun tower.

Water Effluents and Control

The acid residue from the acid stripping column is the major waste stream generated in the process. This waste stream is sent either to the SAR unit previously mentioned or it is discharged into sewers. The waste streams generated as bottoms from various stills are combined with the acid residue for spent acid recovery. Water samples from streams entering and exiting the SAR unit have been analyzed (EN-153), and the results are shown in Table 3.6-5.

TABLE 3.6-5

CHARACTERISTICS OF WATER EFFLUENT FROM SPENT ACID RECOVERY UNIT

	SAR Influent	SAR Effluent
Flow	4440 l/MT	3550 l/MT
COD	178,000 mg/l	110 mg/l
BOD_5	20,700 mg/l	15 mg/l
TOC	69,998 mg/l	18 mg/l

The stream entering the SAR has a high concentration of floating solids. The floating solids removed in the SAR may be incinerated. High concentrations of metal contaminants such as copper and iron are also indicated. A large portion of the metals is removed along with floating solids in the SAR unit; however, the metal concentration in the streams discharged to sewers is still higher than general discharge criteria for biological processes. The sulfuric acid concentration is reduced from 40 percent by weight in the influent to the SAR to 1 percent by weight in the effluent, but the sulfate concentration in the discharge stream is still high enough to inhibit the normal functioning of a biological treatment process.

Because of the highly exothermic reactions involved, the process requires a large amount of cooling water. The survey data (EN-163) show that gross cooling water usage amounts to 366 kg per kg of methyl methacrylate. Process water, 0.56 kg per kg of product, is introduced into the system as direct stream stripping.

The BATEA for this process is a Spent Acid Recovery unit. The economics of a 220,000 MT/yr spent acid recovery plant have been estimated (EN-153) for two different processes: spent acid recovery by neutralization and by complete combustion. A possible alternative to SAR, where geology is favorable, is deep well disposal.

The use of SAR throughout the industry would reduce effluent organic levels by 26,900 MT organic/yr. The BOD_5, COD, TOC and organic effluent loads are presented in Table 3.6-2.

3.7 Noncombustion Organic Chemical Utilization

The noncombustion organic chemical utilization category examines organic emissions from operations which utilize industrial and commercial grade organic chemical products. The bulk of the emissions from this category results from the evaporation of solvents used in various processing and coating operations.

The category is divided into subgroups based upon the industries examined as listed in Table 3.7-1. The major subgroups, including surface coating, graphic arts, dry cleaning, rubber and plastic processing, and fabric treatment, are described in Sections 3.7.1 through 3.7.5. A summary of the air emissions from the industries in this category is presented on Table 3.7-1.

Water effluents and solid wastes were also examined for this category. The only source of water effluents from this category was the tire and inner tube segment of the rubber processing industry. No data was found on solid wastes for any subgroups in this category. Table 3.7-2 contains a summary of the organic water effluents from the tire and inner tube production industry.

3.7.1 Surface Coating

3.7.1.1 Process Description

Surface coating operations consist of one or more of the following processing steps: degreasing, surface coating application, and drying and curing. Each of these steps will be discussed in the following sections.

TABLE 3.7-1

NONCOMBUSTION ORGANIC CHEMICAL UTILIZATION - ATMOSPHERIC EMISSIONS

	Emissions (MT/yr)		
	Year	Volatile Organics	Ref
Noncombustion Organic Chemical Utilization			
Rubber and Plastic Processing	1975	1,280,000	1
Surface Coating			
Paper and Paperboard	1975	475,000	1
Sheet, Strip, and Coil	1975	469,000	1
Automobile and Truck	1975	100,000	1
Major Appliance	1975	30,000	1
Wood Furniture	1975	9,000	1
Industrial Machinery	1975	8,000	1
Metal Furniture	1975	8,000	1
Graphic Arts			
Gravure	1975	107,000	2
Flexography	1975	98,000	2
Letterpress	1975	66,000	2
Lithography	1975	62,000	2
Metal Decorating	1975	59,000	2
Drycleaning	1975	367,000	1
Fabric Treatment	1975	210,000	3

TABLE 3.7-1 (Cont'd.)

NONCOMBUSTION ORGANIC CHEMICAL UTILIZATION - ATMOSPHERIC EMISSIONS

	Emissions (MT/yr)		
	Year	Volatile Organics	Ref
Cast Iron Foundry	1975	102,000	2
Asphalt Batching	1975	53,000	2
Paint Manufacturing	1975	19,000	2
Printing Ink Manufacturing	1975	8,000	2
Varnish Manufacturing	1975	7,000	2
Asphalt Roofing	1975	6,000	2
TOTAL		3,540,000	

References:
1. MO-201
2. HO-244
3. HU-100

TABLE 3.7-2

NONCOMBUSTION ORGANIC CHEMICAL UTILIZATION - ORGANIC EFFLUENTS

	Effluents (MT/yr)				
	Total Organics	BOD	COD	SS	Oil and Grease
Noncombustion Organic Chemical Utilization					
Rubber and Plastic Processing					
Tire and Inner Tube Industry	40	NA	NA	160	40

Ref: EN-154

Degreasing

The surface of metal products is lubricated with oils, greases, or stearates during their fabrication to facilitate the various drawing, forming, and machining operations. These lubricants, as well as dust and dirt, must be removed from the metal surface prior to surface coating. This cleaning operation is called degreasing, and it is used to ensure that the surface coating adheres to the metal surface.

Three chlorinated hydrocarbon compounds are used in units for degreasing. These are trichloroethylene, 1,1,1-trichloroethane, and perchloroethylene. Equipment used includes vapor spray degreasers, dip tank degreasers, liquid spray degreasers, and diphase degreasers employing an aqueous solvent along with the organic solvent.

Surface Coating Application

Manufactured articles often receive coatings for surface decoration and/or protection before being marketed. A number of basic coating operations are utilized for this purpose. Included below is a list of these different operations and a brief description.

- Spraying - Spraying operations are performed in a booth or enclosure vented by a draft fan. In the operation, a coating material is forced through a nozzle which directs the coating as a spray upon the desired surface. The organic solvent vapors are vented through the fume hood system.

- Dip Coating - In dip coating operations, the object to be coated is immersed in a tank containing the surface coating just long enough to be coated completely. The excess paint drains back into the tank.

- Flow Coating - This technique is used on items which cannot be dipped due to the buoyancy. The article is coated by the liquid release from overhead nozzels and flowing in a steady stream over the article. Excess paint drains from the coated object and is recirculated.

- Coil Coating - In this operation, long, flat strips or coils of metal are coated by means of rollers. Three rollers are commonly used, one partially immersed in the coating material and two others which apply the paint by transfer from the first roller.

Drying and Curing

Applied surface coatings are dried and cured by both natural evaporation and by forced evaporation with heating. The forced evaporation of solvent is accomplished in bake ovens. Before entering the oven, the wet, coated object is allowed to dry by natural evaporation to remove the highly volatile solvent components. This is done to prevent the formation of bubbles in the coating during oven drying.

The ovens are designed for either batch or continuous operation. They are equipped with temperature regulation, air-circulation, and exhaust systems. The heat required by a bake oven may be supplied by gas, electric, steam, or waste heat from the other processes.

The evaporated organic vapors from drying and curing are vented through an exhaust system to prevent their escape into the plant. The exhaust system collects these vapors and either vents them to the atmosphere or directs them to a vapor control device for disposal.

3.7.1.2 Atmospheric Emissions and Control

The two types of emissions from surface coating plant operations are point source emissions and fugitive emissions. The point source emissions include the controlled and uncontrolled emissions from the degreasing, surface coating, and drying and curing operations. Other point sources include the degreasing solvent storage tank vent, surface coating solvent vent, and surface coating blending tank vent (HU-100).

The fugitive emission sources include solvent evaporation losses from degreased, coated, and dried products. They also include losses from each piece of processing equipment and from the transfer of organic liquids within the plant.

Table 3.7-3 presents estimates of the quantities of organics emitted yearly to the atmosphere from surface coating operations. Monsanto Research Corporation estimates the quality of this data to be within 50-100 percent of the true value (HU-100).

TABLE 3.7-3

ATMOSPHERIC ORGANIC EMISSIONS FROM SURFACE COATING OPERATIONS

Source	Emissions (MT/yr)
Paper & Paperboard Coating	475,000
Sheet, Strip & Coil Coating	469,000
Automobile & Truck Coating	100,000
Major Appliance Coating	30,000
Wood Furniture Finishing	9,000
Industrial Machinery Coating	8,000
Metal Furniture Coating	8,000
TOTAL	1,099,000

Source: HU-100

The control of organic vapors from surface coating sources can be accomplished by the application of condensation, compression, absorption, adsorption, or incineration technology. The emissions from the degreasing phase are best reduced by carbon adsorption units. They can potentially recover nearly 100 percent of the vapors in exhaust gases from a degreaser. For the actual coating application phase, the evaporated solvents are best controlled by adsorption (should solvent recovery be desired) or incineration (if the solvent is not to be recovered). The emissions from the drying and curing operation are best controlled through incinceration of the solvent vapors (DA-069).

Based on the relatively high reduction efficiencies of these control devices (greater than 90 percent), a high reduction potential is expected for organic emissions from surface coating

operations. An assumed percent reduction for this stationary source is estimate to be as high as 90 percent. This results in a reduction potential of 989,000 MT/year of hydrocarbons from the described surface coating operations.

3.7.2 Graphic Arts

This section reviews the organic emissions from the various printing processes comprising the graphic arts industry. The five processes considered are offset lithography, letterpress, metal decorating, gravure, and flexography. A brief discussion of each of these processes is followed by the organic emission estimates for each segment and the controls used to reduce these emissions.

3.7.2.1 Process Description

Offset Lithography

Lithography involves transferring, by direct contact, an immage on a plate to a paper surface using ink and water. Offset lithography usually involves transferring the image from the plate to a rubber surface on a cylinder in contact with the paper. The image is therefore transferred first from the image plate to the cylinder and then to the paper. The water used in offset lithography may contain as much as 15 to 30 percent isopropanol (GA-168).

From the image transfer operation, the paper is passed through a drier, where the ink is dried. The exhaust from the drier contains organics evaporated from the ink.

Letterpress

In this process, the ink is transferred to the paper from the image surface, which is slightly raised in relation to the nonprinting surface of the plate. As with the offset lithography operation, when the paper exits from the letterpress printing operation it is passed through a drier where most of the ink is dried. The exhaust from the drier contains the organic solvent evaporated from the ink (GA-168).

Metal Decorating

Sheet-fed metal decorating is done with lithographic inks containing mainly alkyd resins and a small amount of solvent. The image is transferred by lithography to a dried lacquer undercoat rather than to the base metal. After printing, the sheet of metal may or not be coated and then it is sent to drying. In the case of metal can decorating, the can receives a coating of varnish following printing.

Since the ink contains little or no solvent, the organic emissions from the lithographing process are insignificant. The points of organic emissions in metal decorating are the roller coating area and the drier exhaust.

Gravure

In this type of printing, ink is transferred directly from the image carrier to the paper or film. The ink used in high speed gravure printing contains a relatively large amount of volatile solvent.

Following printing, the product is dried by a steam drum or hot air drier. The majority of the solvent emissions

from this process are present in the drier exhaust with most of the remainder coming from the press unit.

Flexography

The flexographic process is similar to letterpress in that the image area is raised above the surface of the plate. Ink is transferred directly to the image area of the plate and directly from the plate to the paper or substrate. Flexography includes processes in which the plate is made of rubber and the inks are alcohol based. Flexographic processes differ primarily in the type of ink and solvent used. Following printing, the product is dried by forced evaporation in a hot air drier or steam drum.

As with the other printing processes, the primary sources of solvent vapors are the inking area and the drier exhaust.

3.7.2.2 Atmospheric Emissions and Control

The types and amounts of solvents emitted from printing processes vary widely depending on the printing process being used. The gravure and flexographic processes account for the majority of the organic emissions from graphic arts. There are eight groups making up the solvents commonly used for flexographic and gravure inks: aromatic hydrocarbons, aliphatic hydrocarbons, mixed aromatic and aliphatic hydrocarbons, alcohols, glycol ethers, esters, ketones, and miscellaneous solvents. The solvents used in the letterpress and lithographic inks are either aliphatic hydrocarbons or glycols (MS-001).

Table 3.7-4 presents estimates of the quantitites of organics emitted yearly to the atmosphere from graphic arts processes (HO-244). TRC of New England did not estimate the quality of these emissions.

TABLE 3.7-4
ATMOSPHERIC ORGANIC EMISSIONS FROM
GRAPHIC ARTS PROCESSES

Source	Emissions (MT/yr)
Gravure	107,000
Flexography	98,000
Letterpress	66,000
Lithography	62,000
Metal Decorating	59,000
TOTAL	392,000

Source: HO-244

The control of these emissions may be accomplished by several techniques: modification of process, change of process material, incineration, and adsorption. The application of solventless inks, incineration, or adsorption can reduce the organic emissions from 90 to 100 percent (GA-168). Based on this information, the reduction potential for hydrocarbon emissions from graphic arts is assumed high. The percent reduction achievable is estimated to be 90 percent. This results in a reduction potential of 353,000 MT of organics per year from graphic arts.

3.7.3 Dry Cleaning

Process Description

Clothing and other textiles may be cleaned by treating them with organic solvents. This treatment process involves agitating the clothing in a solvent bath, rinsing with clean solvent, and drying with warm air.

There are basically two types of dry-cleaning installations: those using petroleum solvents and those using chlorinated synthetic solvents (perchloroethylene). The trend in dry-cleaning operations today is toward smaller package operations. Typically, they are located in shopping centers and suburban business districts and handle approximately 675 kg (1,500 lbs) of clothes per week on the average. These plants almost exclusively use perchloroethylene, whereas the older, larger dry-cleaning plants use petroleum solvents. It has been estimated that perchloroethylene is used on 50 percent by weight of clothes dry-cleaned in the United States and that 70 percent of the dry-cleaning plants use perchloroethylene (EN-071).

Atmospheric Emissions and Control

The amount of solvent vapors emitted to the atmosphere from a dry-cleaning plant is dependent upon the type of equipment used, the amount of cleaning performed, and the precautions practiced by the operating personnel (DA-069).

The primary source of organic emissions from dry cleaning is the tumbler through which hot air is circulated to dry the cleaned clothes (EN-071). Other sources of organic emissions include the vents for the washing and extraction equipment for synthetic solvent plants which combine these operations and evaporated solvent which is spilled in transferring wet fabrics from one machine to another. The estimated yearly rate of atmospheric organic emissions from dry-cleaning operations is 367,000 metric tons (MO-201).

Petroleum solvent dry-cleaning operations do not control emissions of evaporated solvents since there is no economic incentive for recovery. The principal control, then, is the prevention of solvent loss and evaporation by proper maintenance and good operating practices.

Synthetic solvent dry-cleaning installations on the other hand lend themselves to easy installation of air pollution control equipment. Adsorption is the most practical means of controlling synthetic solvent vapors from dry-cleaning equipment. Packaged adsorption units employing activated carbon are used most often. Despite the high efficiency of adsorption and the operating methods used to prevent solvent emissions, a reduction of more than 70 percent is seldom achieved, when calculated on the basis of total solvents purchased with and without adsorption control (DA-069). Based on this information, the reduction potential for hydrocarbon emissions from dry-cleaning is expected to be moderate to high. Assuming adsorption control of petroleum solvent dry-cleaning operations would reduce their emissions 70 percent and assuming 25 percent of all synthetic solvent installations are already controlled by adsorption, the percent reduction of atmospheric hydrocarbon emissions from dry cleaning could be as high as 55 percent. This results in a reduction potential of 202,000 MT of organics per year.

3.7.4 Rubber and Plastic Processing

Rubber and plastic processing includes those industries producing products from raw rubber and plastic. The industries are similar in that many ingredients other than the raw base material are added to produce desired properties in the finished product. The ingredients have several functions, and they include plasticizers, antioxidants, vulcanization additives, and fire retardants.

The following sections briefly identify each industry. Because of the similarity in the type and nature of the organic emissions from rubber and plastic processing, the mass emission rates for the two industries are combined.

3.7.4.1 Process Description

Rubber Processing

Rubber in its raw state is too plastic for most commercial applications, and its use is limited to items such as rubber shoe soles, rubber cements, and adhesives. Vulcanization, a curing process, can cause the raw rubber to lose its plasticity and gain elasticity. The most important rubber processing operations up to and including vulcanization are: (1) physical treatment of raw rubber to prepare it for addition of compounding ingredients; (2) incorporation of various substances, especially fillers: (3) pretreatment of mix to make it satisfactory for preparing the final product; (4) forming the final product; and (5) vulcanization or curing the molded article.

The first step in rubber processing is plasticization which can be done in several ways: (1) mechanical plasticization; (2) heat plasticization; and (3) chemical plasticization. Next, various additives are compounded into the rubber to give its desired properties. After the rubber is compounded, it is formed into the desired shape and cured at the required temperature. In the forming steps, large amounts of organic solvents are often used in the form of rubber adhesives. These compounds, known as antioxidants, typically include aromatic amines, aldehyde-amine condensation products, derivatives of secondary naphthylamines, aromatic diamine derivatives, and ketoneamine condensation products (NA-032). Finally, the molded article is vulcanized or cured between 93 and 149°C (200 to 300°F) for periods from a few seconds to several hours. During this operation many of the plasticizers, accelerators, antioxidants, and other organics are volatilized and driven off as air emissions (NA-032).

Plastic Processing

There are numerous possible classifications for plastics; however, nearly all fall into one of two major categories: thermosetting (or thermosets) or thermoplastic materials. Basically, thermosetting plastics are not remeltable, while thermoplastics are. This difference in properties results from different processing techniques.

Thermosetting plastics processing starts with a partially polymerized material that is softened and activated by heating (either in or out of the mold), forcing it into the desired shape by pressure. It is held at the curing temperature until polymerization reaches the point where the part hardens and stiffens sufficiently to keep its impressed shape. Solvents are not used in this processing sequence, thus thermoset processing does not represent a significant source of atmospheric organic emissions.

One typical sequence of thermoplastic processing is to heat the material so that it softens and flows and then to force it through a die or into a mold to give it final shape. This does not represent a source of atmospheric organic emissions. However, the processing of the thermoplastic vinyl chloride polymers and copolymers into permanently pliable materials by addition of suitable plasticizers is a significant source of atmospheric organics. The most common plasticizer used for this purpose is dioctyl phthalate (DOP), and sometimes diisooctyl phthalate (DIOP) is used. The products are cured at high temperatures, causing volatilization of the plasticizers (NA-032).

3.7.4.2 Atmospheric Emissions and Control

For rubber and plastic processing, the primary source of atmospheric emissions is the curing process. This operation drives off volatile organics present in the rubber or plastic at elevated temperatures. The atmospheric emissions of organic chemicals from this industry have been reported to be 1.28×10^6 MT/year (1.41×10^6 short tons per year) (MO-201).

The principal techniques used to control organic air pollutants from rubber processing are: reformulation, condensation, adsorption, absorption, and incineration (NA-032). These methods would be applicable to the control of organics from plastic processing as well. Direct-flame incineration has proven to be very successful in controlling both organics and odors from rubber processing. Recovery efficiencies as high as 97 percent have been achieved in some plants (NA-032). Based on this information, the percent reduction for rubber and plastic processing is estimated to be over 90 percent, assuming limited emission control application to date. This results in a reduction potential of 1,150,000 MT of organics per year.

3.7.4.3 Water Effluents and Control

The tire and inner tube segment of the rubber processing industry discharges organic water effluents. A development document for proposed effluent guidelines and new source performance standards for tire and inner tube processing has been published (EH-154). This publication provides the most recent and comprehensive assessment of the industry's organic effluents and their control. For this reason, the July 1, 1977 effluent limitations

or Best Practicable Control Technology Currently Available (BPCTCA) were selected to describe the current degree of control and the associated organic effluent rate.

This document places limitations on the oil and grease discharge and the suspended solids discharge from tire and inner tube production facilities. The primary source of oil and grease is the leakage of lubricating oils from process machinery into wastewater streams. The suspended solids from normal daily production originate primarily from nonprocess blowdowns and the water treatment wastes. Table 3.7-2 contains estimates of effluents annually discharged from tire and inner tube production.

The best control and treatment technologies currently in use emphasize in-house control of solution wastes with end-of-pipe treatment of combined process and non-process waste waters (EN-154). Control and treatment of oily waste streams involves segregation, collection, and treatment of these wastes. The wastes to be segregated include runoff from oil storage and unloading areas and leakage and spills from the mill and press basins. These waste waters are sent to an API-type gravity separator where the separable oil and solids fraction is removed and disposed.

No additional reduction is proposed for the limitations and standards represented by the BATEA or for new sources coming on stream after effluent limitation guidelines are put into effect (EN-154). Therefore, the reduction potential for organic effluents from the tire and inner tube industry is zero.

3.7.5 Fabric Treatment

Fabric treatment consists of two major processes: finishing and coating. The finishing process is designed to change, improve, or develop the appearance or desired behavior characteristics of the fabric. Most fabrics receive one or more special finishes. The types of finishes used include shrinkproofing, crease resistance, water repellency and waterproofing, flameproofing, stainproofing, antistatic finishing, and others.

The application of the various finishes is followed by a curing step which exposes the fabric to temperatures above 200°C. At these temperatures, the solvents used in the applied finishes, the softeners and conditioners, and the by-products from resin curing are volatilized from the fabric. Drying is achieved using both direct contact driers and by forced air drying.

Atmospheric Emissions and Control

The primary source of atmospheric organic emissions from fabric treatment is the curing or drying operation. The estimated yearly quantity of organics emitted from fabric treatment is 210,000 metric tons (HU-100).

The control of these emissions is similar to that used for paint-baking ovens. The most successful and most often used control is the afterburner. Both thermal and catalytic incinerators may be used. The efficiency for this control device is estimated to be greater than 95 percent. For this reason, the hydrocarbon reduction potential for this industry is assumed to be high. The potential percent reduction in emissions is estimated to be 90 percent. This results in a reduction potential of 189,000 MT of organic per year.

No information was found concerning organic effluents from this industry.

3.8 Agricultural and Forest Products

The agricultural and forest products industry includes a variety of processing steps which convert agricultural and forest products into consumer goods. These processing steps include refining, preservation, product improvement, storage, handling, and packaging. The processing operations involved in this industry produce gaseous, liquid, and solid wastes.

Atmospheric Emissions

Estimates of volatile and particulate organic emissions from major sources in the agriculture and forest products industry are presented in Table 3.8-1. These values were derived from emission factors and estimates found in the various literature sources indicated in the table. The largest emission sources including pulp and paper production, wood waste combustion, beer brewing, fruit and vegetable processing, tobacco manufacture, and grain and feed mills are discussed in detail on the following pages. The reduction potentials shown in Table 3.8-2 were determined by estimating the reductions which would be realized by the application of the best available control methods. In most cases, additional study of specific processes is required to determine the economic feasibility of controls and the best application of available control techniques.

Water Effluents

Many operations involved in the processing of agricultural and forest products are water-intensive and result in organic water pollutants. The wastes generally have high oxygen demands and can make water unsightly, unpalatable and malodorous. Estimated quantities of water effluents from processes in the

TABLE 3.8-1

ATMOSPHERIC EMISSIONS FROM THE AGRICULTURAL AND FOREST PRODUCTS INDUSTRY

Subcategory	Year	Emissions (MT/Yr) Volatile Organics	Ref.	Particulate Organics	Ref.
. Pulp and Paper	1974	143,000	1,2		
. Wood Waste Combustion	1968	137,000	1,2,6	47,400	1,2,6
. Beer	1973	67,800	4	108,000	4
. Fruit and Vegetable Processing	1973	47,700	4	945	4
. Tobacco	1973	39,700	4	794	4
. Charcoal	1973	28,600	4	100,000	4
. Distilled Spirits	1973	10,600	4	13,300	3
. Cottonseed Oil Milling	1973	10,300	4	6,160	4
. Plywood and Veneer	1974	9,070	2	1,220,000	2
. Deep Frying	1975	6,090	3	6,900	3
. Vegetable Oil Milling	1975	3,865	4	23,496	4
. Coffee Roasting	1974	1,400	1,5	7,080	1,5
. Leather Tanning and Finishing	1973	1,100	4		
. Fish and Seafood Processing	1973	745	4	64	3
. Meat Smokehouses	1975	462	3	397	3
. Sawmills	1971	346	2	414,000	2
. Grain and Feed Milling & Storage	1971	-		1,311,000	6
. Grain Food Processing				55,520	
. Sugar Processing	1975	-	4	8,800	4
. Wood Preserving	1971			78	2
CATEGORY TOTAL		507,778		3,323,934	

Sources: 1. EN-071 3. HO-224 5. US-303
2. EN-197 4. MO-201 6. VA-067

TABLE 3.8-2

CONTROL OF ATMOSPHERIC EMISSIONS IN THE AGRICULTURAL AND FOREST PRODUCTS INDUSTRY

Subcategory	Air Emissions (MT/Yr) Volatile Organics (Organic Particulates)	Reduction Potential (%)	Control Methods
Pulp & Paper	143,000	99	Process modifications*
Wood Waste Combustion	137,000	100	Utilization of other disposal methods
	(47,400)	100	" " " " "
Beer	67,800	99	*
	(108,000)	95	**
Processed Fruits & Vegetables	47,700	99	*
	(945)	-	
Tobacco	39,700	99	*
	(794)	-	
Grain & Feed Milling & Storage	(1,311,000)	99	**

*Volatile organic emissions can be controlled by conventional methods including incineration, adsorption, absorption, condensation, and various methods for reducing fugitive emissions. Individual processes must be studied to determine best application of controls.

**Particulate emissions can be controlled by conventional methods including settling chambers, cyclones, electrostatic precipitators, scrubbers, and baghouses. Individual study of processes is required to determine best application of controls.

industry are presented in Table 3.8-3. Effluent quantities were estimated from raw waste loads (RWL) by calculations based on an assumed level of treatment according to effluent guideline limitations.

RWL data were obtained from the various literature sources indicated in Table 3.8-3. These data generally resulted from sampling studies at plants representative of the industry. Effluent guideline limitations for BOD_5 and SS have been developed for some segments of the industry. The development documents for these guidelines provided useful data on reduction factors for waste treatment systems.

Total organic effluents were estimated by assuming that mg/ℓ BOD approximately equals 52 mg/ℓ TOC (SO-080). This correlation was developed for biologically treated municipal wastes. The wastes treated at municipal sewage systems have similar components to the wastes from agricultural and forest processes and operations.

Effluent limitations to be achieved by July 1, 1977 (Best Practicable Control Technology Currently Available, BPCTCA) are generally based upon the average of the best existing performance by processes within the industry. The averages are not based upon a broad range of processes, but are based upon performance levels achieved by exemplary ones. This technology normally involves in-process changes to reduce waste loads and end-of-process treatment consisting of any required primary treatment followed by biological oxidation.

For quantification of effluents in this report, present effluents were assumed to be those resulting from the application of BPCTCA or equivalent technology to the processes. Reduction factors for BPCTCA and effluent guideline limitations (BPCTCA 30-day maximum averages) were used to calculate effluents.

TABLE 3.8-3

WATER EFFLUENTS FROM THE AGRICULTURAL AND FOREST PRODUCTS INDUSTRY

Subcategory	Year	Effluents (MT/yr) BOD	Total Organic	COD	SS	Oil	Ref
· Pulp & Paper Industry	1972	100,000	208,000		196,000		3,9,21
Processed Fruits & Vegetables	1975	44,300	93,200		42,400		2,18
· Beer Brewing	1974	35,500	73,300		36,400		10,20
· Sugar Processing	1974	9,080	18,900		7,160		16,17,20
· Plywood/Veneer	1974	8,600	17,900		8,330		9,13,20
· Grain Mills	1974	7,720	16,100		7,560		5,11
· Red Meat Processing	1972	6,450	13,400		8,330	3,490	15
· Dairy Products	1974	5,810	12,100	10,200	5,990		8,20
· Poultry Processing	1974	3,760	7,820		2,290		4,19,20
· Fish & Seafood Processing	1972	2,840	5,910		1,050	380	12
· Leather Tanning & Finishing	1974	2,830	5,890		3,550	534	6
· Misc. Food Products	1975	2,180	4,530		650		2
· Rayon	1974	1,880	3,910	28,200	3,450		1,7
· Rendering (Independent)	1968	1,680	3,490		2,080	9,910	14
· Distilled Spirits	1974	1,160	2,410				2,19,20
· Wood Preserving	1971			675		21	13
· Hardwood	1972	329	684		629		13

TOTAL BOD: 234,691
TOTAL OIL: 14,355
TOTAL SS: 325,869
TOTAL ORGANIC: 488,044

Sources:
1. AN-134
2. CA-281
3. CL-073
4. EC-010
5. EN-152
6. EN-156
7. EN-160
8. EN-175
9. EN-197
10. EN-294
11. EN-380
12. EN-381
13. EN-382
14. EN-383
15. EN-386
16. EN-387
17. EN-397
18. ME-126
19. SI-206
20. US-393
21. VA-067

Best Available Technology Economically Achievable (BATEA) effluent limitations have been established for some segments of the industry. These guidelines were developed by identifying either the best performance within a given subcategory or the very best control and treatment technology employed by a specific point source within a subcategory. This level of technology emphasizes both in-process improvements and external treatment of the wastewaters.

The reduction potential for water effluents from the industry was determined to be the reduction in effluents below levels with BPCTCA-type controls achieved by the application of BATEA-type controls. These reduction potentials were found by using the reduction factors for BATEA or by the difference between BPCTCA and BATEA effluent guidelines (maximum 30-day averages). Effluents and reduction potentials of processes for which effluent limitations have not been written were estimated by the use of the development documents for effluent limitations guidelines for similar processes.

The major sources of organic water pollutants within the agricultural and forest products industry are discussed on the following pages. These descriptions exemplify the types of effluent sources found within this industry and application of control technologies to the sources. The estimated reduction potentials for water emissions from these sources are presented in Table 3.8-4.

3.8.1 Pulp and Paper Industry

3.8.1.1 Process Description

Most pulp is made by integrated companies and consumed captively. Wood pulp is prepared wither mechanically or

TABLE 3.8-4

CONTROL OF WATER EFFLUENTS IN THE AGRICULTURAL AND FOREST PRODUCTS INDUSTRY

	Water Effluents (MT/Yr)		Reduction Potential (%)		
	BOD_5	Total Organic	BOD_5	Total Organic	Control Methods
Pulp & Paper	100,000	208,000	50	50	*
Processed Fruits & Vegetables	44,800	93,200	75	75	*
Beer	35,500	73,800	75	75	*

*Organic wastewater effluents are controlled by in-process modifications and primary treatment of wastewater followed by biological oxidation and filtration.

chemically. In the mechanical processes, groundwood, defibered and exploded wood are shredded or separated by physical means. Chemical wood pulping involves the extraction of cellulose from wood by dissolving the lignin that holds the cellulose fibers together. The principal chemical pulping processes are kraft, acid sulfite, neutral sulfite semichemical (NSSC), dissolving and soda.

The type of pulping process utilized is determined by the product being made, the type of wood species used, and economic considerations. The kraft, acid sulfite, and NSSC processes account for approximately 80 percent of the pulp produced in the United States (about 65 percent is produced by the kraft process) and have the greatest potential for gaseous emissions (EN-071). These processes will be discussed in this section.

Kraft Pulping

In the kraft process, wood chips are cooked under pressure in the presence of a cooking liquor in either a batch or continuous digester. The cooking liquor (white liquor), an aqueous solution of sodium sulfide and sodium hydroxide, dissolves the lignin.

When cooking is completed, the contents of the digester are fed to the blow tank. The major portion of the spent cooking liquor (black liquor) is drained from the blow tank. The pulp from the blow tank is charged to the knotter where unreacted chunks of wood are removed. The pulp is then washed and sometimes bleached before being pressed and dried into the finished product.

Recovery or the inorganic cooking chemicals and heat content of the black liquor is economically necessary. Recovery is accomplished by concentrating the liquor to a level that will support combustion and then feeding it to a furnace where burning and chemical recovery take place.

The black liquor is concentrated initially in a multiple effect evaporator. Further concentration is achieved in a direct contact evaporator. This is generally a scrubbing device in which combustion gases from the recovery furnace mix with the black liquor.

The concentrated black liquor is sprayed into the recovery furnace. The organic content supports combustion and the inorganic compounds fall to the bottom of the furnace and are then dischared to the smelt dissolving tank. The solution from the smelt dissolving tank (green liquor) is conveyed to a causticizer where calcium hydroxide is added prior to recycling the liquor. Lime sludge from the causticizer can be recycled after being dewatered and calcinated in the hot lime kiln.

Acid Sulfite Pulping

The acid sulfite pulping process is similar to kraft pulping except that different chemicals are used in the cooking liquor. In place of the caustic solution used in the kraft process, a sulfurous acid solution is employed which is buffered by sodium, magnesium, calcium, or ammonium bisulfite.

Due to the variety of chemicals employed in the cooking liquor, numerous schemes for heat and/or chemical recovery have evolved. Chemical recovery is not practical in calcium-base systems, which are used mostly in older mills, and the spent liquor is normally discarded. In ammonium-base mills, heat can

be recovered from the spent liquor through combustion, but the ammonium is consumed. In sodium or magnesium-base mills (the latter being utilized most frequently in newer mills) heat, sulfur, and chemical recovery are all feasible.

The recovery process involves a multiple-effect evaporator and recovery furnace arrangement similar to that in the kraft process. The combustion gases from the furnace pass through absorbing towers where sulfur dioxide is recovered for use in subsequent cooks. The base can be recovered by feeding the inorganic residue from the furnace to the absorbing tower to react with the sulfur dioxide.

Neutral Sulfite Semichemical (NSSC) Pulping

The NSSC pulping process involves the cooking of wood chips in a neutral solution of sodium sulfite and sodium bicarbonate. The major difference between this process and the kraft and acid sulfite processes is that only a portion of the lignin is removed during cooking, after which the pulp is further reduced by mechanical means.

The NSSC process varies since some mills dispose of their spent liquor, some mills recover the cooking chemicals, and some, which are operated in conjunction with kraft mills, mix their spent liquor with the kraft liquor as a source of makeup chemicals. The recovery process, when practiced, involves steps parallel to those of the sulfite process.

Paper Production

Paper is made by depositing, from a dilute water suspension of pulp, a layer of fiber on a fine screen which allows water to drain through but retains the pulp. The fiber layer is

removed from the wire and sent through a series of pressing and drying machines.

Two general types of machines are commonly employed. One is a cylinder machine in which the wire screen is placed on cylinders, and the other is the fourdrinier in which the wire screen is an endless belt. The water draining through the paper machine is known as white water and contains suspended fiber, pulp fines, and chemicals used as additives in the paper or board. White water is commonly used in the paper and board making operation and the pulping process.

3.8.1.2 Atmospheric Emissions and Control

Kraft Pulping

The characteristic odor of kraft mills is caused in part by an assortment of organic sulfur compounds; all have extremely low odor thresholds. Methyl mercaptan and dimethyl sulfide are formed in reactions with lignin. Dimethyl disulfide is formed by the oxidation of mercaptan groups derived from the lignin. Table 3.8-5 shows the quantity of these compounds (expressed as sulfur) emitted from various points in the mill.

Devices for controlling the organic sulfur compounds are generally not applied in kraft mills; however, control of these compounds can be accomplished by process modifications and by optimizing operating conditions. A three-volume report by E. R. Henderson, et al. (HE-128) presents a detailed discussion of control methods for atmospheric emissions from the pulping industry and is summarized in this section.

Black liquor oxidation systems, which oxidize sulfides into less reactive thiosulfates, can reduce odorous sulfur emissions from the direct contact evaporator, although the vent gases

TABLE 3.8-5

UNCONTROLLED EMISSION FACTORS FOR SULFATE PULPING

Source	Emissions of Methyl Mercaptan, Dimethyl Sulfide,[1] Dimethyl Disulfide (kg/MT of Air Dry Pulp)
Digestor Relief and Blow Tank	0.75
Brown Stock Washers	0.1
Multiple-Effect Evaporators	0.2
Recovery Boiler and Direct Contact Evaporator	0.5
Smelt Dissolving Tank	0.2
Lime Kilns	0.125
Turpentine Condenser	0.25
Miscellaneous Sources	0.25[2]

[1] These reduced sulfur compounds are usually expressed as sulfur.

[2] Includes knotter vents, brown stock seal tanks, etc. When black liquor oxidation is included a factor of 0.3 should be used.

Source: EN-071

from such systems become minor odor sources themselves. The sulfur compound emissions from the recovery boiler and direct contact evaporator are typically reduced by 50 percent when black liquor oxidation is employed, but can be cut by 90 to 99 percent when oxidation is complete and the recovery furnace is operated optionally (EN-071). Noncondensable organic sulfur gases vented from the digestor/blow tank system and multiple-effect evaporators can be destroyed by thermal oxidation in the lime kiln or recovery furnace. Using fresh water instead of contaminated condensates in the scrubbers and pulp washers reduces organic sulfur emissions.

Use of these and other control methods could almost completely eliminate the organic sulfur emissions from kraft mills. Organic sulfur emissions could be reduced approximately 135,000 MT per year.

Acid Sulfite Pulping

Volatile reduced sulfur compounds are not products of the lignin-bisulfite reactor involved in acid sulfite pulping; therefore, these organic sulfur compounds are not emitted from acid sulfite pulping mills. No mention of atmospheric emissions of other organic compounds from this pulping process was found in the literature.

NSSC Pulping

The NSSC process differs greatly from mill to mill and there is a scarcity of adequate data. The data in Table 3.8-6 were extracted and compiled from the literature (EN-197). The data for new technology represents improvements made in the past seven to eight years. Combination of NSSC spent liquor with kraft

TABLE 3.8-6

EMISSIONS FROM NSSC PULPING

Source	Pollutant	Emissions (kg/MT Air Dry Pulp) Old Technology	Newer Technology
Recovery Furnace	CH_3SH	0.15	0.05-0.025
Blow Tank	CH_3SH	0.78	0.39
	Other Organic	1.56	0.75
Evaporator	Total Organic S	0.045	0.045
Fluidized Bed	Total Organic S	-	0.002-0.004
Copeland Process	Total Organic S		0.09-0.16

Source: EN-197

black liquor prior to evaporation and combustion results in increased emissions from the kraft recovery system. No quantitative data on this increase in emissions are available.

The emissions from the NSSC processes could be almost completely eliminated by control methods similar to those for the kraft process resulting in a reduction of approximately 6850 MT of organic atmospheric emissions per year.

3.8.1.3 Water Effluents and Control

Information presented in the following section was obtained primarily from the results of plant surveys (EN-147). Wood is received at the mills in various forms and, consequently, must be handled in a number of different ways. In mills receiving chips from saw mills or barked logs which can be chipped directly, little or no water is employed in preparation of the wood and no effluent is produced. Most mills receive logs with bark which must be removed. Logs are frequently washed before dry or wet barking. The water from this operation is very low in BOD_5 and its suspended solids content is largely salt.

Most pulpwood used in the United States is small in diameter and is barked in dry drums. When large diameter or long wood is used, wet barking is commonly employed. Wet barking is accomplished in drums, pocket barkers, or hydraulic barkers.

The wet drum consists of a slotted drum equipped with internal staves rotating in a pool of water. The bark falls through the slots and is removed with an overflow of water. Barkers of this type contribute from 7.5 to 10 kg BOD_5 per MT of wood barked, and from 15 to 20 kg of suspended solids per

MT of wood barked. The water supplied to them is frequently spent process water, and recycling within the barking unit itself is often practiced.

Wet pocket barkers remove bark from timber by jostling and gradually rotating the logs against an endless chain belt equipped with projections. Hydraulic barkers use high pressure water jets to blow bark from the timber.

Water discharged from all three types of wet barking is generally combined with log washwater. This stream first passes through coarse screens to remove the pieces of bark and wood slivers and then through fine screens. Screenings are removed and conveyed away continuously and dewatered in a press. Press water is combined with the fine screen effluent. The total waste flow, about 19,000 to 26,600 liters per cord, generally contains from 0.5 kg of BOD_5 and 3 to 22 kg of suspended solids per ton of product.

Wastewater from unbleached kraft pulping comes primarily from three areas of the process. The effluent from pulp washing accounts for the highest percentage of the total effluent. Currently, the use of hot stock washing has considerably reduced the waste load generated in the washing operation. Another wastewater source is condensate streams. Relief condensate from the digesters is condensed and the terpentine is recovered from it by decantation. The residual water is sewered. Blow and evaporation condensates are contaminated with methanol, ethanol, and acetone to various degrees depending on the wood species pulped. When using surface condensers, the volume of this stream is low and its BOD_5 can be reduced by air or steam stripping. These condensates are frequently reused for pulp washing. Chemical recovery operations and other minor losses also constitute a BOD_5 source. The total raw waste load from unbleached kraft

mills, including both pulping and paper making operations, is typically 15 to 20 kg BOD_5 and 10 to 15 kg of suspended solids per MT of product.

In sodium base NSSC mills, liquor digester relief and blow gases are condensed, and in some mills the condensate is used for pulp washing. Other than spent liquor, the pulping and washing operations discharge little wastewater. Without recovery of the liquor, effluents would range from 1500 to 5000 mg BOD_5/ℓ with a suspended solids content of from 400 to 600 mg/ℓ.

The ammonia base NSSC process is similar to the sodium base process. The four significant sources of wastewater in the ammonia base NSSC pulp manufacturing processes are: the evaporators, the powerhouse and maintenance area, the pulp mill, and the paper machine. The raw waste load from this process averages about 33.5 kg BOD_5 and 17 kg suspended solids per MT of product (EN-147).

The spent sodium base NSSC liquor can be introduced into a kraft recovery system. The raw waste load for unbleached kraft-NSSC (cross recovery) mills averages about 19.4 kg BOD_5 and 20.5 kg suspended solids per MT of product.

The raw waste load of paperboard from waste paper mills comes from the stock preparation area and is a function of the type of raw materials and additives. The raw waste load for these mills averages about 11.2 kg BOD_5 and 2.8 to 81 kg suspended solids per MT of production.

BPCTCA effluent limitations (July 1, 1977 standards) are based upon the average of the best existing performance by

plants of various sizes, ages, and unit processes within the industry. BATEA effluent limitations have been established by identifying the very best control and treatment technology employed by a specific point source, or by applying technology from other industry areas where it is transferable. Technologies have been identified below which will allow mills to meet the limitations, but mills have the option to use other internal and external controls which may prove to be more cost effective.

Identification of BPCTCA

Unbleached Kraft and Kraft-NSSC

1) Hot Stock Screening - a process modification in which the pulp is passed through a fibrolizer to fractionate knots and then through a hot stock screen to remove shives.

2) Spill Evaporator Boil-Out Storage - material from these sources can be stored in a tank from which it can be slowly returned to the process or discharged to the wastewater treatment system.

3) Efficient Pulp Washing - the use of multistage countercurrent washers for more efficient recovery of black liquor.

Sodium and Ammonia-Base NSSC

Non-Polluting Spent Liquor Disposal - partial evaporation followed by incineration.

Paper Machines

1) Water Showers - use of low-volume and high-pressure showers in the machines.

2) Segregation of White Water Systems - permits maximum reuse of white water and allows only low fiber content white water to enter the sewer.

3) Press Water Filtering - use of a vibrating or centrifugal screen to remove felt hairs prior to press water reuse.

4) Collection System for Vacuum Pump Seal Water - collection for partial reuse.

5) Save-all and Associated Equipment - recovery of fibrous and other suspended material which escapes from the paper machine.

6) Gland Water Reduction - flow control of seal water to equipment packing glands.

External Treatment

1) Suspended Solids Reduction - This step involves removal of the suspended solids from the raw waste stream. Screens can be used to remove coarse solids. The suspended solids removal can incorporate: a) an earthen stilling basin; b) mechanical clarification; and/or c) dissolving air floatation.

2) BOD_5 Reduction - BOD_5 removal is accomlished by biological oxidation with nutrient addition. The treatment system can consist of an activated sludge process (AS), aerated stabilization basins (ASB), and/or storage oxidation ponds (SO).

3) Biological Solids Removal - Biological solids may be removed by either mechanical clarifiers, stilling ponds (or an SO following an ASB), or a quiescent zone in an ASB beyond the influence of the aeration equipment.

4) Sludge Disposal - Stilling pond disposal of biological sludge or sludge thickening and dewatering with ultimate disposal by incineration or sanitary landfilling.

Identification of BATEA

BATEA consists of the BPCTCA defined above plus the following additional mill improvements and external advanced wastewater treatment practices.

Internal Controls

Pulping operations of all applicable subcategories can implement modification and procedures for:

1) Reuse of fresh water filter backwash;

2) Control of spills such that major pollution loads enter a retention basin and are ultimately either reused, greadually discharged into the treatment system, or treated separately;

3) Minimize pulp wash and extraction water without decreasing washing efficiencies;

4) Extensive internal reuse of process waters;

5) Segregation and reuse of cooling waters; and

6) Extensive reduction of gland water spillage.

All of the above procedures, except (1) and (3), can be implemented by paper machine systems.

External Treatment

BATEA external treatment is defined as BPCTCA with the addition of the following external processes:

1) BOD_5 Reduction - treatment system consisting of biological oxidation with nutrient addition for further removal of BOD_5.

2) Suspended Solids Reduction - additional suspended solids removal can be achieved by mixed media filtration with, if necessary, chemical addition and coagulation.

3) Color Reduction - color reduction can be achieved by minimum lime treatment and reverse osmosis.

The application of the BATEA limitations to pulp and paper mills would result in an estimated reduction of approximately 49,600 MT BOD_5, 103,000 MT organic, and 132,274 MT of suspended solids per year below effluents with BPCTCA.

3.8.2 Wood Waste Combustion

Process Description

A common method of disposing of wood residues from forestry operations and lumber processing is incineration in conical burners. Approximately 24.9 million MT of wood waste is combusted annually in these incinerators according to a 1971 estimate (VA-067).

Conical burners, truncated metal cones with a screened top vent, are charged by introducing the material to a grate using either conveyer or bulldozer. No supplemental fuel is used, but combustion air is often supplemented by air blown into the chamber below the grate and by air introduced through peripheral openings in the shell.

Atmospheric Emissions and Control

The quantity and types of pollutants emitted from conical burners depend on the composition and moisture content of the waste, control of combustion air, type of charging system used, and the condition in which the incinerator is maintained. The most critical factor seems to be maintenance practices. The burners sometimes have missing doors and holes in the shell, resulting in excessive combustion air, or low temperatures, with resultant high emission rates of organic pollutants.

Emission factors for waste wood incineration in conical burners without controls are about 5.5 kg of hydrocarbons per MT burned and from 1 to 20 kg of particulates per MT burned, depending on the operation and maintenance of the burner (EN-071). Typically, a conical burner produces 5 kg of particulates per ton of waste burned (EN-197), estimated to be approximately 38

percent organic matter (VA-067). Based on these emission factors and the 1971 estimate of 24.9 million MT of wood waste combusted annually, the emissions from conical burners are 137,000 MT hydrocarbons and 47,400 MT organic particulates per year.

Emissions from conical burners can be reduced by using conveyors instead of bulldozers for charging, proper control of combustion air, and good maintenance practices. Particulate control systems have been adapted to conical burners with some success. These control systems include water curtains (wet caps) and water scrubbers (SI-106).

Conical burners have been banned in most states (EN-197). This measure is the most effective method of eliminating emissions from the burners. When using this method the waste wood can be used as a raw material for other processes such as production of pulp or wood chemicals, or disposed of by some other method.

3.8.3 Beer Brewing

Process Description

The four major production stages of brewing operations are listed below (EN-071):

1) Brewhouse operation, which include:

   a) malting of the barley,

   b) addition of adjuncts to barley mash,

   c) conversion of starch in barley and adjuncts to maltose sugar by enzymatic processes,

   d) separation of wort from grain by straining, and

   d) hopping and boiling of the wort.

2) Fermentation, which includes:

   a) cooling of the wort,
   b) addition of yeast cultures,
   c) fermentation for 7 to 10 days,
   d) removal of settled yeast, and
   e) filtration and carbonization.

3) Aging for 1 to 2 months under refrigeration, and

4) Packaging, which includes:

   a) bottling - pasteurization, and
   b) racking draft beer.

Atmospheric Emissions and Control

Gaseous organic chemicals are emitted from the drying of spent grains and yeast in beer. The results of a study of gaseous emissions from whiskey fermentation units, which are similar to those for beer production, showed that at least six organic compounds were emitted from these units: ethyl acetate, ethyl alcohol, isopropyl alcohol, n-propyl alcohol, isoamyl alcohol, and isoamyl acetate (CA-281). Other compounds were detected by chromatograph but were present in trace amounts only. Organic particulate emissions occur from the handling of grain and from the drying operations.

The emissions from malt beverage production in 1973 were estimated to be 67,810 MT of organic chemicals and 108,500 MT of particulates (MO-201). These values are based on totally estimated emission factors of indeterminate accuracy (EI-017).

The application of best available control technology for organic chemicals and particulates can reduce emissions of these pollutants from beer brewing operations by approximately 99 and 95 percent, respectively (HO-244). The application of these reduction factors provides reduction potential of 67,100 MT hydrocarbons and 103,000 MT particulates per year.

Water Effluents and Control

Wash water from the various brewing vessels, general plant washdown, and waste beer from breakage and spillage in the packaging lines contribute large waste loads. Another large waste source is press liquor from grain drying. Some brewers partially dry the spent grain with large mechanical presses prior to selling the grain as feed. The liquor from these presses has a very high BOD content and may constitute 25 percent or more of the total plant BOD load (EN-294).

Effluent characteristics have been reported for ten breweries (EN-294). Individual waste parameters fluctuated considerably over the brewing day because of the batch-type operation. The BOD concentration in the brewery effluents averaged 2200 mg/ℓ and suspended solids concentration averaged 900 mg/ℓ. Soluble BOD constituted about 75 percent of the total BOD. A COD:BOD ratio of about 2:1 was indicated, but this factor was somewhat variable. Water consumption in the industry was found to range from 5 to 15 liters per liter of beer.

Most breweries discharge waste to large municipal sewage systems where it undergoes various types of primary and secondary treatment. The treatment efficiencies for the wastes from the ten breweries studied averaged approximately 90 percent BOD removal and 75 percent suspended solids removal.

Additional treatment similar to that required for BATEA of fruit and vegetable processing wastes could be applied to brewery wastes, i.e., in-plant waste reduction practices plus additional secondary treatment or advanced treatment such as a sand filter and disinfection. Assuming that this additional treatment would result in the same reductions in BOD and suspended solids as those estimated for the fruit and vegetable industry (approximately 75 percent), the effluents from beer production could be reduced by about 26,600 MT BOD_5, 53,500 MT organic, and 27,260 MT suspended solids per year.

3.8.4 Fruit and Vegetable Processing

Process Description

Many of the steps used in the process of canning and freezing of fruits and vegetables are common to the industry as a whole. Typically, the fruit or vegetable is received, washed, and sorted to prepare it for subsequent processing. Commodities such as apples, citrus and potatoes are then usually peeled when the end product is a solid (slices, cubes, or powder). If the final product is a juice or liquid product, the peel is not removed from either the citrus or the apples. Subsequent processing steps include trimming, slicing, blanching, cooking, cooling, transport, etc., and the final canning and freezing operations.

In packing operations for fresh fruits and vegetables, picked fruit is sometimes exposed to heat, moisture, and ethylene to bleach out the chlorophyll masking the color. Some products are dyed with an oil-soluble non-toxic dye and waxed to improve appearance.

Atmospheric Emissions and Control

Atmospheric emissions of volatile organics are known to occur from operations involved in the processing of fruits and vegetables; however, quantitative data for these emissions are practically nonexistent. The most significant sources are probably the cooking operations in the canning and freezing processes and the artificial ripening of fruits and vegetables with ethylene. The volatile organic emissions from these processes would occur in vent streams. Control methods such as incineration and adsorption could be applied to effectively eliminate these emissions. Monsanto Research Corporation estimated that 1974 emissions from the processing of fruits and vegetables were 47,700 MT of hydrocarbons and 945 MT of particulates (MO-201). The data used to obtain these estimates is totally estimated and is of indeterminate accuracy (EI-017). The reduction potential for volatile organics is 47,200 MT/yr.

Water Effluents and Control

Water is used extensively in many phases of the fruit and vegetable processing industry. Waste characteristics have been determined for processing steps for apples, citrus, and potatoes through in-plant sampling and supplemental data from processors. Data from 10 apple plants, 20 citrus plants, and 15 potato plants were used to develop the tabulations of the waste characteristics from these plants presented in Tables 3.8-7, 8, and 9. These tables show the water usage and waste characteristics associated with various operations in the industry.

The total raw waste load due to processing fruits and vegetables has been estimated to be 448,200 MT BOD_5 and 2,118,300 MT SS (SI-106). The use of BPCTCA level controls (in-process

TABLE 3.8-7

WATER USAGE AND WASTE CHARACTERIZATION IN APPLE PROCESSING

Process Steps	Water Usage ℓ /MT	BOD_5 kg/MT	Suspended Solids Kg/MT
Washing	142	0.09	0.03
Peeling			
Mechanical	104	0.16	0.015
Slicing	638	2.49	0.182
Deaeration	71	2.21	0.12
Cooking	267	0.14	0.05
Cooling (1)	58	0.02	0.005
Transport	58	0.02	0.005
Clean-up	1,558	1.90	0.30

(1) 95% recirculated

Source: EN-408

TABLE 3.8-8

WATER USAGE AND WASTE CHARACTERIZATION IN CITRUS PROCESSING

Process Steps	Water Usage ℓ/MT	BOD_5 kg/MT	Suspended Solids kg/MT
Fruit Cleaning	303	0.08	0.04
Extracting	389	0.40	0.27
Pasteurizing/Homogenizing	62	0	0
Cooling (1)			
Juice Products	221	0.03	0.02
Segments		0.01	0.01
Juice Condensing	400	0.06	0.02
Barometric Condensing (2)			
Juice Products	50	0.07	0.09
Waste Heat Evaporator	71	0.15	0.09
Peeled Fruit Washing	129	0.04	0.01
Caustic Treatment	1	0.01	0.01
Centrifuging	144	3.07	0.51
Container Washing	75	0	0
Waste Heat Evaporator Condensate	334	0.33	0.11
Waste Heat Evaporator Scrubber Effl.	351	0.22	0.08
Oil Lean Residue From Separator	126	0.16	0.25
Boiler Blowdown	60	0.01	0.01
Regeneration Brine	13	0	0
Cleanup			
Juice Products	705	0.16	0.16
Segments	371	0.36	0.07
Peel Products	484	0.07	0.11

(1) 90% recirculated
(2) 2% cooling tower blowdown

Source: EN-408

TABLE 3.8-9

WATER USAGE AND WASTE CHARACTERIZATION IN POTATO PROCESSING

Process Steps	Water Usage	BOD_5		Suspended Solids	
	ℓ/MT	kg/MT	lb/T	kg/MT	lb/T
Washing	1,102	0.676	1.35	1.383	2.76
Peeling					
Dry Caustic	1,448	7.325	14.62	9.569	19.1
Wet Caustic	3,000	20.245	40.41	28.662	57.2
Steam	2,391	15.215	30.37	13.427	26.8
Trimming	793	0.777	1.55	0.26	0.52
Slicing					
Dehydrated	764	0.296	0.59	0.701	1.4
Frozen	1,519	2.630	5.25	1.303	2.6
Blanching					
Dehydrated	175	0.701	1.40	0.601	1.2
Frozen	1,043	5.461	10.9	2.104	4.2
Cooling	668	1.172	2.34	-	-
Cooking	448	1.192	2.38	-	-
Dewatering	513	0.471	0.94	0.351	0.70
Fryer Scrubber	417	-	-	-	-
Fryer Belt Spray	417	-	-	-	-
Refrigeration	1,602	-	-	-	-
Transport Water	292	0.261	0.52	-	-
Cleanup	951	2.725	5.44	-	-

Source: EN-408

and end-or-pipe treatment assumed to be currently utilized) results in estimated reductions of 90 percent BOD_5 and 80 percent suspended solids (EN-408). Therefore, the effluents from fruit and vegetable processing are estimated to be 44,820 MT BOD_5, 92,200 MT organics, and 42,370 MT SS per year.

The BATEA control treatment for wastes from apple, citrus, and potato processing includes housekeeping and water use practices to reduce the raw waste, preliminary screening, primary settling, and secondary biological treatment (BPCTCA) plus additional secondary treatment or advanced treatment such as a sand filter and disinfection (EN-408). Several in-plant controls and modifications that provide alternatives and trade-offs between controls and additional treatment facilities required to meet the BATEA effluent guidelines are:

1) recycle of raw material wash water following solids removal and chlorination;

2) utilization of low water usage peel removal equipment;

3) removal of solids from transport and slicing waters;

4) reduction of belt wash water by improved mechanical cleaning of belts;

5) reuse of cooling water; and

6) extensive dry cleanup to replace washing.

The effluent guideline limitations for BATEA average approximately 75 percent less than the limitations for BPCTCA (EN-408). Application of BATEA would therefore result in the reduction of about 34,072 MT of BOD_5, 69,900 MT organic, and 31,780 MT of SS per year from fruit and vegetable processing operations.

3.8.5 Tobacco Manufacture

Process Description

Tobacco manufacturers usually maintain a pack house operation near each major tobacco market for preparing the tobacco for shipment. This preparation consists of pressing leaf into cylindrical wooden containers called hogsheads or bundling in large burlap sheets.

Leaf tobacco is transported to a steaming and/or redrying plant where it is reclassified and rehumidified. The larger leaf stems are removed prior to redrying and pressing into hogsheads. These hogsheads are stored in warehouse-type sheds.

The cigarette manufacturing process begins with removal of tabacco from storage. It is rehumidified and removed from the hogsheads. Leaf strip next passes through various cleaning, tumbling, blending, and treating operations to prepare it for the shredding operation. After shedding, the tobacco is bulk aged and conveyed to cigarette making machines where it is metered, formed, and wrapped with paper into continuous rods. The cigarettes then undergo the final processing and packing operations.

Atmospheric Emissions and Control of Organic Emissions from Tobacco Manufacture

Organic atmospheric emissions from tobacco manufacturing consist of tobacco volatiles and particles. Measured data for these emissions are practically nonexistent, but they have been estimated to be 39,710 MT volatile organics and 794 MT particulates in 1973 (MO-201). The emissions exit in vent streams from the various manufacturing processes and could be elimianted by control devices such as incinerators, adsorbers, scrubbers, and filters. The reduction potential for voaltile organics is 39,300 MT/yr.

3.8.6 Grain and Feed Mills and Elevators

Process Description

Grain elevators are primarily transfer and storage units. In addition, many elevator locations also contain feed manufacturing facilities. A variety of grain handling configurations are used at elevators depending on the number and quantity of grains handled and the amount of processing required. The following operations can occur at grain elevators: receiving, transfer and storage, cleaning, drying, and milling or grinding. Grain processing may include wet and dry milling (cereals), flour milling, oil-seed crushing, and distilling. Feed manufacturing involves receiving, conditioning (drying, sizing, cleaning), blending, packaging, and loading.

Atmospheric Emissions and Control

Particulate emissions occur in grain and feed operations because of the dry, light nature of most grains and the

methods of handling in pneumatic and mechanical conveyors. Emissions from grain operations may be separated into transfer losses and those occurring at processing operations. Loading and unloading areas have the greatest emissions. Conveying equipment and storage bins are also sources of dust emissions. Belt conveyors have less friction than either screw or drag conveyors and generate less dust. Emissions occur at belt transfer points as material moves on or off a belt. The discharge points of pneumatic conveying equipment are potential sources of dust emissions. Storage bins vent dust-laden air during loading operations.

Factors affecting the emissions from grain elevators include the type of grain, the moisture content of the grain, the amount of foreign material in the grain, and the degree of enclosure at loading and unloading areas. Approximately 89 percent of the dust in grain loading areas is organic (VA-067).

Wet milling operations are not conducive to major dust formation, although particulates may escape from drier cyclones. Dry milling is somewhat dusty in its operation. Most handling and transfer in these operations is pneumatic, allowing good dust control. Losses can occur from extracting and drying operations and from cyclone collectors used in oilseed crushing operations.

Heated air in rotary, column, or shelf driers is normally used to dry the grain. The particulate material emanating from the driers is generally classified as chaff or, in the case of corn, "beeswing." Particle size is large, but the particles are extremely light and can be carried miles on a windy day.

Factors affecting emissions from grain processing operations include the type of processing (wet or dry), quantity of grain processed, the amount of cleaning, the degree of drying and heating, the type of drier, the amount of grinding, and the type of grain processed.

The dust from grain and feed mills and elevators may be collected by inertial devices, fabric filters, and electrostatic precipitators. Enclosures or hoods with proper ventilation and recovery should be installed for control of loading and unloading operations. The use of particulate control equipment can reduce the emissions from grain and feed mills and elevators by approximately 99 percent (HO-244). The application of these controls would result in a reduction of about 1,300,000 MT per year of particulates (VA-067).

3.9 Open Sources

This category includes open burning of agricultural, land clearance, and forest wastes. The quantities of organic air pollutants resulting from these practices are shown in Table 3.9-1. It was determined that the reduction potentials in this category are 100 percent based on the elimination of open burning of these wastes. No estimates were made for water effluents or solid waste.

3.9.1 Agricultural Field Burning and Land Clearance

A common method of controlling pests and disposing of agricultural and land clearance wastes such as cut grass, weeds, and field residues is open burning. Agricultural operations contributing heavily to the waste burning problem include grass seed production and maintaining grain fields, rangelands, and sugar cane fields.

Atmospheric emissions from burning straw and stubble are generally characteristic of vegetable plant sources. Cellulose and lignin are the major constituents of the plants. Emissions consist of volatile organic compounds and smoke plus the combustion products. Approximately 10 kg of volatile organics and 8.5 kg of particulates are emitted per ton of waste burned (EN-071).

About 254 million MT of crop residues, brush, weeds, and other vegetation are burned annually (US-336). This open burning produces approximately 2,540,000 MT volatile organics and 820,000 MT organic particulates per year. Regulations against open burning have probably reduced current emissions below these levels. Open burning emissions are affected by

TABLE 3.9-1

ATMOSPHERIC EMISSIONS FROM OPEN SOURCES

Subcategory	Year	Emissions (MT/yr) Volatile Organics	Ref	Particulate Organics	Ref
Open Sources					
• Agricultural Field Burning & Land Clearance	1968	2,540,000	1,5	820,000	4
• Prescribed Forest Burning	1968	471,700	1,3	152,300	1,3,4
TOTAL		3,011,700		972,800	

Sources:
1. US-336
2. WA-252
3. EN-071
4. VA-067
5. MS-001

many factors including wind; ambient temperatures; moisture content, size and shape of the fuel; and compactness of fuel bed (VA-067). The emissions and their effects can be reduced by choosing periods with optimum conditions for burning of the refuse. Collection and incineration of the wastes in properly controlled incinerators could significantly reduce emissions.

The most effective method of controlling the emissions is to use other disposal methods for the wastes and eliminate open burning of agricultural and land clearance waste. Alternatives include abandonment or burying at the site, transport and disposal in remote areas, and waste utilization. Potential harmful aspects of abandoned or buried vegetation such as odor, water pollution, fire hazards, insects and organisms should be considered before employing these methods. Composting and animal feeding are potential alterantives to burning (NA-032).

3.9.2 Prescribed Forest Burning

Prescribed burning of forest wastes has been practiced since the turn of the century. This practice is used in the following instances (EN-186):

1) to reduce the fuel accumulation and therefore the hazard of uncontrollable wildfires;

2) to control undesirable species of trees;

3) to improve the habitat for wildlife;

4) to prepare a seedbed for natural reseeding and for planting of pines;

5) to enhance grazing;

6) to control the brown spot fungus disease of longleaf pine; and

7) to increase volume growth of trees.

The United States Forest Service estimates that 1.42 million hectares (representing 69.3 million MT of combustible material) were burned in controlled forest fires in 1966 (US-336). Open burning of landscape and pruning refuse, representative of forest wastes, produces about 10 kg of organics and 8.5 kg of particulates per MT burned (EN-071). Twenty-four gaseous organic emissions have been identified in slash burning experiments (SA-223). The gas chromatographic analysis of the organic gases showed that 15 to 40 percent of the gas was composed of methane and ethylene and that ethane and acetylene were the next most abundant materials. The smoke from rye-grass burns contained about 38 percent organic matter (VA-067). This value is probably representative of the organic content of particulates from slash burning.

The annual emissions from controlled forest burning are estimated to be 693,000 MT of volatile organics and 224,000 MT of organic particulates. The obvious method of eliminating these organic emissions is to use disposal methods other than combustion for the forest wastes. Forest scraps can be processed by chipping or crushing and used as raw materials for kraft pulp mills or processes producing fiberboard, charcoal, or synthetic firewood. At present, the economic feasibility of alternative methods including collection and transport for landfilling or chipping appears to be low. The cost of eliminating the waste by burning is about $0.91 per MT, whereas disposal by chipping costs about $11 per MT (WA-252). Despite the costs of alternative disposal methods, the reduction potential for prescribed forest

burning is determined to be 100 percent, resulting from complete elimination of open burning of the wastes.

In lieu of complete elimination of open burning, the air pollution aspects of slash burning can be minimized by various practices. Tests have shown that the smoldering phase of combustion is of greatest significance in air pollutant production during slash burning. The initial 80 percent of the fuel burned accounts for only 20 to 30 percent of the organic emissions (SA-223). This suggests that the air pollution from slash burns could be substantially reduced by choosing conditions that promote a high energy fire and by rapid mop-up of the burns.

3.10 Natural Sources

The major natural sources of organic air pollutants that have been identified and for which quantitative estimates of emissions are available include decomposition of organic matter, plant functions, and enteric fermentation in animals. These are discussed in this section.

Natural organic materials contribute to the organic load of waterways in many ways. Sources include dead organic material originating in the water such as fish or aquatic plants and natural organic material in the runoff from watersheds such as leaves, wood, carcasses, and animal waste. This organic material is normally removed in nature by either aerobic or anaerobic processes. No quantitative data on natural water pollutants were available.

Natural processes also produce solid wastes such as plant residues, animal waste, and carcasses. These solid wastes are normally decomposed *in situ* unless they are washed or blown into a body of water. Occasionally, these wastes are burned or otherwide disposed of for safety reasons or to allow utilization of the land.

Quantitative estimates of water quality impact and solid waste contributions from natural processes are not available; therefore, these types of emissions will not be discussed in detail. Estimates of the quantities of atmospheric emissions from major natural sources are shown in Table 3.10-1. The values given in this table are only estimates based on the best data available on natural emissions

TABLE 3.10-1. ATMOSPHERIC EMISSIONS FROM NATURAL SOURCES

SUBCATEGORY	YEAR	Emissions (MT/yr) VOLATILE ORGANICS	REF	PARTICULATE ORGANICS	REF
Decomposition of Organic Material	1968	71,700,000	3	--	-
Plants	1972	9,100,000	4.5,6	1,500,000	2
Enteric Fermentation in Animals	1963	4,500,000	1	--	-
CATEGORY TOTAL		85,300,000		1,500,000	

Sources: 1. KO-172 4. RA-156
2. WA-252 5. AB-044
3. RO-228 6. RA-209

3.10.1 Process Description

Decomposition of Organic Material

Methane is produced by the anaerobic bacterial decomposition of organic matter. This process occurs in such places as lakes, marshes, and paddy fields. Trace quantities of ethane, acetylene, ethylene, propane, and propylene are also products of methane fermentation. Robinson and Robbins (RO-228) estimated that, on a worldwide basis, 13.7×10^8 MT of methane per year are emitted to the atmosphere from swamps, tropical areas, lake sediment, and various soils. They also estimated that carotene decomposition of organic material releases an estimated 63.5 million MT per year of terpene-type hydrocarbons to the atmosphere.

From these global estimates, the annual production rate of organics due to the decomposition of organic material in the United States is estimated to be 71.7 million MT. This estimate was obtained by assuming that the United States' production rate per unit area is one-half that of the average for the vegetated earth surface. This assumption is based on the fact that emission rates are higher in tropical than nontropical areas, and that a significant portion of the global emissions are from paddy fields (KO-172).

There is no feasible method of controlling organic atmospheric emissions from this source. However, when reduction of the area covered by rice paddies and marshes is attractive, this will result in a reduction of atmospheric emissions.

Plant Functions

Plants release a variety of volatile organics. The major organic substances emitted to the atmosphere from plants

are monoterpentenes (C_{10}) such as α-pinene, β-pinene and limonene and the hemiterpene (C_5) isoprene (RA-156). Rasmussen and Went (RA-209) conducted in situ gas chromatographic studies at temperate forests and fields. They reported that the emission rates of organic volatiles from plants show diurnal and temperature variations and are related to the mass and activity of the foliage.

The biological and atmospheric fates of organic foliar emissions are poorly understood. It is believed that significant amounts of the naturally occurring organic compounds are disposed of in a biological sink, i.e., populations of fungi, microbial life growing on vegetation surfaces, and absorption by components in the soil (AB-044). Terpenes which have been studied show the high reactivity predicted by their olefinic structures (RA-156). It has been suggested that these photochemically reactive compounds undergo the photochemical reaction for smog formation in which olefins, nitric oxides, and sunlight react to form ozone, peroxyacyl nitrate-like compounds, and aerosol material (RA-209). The aerosols (Aitken nuclei) produced by this photochemical polymerization process are believed to be responsible for the blue haze associated with vegetation.

Estimates of worldwide volatile organic emissions vary greatly. Table 3.10-2 summarizes global terpene emission estimates determined by various investigators. Went's estimate of 154 million MT of terpenes emitted per year is approximately the median value and corresponds to Rasmussen's estimate at a canopy depth of 75 cm. A United States' emission estimate of 15.4 million MT per year was derived from this global estimate of 154 million MT per year by assuming that the terpene emission rate per unit area for the total United States area (10^{17} cm^2) is equal to that of the total vegetated earth surface (10^{19} cm^2) (RA-156). Abeles, et al., (AB-044) estimated that the natural

TABLE 3.10-2. GLOBAL TERPENE EMISSION ESTIMATES

Investigator	Method	Estimate (10^6 MT/yr)
Rasmussen (1972)	Intact plants in leaf assimilation chambers	23.4 - 464[1]
Went (1960)	Sum of sagebrush emission and terpenes as percentage of plant tissues	154
Rasmussen and Went (1964)	1. Bagging foliage 2. Enclosure forbs 3. *In-situ* ambient concentration	23.4 13.5 432
Ripperton, White and Jeffries (1967)	Rx rate O_3/pinene	2to10 times previous estimates

[1]Emissions vary with canopy depth (10-200 cm canopy depths in study)

Source: RA-156

production of ethylene from plants in the United States is approximately 18,000 MT per year.

Ragweed, goldenrod, bermuda grass, walnut trees, and numerous other weeds, economic plants, and trees produce pollens. There is evidence that 1.5 million MT of pollen move into the atmosphere over the United States every year (WA-252). The major detrimental effect of pollen is, of course, its allergenic nature.

Enteric Fermentation in Animals

Methane is produced as the result of enteric fermentation in animals. The global production of methane from this source is estimated to be approximately 45 million MT (KO-172). The United States' methane emissions from this source are about 4.5 million MT per year assuming that the animal population is uniformly distributed over all vegetated land areas.

3.10.2 Control of Emissions

The only method of controlling emissions from natural processes is to reduce the quantity of plants and animals causing the emissions. This control method is not practical in most cases; therefore, the reduction potential for emissions from natural process is negligible.

3.11 Solid Waste Disposal

This section describes techniques and processes for the disposal of the following solid wastes:

1) Wastes generated by urban, rural, commercial, municipal, institutional and industrial sources, collected and disposed of by municipal agencies.

2) Municipal sewage solids.

3) Solid waste disposed of by non-industrial intermediate size incinerators, such as apartment house incinerators. This category does not cover, however, industrial wastes handled on-site or off-site by the industries themselves or by private contractors who do not use municipal facilities.

4) Non-collected urban and rural solid wastes which are disposed of by various unidentified and/or unquantified methods.

Subcategories within the agricultural and forest products industry also produce organic solid wastes. Table 3.11-1 shows the composition of solid wastes generated by various processes within the industry. These wastes are normally either allowed to decompose in situ or are disposed of by methods including incineration, open burning, landfills and spreading, open dumping, or utilization within another process.

Eventually all solid waste is disposed of by some type of open dumping or landfilling. Incineration merely produces

TABLE 3.11-1. SOLID WASTES IN THE AGRICULTURAL AND FOREST PRODUCTS INDUSTRY

Subcategory	Solid Waste Composition	Ref
• Livestock/Poultry	Manure, carcasses	2
• Grains	Field residue	2
• Logging Operations	Logging residue	4
• Fruits & Vegetables	Field residue	2
	Residual from canning & freezing	2
• Sawmills	Unused sawdust	2
• Pulp & Paper	Pulp residue & unusable paper residue	2
• Secondary Wood Mfg.	Chips, shavings, sawdust	2
• Processed Foods	Processing residuals	2
• Meat Products	Paunch manure	2
• Paper Products	Contaminated or unusable paper and wood	2
• Leather	Flesh scrapings, hair & nonleather residuals	2
• Fats, Oil, Misc. Foods	Various processing residuals	2
• Bakery	Residuals & unusable materials & products	2
• Coffee Roasting	Chaff	1,3
• Tobacco	Fines, lints, unacceptable material	2

Sources:
1. DA-069
2. EN-067
3. US-303
4. WA-234

a less voluminous, more stable product for landfilling. Today, other reasons such as recovering heating value and recycling of valuable metals have made incineration even more attractive. Table 3.11-2 lists the types of solid waste disposal techniques examined in this category.

The organic atmospheric emissions, liquid effluents, and solid wastes from the disposal methods are described in this section. The organics were quantified and are listed in Tables 3.11-3, 3.11-4, and 3.11-5. The values are based on a collected municipal refuse rate of 240 x 10^6 MT/year and a conversion factor of 25 mg/ℓ BOD approximately equals 52 mg/ℓ total organics (SO-080).

3.11.1 Process Description

Open Dumping

Burning at open dumps is the largest single atmospheric emitter of organics of all the solid waste disposal methods. The total emission rate in 1970 was approximately two million metric tons per year of both volatile organics and organic particulates. Since that time there has been a major effort to shut down all burning dumps in the United States. The success of this effort has not been documented, but it is believed to be only partially completed.

If waste at the dumps is not burned, decomposition of the organic matter will produce organic gases consisting mainly of methane. The methane produced in open dumps is estimated at 67,000 metric tons per year. This emission rate is, at best, an order-of-magnitude estimate due to the complicated and variable processes involved in the decomposition of the organic material.

TABLE 3.11-2. SOLID WASTE DISPOSAL METHODS

1) Open Dumps
   a) Open burning - collect and uncollected refuse
   b) Open dumping
   c) Sewage sludge lagooning and dumping

2) Landfills
   a) Landfill
   b) Sanitary Landfill

3) Incineration
   a) Municipal incinerators
   b) Intermediate non-industrial incinerators
   c) Sewage sludge incinerators
   d) Incineration of uncollected urban and rural refuse

TABLE 3.11-3. ATMOSPHERIC EMISSIONS FROM SOLID WASTE DISPOSAL OPERATIONS IN METRIC TONS PER YEAR

	Year	Volatile Organics	Ref	Organic Particulates	Ref
Open burning of collected refuse	1963	1,656,000	1	378,000	7
Open burning of uncollected urban refuse	1972	345,000	2	80,000	2
Open burning of uncollected rural refuse	1972	322,000	2	74,000	2
Methane from decomposition in dumps and landfills	1974	246,900	3	0	8
Municipal incineration	1974	51,500	4	65,400	4
Intermediate size incinerators	1972	59,800	5	38,450	5
• Schools	1972	35,300	5	18,100	5
• Commercial	1972	18,600	5	16,500	5
• High-rise apartments	1972	3,280	5	1,800	5
• Medical	1972	2,640	5	2,050	5
Sewage sludge incinerators	1974	4,150	6	4,900	6

Sources - 1. LA-204
2. MS-001
3. MA-256
4. CH-281
5. BR-279
6. EN-341
7. HE-159
8. FO-001

TABLE 3.11-4. WASTEWATER EFFLUENTS FROM SOLID WASTE DISPOSAL IN METRIC TONS PER YEAR

	Year	Total Organics	BOD	COD	Suspended Solids	Ref
Leachate from open dumps	1974	293,000	141,000	176,000	106,000	1
Leachate from burning dumps	1974	245,000	118,000	141,000	70,600	1
Leachate from landfills	1974	171,000	82,300	103,000	61,700	2
Leachate from sanitary landfills	1974	24,500	11,800	14,700	8,800	3
Leachate from lagoons and oxidation ponds	1974	850	410	1,500	--	1
TOTAL		736,000	354,000	436,000	247,000	

Sources:
1. SA-103
2. BO-181
3. HO-250

TABLE 3.11-5. ORGANIC SOLIDS FROM SOLID WASTE DISPOSAL OPERATIONS

	Year	Organic Solids (MT/Yr)	Ref
Bottom ash from non-industrial intermediate size incinerators	1972	257,000	1
Bottom ash from municipal incinerators	1970	154,000	2
Bottom ash from sewage sludge incinerators	1974	77,400	3
Collected fly ash from municipal incinerators	1970	47,600	2

Sources:
1. BR-279
2. CH-281
3. EN-341

The majority of the liquid organic effluent from open dumps is leachates formed by percolation of rainfall and infiltration of ground water. The leachate rate is estimated at 1.76×10^{10} liters per year. This value is an order-of-magnitude estimate. The actual leachate rate will depend on hydrology, geology, topography, type of refuse, and age of the refuse. The estimated leachate quality for open dumps and burning dumps is shown in Table 3.11-6.

Also considered in open dumping is the lagooning of sewage sludge. Lagooning is the most popular method of handling sewage solids. Air emissions can result from the lagoons due to aerobic and anaerobic decomposition of organics within the sludge liquor. The gaseous products are mainly H_2S and methane. Although the total gas quantity is relatively small, the gas produced is often offensive in odor and may be a nuisance.

Infiltration of wastewater into the soils making up the pond may also be considered a source of organic effluents. The estimated volume for this leachate was the smallest of all those calculated in this solid waste category. The BOD, COD, and total organics emitted are estimated to be 410, 1,300, and 850 metric tons per year, respectively. These numbers are order of magnitude estimates.

Open Burning of Uncollected Refuse

A 1972 report estimated the volume of uncollected urban and rural residential and municipal refuse to be 58×10^6 MT/year (MS-001). Of this amount approximately 29×10^6 MT/year was open burned. The emissions from open burning were estimated from the same emission factors used for the open burning dump.

TABLE 3.11-6. ESTIMATED QUALITIES OF DUMP AND LANDFILL LEACHATES

	BOD mg/ℓ	COD mg/ℓ	Dissolved Solids mg/ℓ	Total Solids mg/ℓ
Open Dump	8,000	10,000	2,000	8,000
Burning Dump	10,000	12,000	6,000	12,000
Landfills	8,000	10,000	2,000	8,000
Sanitary Landfills	8,000	10,000	2,000	8,000

Sources: SA-103, RO-211, HU-111, BO-181, LO-250, EM-007, FU-021, EM-003.

The remaining 29 x 10^6 MT/year was disposed of by intermediate size incinerators to be discussed later and by open dumping. Approximately 90 percent of the remaining refuse was open dumped in unidentified locations. There were no calculated emissions for the open dumped uncollected solid waste.

Landfills

Regular landfills covered with soil periodically and those classified as the sanitary-type covered on a daily basis are similar in design and, therefore, have similar emissions and effluents. The effluent source from landfills is leachates from the landfill sites. The emissions result from gases produced by decomposition of the organic matter.

The leachate from landfills results from percolation of rainfall infiltration of ground waters into the fill site. In the United States, the volume of such leachates has been estimated as 1.03 x 10^{10} liters per year for regular landfills and 1.47 x 10^9 liters per year for sanitary landfills. The estimated quality of leachates is shown in Table 3.11-7. The actual composition depends on hydrology, geology, topography, type of refuse, and age of the refuse.

The main organic constituent of the gases formed during the decomposition of organic materials is methane. The atmospheric emissions from regular landfills are estimated to be 157,000 metric tons per year, and for sanitary landfills 22,400 metric tons per year.

TABLE 3.11-7. POTENTIAL REDUCTION OF ORGANIC EMISSIONS AND EFFLUENTS

REDUCTION METHOD	ATMOSPHERIC EMISSIONS REDUCTIONS (MT/YR)		WATER EFFLUENTS REDUCTIONS (MT/YR)			
	Volatile Organics	Organic Particulates	Total Organics	BOD	COD	SS
1. Replacement of open burning dumps and open dumps with sanitary landfills	1,520,000	378,000	48,900	23,500	23,500	--
2. Replacement of open burning of uncollected refuse with collection and sanitary landfilling.	607,000	154,000	22,000	--	--	--
3. Containment of leachates and flaring decomposition gases from existing sanitary landfills.	21,000	--	--	10,600	13,200	8,380
4. Application of afterburners or auxiliary burners to						
• municipal incinerators	48,900	62,100	--	--	--	--
• intermediate incinerators	12,000	7,740	--	--	--	--
• sewage sludge incinerators	3,900	4,660	--	--	--	--
TOTAL	2,210,000	607,000	70,900	34,100	66,700	8,380

Incineration

As mentioned previously, incineration produces a more stable and less voluminous material which is suitable for landfilling. Variations in emissions from municipal, non-industrial, and sewage sludge incineration processes result from the type of incinerator, the size of the incinerator, the kind of refuse incinerated, and the controls used. Wastes from incinerators include combustion products emitted in stack gases, bottom ash and collected fly ash, and wastewater from the ash handling systems and flue gas scrubbing systems.

About six percent of the ash material is organic (HO-122). The organic content of ash generated by municipal incinerators, intermediate non-industrial incinerators, and sewage sludge incinerators is 2[illegible],000 MT/year, 257,000 MT/year, and 77,400 MT/year, respectively.

Ten percent of all generated and collected residential, municipal, commercial, institutional, and industrial solid wastes are combusted in municipal incinerators. The estimated volatile organic and organic particulate emissions from these units are 51,500 and 65,400 metric tons per year, respectively.

Intermediate size incinerators are employed in schools, stores, office buildings, high-rise apartments, and hospitals.

There is much less wastewater effluent from ash handling systems and particulate scrubbers than other wastewater streams in the solid waste cateogry. Since ash sluice water and scrubber water are generally treated and recycled, the final effluent streams are easily handled by municipal sewage systems or on-site evaporation ponds.

3.11.2 Control of Emissions and Effluents

Both open dumping and open dump burning are inadequate methods for waste disposal. A major effort has been undertaken in the United States in recent years to replace all open and burning dumps with landfills.

The major pollutants from sanitary landfills are leachates and gases formed during decomposition of organic matter within the landfill. To control leachates, the solid materials should be contained and water flow through it minimized. Control systems for gases such as methane, which is an environmental and a safety hazard, include containment, venting, and flaring.

Control of volatile organics from incineration is accomplished by three methods. Close control of incinerator operating parameters may be employed. Design of multiple chamber incinerators reduces emissions. The use of auxiliary fuel-fired burners in the mixing chamber increases the combustion temperature which results in more complete combustion.

The add-on controls presently used on municipal incinerators are designed for removal of particulates but not for the control of volatile organics. These controls include expansion chambers, spray chambers, wet and dry scrubbers, electrostatic precipitators, and fabric filters. Organics are, however, controlled by design of the incinerator with multiple chambers or afterburners.

Intermediate size non-industrial incinerators are smaller and have irregular loading rates. Regulation of excess air, firebox temperature, and residence time for these incinerators is more difficult than for larger ones. Approximately 70 to 90 percent of these incinerators are equipped with afterburners

which eliminate approximately 95 percent of the organic emissions (BR-279). Some intermediate size incinerators have particulate control systems which further reduce the organic particulates in the stack.

Sewage sludge incinerator controls are similar to the municipal and intermediate incinerator control systems. The control systems are usually designed to control particulates and not volatile organics. Before 1960, most sewage sludge incinerators had no air pollution controls. Between 1961 and 1967, most new installations were equipped with low energy venturi scrubbers to meet the 1960 ASME particulate standards. After 1967, stricter standards required the installation of impingement plate scrubbers or high energy venturi type scrubbers on all new installations.

To eliminate air pollution problems associated with incineration, sanitary landfills could be employed as an alternative disposal method. However, landfill requires six to ten times the land area necessary for incineration and water effluents are a potential problem.

3.11.3 Potential Reduction of Emissions and Effluents

Table 3.11-7 summarizes the potential reductions in organic emissions and effluents from solid waste disposal operations. Reductions can be achieved by:

1) replacement of open burning and dumping of collected and uncollected refuse with sanitary landfills,

2) containment of leachates from existing landfills,

3) flaring decomposition gases from existing landfills, or

4) application of afterburners or auxiliary burners to incinerators.

The total potential reduction in volatile organics is 2,210,000 MT/year. The potential for reduction of organic particulates is 607,000 MT/year. Organic water effluents can be reduced by 70,900 MT/year.

There are some alternative control methods to sanitary landfilling and incineration. These methods are composting, pyrolysis, and salvage-recycle operations. These methods have yet to be proven on a large-scale nationwide basis.

Composting has been proven in Europe as a viable solid waste control method, although it has yet to be accepted on a large-scale in the United States. Composting is generally more expensive than landfilling and incinerating and also has problems with odors and vermin. Both of these problems can be reduced by use of covering material, insecticides, and pesticides. Composting has the advantages of requiring less land than the landfill and of recycling the decomposed material as a useful product.

Pyrolysis is still in the pilot-plant stage of development. If it is perfected, pyrolysis could effect a reduction in organic emissions from solid waste handling due to the fact that waste streams are collected and treated. Added incentive to develop the process is the potential for production of valuable fuels such as light oils and fuel gas.

A method of reducing the volume of refuse is to remove and recycle all valuable, reusable constituents. These constituents include ferrous metals, non-ferrous metals (especially aluminum), glass, and plastics. Ash material from incinerators can also be classified and recycled. Major recycle operations are also carried out in the area of bulky metal wastes (such as junk automobiles and heavy household appliances), paper products, aluminum cans, and used tires. Recycle operations eliminate the need for disposal of a fraction of the original solid waste by eliminating organic wastes from the solid waste disposal process. However, some wastes will still be generated from the recycle process.

3.12 Municipal Wastewater Treatment

Processes for treatment of all sewered and unsewered residential wastewaters and for all sewered commercial, industrial, and institutional wastewaters treated in municipal facilities are included in this cateogry. All unsewered wastewaters are assumed to be handled by septic tanks.

Figure 3.12-1 shows the available wastewater treatment alternatives discussed in this section. Modern designs of large treatment facilities include some type of secondary organic removal process along with lagoons or drying beds for handling the sludge.

The BOD, COD, suspended solids, and total organic from each of the different types of waste treatment facilities were quantified. EPA estimates were used to estimate the extent of use of each type of facility. These estimates included only the sewered United States wastewater. The quality of the wastewaters from the wastewater treatment facilities was based on an average of effluents given in literature (BA-416, RE-176). The quantity and quality of the wastewaters from each type of facility were combined to give the total effluents contained in Table 3.12-1. The values for total organics were calculated by the conversion factor of 25 mg/ℓ BOD approximately equals 52 mg/ℓ total organics (SO-080). The handling and disposal of sludge solids generated by the wastewater processes are discussed in Section 3.11.

3.12.1 Effluent Sources

Unsewered septic tanks are calculated to be the largest sources of BOD, COD and suspended solids. The BOD and COD concentrations of septic tank effluents are comparable to those of

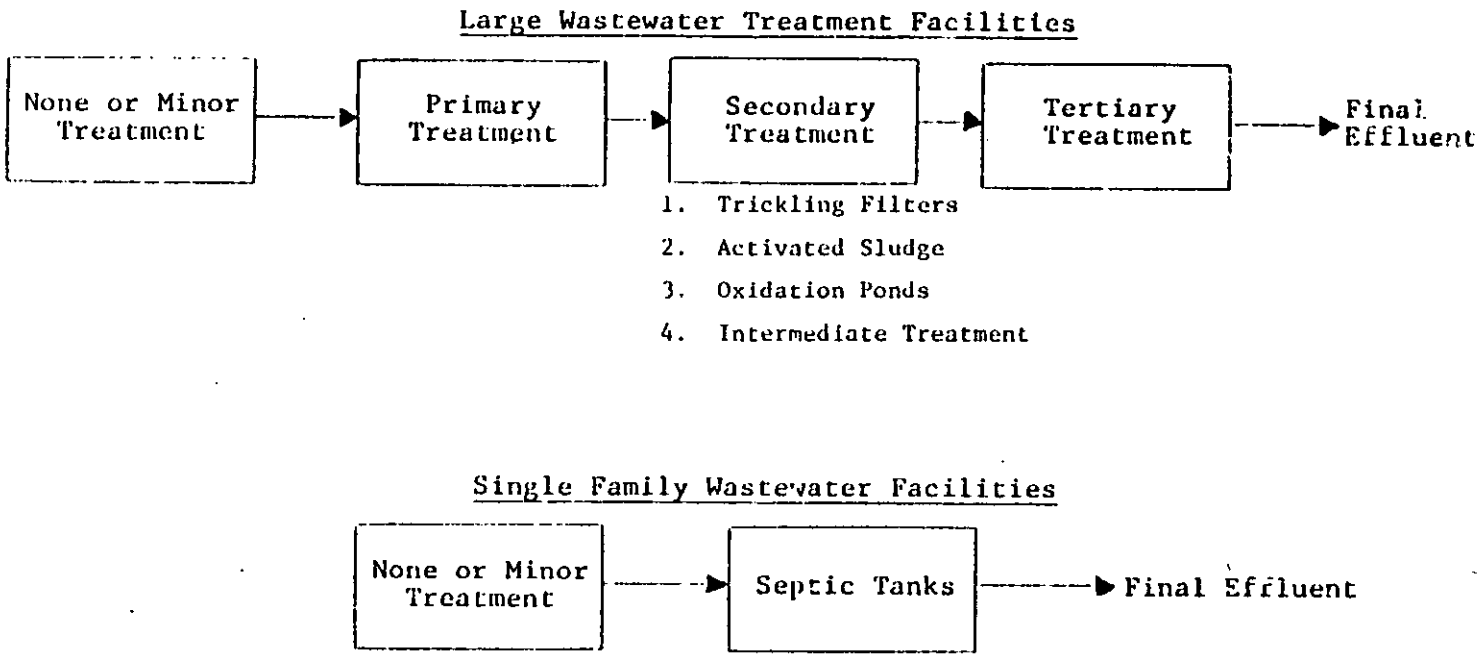

FIGURE 3.12-1. WASTEWATER TREATMENT ALTERNATIVES

TABLE 3.12-1. WASTEWATER EFFLUENTS (MT/YR)

Method of Wastewater Treatment	Year	Total Organics	BOD	COD	Suspended Solids	REF
None or minor	1974	1.02×10^6	0.49×10^6	1.23×10^6	0.369×10^6	1,3
Septic tank	1974	0.603×10^6	0.29×10^6	0.46×10^6	0.057×10^6	2,3
Septic tank (unsewered)	1974	5.70×10^6	2.74×10^6	4.33×10^6	0.526×10^6	2,3
Primary	1974	1.37×10^6	0.66×10^6	1.52×10^6	0.436×10^6	1,3
Intermediate	1974	0.27×10^6	0.13×10^6	0.39×10^6	0.028×10^6	1,3
Trickling filters	1974	0.201×10^6	0.097×10^6	0.77×10^6	0.080×10^6	1,3
Activated sludge	1974	0.395×10^6	0.19×10^6	1.55×10^6	0.136×10^6	1,3
Oxidation ponds	1974	0.208×10^6	1.10×10^6	0.36×10^6	0.020×10^6	1,3
Secondary unknown	1974	0.201×10^6	0.097×10^6	0.48×10^6	0.039×10^6	1,3
Tertiary	1974	0.010×10^6	0.005×10^6	0.037×10^6	0.003×10^6	1,3
		9.98×10^6	4.81×10^6	11.1×10^6	1.68×10^6	

Sources:
1. RE-176
2. BA-416
3. MI-208

medium to strong raw municipal wastewater. The septic effluents are usually evaporated to the surrounding environment from an absorption field.

Primary wastewater treatment facilities are the second largest source of pollutant effluents. These facilities provide pretreatment (i.e., grit removal, flocculation, etc.) and suspended solids removal, but not biological treatment. The effluent from primary treatment processes is characterized by BOD, COD, and suspended solids concentrations of approximately 150 mg/ℓ, 350 mg/ℓ, and 100 mg/ℓ, respectively (RE-176, CE-014).

Most new designs for large wastewater treatment facilities employ secondary biological treatment of the wastewater. These processes include trickling filters, activated sludge, and aerated lagoons or oxidation ponds. Biological treatment provides BOD and COD reduction of 55 to 95 percent and suspended solids reduction of 65 to 92 percent. Any desired degree of reduction can usually be attained through proper design of the facility. Secondary biological treatment generally provides enough pollutant reduction to meet all existing wastewater effluent guidelines. In 1974, approximately 49 percent of the United States population was serviced by some type of secondary biological treatment facility (MI-028).

Tertiary treatment of municipal wastewater removes particularly hard to treat pollutants or meets very stringent wastewater effluent standards. Tertiary processes include ion exchange, membrane separation processes (i.e., reverse osmosis), activated carbon, microfiltration, and chemical treatment such as chlorination. All of the above listed processes have been proven on full-scale municipal wastewater operations. Only slightly over one percent of the United States population is served by a tertiary treatment facility.

Organic gases from a municipal treatment facility are difficult to quantify but are expected to be relatively small. These vapors are emitted from screening areas, aeration tanks, trickling filters, and clarifiers. The emission rates are low, but the constituents generally cause odor problems. The activated sludge treatment plant emits more volatile organics than does the screening area or the settling ponds. The emissions from activated sludge treatment result from the partial stripping from the liquor of various volatile oils, fats, and other organic compounds present in the sewage (NA-032).

3.12.2 Application of Control Technology

Although the single-family septic tanks have been designated as the greatest impactor in the wastewater category, there is currently no viable substitute for septic tanks. In areas where septic tanks have been used and the population has now grown reasonably close together, one possible alternative is to gather all the wastewater to a common treatment facility. Generally, this is not feasible in rural areas, and the septic tank is the only alternative.

Of the wastewater which is currently gathered and treated at one site, a reduction in the total BOD, COD, and suspended solids can occur with upgrading of the existing facilities. One step in upgrading would be the addition of secondary biological treatment to plants which have no treatment or only primary treatment. The estimated reduction achieved by upgrading to secondary treatment is shown in Table 3.12-2.

If more stringent wastewater effluent guidelines are adopted, addition of tertiary processes to all wastewater treatment facilities may be required. The expected reduction

TABLE 3.12-2. POTENTIAL REDUCTION OF ORGANIC WATER EFFLUENTS FROM MUNICIPAL WASTEWATER TREATMENT FACILITIES

	Water Effluent Reductions MT/yr			
	Total Organics	BOD	COD	Suspended Solids
1. Upgrading of nonexistant treatment and primary treatment to secondary biological treatment facilities	2.08×10^6	1.00×10^6	1.11×10^6	0.728×10^6
2. Converting all the upgraded facilities listed in 1. to tertiary treatment facilities	1.05×10^6	0.503×10^6	2.37×10^6	0.189×10^6
3. Reuse of the treated wastewater from the tertiary facilities listed in 2. with 50% used for irritation and 50% used for industrial process cooling water	0.263×10^6	0.141×10^6	1.13×10^6	0.105×10^6
Total	3.42×10^6	1.64×10^6	4.61×10^6	1.02×10^6

resulting from addition of tertiary control is also shown in Table 3.12-2. The cost of the tertiary controls is expected to be relatively expensive for the amount of reduction.

As water resources become scarce and wastewater quality requirements more stringent, wastewater reclamation and reuse will become increasingly popular. Areas where wastewater reuse is currently being practiced are:

1) irrigation and other agricultural uses,

2) cooling water,

3) industrial process water,

4) boiler feed water,

5) recreational lakes,

6) fish propagation, and

7) nonpotable domestic use.

In 1971, the greatest amount of reuse was for irrigation and industrial process water. With proper crop selection and irrigation management, even very poor quality effluents were used successfully. The total water reuse that same year amounted to less than the annual water use of New York City.

Wastewater reuse is economically feasible under the following conditions (SC-310):

1) Existing freshwater supplies are limited, and substantial future expenditures are contemplated, making it essential to develop additional supplies.

2) Existing freshwater supplies are relatively expensive.

3) Private or public developments with need for large volumes of water exist in the area.

4) The treatment provided the wastewater produces an effluent of very high quality that is not wasted into receiving waters.

5) Regulatory agencies are planning to require a higher degree of treatment for discharge to receiving waters, such as nutrient removal.

Increased reuse of treated municipal wastewater could provide a reduction in organic water from municipal water treatment. An estimation of the reduction was made based on the following assumptions:

1) Approximately 50 percent of the wastewater is reused as irrigation water and thus has an environmental impact.

2) The other 50 percent of the wastewater is reused in industrial process and cooling waters and will not impact the environment.

3) Wastewater from septic tanks is not recycled.

If these three assumptions are included with the upgrading of all the existing wastewater treatment facilities to tertiary type controls, the expected organic reduction in total organic effluents would be 3.42×10^6 MT/year.

3.13 Other Sources

Known sources of organic pollutants not previously discussed are included in this cateogry. Included here are forest wildfires, coal refuse fires and structural fires. The quantities of volatile organics and organic particulates emitted from these sources are shown in Table 3.13-1. These emission estimates are based on numerous assumptions and are "ball park" values. The emissions from these fires can be reduced by more extensive application of control and prevention methods, but it was not possible to determine reduction potentials associated with the methods.

3.13.1 Forest Wildfires

The size, intensity, and occurrence of wildfires are dependent on such variables as local meteorological conditions, the species of trees and their moisture content, and the weight of combustible fuel per unit area (fuel loading). After ignition, small dry matter burns first, then larger living plants.

The United States Forest Service is developing a nation-wide fuel identification model to provide estimates of fuel loading by tree size class. A National Fire Danger Rating System (NFDR) is produced when wind, slope, and expected moisture changes are superimposed on this fuel model.

Hypothetically, the nature and quantity of pollutant emissions are related to the intensity of the wildfire, its direction relative to the wind, and the rate at which it spreads (EN-071). Laboratory tests have shown that the smouldering phase of combustion is a major source of pollution. The initial 80 percent of the fuel burned accounts for only about 20-30 percent of the organic emissions (SA-223).

TABLE 3.13-1. ATMOSPHERIC EMISSIONS FROM OTHER SOURCES

Sub-Category	Year	Emissions (MT/yr) Volatile Organic	Ref	Particulate Organic	Ref
Forest Wildfires	1971	791,000	1	213,000	1,2
Structural Fires	1973	64,800	4,6	20,900	2,6
Coal Refuse Fires	1972	61,200	3,5,6	N/A	
Category Total		917,000		233,900	

Sources: 1. EN-071 4. NA-032
2. VA-067 5. EN-226
3. MS-001 6. MO-201

Gas chromatographic analysis of emissions from the burning of ponderosa pine showed that 15-40 percent of this gas was methane and ethane (SA-223). Ethane and acetylene were the next most abundant compounds of the 24 organic compounds identified by the analysis. The smoke from rye grass burns contains about 38 percent organic matter (VA-067) and is thought to be representative of particulate matter from forest wildfires.

Forest wildfires produce about 791,000 MT of organics (as methane) and 560,000 MT of particulate matter (213,000 MT organic particulates assuming 38 percent organic content) annually (EN-071). These rough estimates were obtained by using data on areas consumed by wildfires in 1971, the fuel loading in the areas consumed, and emission factors.

The most effective control method for forest wildfires is fire prevention. Considerable activity has been, and is being, directed toward reducing the number and severity of wildfires. These activities include publishing information on fire prevention and control, surveillance of forest areas where fires are likely to occur, prevention of recreational usage of these areas, prescribed controls for burning of litter and underbrush, and various firefighting and control activities. The tests mentioned previously indicate that emissions could be substantially reduced by rapid mop-up operations to minimize smoldering. The reduction potential associated with these techniques cannot be quantitatively estimated.

3.13.2 Structural Fires

Approximately one million buildings are damaged annually by fires in the United States (US-336). Emissions from these fires can be roughly approximated by using various

assumptions for the quantity of combustibles and emission factors. Monsanto Research Corporation estimated that in 1973 structural fires emitted 64,800 MT of volatile organics and 55,100 MT of particulates. The emission of organic particulates equals about 20,900 MT per year, assuming that the smoke from these fires is represented by that from rye grass burns which contain about 38 percent organic matter (VA-057).

Prevention and control techniques can reduce these emissions. Fire prevention techniques include the use of fire-proof construction materials; information programs on fire prevention; and proper handling, storage, and packaging of flammable materials. Fire control techniques include methods for rapidly extinguishing fires such as the use of sprinklers, foam, and inert gas systems, and provision of adequate alarm systems, firefighting facilities, and personnel.

3.13.3 Coal Refuse Fires

Large amounts of refuse are generated during the cleaning of coal. About 80 percent of the total bituminous coal production in 1968 was cleaned, generating 88 million MT of refuse, or about 18 percent of the total production (MS-001). These wastes are normally disposed of in hillside dumps, valley fills, and earthen dumps. The wastes cover many thousands of hectares of land. For example, in Pennsylvania and West Virginia alone, the disposal of deep mine wastes has covered 16,000 hectares of land (CO-168).

Fires have been burning for many years in accumulations of coal refuse. The most important causes of these fires are (CO-168):

1) spontaneous combustion,

2) intentional ignition to obtain "red dog" for use as a road base material,

3) camp fires left burning near disposal sites,

4) forest fires, and

5) careless burning of trash on or near the refuse piles.

It was estimated that 538 million cubic meters of burning coal refuse piles existed in the United States in 1964. A more recent study cited reports which estimated that in 1969 there were 292 burning refuse piles, with a total volume of 206 million cubic meters and containing an estimated equivalent of 16 million MT of coal (NS-001). These figures indicate significant progress has been made in efforts to extinguish and prevent fires in coal refuse piles.

By using assumed densities, average lives for coal piles, and emission factors, a rough estimate of emissions can be obtained. Burning coal refuse piles emitted about 61,200 MT of volatile organics in 1973 (MO-201). The composition of the gaseous organics is not known. The emission rate for organic particulates is unknown. Total particulates are emitted at a rate of 123,000 MT/yr. (CO-168, US-144).

There are numerous approaches for control and prevention of fires in coal refuse piles. Control methods include various ways of applying water and slurries of non-combustibles

to the fires and the use of bulldozers to isolate and extinguish the fires. Prevention methods include proper choice and preparation of the dump sites, minimizing the quantity of combustibles in the refuse, systematic dumping techniques, compaction, and sealing of the piles. The Office of Coal Research has prepared a report concerning the stabilization, reclamation, and utilization of coal refuse piles which examines these control and prevention techniques and their application (CO-163). The reduction potential associated with more stringent application of the control and prevention methods is unknown.

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APPENDIX

TABLE A-1
AIR EMISSIONS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Production (10^3MT/yr)	"Best Estimate" of Organic Air Emissions[1] Volatiles (MT/yr)	Ref	Q	Particulates (MT/yr)	Ref	Q	Additional Estimates of Volatile Organic Emissions (MT/yr)	Ref	Q	(MT/yr)	Ref	Q	(MT/yr)	Ref	Q
Ammonia	13,694 (1974)	322,700	1	A				616,256	9	B	753,000	3	C			
Carbon Black	1,520 (1974)	96,700			3,700	2	B	83,250	1	B	39,540	3	C			
Acrylonitrile	635 (1974)	83,000	2	B	0	2	B	134,600	1	B	1,714	8	C	30,838	3	C
Ethylene Dichloride	3,493 (1974)	56,300	2	B	0	2	B	135,788	1	B	18,146	3	C	54,795	5	
Toluene	3,398 (1974)	51,000	4	D												
Carbon Tetrachloride	460 (1974)	43,400	1	B				7,122	5	D						
2-Ethylhexanol	182 (1974)	41,400	1	B												
Dimethyl Terephthalate	1,243 (1974)	41,300	2	B	600	2	B	49,440	1	C						
Ethylene Oxide	1,763 (1974)	38,900	2	B	0	2	B	84,850	1	B	239,000	3	C			
Ethyl Benzene	2,586 (1974)	38,800	4	D												
High Density Polyethylene	1,283 (1974)	35,800	2	B	1,000	2	B									
Low Density Polyethylene	2,703 (1974)	34,000	2	B	600	2	B	31,900	1	B	8,163	3	C			
Cyclohexanone and Cyclohexanol	574 (1972)	31,700	2	B	0	2	B	31,240	1	B						
p-Xylene	1,214 (1974)	28,800	1	B												
Polyvinyl Chloride and Copolymers	2,250 (1974)	28,100	2	B	5,400	2	B	76,110	1	B	9,977	3	C			
Ethylene-Propylene Polymers	1,690 (1972)	24,500	1	C												
Propylene Oxide	789 (1974)	23,900	1	B												
Methyl Methacrylate	290 (1973)	23,400	1	B												
Formaldehyde (37%)	2,654 (1974)	22,400	2	B	0	2	B	22,440	1	C	30,838	3	C			
Butylenes	1,074 (1971)	21,500	4	D												

TABLE A-1 (Continued)
AIR EMISSIONS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Production (10^3MT/yr)	"Best Estimate" of Organic Air Emissions[1] Volatiles (MT/yr)	Ref	Q	Particulates (MT/yr)	Ref	Q	Additional Estimates of Volatile Organic Emissions (MT/yr)	Ref	Q	(MT/yr)	Ref	Q	(MT/yr)	Ref	Q
Butadiene	1,663 (1974)	21,000	1	B												
Acetic Acid	1,030 (1974)	20,900	2	B	8,000	1	B									
Acrylic Acid	430 (1974)	18,500	1	B												
Methanol	3,112 (1974)	17,100	1	C												
Polypropylene and Copolymers	1,048 (1974)	17,000	2	B	50	2	B	9,768	1	B	362	3	C			
Maleic Anhydride	128 (1974)	15,400	2	B	0	2	B	16,630	1	B	15,328	3	C			
Phenol	1,044 (1974)	11,000	2	B	0	2	B	2,026	1	B	3,221	5				
Trichloroethylene	197 (1974)	10,200	1	B				1,693	6	C	2,041	5				
Polystyrene Copolymers	2,431 (1974)	9,100	2	B	200	2	B	16,740	1	C	3,900	3	C			
Glycerol	165 (1972)	9,000	2/1	B/C	0	2	B	21,798	1	C/B						
Acrylics	286 (1974)	8,300	3	C												
Acetaldehyde	635 (1974)	8,200	2	B	0	2	B									
Cyclohexane	1,061 (1974)	7,800	1	C												
Printing Ink	301 (1975)	7,700	3	C				17,010	1	D						
Pesticides	571 (1972)	7,000		D												
Ethylene from Chemical Conversion	10,699 (1974)	6,800	2	B	100	2	B	10,060	1	B						
1,1,1-Trichloroethane	267 (1974)	6,100	1	B				5,085	6	C	2,495	5				
Polychloroprene Rubber (Neoprene)	177 (1972)	5,700	1	C												
o-Xylene	475 (1974)	5,400	1	C												
Methylisobutyl Ketone	73 (1974)	5,200	1	C												
Adiponitrile	324 (1974)	5,000	2	B	0	2	B	4,715	1	C						
Ethyl Chloride	299 (1974)	4,900	1	B				5,005		B	30	5				

TABLE A-1 (Continued)
AIR EMISSIONS FROM ORGANIC PROCESSING IN METRIC TONS/YR

Product	Production (10^3MT/yr)	"Best Estimate" of Organic Air Emissions[1] Volatiles (MT/yr)	Ref	Q	Particulates (MT/yr)	Ref	Q	Additional Estimates of Volatile Organic Emissions (MT/yr)	Ref	Q	(MT/yr)	Ref	Q	(MT/yr)	Ref	Q
Chloroprene (2 chloro-1,3-butadiene)	80 (1972)	4,800	1	B												
Acetone	934 (1974)	4,700	1	C												
Vinyl Chloride	2,541 (1974)	4,500	1	D				22,455	6	C	6,577	5				
Styrene-Butadiene Rubber	1,465 (1974)	4,300	2	B	700	2	B	0	1	B	3,265	2	B			
Methyl Chloride	208 (1974)	3,700	6	C				4,953	1	C	1,724	5				
Methylene Chloride	268 (1974)	3,700	1	B				4,817	6	C	2,359	5				
Nitrobenzene	297 (1974)	3,400	1	B	0	8	C	2,466	8	C						
Ethylene Glycol	1,411 (1974)	3,000	1	B												
Acetylene	181 (1974)	2,800	1	C												
Ethyl Acrylate	75 (1968)	2,400	1	D												
Vinyl Acetate	635 (1974)	2,400	2	B	0	2	B	13,278	1	B						
Chloroform	136 (1974)	2,300	1	B				2,450	6	B	1,724	5				
Phenolic & Other Tar Resins	599 (1974)	2,300	3	C												
Dyes & Pigments (Organic)	160 (1973)	2,000		D												
Styrene	2,694 (1974)	2,000	2	B	30	2	B	2,203	1	B						
Cellulose Acetate	172 (1974)	1,900	1	C												
Acrolein	28 (1974)	1,900	1	B												
Cumene	1,302 (1974)	1,700	1	C												
Dodecylbenzene Sulfonic Acid-Sodium Salt	181 (1974)	1,700	1	C												
Ethanolamines	138 (1974)	1,500	1	C												

TABLE A-1 (Continued)
AIR EMISSIONS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Production (10^3MT/yr)	"Best Estimate" of Organic Air Emissions[1] Volatiles (MT/yr)	Ref	Q	Particulates (MT/yr)	Ref	Q	Additional Estimates of Volatile Organic Emissions (MT/yr)	Ref	Q	(MT/yr)	Ref	Q	(MT/yr)	Ref	Q
s-Butyl Alcohol	525 (1974)	1,500	1	C												
Ethanol (synthetic)	816 (1974)	1,500	1	B												
Acetic Anhydride	775 (1974)	1,400	2	B	0	2	B	12,361	1	B						
Polyamid Resins	47 (1970)	1,300	1	C												
Urea-Formaldehyde Resins	454 (1970)	1,300	3	C												
Dichlorobenzene	63 (1972)	1,300	1	B												
Chlorobenzene	183 (1973)	1,300	1	B												
Rayon	372 (1974)	1,200	1	B												
Naphthalene	254 (1970)	1,200	1	C												
Tetraethyl & Tetramethyl Lead	272 (1970)	1,200	1	C												
Polybutadiene Rubber	326 (1974)	1,200	1	B												
Polyester Resins	1,334 (1974)	1,100	1	C				1,207	3	C						
Cresol (Synthetic)	41 (1970)	1,100	1	B												
Cresylic Acid	31 (1971)	1,100	1	B												
Toluene Diisocyanates	290 (1974)	1,000	1	C												
Pentaerythritol	47 (1973)	1,000	1	C												
Fluorocarbon 12	231 (1974)	800	1	C				2,223	5							
Acetonitrile	68 (1973)	800	4	D												
Diethylene Glycol	152 (1973)	800	4	D												
Dodecyl Benzene Sulfonic Acid	63 (1970)	700	1	C												
Isodecanol	82 (1973)	700	4	D												

TABLE A-1 (Continued)
AIR EMISSIONS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Production (10^3MT/yr)	"Best Estimate" of Organic Air Emissions[1] Volatiles (MT/yr)	Ref	Q	Particulates (MT/yr)	Ref	Q	Additional Estimates of Volatile Organic Emissions (MT/yr)	Ref	Q	(MT/yr)	Ref	Q	(MT/yr)	Ref	Q
Fluorocarbon 22	64 (1974)	600	5													
Melamine Resins	77 (1974)	300	3	C												
Acetone Cyanohydrin	244 (1969)	300	1	C												
Perchloroethylene	332 (1974)	300	1	B				272	6	C						
Hydrogen Cyanide	138 (1973)	200	2	B	0	2	B	0	1	B						
Benzoic Acid	36 (1974)	200	1	C												
Isoprene	181 (1974)	200	1	C												
Epoxy Resins	82 (1972)	200	1	C												
Methyl Ethyl Ketone	229 (1974)	200	1	B												
Diisodecyl Pathalate	70 (1970)	200	1	C												
Heptenes	54 (1971)	100	1	C												
Polyisoprene Rubber	91 (1974)	100	1	C												
Isophthalic Acid	54 (1974)	100	1	B												
Aniline	242 (1974)	100	1	C												
Benzyl Chloride	41 (1971)	100	1	C												
Nonyl Phenol	81 (1970)	100	1	C												
Benzene from Chemical Conversion	5,021 (1972)	80	1	C												
Ethyl Ether	80 (1974)	80	1	C												
Chloroacetic Acid	29 (1969)	70	1	C												
Carbon Disulfide	348 (1972)	70	2	B	0	2	B									
2-Methoxyethanol	77 (1972)	50	1	C												
Phthalic Anhydride	467 (1974)	50	2	B	3,200	2	B	1,450	1	B	12,700	3	C	2,568	7	D
Isooctyl Alcohols	45 (1970)	40	1	C												

TABLE A-1 (Continued)
AIR EMISSIONS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Production (10^3MT/yr)	"Best Estimate" of Organic Air Emissions[1] Volatiles (MT/yr)	Ref	Q	Particulates (MT/yr)	Ref	Q	Additional Estimates of Volatile Organic Emissions (MT/yr)	Ref	Q	(MT/yr)	Ref	Q	(MT/yr)	Ref	Q
Polyisobutylene - Isoprene (Butyl) Rubber	163 (1974)	40	1	C												
n-Butyl Acetate	43 (1972)	40	1	C												
2-Butoxyethanol	52 (1971)	40	1	C												
2-Ethoxyethanol	71 (1971)	30	1	C												
n-Octyl-n-Decyl Phthalate	91 (1970)	30	1	C												
Fluorocarbon 113	64 (1974)	30	1	D				272	5							
Dinitrotolvene	131 (1970)	20	1	C												
Fluorocarbon 114	12 (1970)	20	1	C				136	5							
Hexamethylene Diamine	322 (1971)	10	1	C												
Isopropyl Alcohol	866 (1974)	10	1	B												
Allyl Chloride	395 (1970)	10	1	B				10,655	6	C						
Acrylonitrile-Butadiene Styrene Resins	238 (1970)	10	1	C				687	3	C						
Fluorocarbon 11	157 (1974)	3	5													
Acrylonitrile-Butadiene Rubber (Nitrile)	86 (1974)															
Cellopane	141 (1972)															
Nylon 6	445 (1970)	0	2	B	1,400	2	B	1,364	1	B						
Nylon 66	921 (1970)	0	2	B	2,400	2	B	2,858	1	B						
Phosgene	330 (1973)	0	1	B				413	6	C						
Soap & Detergent	5,840 (1973)		1	C	18,400	3	C									
Urea	3,348 (1974)		1	C												

[1]Estimates rounded to nearest 100 metric tons.
SOURCES: MO-201, PE-160, HO-244, ER-030, SH-241, PR-116, EN-071, PR-115, CL-011

TABLE A-2

WATER EFFLUENTS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Current Emissions (MT/yr) (BPCTCA)[1]				Potential Level of Control (MT/yr) (BATEA)[2]			
	Total Organics	BOD_5	COD	TOC	Total Organics	BOD_5	COD	TOC
Acetaldehyde	4,584	162	777	2,505	597	17.8	241	326
Acetic Acid	484	46.9	225	194	62.8	5.16	69.7	25.1
Acetic Anhydride	2,122	84.6	861	996	275	9.31	267	129
Acetone	4,780	926	5,240	2,970	621	102	1,630	386
Acetone Cyanohydrin (2-methyllactonitride)	3,628	723	4,106	2,050	471	79.6	1,273	266
Acetonitrile (vinyl cyanide, propane nitrile)	149	7.42	75.6	87.4	19.5	0.82	23.4	11.4
Acetylene	147	45.2	302	136	19.1	4.97	93.5	17.7
Acrolein	no data							
Acrylic Acid	553	41.2	197	276	71.8	4.53	61.2	35.9
Acrylics	3,960	838	3,125	2,690	522	92.2	969	350
Acrylonitrile	4,508	974	5,690	3,067	587	107	1,764	399
Acrylonitrile-Butadiene-Styrene Resins (ABS)	2,390	642	2,240	1,930	311	70.6	694	251
Acrylonitrile-Butadiene Rubbers (Nitrile)	1,080	52.9	874	752	141	5.82	271	97.8
Adipic Acid	7,048	2,042	11,594	5,788	917	225	3,594	752
Adiponitrile	8,990	809	12,258	5,993	1,170	89.0	3,800	779
Alkyd Resins	10,100	680	5,400	4,640	1,310	74.8	1,674	603
Allyl Chloride	no data							
Ammonia (Synthetic, anhydrous)	1,870	210	1,090	937	244	23.2	337	122
Aniline (Aminobenzene)	3,775	6.62	1,435	1,950	438	0.07	445	253

TABLE A-2 (Continued)

WATER EFFLUENTS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Current Emissions (MT/yr) (BPCTCA)[1]				Potential Level of Control (MT/yr) (BATEA)[2]			
	Total Organics	BOD_5	COD	TOC	Total Organics	BOD_5	COD	TOC
Benzene	34.3	9.79	74.5	31.6	4.43	1.08	23.1	4.1
Benzoic Acid	438	122	522	302	57.0	13.4	162.0	39.3
Benzyl Chloride	79.0	4.46	45.4	52.5	10.3	0.49	14.1	6.82
Bisphenol A	480	-	843	379	62.6	-	261	49.3
Butadiene	651	388	1,227	562	84.7	42.7	380	73.0
n-Butyl Acetate	536	129	730	364	69.7	14.2	226	47.4
n-Butyl Alcohol (n-Butanol)	3,168	726	4,121	2,057	411	79.8	1,278	267
s-Butyl Alcohol	3,681	440	2,587	2,390	479	48.4	802	311
Butylenes (1-,2-,iso-)	1,495	117	1,194	1,380	193	12.9	370	179
Caprolactam	218	1,120	537	146	28.4	123	166	18.9
Carbon black			no data					
Carbon disulfide	2,840	38.0	387	448	369	4.18	120	58.2
Carbon Tetrachloride	996	14.3	132	77.7	129	1.57	40.8	10.1
Cellopane			no data					
Cellulose Acetate (Resins and Fibers)	12,200	2,780	6,050	5,200	1,590	306	1,870	676
Chloroacetic Acid	963	86.7	442	246	125	9.54	137	32.0
Chlorobenzene	28.6	0.36	19.7	18.3	3.71	0.04	6.11	2.38
Chloroform (Trichloromethane)	211.0	3.90	35.9	21.2	27.5	0.43	11.1	2.76
Chloroprene	1,240	238	1,351	674	161	26.2	419	87.7
Cresol (Synthetic)	761	253	1,154	595	98.9	27.8	358	77.3

TABLE A-2 (Continued)

WATER EFFLUENTS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Current Emissions (MT/yr) (BPCTCA)[1]				Potential Level of Control (MT/yr) (BATEA)[2]			
	Total Organics	BOD_5	COD	TOC	Total Organics	BOD_5	COD	TOC
Cresylic Acid	532	94.0	534	266	69.2	10.3	165	34.6
Cumene	0.06	0.02	0.11	0.06	0.01	neg	0.03	0.01
Cyclohexane	no discharge							
Cyclohexanone and Cyclohexanol (coproducts)	58.5	7.46	35.3	40.9	7.34	0.82	11.0	5.32
Dichlorobenzene (m-,o-,p-)	164	6.92	70.4	81.4	21.3	0.76	21.8	10.6
Diethylene glycol	2,830	450	2,560	1,280	367	50	793	166
Di(2-ethylhexyl) phthalate	312	21.5	219	254	40.5	2.37	68.0	33.0
Diisodecyl phthalate	104	7.59	77.3	89.4	13.6	0.84	24.0	11.6
Dimethyl terephthalate	8,530	3,942	13,300	4,700	1,110	434	4,120	611
Dinitrotoluene	2,400	390	2,210	1,100	312	42.9	686	144
Dodecyl benzene sulfonic acid	no data							
Dodecyl benzene sulfonic acid, sodium salt	no data							
Dyes and pigments	60,800	8,230	73,300	30,400	7,890	905	22,700	3,946
Epichlorohydrin	4,830	665	3,780	1,880	627	73.2	1,170	245
Epoxies	2,980	746	1,814	1,562	388	82.1	562	203
Ethanol (Synthetic)	7,990	1,320	7,720	4,160	1,040	145	1,290	541
Ethanolamines (mono-,di-,tri-)	21.6	1.80	8.52	9.88	2.80	0.20	2.64	1.28
Ethyl acetate	2.01	0.49	2.20	1.10	0.26	0.05	0.68	0.14
Ethyl acrylate	4,126	458	2,464	2,500	536	50.4	764	325

TABLE A-2 (Continued)

WATER EFFLUENTS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Current Emissions (MT/yr) (BPCTCA)[1]				Potential Level of Control (MT/yr) (BATEA)[2]			
	Total Organics	BOD_5	COD	TOC	Total Organics	BOD_5	COD	TOC
Ethylbenzene (phenylethane)	788	45.7	1,361	71.7	103	5.03	422	93.2
Ethyl chloride	57.5	3.89	18.4	21.4	7.48	0.42	5.72	2.78
2-Ethoxyethanol	9.51	0.92	4.37	5.06	1.21	0.10	1.35	0.66
Ethylene (chem)	5,520	1,168	8,960	4,718	717	128.5	2,780	613
Ethylene dibromide	1,508	16.5	168	195	196	1.82	52.2	25.3
Ethylene dichloride	5,270	-	4,732	1,305	687	-	1,470	170
Ethylene glycol	6,925	62.4	3,464	2	900	6.86	1,074	349
2-Ethyl hexanol	2,060	539	3,070	1,5[illegible]	269	59.3	951	199
Ethylene oxide	3,940	162	3,800	2,150	512	17.9	1,180	280
Ethylene-propylene polymers	430	24.8	427	368	55.9	2.73	132	47.8
Ethyl ether	593	122	715	385	77	13.5	222	50
Fluorocarbon 11	2,290	17.2	175	202	297	1.89	54.2	26.3
Fluorocarbon 12	2,970	25.2	257	297	386	2.77	79.6	38.6
Fluorocarbon 22	590	6.98	71.1	82.2	76.7	0.77	22.0	10.7
Fluorocarbon 113	289	3.17	32.2	37.3	37.5	0.34	10.0	4.84
Fluorocarbon 114	111	1.34	13.6	15.7	14.5	0.14	4.22	2.05
Formaldehyde (37%)	8,530	290	2,950	3,410	1,110	31.9	914	443
Glycerol	2,050	254	1,480	800	266	27.9	460	104
Glycol monobutyl ether	6.14	0.68	3.21	3.72	0.79	0.07	1.00	0.48
Heptenes (mixed)	4.49	0.70	3.32	3.85	0.58	0.77	1.03	0.50
Hexamethylene diamine	832	166	1,480	517	108	18.2	458	67.2
Hexamethylene tetramine	365	54.6	376	188	47.3	6.01	116	24.4

TABLE A-2 (Continued)

WATER EFFLUENTS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Current Emissions (MT/yr) (BPCTCA)[1]				Potential Level of Control (MT/yr) (BATEA)[2]			
	Total Organics	BOD_5	COD	TOC	Total Organics	BOD_5	COD	TOC
Hydrogen Cyanide	2,608	20.9	2,320	1,160	808	2.30	720	359
Isodecyanol	86.2	34.0	96.7	65.8	11.2	3.74	30.0	8.56
Isooctyl alcohols	48.9	18.8	53.8	36.5	6.35	2.07	16.7	4.74
Isophthalic acid	119	5.84	59.5	68.8	15.5	0.64	18.4	8.94
Isoprene	264	19.9	202	234	34.4	2.18	62.7	30.4
Isopropyl alcohol	802	112	725	480	104	12.3	225	62.4
Maleic anhydride	13,500	1,803	10,300	647	17,500	198	3,190	841
Melamine resins	unknown							
Methanol	1,850	372	1,516	693	240	40.9	470	90.0
Methyl chloride	2,410	242	1,851	547	314	26.6	573	74.7
2-Methoxyethanol	10.4	1.00	4.75	5.51	1.35	0.11	1.47	0.72
Methylene chloride	294	7.65	70.4	41.6	38.3	0.84	21.8	5.41
Methyl ethyl ketone	98.5	117	137	65.7	12.8	12.9	42.5	8.54
Methyl isobutyl ketone	1,153	216	1,230	613	150	23.8	381	79.7
Methyl methacrylate	30,900	1,690	31,300	18,500	4,020	186	9,720	2,407
Naphthalene	19.4	3.30	15.6	18.1	2.52	0.36	4.85	2.36
Nitrobenzene	3,190	881	5,000	2,490	415	96.9	1,550	324
Nonyl phenol	6.97	1.05	4.97	5.76	0.90	0.12	1.54	0.74
Nylon 6 (resins and fibers)	1,410	685	1,047	900	184	75.4	324	117
Nylon 66 (resins and fibers)	3,530	830	2,620	2,250	460	91.3	811	293
n-Octyl-n-decylphthalate	152	9.91	101	116	19.9	1.09	31.2	15.2

TABLE A-2 (Continued)

WATER EFFLUENTS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Current Emissions (MT/yr) (BPCTCA)[1]				Potential Level of Control (MT/yr) (BATEA)[2]			
	Total Organics	BOD_5	COD	TOC	Total Organics	BOD_5	COD	TOC
Paint Manufacture	no data							
Pentaerythriol	23,900	2,370	20,700	16,300	3,100	261	6,418	2,120
Perchloroethylene	158	18.9	262	23.1	20.5	2.08	81.1	3.00
Phenol	258	760	3,240	197	33.5	83.6	1,000	25.6
Phenolic resins (and other tar resins)	15,600	2,570	12,900	11,100	2,020	283	4,000	1,449
Phosgene	192	4.29	20.3	23.6	25.0	0.47	6.30	3.06
Phthalic anhydride	6.04	7.77	83.9	3.90	0.78	0.85	26.0	0.51
Polyamid resins	no data							
Polybutadiene resins	929	54.0	930	801	121	5.93	288	104
Polychloroprene rubber	1,830	58.9	1,060	908	237	6.48	327	118
Polyester (resins and fibers)	7,060	682	4,550	3,920	918	75.0	1,410	510
Polyethylene								
low density	8,900	1,504	8,840	7,607	1,160	165	2,740	989
high density	405	156	402	346	52.7	17.1	125	45.0
Polyisobutylene-isoprene (Butyl) rubbers	390	23.9	412	355	50.7	2.63	128	46.1
Polyisoprene rubber	341	20.4	351	302	44.4	2.24	109	39.3
Polypropylene and copolymers	2,760	63.7	2,740	2,360	359	70.0	850	307
Polystrene and copolymers	1,620	271	1,750	1,500	212	29.8	542	196
Polyvinyl acetate	130	36.[illegible]	84.3	72.5	16.9	4.02	26.1	9.43

TABLE A-2 (Continued)

WATER EFFLUENTS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Current Emissions (MT/yr) (BPCTCA)[1]				Potential Level of Control (MT/yr) (BATEA)[2]			
	Total Organics	BOD_5	COD	TOC	Total Organics	BOD_5	COD	TOC
Polyvinyl chloride and copolymers	32,100	1,530	14,500	12,500	4,180	168	4,490	1,620
Printing inks	no data							
Propylene	2,290	486	3,730	1,960	298	53.5	1,160	255
Propylene glycol	1.29	4.74	37.4	0.61	0.17	0.52	11.6	0.08
Propylene oxide	11,400	3,015	31,600	7,061	1,480	332	9,790	917
Rayon	no data							
Soap and Detergent	no data							
Styrene	147	133	1,760	136	19.0	1.47	547	17.6
Styrene-butadiene rubber	9,230	579	9,570	8,241	1,200	63.7	2,970	1,070
Terephthalic acid	18,200	3,700	14,100	9,200	2,380	406	5,930	1,200
Tetraethyl and tetra-methyl lead	2,149	141	8,380	640	280	15.6	2,600	83.2
Toluene	23.5	6.59	50.4	21.4	3.06	0.72	15.6	2.78
Toluene diisocyanates	3,290	861	4,880	2,440	428	94.8	1,510	317
1,1,1 Trichloroethane	1,860	29.3	298	344	242	3.22	92.4	44.8
Trichloroethylene	1,370	21.5	219	253	178	2.37	67.9	32.9
Urea	21,500	266	3,720	4,302	2,800	40.2	1,153	559
Urea-formaldehyde resins	no data							
Vinyl acetate monomer	115	3.03	23.1	66.7	15.0	0.36	7.16	8.67
Vinyl chloride monomer	916	155	5,450	352	119	17.1	1,690	45.8
Vinylidene chloride	396	8.42	79.9	99.1	51.6	0.92	24.8	12.9

TABLE A-2 (Continued)

WATER EFFLUENTS FROM ORGANIC CHEMICAL PROCESSING IN METRIC TONS/YR

Product	Current Emissions (MT/yr) (BPCTCA)[1]				Potential Level of Control (MT/yr) (BATEA)[2]			
	Total Organics	BOD_5	COD	TOC	Total Organics	BOD_5	COD	TOC
m-Xylene and mixed xylenes	1.52	0.42	3.26	1.39	0.20	0.05	1.01	0.18
o-Xylene	3.29	0.92	7.05	2.99	0.43	0.10	2.18	0.39
p-Xylene	3.93	1.58	8.50	3.57	0.51	0.17	2.63	0.46

[1]Best practicable control technology currently available.
[2]Best available technology economically achievable