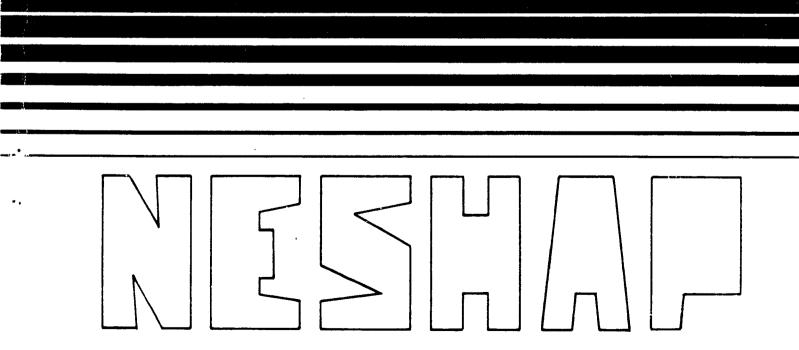
Office of Air Quality Planning and Standards Research Triangle Park NC 27711

EPA-450/3-88-003 October 30 1986

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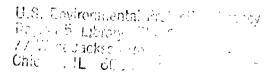


# Summary of Emissions Associated with Sources of Naphthalene



# Summary of Emissions Associated with Sources of Naphthalene

**Emission Standards Division** 



U.S. ENVIRONMENTAL PROTECTION AGENCY Office of Air and Radiation Office of Air Quality Planning and Standards Research Triangle Park, North Carolina 27711

October 30, 1986

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#### 1.0 INTRODUCTION AND SUMMARY

The purpose of this document is to identify and quantify, on a preliminary basis, all emission sources of naphthalene. These estimates will be used to estimate public exposure to naphthalene using EPA's human exposure model (HEM). Information used to assemble this document came from existing information sources, including previously published EPA documents and reports, general chemical and engineering references, current literature and periodicals, and State agency files. In addition, information was obtained through telephone conversations with State air pollution control personnel and/or visits to State agencies.

In most cases there was little information available for individual producers and users of naphthalene. The scope and purpose of this project did not allow, in many instances, the desired investigation or follow up to fill information gaps. Therefore, where information was not available, assumptions were made.

#### SUMMARY

There are 17 producers of crude and/or refined naphthalene in the U.S. Twleve of these producers are coke by-product recovery plants that may refine naphthalene or manufacture a coal tar product containing naphthalene. Two of the 17 producers use coal tar as a raw material to manufacture chemical-grade naphthalene, and three other producers use petroleum as a raw material to produce chemical-grade naphthalene.

Naphthalene is used primarily as an intermediate in the production of organic chemicals, including phthalic anhydride (mainly), carbamate insecticides, surface active agents, synthetic tanning agents, and miscellaneous organic chemicals. The only direct use of naphthalene is for moth repellant. Koppers in Follansbee, WV, which manufactures naphthalene from coal tar, is the only producer that uses some of the naphthalene it produces on-site for the production of an end-use chemical, namely, phthalic anhydride. All other producers sell naphthalene to various customers for the manufacture of other end-use chemicals.

Emission sources from the production and use of naphthalene are primarily from distillation unit vents, equipment leaks from pump seals

and flanges, and naphthalene storage tanks. Process emissions may be vented to a flare or other control device, although information was not usually available to indicate what emission controls, if any, are used. Total naphthalene process emissions from production and use are estimated to be about 85 Mg/yr. Fugitive emissions of naphthalene are approximately 43 Mg/yr, and total storage emissions of naphthalene are estimated to be about 84 Mg/yr. Naphthalene emissions to the atmosphere from all sources are about 213 Mg/yr. The largest contributors of naphthalene emissions are coke by-product recovery plants and naphthalene users, emitting about 38 and 35 percent of total naphthalene emissions, respectively. Naphthalene producers contribute about 25 percent of the total. Less than 3 percent of naphthalene emissions originate from combustion processes, primarily residential wood and coal heating.

#### 2.0 NAPHTHALENE PRODUCTION AND END USES

#### 2.1 INTRODUCTION

Naphthalene is produced from either coal tar or petroleum as raw materials. Approximately 55 percent of the total annual capacity of chemical-grade naphthalene is recovered from coal-tar-based feedstocks, while the remainder is from petroleum refinery streams. Crude naphthalene from coal tar may be produced at one of twelve coke by-product recovery plants in the U.S. Five U.S. companies currently produce chemical-grade naphthalene from either coal tar or petroleum at facilities operating with a total annual capacity of 184 gigagrams (Gg), based on a January 1985 estimate. In addition, two other companies, U.S.S. Chemicals and Ashland Chemical Company, have a total of three facilities to produce chemical naphthalene; however, all three are closed due to market conditions. 1,2

Since the early 1970's, naphthalene production as a whole has decreased at an average rate of about 3 percent per year, from 326 Gg in 1970 to 184 Gg in 1985. 1,3 The decline in naphthalene production primarily resulted from competition with ortho-xylene as the feedstock for phthalic anhydride, the major chemical derivative of naphthalene. 4 Since ortho-xylene is currently the preferred raw material for phthalic anhydride manufacture, only about one-fourth to one-third of phthalic anhydride produced in the United States is based on naphthalene feed.

#### 2.2 NAPHTHALENE PRODUCTION PROCESSES

#### 2.2.1 Naphthalene from Coal Tar

2.2.1.1 <u>Coke By-product Recovery Plants</u>. Coal-tar naphthalene may be recovered as a crude by-product from the coking of coal at some coke-oven by-product plants. Table 2-1 lists the twelve U.S. coke by-product recovery plants that handle and/or process naphthalene. Naphthalene, which is present as a constituent of coke oven gas, is removed from the gas stream after the coke oven gas leaves the ammonia adsorber. The naphthalene-containing gas is cooled in a tower scrubber (called a final cooler) by direct contact with water to condense most

Table 2-1. U.S. COKE BY-PRODUCT RECOVERY PLANTS HANDLING/PROCESSING NAPHTHALENE\*

Plant	Location	Coke Production Capacity (1,000 Mg/yr)
Empire Coke	Holt, AL	161
Republic Steel	Gadsden, AL	758
National Steel	Granite City, IL	570
Interlake	S. Chicago, IL	582
Indiana Gas & Chemical	Terre Haute, IN	132
U.S. Steel	Gary, IN	4,228
Rouge Steel Co.	Dearborne, MI	778
National Steel	Detroit, MI	1,397
Bethlehem Steel	Bethlehem, PA	2,253
Chattanooga Coke & Chemical	Chattanooga, TN	130
Lone Star Steel	Lone Star, TX	5 0 7
J&L Steel (LTV Steel)	Pittsburgh, PA	1,792

<sup>\*</sup>Reference 5.

of the naphthalene and any entrained tar and vapors, thus separating naphthalene from the gas stream before the gas is processed further. 6 The condensed naphthalene floats to the top of the water in the final cooler, is skimmed and collected in open sumps as an impure, yellow-brown slurry containing about 50 to 60 percent water. 5,7 Separation may be enhanced with a froth flotation separator or similar equipment. The naphthalene slurry may be pumped into a tank where water is removed by gravity separation, which crystallizes the product. The resulting crude naphthalene may be dissolved in coal tar after physical separation and sold as a commercial feedstock. A typical dry coal tar processed in the United States contains approximately 8 to 10 weight percent naphthalene. 4,8 Although crude naphthalene has little market value, about 40 percent of coke by-product recovery plants handle and/or process naphthalene in some manner.

If the crude naphthalene is further refined on-site, the crystallized product may be refined through drying when the crystals are melted in a separate rectangular tank equipped with coils for either cold water or steam circulation. After 24 hours in the vessel, an upgraded (chemical-grade) naphthalene (>78°C crystallization point) is generated. Figure 2-1 is a flow diagram of a final cooler and recirculating water circuit with naphthalene collected by physical separation at a typical coke by-product recovery plant that handles and/or processes naphthalene.

2.2.1.2 <u>Coal-tar Naphthalene Producers</u>. As discussed above, the naphthalene product that is dissolved in coal tar at coke by-product recovery plants may be sold as a commercial feedstock to companies that produce chemical-grade naphthalene as an intermediate product for various end uses. Coal-tar naphthalene accounts for about 55 percent of the total annual chemical naphthalene capacity. There are only two U.S. producers of chemical naphthalene in operation that use coal tar as a raw material, namely, Allied Chemical in Ironton, Ohio, and Koppers Company in Follansbee, West Virginia. These plants and their location and capacities are listed in Table 2-2.

Figure 2-2 depicts a general process for the production of chemical naphthalene from coal tar. To recover naphthalene from coal tar, the crude tar is distilled and fractionated. The crude coal tar is generally

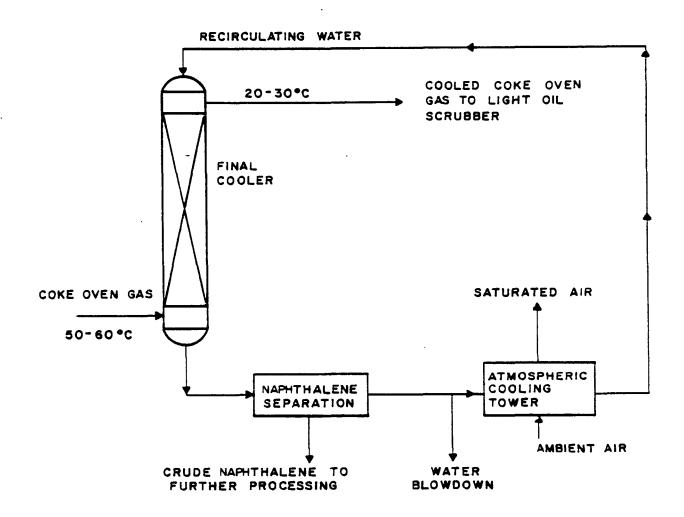


Figure 2-1. Final cooler with naphthalene separation.<sup>6</sup>

Table 2-2. CURRENT AND POTENTIAL U.S. NAPHTHALENE PRODUCERS AND CAPACITIES, 1985

Producer	Location	Capacity (Mg/yr)	Raw Material Used/Remarks
Coal-tar naphthalene			
Allied Chemical	Ironton, OHª	34,000 <sup>b</sup>	Coal tar/product is sold.
Koppers Co.	Follansbee, WV <sup>a</sup>	68,000 <sup>b</sup>	Coal tar/product is both sold and captively consumed.
U.S.S. Chemicals	Clairton, PAC Gary, INC	90,000 <sup>d</sup> ,e	Coal tar. Coal tar.
Petroleum naphthalene			
Chemical Exchange Industries (Advanced Aromatics Chemical Co.)	Baytown, TX <sup>a</sup>	14,000 <sup>b</sup>	Petroleum naphtha stream/ product is sold.
DuPont	Chocolate Bayou, TXª	41,000 <sup>b</sup>	Petroleum (ethylene by-product), product is sold.
Texaco Chemical	Delaware City, DEª	27,000b	Petroleum/product is sold.
Ashland Chemical	Ashland, KYC	41,000 <sup>d</sup>	Petroleum/product is sold.
Total capacity (plants ope	erating) coperating)	184,000 Mg/ 131,000 Mg/	•

<sup>&</sup>lt;sup>a</sup>Current producer - plant in operation, based on information obtained in Reference 1.

 $<sup>{\</sup>tt bSRI}$  International estimates as of January 1, 1985 (Reference 1).

Cplant not operating. This plant is on standby and can be restarted if market conditions warrant (Reference 9).

dEstimates as of October 1984 (Reference 2).

eCombined capacity for facilities in Clairton, PA, and Gary, IN.

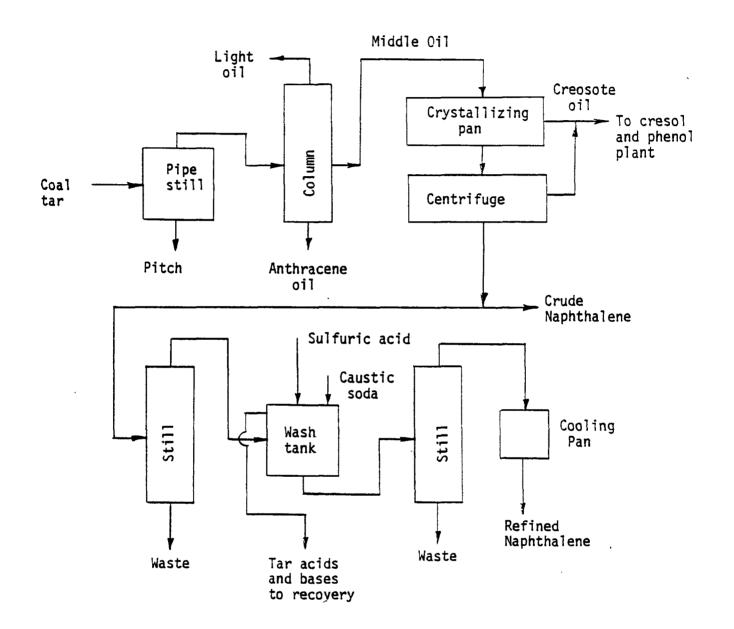


Figure 2-2. Naphthalene production from coal tar. 10

distilled in pipe stills in either a batch or continuous process. The tar is discharged into a flash tank from which the vapors pass to condensers; the still bottom and the pitch are sent to receiving tanks. If the total distillate is condensed, the distillate is fractionated in four fractions: light oil, middle oil, heavy oil, and anthracene oil. The middle oil fraction contains most of the naphthalene and tar acids.

The middle oil fraction, containing naphthalene, phenols, and cresols, is pumped hot into shallow pans where it is cooled, allowing the naphthalene to crystallize. After draining, the crystalline coke is then broken up and charged into batch centrifuges. The mother liquors are combined and sent to phenol and cresol recovery units. The naphthalene coke is washed with hot water to increase its purity before it is discharged as crude naphthalene. This material is suitable for phthalic anhydride manufacture and is graded and sold according to its melting point.

For refined naphthalene, the crude material is further distilled. The distillate is first washed with a hot caustic soda solution to remove phenolic compounds and then washed with concentrated sulfuric acid to remove basic substances. To yield a refined product, the washed naphthalene is redistilled. The distillate from the final still is either cast into forms or is cooled and subsequently crushed. The refined material is suitable for manufacture of flakes or pellets for insecticide use (i.e., mothballs or flakes). 10 However, the production of refined naphthalene from coal tar essentially has ceased in the United States due to costs of refining and costs of disposing significant amounts of waste sludge that is generated by the process. 4

#### 2.2.2 Naphthalene from Petroleum

There are three U.S. producers of naphthalene in operation that use petroleum as a raw material, namely, Chemical Exchange Industries, Baytown, Texas; duPont, Chocolate Bayou, Texas; and Texaco Chemical, Delaware City, Delaware. One potential producer, Ashland Chemical Co. in Ashland, Kentucky, is not currently operating, but may restart if market conditions warrant. These plants and their capacities are listed in Table 2-2.

The production of naphthalene from petroleum involves two principal steps. The first is the production of an aromatic fraction in the naphthalene-alkylnaphthalene boiling range, usually by hydroaromatization or cyclization. The second step is the dealkylation of the aromatic fraction either thermally or catalytically. The naphthalene that is produced is recovered as a high quality product, usually by fractional distillation. Suitable feedstocks may be the bottoms distilled from catalytic reformate or a narrow cut distilled and concentrated from refractory cycle oils. Figure 2-3 presents a general process used to produce petronaphthalene.

The feedstock and a hydrogen-rich gas are pumped to a dealkylation reactor. The reactor product is quenched and is then sent to a separator from which part of the hydrogen-rich gas is recycled and part burned as fuel. The liquid product is distilled to separate naphthalene, gasoline, and fuel oil. The naphthalene produced by this process is usually better than 99 percent pure and is low in sulfur content. Naphthalene may also be recovered from the stream of naphthalene-methyl naphthalene formed in the cracking of heavy liquids for ethylene production. 10

#### 2.3 NAPHTHALENE USAGE

Naphthalene is used almost exclusively as an intermediate in the manufacture of organic chemicals. The only direct use of naphthalene is as a moth repellant. The U.S. naphthalene consumption by end use (based on 1983 data) is presented in Table 2-3. Demand for naphthalene and consumption patterns are not expected to change significantly through 1988, according to October 1984 estimates.<sup>2</sup>

Naphthalene derivatives are numerous and can be classified as  ${\sf follows:}11$ 

Alkylnaphthalenes
Chlorinated naphthalenes
Hydrogenated naphthalenes
Naphthalenecarboxylic acids
Naphthalenesulfonic acids
Nitronaphthalenes and nitronaphthalenesulfonic acids
Naphthylamines

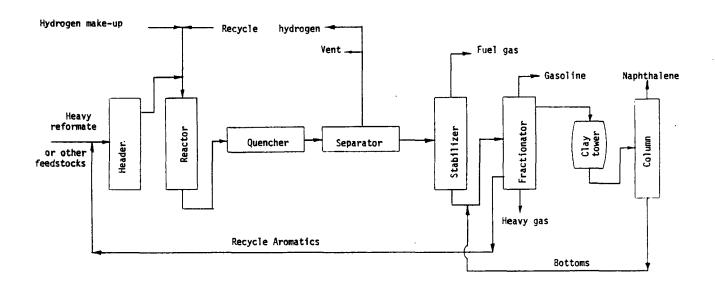


Figure 2-3. Production of naphthalene from petroleum fractions. 10

Table 2-3. U.S. NAPHTHALENE CONSUMPTION, 1983a

Use	Naphthalene consumption (Gg)	% of Total
Phthalic anhydride	233	74
Carbamate insecticides	23	7
Surface-active agents	23	7
Synthetic tanning agents	18	6
Moth repellent	13	4
Miscellaneous organic chemicals	5	2
2-naphthol	Ор	0
Total	315	100

aReference 9.

bAmerican Cyanamid, Willow Island, WV, the sole U.S. producer of 2-naphthol, ceased production in 1982 (Reference 9). All 2-naphthol consumed in the U.S. is now imported.

Aminonaphthalenesulfonic acids
Naphthols
Hydroxynaphthalenesulfonic acids
Aminonaphthols
Aminohydroxynaphthalenesulfonic acids

The three major uses of naphthalene, which represent 88 percent of naphthalene consumption, are as feedstocks for the production of phthalic anhydride, carbamate insecticides, and surface-active agents. The remaining 12 percent of naphthalene consumption is used in a variety of applications, including usage as a feedstock in the production of synthetic tanning agents, in moth repellant, and in the manufacture of miscellaneous organic chemicals. Figure 2-4 presents a general diagram of naphthalene use. A brief description of each of the major uses and its processes is presented below.

#### 2.3.1 Phthalic Anhydride

Seventy-four percent of naphthalene produced is consumed in the manufacture of phthalic anhydride. Phthalic anhydride is derived from one of two raw materials, naphthalene or ortho-xylene. For many years coal tar naphthalene was the only raw material used for phthalic anhydride production. However, ortho-xylene has gradually replaced naphthalene as the principal feedstock for phthalic anhydride manufacture; only about 25 to 35 percent of phthalic anhydride is derived from naphthalene. Koppers Company, Cicero, Illinois, operates the only naphthalene-based phthalic anhydride plant in the U.S., with an annual production capacity of 20,400 Mg. 12 Koppers shut down its Bridgeville, Pennsylvania, plant upon restarting its Cicero unit in 1985. The Cicero unit was idle while more than one-half of its capacity was converted from orthoxylene to naphthalene feedstock. Two other phthalic anhydride producers, Monsanto and USS, closed their New Jersey and Pennsylvania units in early 1986 and fall of 1983, respectively.

The phthalic anhydride plant at Koppers in Cicero, Illinois, is broken down into two operational areas, oxidation and refining. Each of these sections has a dedicated heat transfer oil system used to regulate temperature during the process. The facility can use either naphthalene or ortho-xylene as a raw material. 13

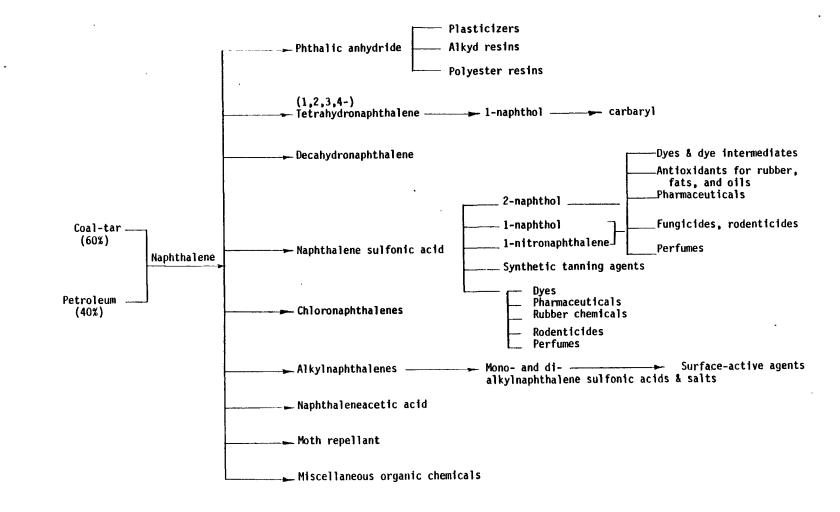


Figure 2-4. End uses of naphthalene. 14-16

The oxidation section consists of four production trains, two of which are deactivated. This operation is broken down into seven subsections: air compressing and heating, ortho-xylene and naphthalene feed systems, reaction and gas cooling, condensing, scrubbing and incineration, and Mobiltherm oil system. A diagram of the oxidation operation is presented in Figure 2-5(a). In the oxidation process, coal tar naphthalene and/or o-xylene is vaporized, mixed with air and fed to the reactors. The catalytic oxidation reactors convert the feedstock to phthalic acid and other by-products. Reactor off gases are cooled and sent to a bank of six switch condensers which capture and solidify the product. According to a preset cycle, one of the condensers is taken out of line and heated to melt out the crude acid which is then transferred to storage. Condenser off gases are then scrubbed using venturi and packed-bed scrubbers before release to the atmosphere. The phthalic anhydride section also has seven subsections consisting of crude storage, decomposing, predistillation, stripping, refining, refined storage and marlotherm heat transfer oil system. A diagram of the refining section is presented in Figure 2-5(b). Crude phthalic anhydride feed is sent to a series of four decomposers where some by-products are removed and the acid converted to phthalic anhydride. This then goes to predistillation where nonvolatile by-products are removed. Light ends are removed in the stripping and the product polished in the refining step. Phthalic anhydride (99.8 percent pure) is then sent to storage until sold or used in polyester production. 13

Approximately 50 percent of current phthalic anhydride production is used for plasticizers, 25 percent for alkyd resins, 20 percent for unsaturated polyester resins, and 5 percent for miscellaneous and exports. 17

#### 2.3.2 Carbamate Insecticides

The second largest use of naphthalene is as a raw material for the manufacture of carbarmate insecticides, of which carbaryl (Sevin®) is the most important. Carbaryl is used as a substitute for DDT and other chlorinated compounds that have become environmentally unacceptable. It is registered for use on about 70 crops and is used chiefly in the South and West. Union Carbide at Institute, West Virginia, is the only domestic producer of carbaryl. 1

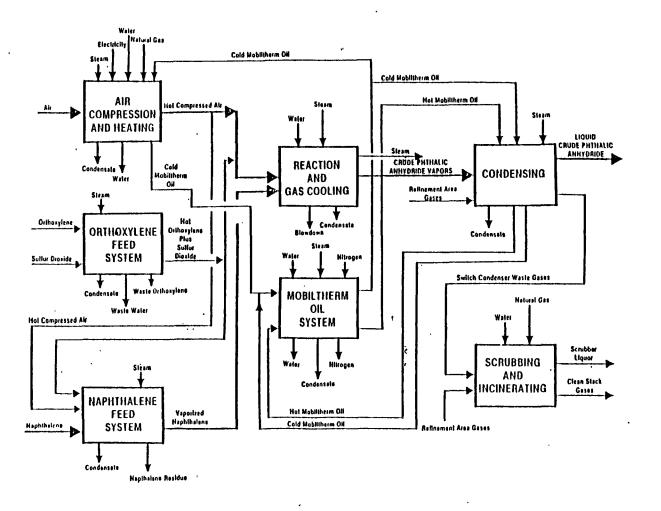


Figure 2-5(a). Flow diagram for oxidation process in production of phthalic anhydride.  $^{13}$ 

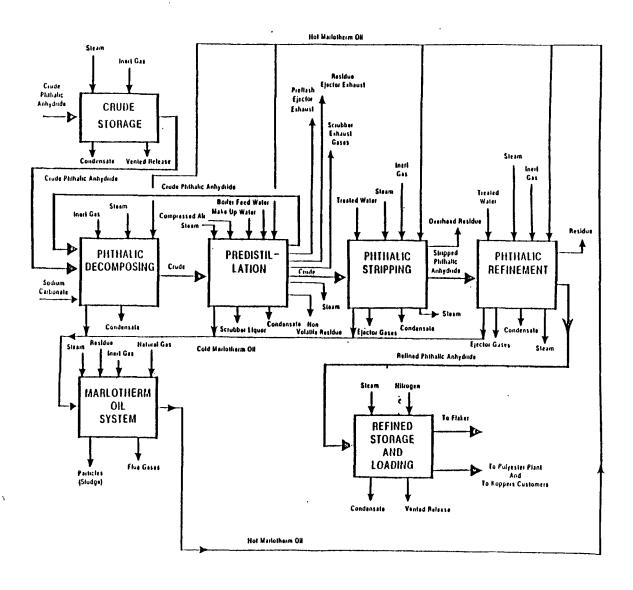


Figure 2-5(b). Flow diagram for refining process in production of phthalic anhydride.  $^{13}$ 

Crude or semirefined coal tar or petroleum naphthalene can be used for carbaryl manufacture. Production involves the following steps: (I) hydrogenation of naphthalene to produce 1,2,3,4-tetrahydro-naphthalene; (2) oxidation of this compound to produce 1-naphthol; and (3) reaction of 1-naphthol with methyl isocyanate to produce 1-naphthyl-n-methyl carbamate (carbaryl). Intermediate products of this process -- 1,2,3,4-tetrahydronaphthalene and 1-naphthol -- are also used as insecticides. Figure 2-6 depicts the production process for carbaryl.

#### 2.3.3 2-Naphthol

A third major use of naphthalene is for the manufacture of 2-naphthol (beta-naphthol or 2-naphthalenol). It is an intermediate primarily used in the manufacture of a variety of dyes or dye intermediates. Other applications include its use as insecticides; antioxidants for rubber, fats, and oils; and in the synthesis of fungicides, pharmaceuticals, and perfumes. American Cyanamid Company in Willow Island, West Virginia, the only U.S. producer of 2-naphthol, closed in 1982. All 2-naphthol consumed in the U.S. is now imported.

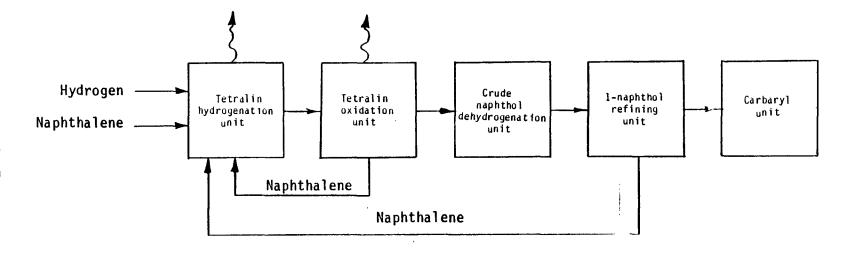
The production process uses high quality petroleum naphthalene as a feedstock, which is reacted with sulfuric acid. The sodium salt of the resulting 2-naphthalenesulfonic acid is treated with sodium hydroxide. The product is then distilled and sublimed. 9,19

#### 2.3.4 Synthetic Tanning Agents

Synthetic tanning agents (syntans) are primarily derivatives of 1- and 2-naphthalenesulfonic acids, their salts, and the sodium salts of the reaction products of the sulfuric acid and formaldehyde. 20 Approximately 6 percent of the U.S. naphthalene supply is consumed in the manufacture of these compounds. Synthetic tanning agents are used for both vegetable and chrome tanned leather. 19 Producers of synthetic tanning agents and their locations are listed in Table 2-4.

#### 2.3.5 Surface Active Agents (Naphthalenesulfonic acids)

Surface active agents (also known as surfactants) are naphthalenesulfonate compounds consisting primarily of 2-naphthalenesulfonic acid, its alkyl derivatives, and their salts. Naphthalene derivatives, however, represent a small portion (less than 0.5 percent) of the total production of surface active agents. The products are used as wetting



= Primary naphthalene emission point

 $_{\scriptscriptstyle \parallel}$  Figure 2-6. Flow diagram for carbaryl production using naphthalene. $^{21}$ 

Table 2-4. PRODUCERS OF SYNTHETIC TANNING AGENTS<sup>1</sup>, 18

Producer	Location
Morflex, Inc. (formerly Ciba-Geigy Dyestuff Division)	Greensboro, NC
Diamond Shamrock	Carlstadt, NJ Cedartown, GA
Georgia Pacific Corp.	Bellingham, WA
Rohm and Haas Co.	Philadelphia, PA

agents and dispersants in paints, dyes, pigments, coatings, polymerization emulsifiers, and concrete additives, as well as in a variety of pesticides and cleaner formulations. The application of naphthalenesulfonate compounds as surface active agents is expected to continue as a low-growth item; however, recent use of these products as concrete additives (i.e., plasticizers) may alter this pattern. These products, primarily from the sodium and calcium derivatives of naphthalenesulfonic acid, formal dehyde condensates, increase the flow of concrete without decreasing its strength.

Naphthalene sufonation leads to a mixture of products. When the process is controlled at less than about 100°C, 1-naphthalenesulfonic acid is predominantly produced. Sulfonation of naphthalene at above 150°C yields 2-naphthalenesulfonic acid as the main product. 11 At one time naphthalenesulfonic acid production technology included only batch operations but now emphasizes continuous processes, removal of excess sulfonating agent by stripping under vacuum, and the use of chlorosulfonic acid or sulfur trioxide to minimize the need for excess sulfuric acid. The improved analytical methods have contributed to the success of process optimization.

A schematic diagram of the main naphthalene sulfonation pathways is presented in Figure 2-7.

1-Naphthalenesulfonic acid. The sulfonation of naphthalene with excess sulfuric acid at less than 80°C gives some 1-naphthalenesulfonic acid, while the majority is 2-naphthalenesulfonic acid. 11 Older methods, however, have been replaced by methods which require less, if any, excess sulfuric acid. For example, sulfonation of naphthalene can be carried out in tetrachloroethane solution, followed by separation of the precipitated 1-naphthalenesulfonic acid; the filtrate can be reused as the solvent for the next batch.

1-naphthalenesulfonic acid can be converted to 1-naphthalenethiol by reduction of the related sulfonyl chloride; this product is used as a dye intermediate, and is converted by reaction with alkyl isocyanates, to S-naphthyl-N-alkylthiocarbamates which are used in pesticides and herbicides.

2-Naphthalenesulfonic acid. The standard manufacture of 2-naphthalenesulfonic acid involves the batch reaction of naphthalene

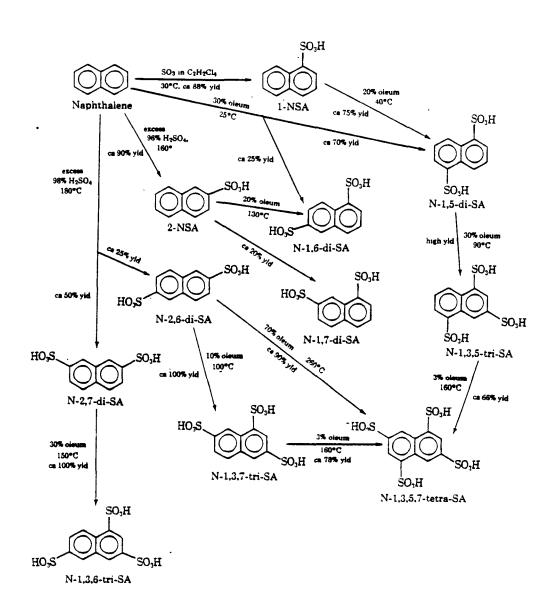


Figure 2-7. Selected paths to naphthalenesulfonic acids.  $^{11}$ 

Key: N = naphthalene
SA = sulfonic acid
yld = yield

with sulfuric acid at about  $160^{\circ}\text{C}$  for approximately 2 hours. The product contains the 1- and 2-isomers in about a 15/85 ratio. 11

Sulfonation can be conducted with a mixture of naphthalene and sulfuric acid with staged acid addition at 160°C over 2.5 hours to give a 93 percent yield of the desired product. Continuous monosulfonation of naphthalene with sulfuric acid in a cascade reactor at about 160°C gives 2-naphthalenesulfonic acid and small amounts of by-product naphthalenedisulfonic acids.

Alkylnaphthalenesulfonic acids and naphthalenesulfonic acid-formal-dehyde condensates. The alkylnaphthalenesulfonic acids can be made by sulfonation of alkylnaphthalenes, e.g., with sulfuric acid at 160°C, or by alkylation of naphthalenesulfonic acids with alcohols or olefins. 11 These products, as the acids or their sodium salts, are commercially important as textile auxiliaries, surfactants, wetting agents, dispersants, and emulsifying aids, (e.g., for dyes, wettable powder pesticides, tars, and clays). The sodium salts of the condensation products of naphthalenesulfonic acid with formaldehyde constitute the most important class of synthetic tanning agents for hides, which were discussed in Section 1.3.4. The naphthalenesulfonic acid-formaldehyde condensation products are also used as plasticizers for concrete, as stated earlier.

Release of naphthalene from the use of surface active agents occurs indirectly, possibly from their degradation. <sup>18</sup> Since 2-naphthalene-sulfonic acid hydrolyzes to naphthalene in the presence of steam, naphthalene detected in paint, textile, and ink discharge streams is most likely a degradation product formed when vats and tanks are cleaned by injecting steam. These industries use both surface active agents and naphthalene-containing dyes; it is difficult to determine from which product the naphthalene arises.

A partial listing of producers of surface active agents and their locations is given in Table 2-5.

#### 2.3.6 Moth Repellant

Moth repellant accounts for about 4 percent of the U.S. naphthalene consumption. The production of naphthalene-based moth repellant is decreasing, however, due to the availability of para-dichlorobenzene and the increased use of synthetic fibers. <sup>18</sup> Moth repellant is the only consumer product manufactured directly from naphthalene. The

Table 2-5. PRODUCERS OF SURFACE ACTIVE AGENTS FROM NAPHTHALENE DERIVATIVESa-c

Producer	Location	Chemical
Allied Chemical	Claymont, DE <sup>a</sup>	2-naphthalenesulfonic acid
American Cyanamid	Linden, NJ <sup>a</sup> Mariétta, OH <sup>b</sup>	1- and 2-Naphthalenesulfonic acids 2-naphthalenesulfonic acid
Ciba-Geigy	Toms River, NJ <sup>a</sup>	1-naphthalenesulfonic acid
Morflex, Inc.	Greensboro, NCª	1-naphthalenesulfonic acid
DeSoto, Inc.	Fort Worth, TXª	1- and 2-Naphthalenesulfonic acids
Diamond Shamrock	Carlstadt, NJ <sup>a,c</sup> Cedartown, GA <sup>a</sup>	<pre>1-naphthalenesulfonic acid 1-naphthalenesulfonic acid</pre>
DuPont	Deepwater, NJ <sup>a</sup>	1- and 2-Naphthalenesulfonic acids
Emkay Chemical Co.	Elizabeth, NJ <sup>a</sup>	1- and 2-Naphthalenesulfonic acids
Georgia Pacific	Bellingham, WA <sup>a</sup>	1-naphthalenesulfonic acid

aReference 22.

bReference 18.

<sup>&</sup>lt;sup>C</sup>Reference 23.

product is manufactured as a solid flake, powder, or ball, and repackaged for shipment. All of the naphthalene contained in moth repellant is emitted to the atmosphere.

There is one U.S. producer of moth repellant from naphthalene, Morflex, Inc. (formerly Ciba-Geigy), in Greensboro, NC. $^{23}$  Kincaid Enterprises in Nitro, WV, is believed to be shut down or no longer uses naphthalene in the production of moth repellant. $^{24}$ 

#### 2.3.7 Miscellaneous Uses

Approximately 2 percent of naphthalene consumption is used in the manufacture of various organic chemicals and intermediates. These chemicals, some of which are listed below, are produced in relatively small amounts and cannot be separately quantified. Process descriptions are not available for most of these compounds. Table 2-6 lists the miscellaneous chemicals and producers.

1-naphthol. 1-naphthol (1-naphthalenol, alpha-naphthol) is used as an intermediate in the manufacture of several agricultural chemicals, i.e., Carbaryl (Sevin®), napropamide (Stauffer's Devrinol®), and 1-naphthoxyacetic acid). 11 In addition, several drugs are derived from 1-naphthol. For example, the magnesium salt of 3- (4-methoxy -1-naphthoyl) propionic acid (Hepalande®) is used as a choleretic; propranolol (Inderal®) is an important adrenergic blocking agent used in the treatment of angina and cardiac arrhythmias; and 1-naphthyl salicylate (Aphol®) has been used as an antiseptic and antirheumatic.

l-naphthol is also used in the preparation of dyes and dye intermediates and as an antioxidant for gasoline. Some of its alkylated derivatives are stabilizers for plastics and rubber. It is an intermediate in the manufacture of synthetic perfumes.  $^{25}$ 

Union Carbide, the only U.S. producer of 1-naphthol, manufactures the chemical by the oxidation of 1,2,3,4-tetrahydronaphthalene (tetralin) in the presence of a metal catalyst to an intermediate product which is dehydrogenated and aromatized to 1-naphthol.  $^{11}$ 

1,2,3,4-tetrahydronaphthalene. This naphthalene derivative (also called Tetralin) is used as an insecticide and as a specialty solvent. It is a powerful solvent for oils, resins, waxes, rubber, asphalt, and aromatic hydrocarbons. Its high flash point and low vapor pressure make it useful in the manufacture of paints, lacquers, and varnishes;

Table 2-6. MISCELLANEOUS NAPHTHALENE DERIVATIVES AND PRODUCERS

Chemical	Producer	Location
Naphthalenols		
<ul><li>1-naphthol</li><li>Napropamide</li></ul>	Union Carbide <sup>a</sup> Stauffer Chemical Co. <sup>l</sup>	Institute, WV
1,2,3,4-tetrahydronaphthalene	DuPont <sup>a</sup> Union Carbide <sup>a</sup>	Deepwater, NJ Institute, WV
Decahydronaphthalene	DuPont <sup>a</sup>	Deepwater, NJ
Naphthaleneacetic acids	Rorer-Amchem <sup>b</sup>	d
• 1-naphthaleneacetic acid	Greenwood Chemical <sup>C</sup> Union Carbide <sup>C</sup>	Greenwood, VA Ambler, PA
Naphthylamines .		
<ul><li>1-naphthylamine</li><li>Naptalam</li></ul>	Sigma Chemical Co. <sup>e</sup> Uniroyal, Inc. <sup>c</sup>	St. Louis, MO Gastonia, NC
1-bromonaphthalene	RSA Corp.f	Ardsley, NY
Alkylnaphthalenes		
<ul><li>1-methylnaphthalene</li><li>methylnaphthalene</li></ul>	Chemical Exchange9 Koppers Co.9 Crowley Chemical9	Houston, TX Follansbee, WV Kent, OH
1-naphthaleneacetamide	Greenwood Chemical Co. <sup>C</sup> Union Carbide <sup>C</sup>	Greenwood, VA Ambler, PA
Chloronaphthalenesh,k	d	d
• Dichlone	Uniroyal, Inc.	d
Nitronaphthalenes		
<ul> <li>1-nitronaphthalene<sup>i</sup></li> <li>2-nitronaphthalene<sup>i</sup></li> </ul>	d d	d d
Nitronaphthalenesulfonic acids	Ciba-Geigy Corp.9	Toms River, NJ
Aminonaphthalenesulfonic acids <sup>i</sup>	d	d
Hydroxynaphthalenesulfonic acids <sup>†</sup>	d	d
Naphthalenecarboxylic acids <sup>i</sup>	<b></b> d	d

Table 2-6. MISCELLANEOUS NAPHTHALENE DERIVATIVES AND PRODUCERS (concluded)

Chemical .	Producer	Location
Anthraquinone <sup>h</sup>	d	d
Sebacic acid <sup>j</sup>	d	d

aReference 25.

bReference 26.

CReference 27.

d<sub>Not</sub> available.

eReference 23.

fReference 28.

9Reference 29.

hReference 20.

iReference 11.

jReference 30.

kReference 31.

<sup>1</sup>Reference 32.

for cleaning printing ink from rollers and type; in the manufacture of shoe creams and floor waxes; as a solvent in the textile industry; and for the removal of naphthalene deposits in gas-distribution systems.<sup>33</sup>

Tetrahydronaphthalene is produced by the catalytic treatment of naphthalene with hydrogen. Nickel or modified nickel catalysts generally are used commercially; however, they are sensitive to sulfur, and only naphthalene that has very low sulfur levels can be used. Thus, sodium treatment and catalytic hydrodesulfurization processes have been used to remove the sulfur from naphthalene; the latter treatment is preferred because of the hazardous nature of sodium treatment. 33

Decahydronaphthalene. Decahydronaphthalene (also called Decalin) is used as a solvent for resins and coatings. 26 It is produced commercially by the catalytic hydrogenation of naphthalene or 1,2,3,4-tetrahydronaphthalene. Decahydronaphthalene can be converted to naphthalene by heating with platinum, palladium, or nickel catalyst at 300°C.33

Naphthaleneacetic acid (naphthylacetic acid). This naphthalenederived chemical is used as a plant growth regulator to induce rooting of plant cuttings, as a germination suppressor for potatoes, and an intermediate for drug manufacture. 26,34 1-naphthaleneacetic acid (NAA®) can be produced by side-chain chlorination of 1-methyl-naphthalene to 1-chloromethylnaphthalene and formation of naphthaleneacetonitrile. 34 Alternatively, the chemical may be produced by the reaction of naphthalene with chloroacetic acid in the presence of potassium bromide as a catalyst. 32

Naphthylamines. Naphthylamines and their derivatives (e.g., 1-naphthylamine) are used in the manufacture of azo dyes, diazo components, and coupling components. 11 1-naphthylamine is a dye intermediate and is used as a raw material in the manufacture of rodenticides, insecticides, miticides, herbicides, and rubber antioxidants. 1-naphthylamine can be made from 1-nitronaphthalene by reduction with iron-dilute HCl, or by catalytic hydrogenation. Naptalam (Alanap®), a herbicide, is a derivative of 1-naphthylamine, prepared by reacting phthalic anhydride with 1-naphthylamine. 32

2-naphthylamine is recognized as a human carcinogen, producing bladder cancer from prolonged exposure.  $^{11}$  Therefore, this chemical is

no longer commercially produced or used in the U.S. It was used at one time in the production of dyes and rubber antioxidants.

<u>1-bromonaphthalene</u>. This is a specialty chemical used to calibrate refractometers.  $^{35}$  It is produced by mixing sodium bromate and water with naphthalene at room temperature. It is usually batch produced (as needed) in relatively small quantities (50 to 250 kg).

Alkylnaphthalenes. Methyl- and dimethylnaphthalenes are contained in coke-oven tar and in certain petroleum fractions in significant amounts. A methylnaphthalene-rich fraction is usually extracted and used as solvents for pesticides, sulfur, and various aromatic compounds. They can also be used as low freezing, stable heat-transfer fluids. Mixtures rich in monoethylnaphthalene content have been used as dye carriers for color intensification in the dyeing of synthetic fibers. They also are used as the feedstock to make naphthalene in dealkylation processes. Phthalic anhydride can also be made from methylnaphthalene mixtures by an oxidation process that is similar to the one used for naphthalene.<sup>34</sup>

A mixed monomethylnaphthalene-rich material can be produced by distillation and can be used as feedstock for further processing. By cooling this material to about  $0^{\circ}\text{C}$ , an appreciable amount of 2-methylnaphthalene crystallizes leaving a mother liquor consisting of about equal quantities of 1- and 2-methylnaphthalene. Pure 2-methylnaphthalene is used primarily as a raw material for the production of vitamin K preparations. 34

·1-methylnaphthalene can be used as a general solvent because of its low melting point. It also is used as a test substance for the determination of the cetane number of diesel fuels. In addition, as described earlier, 1-methylnaphthalene is used in the production of 1-naphthaleneacetic acid, a plant growth regulator and an intermediate for drug manufacture. 34

<u>1-naphthaleneacetamide</u>. This naphthalene derivative is used as a pesticide. Two producers of the compound were identified, Greenwood Chemical Company, Greenwood, VA, and Union Carbide, Ambler,  $PA.^{30}$  However, no information on the chemical, including process descriptions, was available in state permit files. $^{36},^{37}$ 

Chloronaphthalenes. There are 77 possible chloronaphthalenes, but not all are known or precisely identified materials. 31 Some past commercial uses of this class of compounds have included electrical insulating materials (mixtures containing tri- to hexachloronaphthalene) and fungicides, algicides, bactericides, and colorants for plastics (from mixtures containing octachloronaphthalene). Technical octochloronaphthalene has been recommended as an additive in grinding—wheel media and cutting—oil coolants. Monochloronaphthalene and mixtures of mono— and dichloronaphthalene have been used or recommended for chemical—resistant gage fluids and instrument seals, as heat exchange fluids, high—boiling specialty solvents, for color dispersions, as engine crank case additives to dissolve sludges and gums, and as ingredients in motor tuneup compounds. In addition, monochloronaphthalene has been used as a raw material for dyes and as a wood preservative with fungicidal and insecticidal properties.

One example of a dichloronaphthalene is dichlone (Phygon®), a fungicide.<sup>32</sup> Dichlone may be manufactured by chlorinating 1,4-naphthoquinone in a single step in the presence of a catalyst at a temperature of 80-120°C. Alternatively, naphthalene may be used as the starting material. The chlorination of naphthalene produces a chlorinated tetrahydronaphthalene intermediate, which is hydrolyzed and then oxidized by nitric acid to a chlorinated naphthaquinone, which is further chlorinated to the final product.

The trichloronaphthalenes and higher products have been used as impregnants for condensers and capacitors as well as dipping compounds in electronic and automotive applications; as temporary binders in the manufacture of ceramic components; in paper coating and impregnation; in precision casting of alloys; in electroplating stop-off compounds; as additives in gear oils and cutting compounds; as flame retardants; as moisture-proof sealants; and as separators in batteries.

Chlorinated naphthalenes are currently used only as refractive index oils and as impregnants for capacitors.<sup>38</sup> Refractive index oils are produced by mixing monochloronaphthalene with mineral oils to yield testing oils with various high refractive indices. These refractive index oils are used in small amounts during the preparation of slides

for observation in crime and petrographic laboratories. Chloronaphthalenes are still used in some capacitors, primarily for military applications.

Commercial chloronaphthalenes are manufactured by the metal halide-catalyzed chlorination of molten naphthalene to the desired chlorination stage at a temperature slightly above the melting point of the desired product. The hydrogen chloride produced in the reaction must be treated when used for hydrochloric acid manufacture due to the possible presence of unreacted chlorine and entrained or vaporized organics. Crude chloronaphthalenes are treated with soda ash or caustic soda, fractionated under reduced pressure, and purified with activated clay.

Since the 1920's the use of chlorinated naphthalenes has declined steadily. Domestic production of chloronaphthalenes ceased in 1980. 38 Only about 13.6 Mg of these compounds are imported and processed annually, the largest percentage of which (about 70 percent) is for use in refractive index oils. The decline of chloronaphthalenes in the U.S. has been attributed to rising costs, competing products, shifting markets, and increasingly stringent industrial health and safety regulations.

Certain manufacturers and importers of 19 chlorinated naphthalenes are required under Section 8(a) of the Toxic Substances Control Act, 15 U.S.C. 2607(a), to notify EPA of current and prospective manufacture or import of the compound. 38 The rule requires current and prospective manufacturers and importers to notify EPA of any current or prospective manufacture or import of chlorinated naphthalenes. The notice must state whether a person is manufacturing these compounds, or is importing or is proposing to import chloronaphthalenes. Reporting requirements include information on intended or expected uses, production quantities, chemical composition, and wastes.

Nitronaphthalenes. Many of the nitronaphthalene compounds are not formed by direct nitration of naphthalene but are made by indirect methods, such as nitrite displacement of diazonium halide groups in the presence of a copper catalyst, decarboxylation of nitronaphthalene-carboxylic acids, or decontamination of nitronaphthalene amines. 11

1. 1-nitronaphthalene. This compound has been used as a deblooming agent for petroleum and oils, for the manufacture of dyes

and intermediates, and as a component of commercial explosives.  $^{11}$  1-nitronaphthalene is important for the manufacture of 1-naphthylamine. It is manufactured by nitrating naphthalene with nitric and sulfuric acids at  $40\text{--}50^{\circ}\text{C}$ .

2. <u>2-nitronaphthalene</u>. This naphthalene derivative is present in 1-nitronaphthalene (about 3-10 percent by weight). It is metabolized to the carcinogenic 2-naphthylamine in the human body. <sup>11</sup> In making this compound as a by-product, respirators, protective clothing, proper engineering controls, and medical monitoring programs for workers should be used.

Nitronaphthalenesulfonic acids. These chemicals are primarily used in the preparation of dye intermediates. Nitronaphthalenesulfonic acids are prepared by sulfonization of 1-nitronaphthalene with oleum at a low temperature. 11

Aminonaphthalenesulfonic acids. Many of these naphthalene derivatives are used in the manufacture of azo dyes or used to make intermediates for azo acid dyes, direct, and fiber-reactive dyes. The aminonaphthalenesulfonic acids are generally made by either sulfonation of naphthylamines, nitration-reduction of naphthalenesulfonic acids, amination of naphtholsulfonic acids, or desulfonation of aminonaphthalene di- or tri-sulfonic acid.

Hydroxynaphthalenesulfonic acids. Hydroxynaphthalenesulfonic acids are important as intermediates either for coupling components for azo dyes or azo components and for synthetic tanning agents. Hydroxynaphthalenesulfonic acids can be manufactured either by sulfonation of naphthols or hydroxynaphthalenesulfonic acids, by acid hydrolysis of aminonaphthalenesulfonic acids, by fusion of sodium naphthalenepolysulfonates with sodium hydroxide, or by desulfonation or rearrangement of hydroxynaphthalenesulfonic acids.

Naphthalenecarboxylic acids. These compounds are generally used as intermediates for azo dyes, pigments, and synthetic tanning agents. 11 The 1- and 2-naphthalenecarboxylic acids are prepared readily by the oxidation of 1- or 2-alkylnaphthalenes with dilute nitric acid, chromic acid, or permanganate. Some of these acids are useful as herbicides, plant growth regulators and insecticides. Tetrahydrozoline (Visine®, Tysine®), a nasal decongestant, is a derivative of these acids.

Anthraquinone. One new use of naphthalene that could potentially be produced in significant quantities is the manufacture of anthraquinone. It is used as a dyestuff intermediate and in the wood pulp industry. In addition, a by-product of anthraquinone is phthalic anhydride. At present, almost all anthraquinone worldwide is made by the oxidation of anthracene, an expensive chemical recovered from coal tar. The first attempt (joint venture of Bayer and Ciba-Geigy) to operate the world's first naphthalene-based anthraquinone plant (in Japan) failed, however, due to clogging of a scaled-up commercial unit. 39 After considering process changes that would have required 3 more years of study and a costly new investment, the company closed the plant and planned to use the equipment elsewhere.

In the process, coal-tar naphthalene is oxidized with air to naphthoquinone and phthalic anhydride using a vanadium oxide catalyst. 20 Without prior separation, the naphthoquinone reacts with butadiene to form tetrahydroanthroquinone, which is dehydrogenated to anthraquinone. Subsequent separation and purification yield the main product, anthraquinone, and phthalic anhydride as a by-product. This naphthalene-based process is more economical than the conventional anthracene-based process, reducing production costs by 50 percent because of lower feedstock costs despite more complex processing and a higher investment than the conventional process. 20,39

Sebacic acid. Another potential market for naphthalene may be in the production of sebacic acid. The process uses naphthalene as a raw material along with hydroperoxide. 30 Decalin hydroperoxide (HPO) is obtained by autoxidation, and the cleavage reaction of HPO and subsequent dehydration reaction results in 5-cyclodecen-1-one. By reducing and reoxidizing it, sebacic acid is produced. A Japanese chemical company has applied for a patent for this new industrial process for manufacturing sebacic acid. Sebacic acid is used in high-quality plasticizers, engineering plastics, etc. Other methods have been proposed to synthesize sebacic acid from naphthalene, but these processes have either caused problems in operation and equipment or have been unable to manufacture sebacic acid on an industrial scale.

## 3.0 NAPHTHALENE EMISSION SOURCES AND ESTIMATES

This chapter discussed the types of emission sources that release naphthalene to the environment and also presents estimates of naphthalene emissions to the atmosphere. Section 3.1 describes the general types of emission sources (process, fugitive, and storage) of naphthalene. Section 3.2 discusses naphthalene emissions to the atmosphere from production and various end uses; Section 3.3 presents estimates of naphthalene discharged to water; and Section 3.4 discusses solid waste impacts from naphthalene.

#### 3.1 NAPHTHALENE EMISSION SOURCES

Naphthalene emissions may be released to the environment from numerous sources. As discussed in Section 2.2.1.1, naphthalene emissions from coke by-product recovery plants originate primarily from naphthalene separation and handling in open sumps and naphthalene melting/drying tanks. The bulk of naphthalene emissions to the atmosphere from production processes is expected from distillation unit vents, pump seals and flanges, and naphthalene storage tanks.<sup>40</sup> For processes that use a catalyst, catalyst decoking operations can be expected to release particulates that may contain naphthalene. In addition, waste streams resulting from cooling water treatment may contain naphthalene. Spent catalyst and acid-treated clay used in purification may also contain traces of naphthalene, and these solid wastes are usually land disposed.

Little or no information is available on naphthalene emission sources from the production of phthalic anhydride, carbamate insecticides, or other naphthalene derivatives. The major contributor of phthalic anhydride emissions from the naphthalene-based process is the reactor and condenser effluent, which is vented from the condenser unit. Other emision sources of the naphthalene-based phthalic anhydride process include the control catalyst and product storage in the liquid phase. Naphthalene storage emissions are small and are presently not controlled.

In addition, there are emissions from "inadvertent" sources such as combustion sources, largely due to residential wood and coal heating,

and aquatic discharges from cooling water treatment and various industries, including wood preserving, paint, ink, and textile. $^{10,41}$ 

#### 3.2 AIR IMPACTS

## 3.2.1 Emissions from Handling and Production of Naphthalene

Only crude estimates of naphthalene from production sources are available from the literature. According to one source, nationwide production of naphthalene accounted for approximately 34 Mg annually (1976 estimate) to the atmosphere, which may be attributed primarily to distillation unit vents (process emissions), leaks from pump seals (fugitive emissions), and flanges. 10 Other estimates indicate that 40 Mg of naphthalene are released annually to the atmosphere (1975 estimate). 41

This section presents estimated atmospheric emissions from the handling and production of naphthalene based on limited data from State permit files and from January 1985 production capacity estimates from Reference 1. Table 3-1 summarizes process, fugitive, and storage emissions of naphthalene from coke by-product recovery plants that handle and/or process crude naphthalene. Approximately 80 Mg/yr of naphthalene are emitted to the atmosphere from coke by-product recovery plants that process crude naphthalene. Table 3-2 summarizes process, fugitive, and storage emissions of naphthalene from the five current U.S. producers of chemical-grade naphthalene. Naphthalene emissions from the production of chemical-grade naphthalene are about 50 Mg/yr. Appendix A, Sections A.2 and A.3, presents the methods and assumptions used to estimate emissions from coke by-product plants and naphthalene production facilities, respectively. Appendix B includes a memorandum describing two procedures for estimating naphthalene emissions specifically from coke by-product plants. The procedure that was selected is included in Appendix A.

## 3.2.2 Emissions from Naphthalene End Uses

Naphthalene emissions to the atmosphere originate from its uses in the manufacture of phthalic anhydride, carbamate insecticides, synthetic tanning agents, moth repellant, surface active agents, and miscellaneous organic chemicals. In the manufacture of phthalic anhydride and miscellaneous organic chemicals, it has been reported that naphthalene may be emitted to the atmosphere from leaks in column vents, pump seals, and flanges.<sup>42</sup>

TABLE 3-1. NAPHTHALENE EMISSIONS FROM COKE BY-PRODUCT RECOVERY PLANTS

Plant <sup>a</sup>	Location	Emissions Process	by Type (kg, Fugitive	/yr) <sup>b</sup> Storage	Plant Total (kg/yr)
Empire Coke	Holt, AL	330	330	330	1,000
Republic Steel	Gadsden, AL	1,700	1,700	1,700	5,000
National Steel	Granite City, IL	1,000	1,000	1,000	3,000
Interlake	S. Chicago, IL	1,000	1,000	1,000	3,000
Indiana Gas & Chemicals	Terre Haute, IN	330	330	330	1,000
U.S. Steel	Gary, IN	10,000	10,000	10,000	30,000
Rouge Steel	Dearborne, MI	1,600	1,600	1,600	5,000
National Steel	Detroit, MI	2,700	2,700	2,700	8,000
Bethlehem Steel	Bethlehem, PA	3,300	3,300	3,300	10,000
Chattanooga Coke & Chemicals	Chattanooga, TN	330	330	330	1,000
Lone Star Steel	Lone Star, TX	1,000	1,000	1,000	3,000
J&L Steel (TLV Steel)	Pittsburgh, PA	3,300	3,300	3,300	10,000
	TOTAL	26,600	26,600	26,600	80,000

aReference 5.

<sup>&</sup>lt;sup>b</sup>See Appendix A, Section A.2, for discussion of the method used to estimate emissions from handling and/or processing crude naphthalene at coke by-product recovery plants.

Table 3-2. NAPHTHALENE EMISSIONS FROM PRODUCTION OF CHEMICAL-GRADE NAPHTHALENE\*

Plant	Location		s by Type Fugitive		Plant Total
Coal-Tar Naphthalene					
Allied	Ironton, OH	8,100	580	770	9,450
Koppers Co.	Follansbee, WV	19,300	580	1,540	21,420
Petroleum Naphthalene					
Chemical Exchange Industries	Baytown, TX	3,300	340	320	3,960
DuPont	Chocolate Bayou, TX	9,800	340	930	11,070
Texaco Chemical	Delaware City, DE	6,400	340	610	7,350
	TOTAL	46,900	2,180	4,170	53,200

<sup>\*</sup>See appendix A, Section A.3, for discussion of the method used to estimate emissions.

This section presents estimates of process, fugitive, and storage emissions from naphthalene end uses based on an apportioning technique and limited data from State permit files. A discussion of the methods and assumptions used to calculate these emissions is presented in Appendix A, Sections A.4 through A.10. Table 3-3 summarizes process, storage, and fugitive emissions from production of naphthalene end use compounds. Total naphthalene emissions from production of these compounds are about 75 Mg/yr.

# 3.2.3 Naphthalene Emissions from "Inadvertent Sources"

No estimates are available for atmospheric naphthalene emissions from inadvertent sources, such as combustion processes. One report indicates, however, that combustion sources account for most of the annual atmospheric emissions of naphthalene (5,100 Mg), primarily attributed to residential wood and coal heating. 43 Other inadvertent sources, such as wood preserving, paint, ink, and textile industries use naphthalene-containing products (i.e., creosote, dyes, surface active agents), release traces of naphthalene to waste streams instead of to the atmosphere. 44

## 3.2.4 Naphthalene Emission Summary

Total naphthalene emissions from all sources (i.e., coke by-product recovery, naphthalene production, naphthalene end uses, and inadvertent sources) are approximately 213 Mg/yr. This emission summary is presented in Table 3-4.

#### 3.3 WATER IMPACTS

Only crude estimates of naphthalene discharges to water are available from the literature. Annual discharges from naphthalene production are estimated to be 4.5 Mg, primarily from coal tar production (extraction and wash tank effluents), distillation, and water treatment.  $^{10}$ ,  $^{43}$ ,  $^{45}$  Large amounts of naphthalene discharged to surface waters are expected to volatize to the atmosphere and, to a lesser extent, removed to the sediment by adsorption.  $^{43}$ 

The only available estimate of water impacts from naphthalene end uses is for its use as carbamate insecticides, from which 2640 Mg of naphthalene is discharged (1976 estimate). Water impacts from other naphthalene uses are expected to be negligible (i.e., less than 1 Mg per year), based on EPA descriptions of waste treatment practices and EPA

Table 3-3. NAPHTHALENE EMISSIONS FROM MAJOR USERSa

Naphthalene End-Use Compound	Plant	Location		s by Type Fugitive		Plant Total (kg/yr)
Phthalic anhydride	Koppers	Cicero, IL	0	8,470	46,300	54,770
Carbamate insecticides	Union Carbide	Institute, WV	1,402	1,250	1,905	4,557
2-naphthol	American Cyanamid	Willow Island, WV	Ор	Oρ	Ор	ეი
Synthetic tanning agents	Morflex, Inc.	Greensboro, NC	430	430	430	1,300
from 1- and 2-naphthalenesulfonic acids)	Diamond Shamrock	Carlstadt, NJ Cedartown, GA	430 430	430 430	430 430	1,300 1,300
	Georgia Pacific	Bellingham, WA	430	430	430	1,300
	Rohm & Haas	Philadelphia, PA	430	430	430	1,300
	Subtotal Synthetic Ta	2,130	2,130	2,130	6,400	
Surface active agents						
-naphthalenesulfonic acid	American Cyanamid	Linden, NJ	41	41	41	120
1-NSA)	Ciba-Geigy	Toms River, NJ	41	41	41	120
	DeSoto, Inc.	Fort Worth, TX	41	41	41	120
	Diamond Shamrock	Carlstadt, NJ	41	41	41	120
	Diamond Shamrock	Cedartown, GA	41	41	41	120
	duPont	Deepwater, NJ	41	41	41	120
	Emkay Chemicals	Elizabeth, NJ	41	41	41	120
	Morflex, Inc.	Greensboro, NC	41	41	41	120
	Georgia Pacific	Bellingham, WA	41	41	41	120
	Subtotal 1 - NSA		370	370	370	1,100
2-naphthalenesulfonic acid	Allied Chemicals	Claymont, DE	350	350	350	1,050
(2-NSA)	American Cyanamıd	Marietta, OH	350	350	350	1,050
	American Cyanamid	Linden, NJ	350	350	3 <b>5</b> 0	1,050
	DeSoto, Inc.	Fort Worth, TX	350	350	350	1,050
	duPont	Deepwater, NJ	350	350	350	1,050
	Emkay Chemicals	Elizabeth, NJ	350	350	350	1,050
	Subtotal 2 - NSA		2,100	2,100	2,100	6,300

Table 3-3. NAPHTHALENE EMISSIONS FROM MAJOR USERS<sup>a</sup> (concluded)

Naphthalene End-Use Compound	Plant	Location	Emissions Process F			Plant Total (kg/yr)
Moth repellant	Morflex, Inc. Kincald Enterprises	Greensboro, NC Nitro, WV	0q 0c	0q 0c	Oq Oc	0c
Miscellaneous Chemicals						
l-naphthol	Union Carbide	Institute, WV	Оe	0 <b>e</b>	0e	ეe
1,2,3,4-tetrahydronaphthalene (tetralin)	DuPont Union Carbide	Deepwater, NJ Institute, WV	50 Of	50 Of	50 Of	150 0f
Decahydronaphthalene (decalin)	DuPont	Deepwater, NJ	50	50	50	150
l-naphtnaleneacetic acid	Greenwood Chemical Union Carbide	Greenwood, VA Ambler, PA	0 <b>9</b> 50	09 50	09 50 .	09 150
l-naphthylamine	Sigma Chemical Co.	St. Louis, MO	50	50	50	150
Naptalam	Uniroyal, Inc.	Gastonia, NC	50	50	50	150
1-bromonaphthalene	RSA Corp.	Ardsley, NY	0.13	0.13	0.13	0.4
l-methylmaphthalene	Chemical Exchange	Houston, TX	50	50	50	150
methylnaphthalene	Koppers Co. Crowley Chemical Crowley Chemical	Follansbee, WV Kent, OH Oklahoma City, OK	50 0h 01	50 Oh O¹	50 50 50	150 50 50
l-napnthaleneacetamide	Greenwood Chemical Co. Union Carbide	Greenwood, VA Ambler, PA	09 50	09 50	09 50	09 150
Nitronaphthalenesulfonic acids	Ciba-Geigy Corp.	Toms River, NJ	50	50	50	150
	Subtotal Miscellaneous	Chemicals	450	450	550	1,450
	Total Naphthalene Emis End-Use Compounds	sions from all	6,450 1	4,800	53,400	74,600

NOTE: Totals may not sum due to rounding.

# TABLE 3-3. NAPHTHALENE EMISSIONS FROM MAJOR USERSa (concluded)

### **FOOTNOTES**

<sup>a</sup>See Appendix A for discussion of procedures used to calculate emissions from production of each naphthalene end-use compound.

b2-naphthol is no longer produced in the U.S. All 2-naphthol consumed in the U.S. is now imported (Reference 9). American Cyanamid closed its Willow Island, WV, facility in mid-1982 (Reference 46). When it was in operation, 1981 emissions of naphthalene were reported to be about 17 Mg/yr (Reference 47).

CNaphthalene emissions from production and handling of moth repellant at Morflex, Greensboro, NC, are included in estimates for general production of naphthalene (Table 3-2). The product is made directly from the production of naphthalene at one of the five naphthalene producers in Table 3-2 as a solid flake, powder, or ball, and is then usually repackaged as a consumer product at another facility (Reference 17, p. 26). PES assumes that the Morflex facility only repackages the naphthalene product that is already manufactured in a crystallized form by one of the naphthalene producers. Therefore, no emissions of naphthalene are expected from the facility.

dBased on information from the West Virginia Air Pollution Control Commission that the facility is either no longer in production or does not use naphthalene to make moth repellant (References 24 and 48), PES assumes no emissions of naphthalene from Kincaid Enterprises.

eEmissions of naphthalene from 1-naphthol production at Union Carbide, Institute, WV, are included in naphthalene emissions from carbaryl production (Reference 21): process emissions from 1-naphthol production = 0.82 kg/yr; fugitive emissions = 249 kg/yr; and storage emissions = 17.3 kg/yr. Total naphthalene emissions from 1-naphthol production = 270 kg/yr.

fEmissions of naphthalene from tetralin production (tetralin hydrogenation and oxidation) at Union Carbide, Institute, WV, are included in naphthalene emissions from carbaryl production (Reference 21): process emissions = 1,400 kg/yr; fugitive emissions = 963 kg/yr; and storage emissions = 1,844.7 kg/yr. Total naphthalene emissions from tetralin production = 4,207.7 kg/yr, or 4.2 Mg/yr, which represents 92% of total emissions from carbaryl production.

9No longer in operation due to explosion and fire destroying facility in April 1985; no plans to rebuild (Reference 49).

hStorage emissions only (Reference 50).

<sup>1</sup>Storage emissions only (Reference 51).

TABLE 3-4. SUMMARY OF NAPHTHALENE EMISSIONS FROM ALL SOURCES

Emission Source	Source T Process	otal by Type Fugitive	, Mg/yr Storage	Source Total, Mg/yr
Coke by-product recovery	26,6	26.6	26.6	79.8
Naphthalene production				
Coal tar Petroleum	27.4 19.5	1.16 1.02	2.31 1.86	30.8 22.4
Naphthalene end uses	6.5	14.8	53.4	74.6
Inadvertent sources*	5.1			5.1
Total All Sources	85.4	43.0	84.2	212.7

NOTE: Totals may not sum due to rounding.

<sup>\*</sup>Naphthalene emissions from combustion processes, primarily residential wood and coal heating (Reference 43). For the purposes of this analysis, these emissions are classified as process emissions.

effluent guidelines.  $^{18}$  Discharges to POTW's are estimated to be about 2 Mg (1976 and 1979 estimates) from the leather tanning industry.  $^{18,52}$  Less than 0.1 Mg is directly dicharged from this industry (1979 estimate).  $^{18}$  These direct dischargers treat wastewater streams primarily by activated sludge or aerated lagoons.

Traces of naphthalene contained in creosote, dyes, surface active agents, etc. have also been detected in wastewater streams from "inadvertent" sources, such as the woodpreserving, paint, ink, and textile industries. Detection in these waste streams is most likely attributed to the degradation of these compounds. An Naphthalene losses to water from oil spills represents another "inadvertent" source. An estimated 12 Mg (1976 estimate) of naphthalene was reported to be released to the aquatic environment through crude oil spills. 53

#### 3.4 SOLID WASTE IMPACTS

Solid waste from naphthalene production originates from spent catalyst, acid treated clay (from petroleum purification processes), process sludge, and onsite wastewater treatment sludge.  $^{40}$ ,  $^{45}$  An estimated 32 Mg of naphthalene is generated as solid waste from production processes.  $^{10}$ 

Solid waste generated from naphthalene end uses is estimated to be 20,240 Mg (1976 estimate).  $^{26}$  Some solid waste containing traces of naphthalene is expected to originate from process purification activities.  $^{42}$ 

No estimates are available for solid waste generated from "inadvertent" sources of naphthalene. However, an estimated 5 Mg (1976 estimate) of naphthalene is reported lost to the land from crude oil spills.<sup>53</sup>

# 4.0 REGULATIONS AFFECTING THE ENVIRONMENTAL RELEASE OF NAPHTHALENE

Two environmental regulations are known to be in effect specifically to control emissions of naphthalene derivatives. The Toxic Substances Control Act specifies certain reporting and recordkeeping requirements for current and future production or import of chloronaphthalene compounds. In addition, emissions of a number of naphthalene derivatives are regulated under the New Source Performance Standards (NSPS) for Equipment leaks of VOC in the Synthetic Organic Chemical Manufacturing Industry (SOCMI). These environmental regulations pertaining to naphthalene derivatives are discussed below. In addition the Occupational Safety and Health Administration (OSHA) has set limits for occupational exposure to naphthalene. No water criterion has been established; however, a Health Advisory is currently being developed.

#### 4.1 TOXIC SUBSTANCES CONTROL ACT

Section 8(a) of the Toxic Substances Control Act, 15 U.S.C. 2607(a), requires certain manufacturers and importers of 19 chlorinated naphthalenes to notify EPA of current and prospective manufacture or import of the compounds.<sup>38</sup> These manufacturers and importers are required to report to EPA and keep records of information on intended or expected uses, production quantities, chemical composition, and wastes.

### 4.2 NSPS FOR SOCMI EQUIPMENT LEAKS

Equipment leaks of certain naphthalene derivatives are regulated under Subpart VV of the NSPS for Equipment Leaks of VOC in SOCMI.54

Naphthalene itself is not regulated by this standard because it is not a synthetic organic chemical. Equipment subject to the standards include valves, pumps, compressors, pressure relief devices, sampling systems, and open-ended lines in VOC service. The standards require:

(1) a leak detection and repair program for valves in gas/vapor and light-liquid service and for pumps in light-liquid service; (2) equipment for compressors, sampling systems, and open-ended lines; and

(3) no detectable emissions (500 ppm as determined by Reference Method 21) for pressure relief devices in gas/vapor service during normal operation. Naphthalene derivatives listed in Section 60.489 that are

subject to the standards include alkylnaphthalene, anthraquinone, bromonaphthalane, chloronaphthalene, 1- and 2-naphthalenesulfonic acids, 1-naphthol, 2-naphthol, phthalic anhydride, and tetrahydronaphthalene.

#### 5.0 AMBIENT AIR MONITORING DATA FOR NAPHTHALENE

Few ambient air monitoring data for naphthalene are available. In one study data were compiled for quarterly naphthalene concentrations in 13 cities across the United States. No annual estimates are available. The highest reported quarterly mean for naphthalene is 12.0  $\mu g/m^3$  (2.09 ppb) at Upland, California.

Other monitoring data show that ambient air concentrations of naphthalene are 3.5 x  $10^{-4}~\mu g/m^3$  (6.1 x  $10^{-5}~ppb$ ) in an urban area and 5.0 x  $10^{-5}~\mu g/m^3$  (8.7 x  $10^{-6}~ppb$ ) in a rural area.<sup>43</sup> It was not stated, however, whether these readings were hourly, daily, quarterly, or annual averages.

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#### APPENDIX A

# DOCUMENTATION FOR HUMAN EXPOSURE MODEL INPUT DATA

### A.1 INTRODUCTION

This appendix documents the Human Exposure Model (HEM) input parameters for naphthalene. For each naphthalene source category, these parameters include:

SIC code
plant name
latitude and longitude
stack release height (meters)
cross-sectional downwash area (meters<sup>2</sup>)
gas exit velocity (meters/second)
vent type/diameter (meters)
gas temperature (degrees, Kelvin scale)
emission rate (kilograms/year

The sections below cite the references or provide the basis for the modeling parameters and describe the methods used to calculate naphthalene emissions from a given source category (i.e., naphthalene production or end use). The source categories are included in the following sections:

- A.2 Naphthalene from Coke By-product Recovery Plants
- A.3 Naphthalene Production
- A.4 Phthalic Anhydride End Use
- A.5 Carbamate Insecticides End Use
- A.6 2-naphthol End Use
- A.7 Synthetic Tanning Agents End Use
- A.8 Surface Active Agents End Use
- A.9 Moth Repellant End Use
- A.10 Miscellaneous Organic Chemicals End Use

Tables A-1 through A-10 present the modeling parameters described in this appendix.

- A.2 NAPHTHALENE FROM COKE BY-PRODUCT RECOVERY PLANTS
- A. SIC Code

Reference 1.

B. Plant Name

Reference 15, Table 3-3 (revised since proposal), is the basis for the list of coke by-product recovery plants, which include only facilities that produce coal tar naphthalene.

C. Latitude/Longitude

Reference 15, Table E-1 (revised since proposal).

#### D. Urban

All plants are located in urban areas for modeling purposes.

## E. City, State

Locations of coke by-product recovery plants from Reference 15, Table 3-3 (revised since proposal).

### F. Emission Type

Process (P), storage (S), and fugitive (F) emission points were based on information in References 15 and 16. Process emissions are considered to be emitted from a stack or vent. Most naphthalene emissions from coke by-product recovery plants originate from naphthalene processing, specifically separation and drying, which usually occur in partially open, but vented, tanks; therefore, some emission points may be both fugitive and process emission sources. Storage emissions of naphthalene originate from naphthalene storage tanks and some coal tar storage tanks (containing a mixture of coal tar and naphthalene).

#### G. Stack Number

Corresponds to an emission point, either process, fugitive, or storage. When stack parameters for different emission points are identical, they are assigned one number and emissions from these points are combined.

### H. Stack Parameters

Reference 15, Table E-2. Stack parameters for the naphthalene drying tank were selected for modeling purposes. Storage tank release height is based on height of tar storage tank (containing naphthalene) also from Table E-2. For cross-sectional downwash area (fugitive emission points) areas of 200m x 100m for large plants (coke capacity greater than 1 million Mg/yr), 100m x 100m for middlesized plants (coke capacity between 500,000 Mg/yr and 1 million Mg/yr), and 75m x 65m for smaller plants (coke capacity less than 500,000 Mg/yr) are used.

#### I. Emissions

A plant-wide naphthalene emission factor is developed for naphthalene-handling coke by-product recovery plants. This factor is based on a material balance of a representative coke by-product recovery plant and the amount of naphthalene estimated in coal tar production. A naphthalene emission factor is needed on a "kilogram (kg) of naphthalene per megagram (Mg) of coke produced" basis because coke production rates are available for each coke by-product plant. To derive this factor, the following procedure is used.

1. Estimate annual coal tar production based on (1) the amount of naphthalene in coal tar produced (1978 estimate) and (2) the weight percent of naphthalene in dry coal tar:

1978 coal-tar npahthalene production = 230,000 Mg (Reference 10, pp. 27-28)

Average Weight % naphthalene of dry tar (U.S.) = 8.80% (Reference 11, p. 572).

Coal\_Tar Production = 
$$\frac{230,000 \text{ Mg}}{0.088}$$
 = 2.6 Tg

2. Estimate relative amount of coal tar produced per megagram of coke from material balance of a representative coke by-product recovery plant:

 $\frac{380 \text{ Mg Coal Tar}}{7370 \text{ Mg Coke}} = \frac{0.052 \text{ Mg Coal Tar per Mg Coke}}{\text{p. } 23)}$ 

3. Estimate annual coke production based on steps (1) andf (2) above:

$$\frac{2.6 \text{ Tg coal tar}}{0.052 \text{ Mg coal tar/Mg coke}} = 50 \text{ Tg coke production, U.S.}$$

$$(1978 \text{ estimate})$$

Note: This estimate approximates 1979 U.S. coke production figure (48.0 Tq) from Reference 41.

4. Calculate naphthalene emission factor from estimate of total naphthalene emissions to atmosphere from coal tar production (Reference 10) and total U.S. coke production from step (3) above:

300 Mg naphthalene = 6 Mg naphthalene per Tg coke produced, 50 Tg coke produced or 0.006 kg naphthalene per Mg coke produced.

A plant-specific emission total was calculated using the above method. The total was divided by three to allocate emissions to process, fugitive, and storage vents.

- A.3 NAPHTHALENE PRODUCTION
- A. SIC Code

Reference 1.

B. Plant Name

Plants 1-5 from References 2, 3, 4 represent U.S. producers of naphthalene from both coal tar and petroleum.

Plants 6-9 are on standby or not operating due to market conditions based on information from References 2, 3, and 4. Therefore, plants 6-9 are not modeled.

C. Latitude/Longitude

Plant 1 - Reference 5. Plants 2,3 - Reference 6. Plant 4 - Reference 7. Plant 5 - Reference 8.

#### D. Urban

This information is not available from State Permit files or other available sources. All plants are assumed to be located in urban areas.

## E. City, State

Location of plant numbers 1-9 from References 2, 3, 4.

### F. Emission Type

Process (P), storage (S), and fugitive (F) emission points were based on information in Reference 9.

#### G. Stack Number

Corresponds to an emission point, either process (P), fugitive (F), or storage (S). When stack parameters for different emission points are identical within a given type, they are assigned one number, and emissions from those points are combined.

### H. Stack Release Height

A stack release height of 13m from all process stacks at naphthalene production facilities was used based on average of stack heights from Reference 9. Other assigned values are as follows:

- Plant 1 Release height of 3m for fugitives; release height of 7.6m for each of 5 storage tanks (estimated average of heights of 7 tanks from Reference 9).
- Plant 2 Three meters for fugitives; 2 storage tanks both having a height of 7.6m (based on average height of storage tanks, Reference 9).
- Plant 3 Three meters for fugitives; release height of 7.6m for 6 storage tanks (based on Reference 9).
- Plant 4 Three meters for fugitive releases; storage release height based on 7.6m from storage tank height (Reference 9).
- Plant 5 Three meters for fugitives. Three storage tanks, all having a height of 7.6m (based on Reference 9).

#### I. Cross-Sectional Downwash Area

For fugitive emissions, a cross-sectional downwash area of  $20,000m^2$  was used for all naphthalene production facilities, based on model input parameters for xylene reported in Reference 40.

#### J. Vent Type

Vertical (0) for process and storage emission points, and nonvertical (1) for fugitive emissions are assumed.

#### K. Vent Diameter

For process emissions, Reference 9 (average of stack diameter).

For storage emissions, unless assigned plant-specific information was available, a storage tank is assigned a diameter of 0.076m, based on vent diameters of 0.17 ft, 0.25 ft, and 0.33 ft. reported in Reference 40, Table 29-20, for xylene vent parameters.

## L. Gas Exit Velocity

No plant-specific information was available. Therefore, PES used an estimate of 6.3 m/s from Reference 9 is used as a representative exit velocity for process stacks at naphthalene production facilities, and 0.01 m/sec for fugitive and storage emission points.

## M. Gas Temperature

An estimate of 320°K from Reference 9 is selected as a representative exit gas temperature for process stacks at naphthalene production facilities, and 293°K (ambient) for fugitive and storage emission points.

#### N. Emissions

Plant 1 - Allied Chemical, Ironton, OH.

No plant-specific information was available to calculate naphthalene emissions (Reference 12).

Naphthalene Distillation Process - Process, fugitive, and storage emissions are based on plant-specific information from the Koppers facility in Follansbee, WV (Reference 9). Since no process description was available for Allied, the process is assumed to be identical to the one at Koppers. Like Koppers, the facility uses coal tar as a raw material.

### a. Process Emissions

A naphthalene emission factor for process emissions was derived from the polycyclic organic matter (POM) emissions reported in the 1984 Emissions Inventory submitted by Koppers Co., Follansbee, WV (Reference 9). The factor is expressed in terms of kilograms of naphthalene per megagram of naphthalene produced. Based on 20.6 ton POM/yr and based on an estimate from Reference 10 that 87% of POM emissions from naphthalene production are assumed to be naphthalene, the following emission factor for process emissions is calculated:

0.87 x 20.6 
$$\frac{\text{ton}}{\text{yr}}$$
 x  $\frac{2,000 \text{ lb}}{\text{ton}}$  x  $\frac{0.454 \text{ kg}}{\text{lb}}$  x  $\frac{1}{68 \times 10^3 \text{ Mg/yr}}$  = 0.239 kg naphthalene/Mg produced

Using this emission factor, process emissions of naphthalene from the Allied facility with production rate of 34,000 Mg (Reference 13) are calculated as:

0.239 
$$\frac{\text{kg}}{\text{Mg}} \times 34,000 \frac{\text{Mg}}{\text{yr}} = 8,100 \text{ kg/yr}$$

## b. Fugitive Emissions

No information was available on the number of components containing or contacting naphthalene at the Allied facility.

Therefore, fugitive emissions at Allied are estimated to be 580 kg/yr as reported for the fugitive emissions from naphthalene distillation and desulfurization at the koppers facility (Reference 9).

## c. Storage Emissions

Storage emissions of naphthalene from the Allied facility were based on storage emissions from the Koppers, Follansbee, WV, facility (Reference 9), and the 1985 production capacity for the Allied facility from Reference 13. Storage emissions factor is calculated as follows:

$$\frac{1,545 \text{ kg}}{68,000 \text{ Mg}} = \frac{0.0227 \text{ kg}}{\text{Mg}}$$

Therefore, storage emissions from the Allied facility are:

0.0227 
$$\frac{kg}{Mg} \times 34,000 \frac{Mg}{yr} = 770 \frac{kg}{yr}$$

Therefore, total emissions from the Allied facility are 9,450 kg/yr, or 9.4 Mg/yr. As a basis of comparison, nationwide estimates of naphthalene emissions from production (Reference 14) can be apportioned among the five naphthalene producers. Reference 14 reports that from 0.0004 to 0.07% of the annual U.S. production of naphthalene is lost from the plant during its manufacture, and that 48% of these emissions are released to the atmosphere. Using a conservative estimate of 0.0336% (0.0007 x 0.48) as the percentage of naphthalene production emitted and the total naphthalene production of 184,000 Mg/yr (Reference 4), naphthalene emissions to the atmosphere can be calculated as:

$$0.000336 \times 184,000 \, \text{Mg/yr} = 61.8 \, \text{Mg/yr}.$$

Apportioning this total among the five naphthalene producers based on production rate, naphthalene emissions are the following:

Plant	1	-	Allied	11.4 Mg
Plant	2	_	Chemical Exchange	4.7 Mg
Plant	3	-	DuPont	13.8 Mg
Plant	4	-	Koppers	22.8 Mg
Plant	5	-	Texaco Chemical	9.1 Mg
•	~		Total	61.8 Mg

Plant 2 - Chemical Exchange Industries, Baytown, TX.

No plant-specific information was available from State permit files from which to calculate naphthalene emissions (Reference 6).

This plant uses a petroleum-based feedstock (e.g., heavy reformate) in the production of naphthalene. In a comparison of coal tar and petroleum-based processes, certain steps are similar, such as distillation and fractionation. In addition, some petroleum naphthalene producers may also process coal-derived material (Reference 33, p. 25). Although admittedly there are differences in naphthalene contents between coal tar and petroleum, no information is available on the relative percentage of naphthalene in petroleum streams or the percentage of naphthalene emissions of total polycyclic organic matter. Therefore, the only basis for estimating emissions from a petroleum-based naphthalene process is the estimating procedure used above to estimate coal tar-based naphthalene emissions.

## a. Process Emissions

A naphthalene emission factor (0.24 kg naphthalene/Mg napthalene produced) derived from the Koppers facility, Follansbee, WV (Reference 9) was used to estimate process emissions from the Chemical Exchange facility. The same procedure was followed as in Plant 1, assuming 87% of POM emissions are naphthalene (based on Reference 10); and based on a production rate of 14,000 Mg/yr for the Chemical Exchange facility.

Process emissions of naphthalene are calculated as:

 $0.239 \text{ kg/Mg} \times 14,000 \text{ Mg/yr} = 3,300 \text{ kg/yr}.$ 

## b. Fugitive Emissions

No information was available on the number of components containing or contacting naphthalene at the Chemical Exchange Facility. Since there is no desulfurization section in the petroleum-based process, only the distillation process information from the Koppers facility (Reference 9) is used.

Fugitive emissions af heavy liquid coal tar distillate = 1.26 lb/hr (Reference 9)

Weight of naphthalene in dry coat tar, (Reference 11) = 8.8%

Hours of Operation per year, (Reference 44) = 6,745

0.088 x 1.26 lb/hr x 6,745 x 0.454 
$$\frac{kg}{lb}$$
 = 340  $\frac{kg}{yr}$ 

## c. Storage Emissions

-Same procedure as Plant 1, Storage Emissions.

Storage emissions from the Chemical Exchange facility are:

$$0.0227 \frac{\text{kg}}{\text{Mg}} \times {}^{14,000} \frac{\text{Mg}}{\text{yr}} = 320 \text{ kg/yr}.$$

Total naphthalene emissions from Chemical Exchange Industries are 3,960 kg/yr, or 4.0 Mg, which compares favorably with the emissions estimate of 4.7 Mg based on the apportioning technique described above.

<u>Plant 3</u> - E.I. DuPont de Nemours, Chocolate Bayou, TX.

No plant-specific information was available from State permit files from which to calculate naphthalene emissions (Reference 6).

The plant uses a petroleum-based feedstock in the production of naphthalene. The same basis that was used to calculate emissions from the other facilities was used here, based on plant-specific information from Reference 9.

## a. Process Emissions

Same procedure as Plant 1, Process Emissions.

Process emissions from the DuPont facility are calculated as:

0.239 
$$\frac{\text{kg}}{\text{Mg}} \times 41,000 \frac{\text{Mg}}{\text{g}} = 9.800 \text{ Kg/yr}$$

### b. Fugitive Emissions

Same procedure as Plant 2, Fugitive Emissions.

Fugitive emissions from the DuPont facility are calculated as:

$$0.0084 \frac{\text{kg}}{\text{Mg}} \times 41,000 \frac{\text{Mg}}{\text{yr}} = 340 \frac{\text{kg}}{\text{yr}}$$

#### c. Storage Emissions

Same procedure as Plant 1, Storage Emissions.

Storage emissions from the DuPont facility are calculated as:

$$0.0227 \frac{\text{kg}}{\text{Mg}} \times \frac{41,000 \frac{\text{Mg}}{\text{yr}}}{\text{yr}} = 930 \frac{\text{kg}}{\text{yr}}$$

Naphthalene emissions from the DuPont facility total 11,070 kg/yr, or 11.1 Mg/yr. This approximates the estimate of 13.8 Mg/yr from the apportioning technique described above.

Plant 4 - Koppers, Follansbee, WV.

# 1. Process #230 (Naphthalene Distillation)

## a. Process Emissions

20.6 tpy POM emitted from distillation process (Reference 9).

87 percent of POM emissions from naphthalene production assumed to be naphthalene (Reference 10, p. 27), based on an estimate that 87% of POM emissions to air is naphthalene in coal tar production.

0.87 x 20.6 
$$\frac{\text{ton}}{\text{yr}}$$
 x  $\frac{2,000}{\text{ton}}$  x  $\frac{1b}{\text{ton}}$  x  $\frac{0.454}{1b}$  = 16,200  $\frac{\text{kg}}{\text{yr}}$ 

## b. Fugitive Emissions

Fugitive emissions of heavy liquid coal tar distillate = 1.26 lb/hr, Reference 9.

Weight percent naphthalene in dry coal tar, = 8.8% Reference 11.

Hours of operation per year (1984), Reference 9. = 7,490

0.088 x 
$$\frac{1.26}{hr}$$
 x  $\frac{1b}{hr}$  x  $\frac{7,490}{yr}$  x  $\frac{hr}{yr}$  x  $\frac{0.454}{1b}$  = 380  $\frac{kg}{yr}$ 

## c. Storage Emissions

2 naphthalene oil storage tanks for naphthalene distillation process (each 60-65% naphthalene Reference 11); the 65% value is used for calculations. Tank 1 corresponds to S-1 at Koppers in Table A-2 of this appendix, and tank 2 corresponds to S-2 at Koppers.

Tank 1 (S-1) = 
$$547 \frac{1b}{yr}$$
 x  $0.454 \frac{kg}{1b}$  x  $0.65 = 160 \frac{kg}{yr}$   
Tank 2 (S-2) =  $590 \frac{1b}{yr}$  x  $0.454 \frac{kg}{1b}$  x  $0.65 = 170 \frac{kg}{yr}$   
Total = 330 kg/yr

# 2. Process 300 - Naphthalene Desulfurization

# a. Process Emissions

Based on (1) POM emissions from naphthalene desulfurization process of 3.9 ton/yr (Reference 9) and (2) 87% of POM is naphthalene (Reference 10), naphthalene process emissions are calculated as:

0.87 x 3.9 
$$\frac{\text{ton}}{\text{yr}}$$
 x 2,000  $\frac{1b}{\text{ton}}$  x 0.454  $\frac{\text{kg}}{1b}$  = 3,100 kg/yr

# b. Fugitive Emissions

Based on:

- (1) Fugitive emissions of total heavy liquid = 0.77 lb (Reference 9);
- (2) Weight % of naphthalene in dry coal tar = 8.8% (Reference 11); and
- (3) Hours of operation per year (1984) = 6,336 (Reference 9);

naphthalene fugitive emissions are calculated as:

$$0.088 \times \frac{0.77 \text{ } \frac{1b}{hr} \times 6,336 \frac{hr}{yr} \times \frac{0.454 \text{ } kg}{1b}}{} = 200 \text{ kg/yr}$$

## Storage Emissions

5 naphthalene storage tanks for naphthalene desulfurization process (Reference 9):

Tank H	<u>(m)</u> <u>D</u>	)(m)		Emission	S	
1 (S3) 1	0.9 6	5.1	575 <u>lb</u> yr x	0.454 <u>kg</u> 1b	=	261 kg/yr
2 (S4)	9.1 7	.6	610 <u>lb</u> yr x	0.454 <u>kg</u> 1b	=	277 kg/yr
3 (\$5)*	6.1 7	7.3	393 <u>1b</u> x	0.454 <u>kg</u> 1b	=	178 kg/yr
4 (S5)*	6.1	7.3	$393 \frac{1b}{yr} x$	0.454 <u>kg</u> 1b	3	178 kg/yr
5 (S6)* 1	.2.8 13	3.7	697 <u>1b</u> x	0.454 <u>kg</u> 1b	=	316 kg/yr
				Total	= 1,	,210 kg/yr

\*Note: Tanks 3 and 4 are modeled as one tank since parameters are identical, and emissions for the two tanks are combined.

Total naphthalene emissions from the Koppers plant are 21,420 kg/yr, or 21.4 Mg/yr, which closely approximates the estimate (22.8 Mg) based on a nationwide apportioning technique discussed in Plant 1 emissions documentation above.

Plant 5 - Texaco Chemical, Delaware City, DE.

No plant-specific information was available from State permit files from which to calculate naphthalene emissions (Reference 8).

The plant uses a petroleum-based feedstock in the production of naphthalene. The same procedure as used in other facilities was used to calculate naphthalene emissions from Texaco Chemical, based on plant-specific information from Reference 9.

## a. Process Emissions

Same procedure as Plant 1, Process Emissions.

Process emissions from the Texaco Chemical facility are calculated as:

0.239 
$$\frac{\text{kg}}{\text{Mg}} \times 27,000 \frac{\text{Mg}}{\text{yr}} = 6,400 \frac{\text{kg}}{\text{yr}}$$

## b. Fugitive Emissions

Same procedure as Plant 2, Fugitive Emissions.

## c. Storage Emissions

Same procedure as Plant 1, Storage Emissions.

Storage emissions from the Texaco Chemical facility are calculated as:

$$0.0227 \frac{\text{kg}}{\text{Mg}} \times 27,000 \frac{\text{Mg}}{\text{yr}} = 610 \frac{\text{kg}}{\text{yr}}$$

Naphthalene emissions from the Texaco Chemical facility total 7,350 kg/yr, or 7.3 Mg/yr, compared to 9.1 Mg/yr using the apportioning technique based on Reference 14.

Total emissions of naphthalene from production at the above five facilities are 53.2 Mg.

## A.4 PHTHALIC ANHYDRIDE END-USE

#### A. SIC Code

Reference 1.

#### B. Plant Name

References 18 and 19. Plant restarted during May 1985 after modification to use naphthalene as a feedstock as well as orthoxylene.

## C. Latitude/Longitude

Derived from zip code conversion to UTM coordinates using computer program from Office of Toxic Substances.

#### D. Urban

The location of the facility is assumed to be in an urban area. E. City, State

Location of facility from Reference 19.

## F. Emission Type

Reported as process (P), fugitive (F), or storage (S) based on information in References 17-19.

#### G. Stack Number

Corresponds to an emission point, either process, fugitive, or storage. When stack parameters for different emission points are identical, they are assigned one number, and emissions from these points are combined.

#### H. Stack Release Height

A height of 3 m is selected for fugitive emissions; release height for storage emissions is based on storage tank height from Reference 20.

#### I. Cross-Sectional Downwash Area

For fugitive emission points,  $100 \text{ m} \times 200 \text{ m}$  is selected from (Reference 40).

#### J. Vent Type

Vertical (0) for storage emission points and nonvertical (0) for fugitive emissions are chosen.

#### K. Vent Diameter

Process emissions - Reference 20, p. 15.

Storage emissions type: same as documentation for naphthalene production, Section A.3, subsection K.

#### L. Gas Exit Velocity

A gas exit velocity of  $0.01\,\mathrm{m/sec}$  for fugitive and storage emission points is used.

#### M. Gas Femperature

An ambient temperature of 68°F, or 293°K is chosen.

#### N. Emissions

Plant 1 - Koppers Co., Bridgeville, PA - not operating.

Plant 2 - Monsanto Co., Bridgeport, NJ - not operating.

Plant 3 - Koppers Co., Stickney, IL - restarted May 1985 (Reference 19).

The facility uses either orthoxylene or naphthalene as feedstock for production of phthalic anhydride. The bulk of total emissions originate from the catalytic oxidation reactor (Reference 17). Emissions from other equipment (e.g., switch condensers, distillation columns, and heat treaters) are negligible.

## a. Process Emissions from Phthalic Anhydride Formation Process

One-hundred percent of naphthalene used in the manufacture of phthalic anhydride is converted to phthalic anhydride in the reactor. Therefore, O process emissions of naphthalene are assumed (Reference 10, p. 41). This is supported by raw material and product information from Reference 20, p. 9-10, which states that 4,386 lb/hr naphthalene is raw material fed to process and 4,386 lb/yr is production rate for crude phthalic anhydride vapor from naphthalene, indicating that all naphthalene as raw material is used in the process.

## b. Fugitive Emissions

VOC emission factors from Reference 24 for equipment leaks from synthetic organic chemical manufacturing plants (SOCMI) are used. All VOC is assumed naphthalene to estimate conservatively.

Number of pumps, valves, and other equipment per process unit is based on SOCMI process unit counts in Reference 24. Only equipment in heavy liquid or gas vapor service is included since naphthalene is considered a heavy liquid on the basis of its Reid vapor pressure (0.007 kPa at 20°C).

Equipment component counts and emission factors for an average SOCMI unit are used to estimate emissions (Reference 24, pp. 1-4, 3-2, 3-6) as follows:

Equipment Component	Component Count	Average SOCMI Emission Factor (kg/hr/source)	Opera- ting hrs per year <sup>a</sup>	VOC Emis- sions <sup>d</sup> (kg/yr)
Heavy Liquid Pumps	5b	0.0214	8,232	881
Heavy Liquid Valves	84	0.00023	8,232	160
Heavy Liquid Safety/ Relief Valves	1	Not avilable	8,232	
Heavy Liquid Open- ended Valves & Lines	48	0.0017	8,232	670
Compressor Seals	1	0.228	8,232	1,880
Sampling Connections	12 <b>c</b>	0.0150	8,232 -	- 1,480
Flanges	500	0.00083	8,232	3,400
		TOTAL	8,470	

Footnotes from table, previous page:

aOperating hours from Reference 20.

bAssumed to have single mechanical seals.

c25% of open-ended lines used for sampling, based on Reference 24,
p. 3-4.

dyoC assumed to be 100% naphthalene for conservative estimate.

### c. Storage Emissions

Emissions of naphthalene from phthalic anhydride production at the facility are primarily from one storage tank (Reference 10).

It is assumed that EPA emission factors from AP-42 (Reference 21) apply for uncontrolled storage tank losses of naphthalene at phthalic anhydride plants. Emissions from naphthalene storage are presently not controlled.

The facility has one naphthalene storage tank.

Emission equations for estimating breathing (LB) and working losses (LW) from fixed-roof tanks storing volatile organic liquids are calculated as follows (PES assumes all organics in tank are naphthalene):

Total Loss =  $L_B + L_W$  $L_B = 2.26 \times 10^{-2} M_V P_A - P$ 0.68  $D^{1.73} H^{0.51} T^{0.50} F_P CK_C$ 

where:

where:

 $L_B$  = fixed roof breathing loss (lb/yr)

 $M_V$  = molecular weight of vapor in storage tank (1b/1b mole)

 $P_A$  = average atmospheric pressure at tank location (psia)

P = true vapor pressure at bulk liquid conditions (psia)

D = tank diameter (ft)

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

T = average ambient diurnal temperature change (°F)

Fp = paint factor (dimensionless)

C = adjustment factor for small diameter tanks (dimensionless)

 $K_C = product factor (dimensionless).$ 

Fixed-roof tank working losses can be estimated from:

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

LW = fixed-roof working loss (lh/year)

 $M_V$  = molecular weight of vapor in storage tank (1b/lb mole)

P = true vapor pressure at bulk liquid temperature (psia)

V = tank capacity (gal)

N = number of turnovers per year (dimensionless)

N = Total throughput per year (gal)

Tank capacity, V (gal)

 $K_N = turnover factor (dimensionless)$ 

 $K_C = product factor (dimensionless)$ 

From References 20 and 21, the following variables for the equations are given:

# Fixed-roof breathing loss, LB (lb/yr):

My = 128.19 (Reference 22)

 $P_A = 14.7 \text{ psia (Reference 23)}$ 

P = 1.84 (Reference 25) true vapor pressure at 60°F

D = 66.5 ft (Reference 20)

H = 16 ft (assume H = 1/2 tank height, Reference 21)

T = 20°F (assumed as typical value, Reference 23)

F<sub>p</sub> = 1.26 (aluminum tank, based on average of several aluminum tank paint factors, Reference 21)

C = 1 (Reference 23, p. 3-26)

 $K_C = 1.0$  (Reference 21, p. 4.3-8)

$$L_B = 25,500 \frac{1b}{yr} \times 0.454 \frac{kg}{1b} = 11,600 \text{ kg/yr}$$

# Fixed-roof working loss, LW (lb/yr):

 $M_V = 128.19$  (Reference 22)

P = 1.84 psia (same assumptions as for breathing loss above)

V = 835,000 gal (Reference 20)

N = 16.17 (Reference 21)

 $K_N = 1.0$  (Reference 21)

 $K_C = 1.0$  (Reference 21)

$$L_{W} = \frac{76,400 \frac{1b}{yr} \times 0.454 \frac{kg}{1b}}{30.454 \frac{kg}{1b}} = 34,700 \frac{kg}{yr}$$

 $L_{B} + L_{W} = 46,300 \text{ kg/yr}$ 

Total Naphthalene Emissions from Phthalic Anhydride Production = 54,754 kg/yr = 54.8 Mg/yr

### A.5 CARBAMATE INSECTICIDES END USE

# A. SIC Code

Reference 1.

### B. Plant Name

Only one plant, Union Carbide, Institute, WV, produces carbamate insecticides (chiefly carbaryl) from naphthalene (References 4 and 9). One other Union Carbide facility, St. Louis, MO, is reported to dilute the carbaryl product it receives from another plant, but it does not produce carbaryl directly and there is no naphthalene storage (Reference 26).

Corresponds to an emission point, either process, fugitive, or storage. When stack parameters for different emission points are identical, they are assigned one number, and emissions from these points are combined.

### H. Stack Parameters

Reference 9 unless indicated otherwise.

- Process emissions from Unit Number 250 corresponds to Stack Number P-1 in Table A-4. Stack parameters from Reference 9.
- 2. Process emissions from Unit Number 251 correspond to Stacks P-2, P-3, and P-4 in Table A-4. Stack P-3 represents 2 identical 4.6-meter stacks with reported average velocity of 0.22 m/sec Stack P-4 represents 5 15-meter stacks with average temperature of 317°K and an average velocity of 2.4 m/sec. Total emissions from Process [251] were apportioned among the stacks based on stack sampling data given in Reference 9.
- 3. Process emissions from Unit No. 252 correspond to Stack Number P-5 in Table A-4. Stack parameters from Reference 27.
- 4. Process emissions from Unit No. 253 correspond to Stack Number P-6 in Table A-4. Stack parameters from Reference 9.
- 5. Fugitive emissions from all process units are reported under one "stack number." Assumptions include a release height of 3 meters above ground, a cross-sectional downwash area of 100 x 200 meters, a velocity of 0.01 m/sec, and temperature of 293°K (ambient). Values of 0.01 m/sec for velocity and 293°K for temperature were assumed.

### C. Latitude/Longitude

Reference 43.

D. Urban

Plant assumed to be located in an urban area.

E. City, State

Reference 4.

### F. Emission Type

Process (P), Fugitive (F), or Storage (S) emission points are based\_on information in Reference 9.

### G. Stack Number

6. Storage emissions:

Unit 250 - 3 tanks 
$$H = 12m$$
,  $D = 15m$  (S-1 in Table A-4)  $H = 11m$ ,  $D = 21m$  (S-2 in Table A-4) Unit 251 - Estimated 1 tank,  $H = 3m$ ,  $D = 3m$  (S-3 in Table A-4) Unit 252 - 3 tanks,  $H = 9.1m$ ,  $D = 7.6m$  (S-4 in Table A-4) Unit 253 - 1 tank,  $H = 3.4m$ ,  $D = 3.5m$  (S-5 in Table A-4)

Values of 0.01 m/sec assumed for velocity and  $293^{\circ}\text{K}$  (ambient) for temperature. Vent diameter of 0.076 m is based on average diameter of xylene storage tank vents from Reference 40.

# I. Vent Type

A vertical vent (0) for process and storage emission points, and nonvertical (1) for fugitive emissions is used.

### J. Emissions

Plant 1 - Union Carbide, Institute, WV.

Emissions information from 1984 Emission Inventory, Summary by Process, Union Carbide, Institute, WV (Reference 9). The following emission estimates are presented by emission type (process, storage, fugitive, emergency) and by carbaryl process unit (hydrogenation, oxidation, dehydrogenation, and refining).

# a. Process Emissions of Naphthalene from Carbaryl Production

No information to indicate emissions are controlled; therefore, no controls are assumed to be in place. The carbaryl process units and reported emissions are listed below:

1. #250 - Tetralin hydrogenation unit:

1,512 
$$\frac{1}{y}$$
r x 0.454  $\frac{kg}{l}$  = 686  $\frac{kg}{y}$ r

2. #251 - Tetralin oxidation unit:

1,573.5 
$$\frac{1b}{yr} \times \frac{0.454 \text{ kg}}{1b} = 714 \text{ kg/yr}$$

3. #252 - Crude naphthol dehydrogenation unit:

2.8 
$$\frac{1b}{yr} \times 0.454 \frac{kg}{1b} = 1.3 \text{ kg/yr}$$

4. #253 - 1-naphthol refining unit:

1.8 
$$\frac{1b}{yr}$$
 x 0.454  $\frac{kg}{1b}$  = 0.82 kg/yr

TOTAL Process Emissions = 1,402 kg/yr

- b. Fugitive Emissions of Naphthalene from Carbaryl Production
- 1. #250 Tetralin hydrogenation unit:

1,279 
$$\frac{1b}{yr} \times \frac{0.454 \text{ kg}}{1b} \approx 581 \text{ kg/yr}$$

2. #251 - Tetralin oxidation unit:

$$\frac{1b}{yr} \times \frac{0.454 \text{ kg}}{1b} = 382 \text{ kg/yr}$$

3. #252 - Crude naphthol dehydrogenation unit:

83.6 
$$\frac{1b}{yr}$$
 x 0.454  $\frac{kg}{1b}$  = 38.0 kg/yr

4. #253 - 1-naphthol refining unit:

$$\frac{1b}{yr} \times \frac{0.454 \text{ kg}}{1b} = 249 \text{ kg/yr}$$

TOTAL Fugitive Emissions = 1,250 kg/yr

- c. Storage Emissions of Naphthalene from Carbaryl Production
- 1. #250 Tetralin hydrogenation unit (4 storage tanks, 4,046.5 lb/yr total emissions):

4,046.5 
$$\frac{1b}{vr} \times \frac{0.454 \text{ kg}}{1b} = 1.837 \text{ kg/yr}$$

2. #251 - Tetralin oxidation unit:

$$\frac{16.9}{yr} \times \frac{1b}{x} = 7.67 \text{ kg/yr}$$

3. #252 - Crude naphthol dehydrogenation unit (3 storage tanks, 31.7 lb/yr each):

$$\frac{95.1 \text{ } \frac{1b}{yr} \times 0.454 \text{ } \frac{kg}{1b} = 43.2 \text{ } \frac{kg}{yr}}{10.454 \text{ } \frac{kg}{10}} = 43.2 \text{ } \frac{kg}{yr}$$

4. #253 - 1-naphthol refining unit:

38.2 
$$\frac{1b}{yr}$$
 x  $\frac{0.454}{1b} = 17.3 \text{ kg/yr}$ 

TOTAL Storage Emissions = 1,905 kg/yr.

- d. Emergency Emissions of Naphthalene from Carbaryl Production
- 1. #250 Tetralin hydrogenation unit:

$$\frac{5}{yr} \times \frac{0.454}{1b} = 2 \text{ kg/yr}$$

2. #251 - Tetralin oxidation unit:

0.1 
$$\frac{1b}{yr}$$
 x  $\frac{0.454}{1b}$   $\frac{kg}{1b}$  = 0.05 kg/yr

3. #252 - Crude naphthol dehydrogenation unit:

1.0 
$$\frac{1b}{vr} \times 0.454 \frac{kg}{1b} = 0.45 \frac{kg}{yr}$$

4. #253 - 1-naphthol refining unit:

No emissions reported (assume 0)  $0 \frac{\text{kg}}{\text{yr}}$ 

TOTAL Emergency Emissions = 2.5 kg/yr

Total naphthalene emissions from carbaryl production (all from Union Carbide, Institute, WV) = 4,560 kg/yr.

A.6 2-NAPHTHOL END USE

2-naphthol is no longer produced in the U.S. All 2-naphthol consumed in the U.S. is now imported (Reference 28).

American Cyanamid, Willow Island, WV, closed in mid-1982 (Reference 29). When it was in operation, 1981 emissions of naphthalene were reported to be 37,509 lb/yr, or 17,029 kg/yr (Reference 30).

A.7 SYNTHETIC TANNING AGENTS END USE

(Production of 1- and 2-naphthalenesulfonic acids).

### A. SIC Code

Reference 1.

# B. Plant Name

Five producers of synthetic tanning agents from naphthalene were identified:

- (1) Diamond Shamrock, Carlstadt, NJ (Reference 4)
- (2) Rohm and Haas, Philadelphia, PA (Reference 4)
- (3) Morflex, Inc., Greensboro, NC (Reference 10, p. 45) (formerly Ciba-Geigy)
- (4) Georgia Pacific, Bellingham, WA (Reference 10, p. 45)
- (5) Diamond Shamrock, Cedartown, GA (Reference 10, p. 45)

# C. Latitude/Longitude

Based on conversion of zip code obtained from Reference 4 or U.S. Postal Service Zip Code Directory to UTM coordinates using computer program from Office of Toxic Substances.

### D. Urban

All plants are assumed to be located in an urban area.

### E. City, State

References 4 and 10.

### F. Emission Type

Process (P), Fugitive (F), and Storage (S).

# G. Stack/Vent Parameters

Same as Section A.8, Surface Active Agents, Part H.

### H. Emissions

Synthetic tanning agents are produced primarily from 1- and 2naphthalenesulfonic acids (NSA), both derivatives of naphthalene.
Plant-specific emissions of naphthalene from the production of 1- and
2-NSA were calculated on the basis of total naphthalene consumption by
the method described in Section A.8 for Surface Active Agents. Calculated
emissions are based on: (1) the assumption that 0.034% of total naphthalene
consumed (315 Gg) is lost to the atmosphere (based on Reference 3,
assuming this percentage is the same for both production and consumption);
and (2) 6% of total naphthalene consumption is from production of synthetic
tanning agents (Reference 3). From the above, total naphthalene emissions
from production of synthetic tanning agents (1- and 2-NSA) are calculated as:

$$0.06 \times 0.00034 \times 315 \text{ Gg} = 0.0064 \text{ Gg}$$
  
= 6.4 Mg.

This total was divided among the five producers of synthetic tanning agents, or 1.3 Mg naphthalene emissions per plant.

### A.8 SURFACE ACTIVE AGENTS END USE

(Production of 1- and 2-naphthalenesulfonic acids)

# A. SIC Code

Reference 1.

### B. Plant Name

References 4 and 31.

# C. Latitude/Longitude

Based on conversion of zip codes from Reference 4 and U.S. Postal Service Zip Code Directory to UTM coordinates using computer program from the Office of Toxic Substances.

### D. Urban

Plants are assumed to be located in an urban area.

# E. City, State

References 4 and 31.

# F. Emission Type

Process (P), Fugitive (F), and Storage (S) emissions.

### G. Stack Number

Corresponds to an emission point, either process, fugitive, or storage. When stack parameters for different emission points are identical, they are assigned one number, and emissions from those points are combined.

### H. Stack Parameters

1. Process emissions - Unless a specific stack height is known, 13 m from average of stack heights was selected, Reference 9; specific stack heights were available for some of the New Jersey plants (Reference 32).

Vents are assumed to be vertical (0) and a stack diameter of 0.15 m (average of stack diameters from Reference 9 is used).

A stack velocity of 6.3 m/sec is selected based on average velocity from Reference 9. If stack velocities are known for specific plants, they are reported (Reference 32).

A stack temperature of 320°K is selected based on average temperatures for process stacks from Reference 9.

- 2. Fugitive emissions A height of 3m, crosssectional area of 200 m  $\times$  100 m (20,000 m<sup>2</sup>) for Plants 1 and 3 and 100 m  $\times$  50 m (5,000 m<sup>2</sup>) for Plants 2 and 4 are used. Horizontal venting is assumed; a velocity of 0.01 m/sec and a temperature of 293°K (ambient) are assumed.
- 3. Storage emissions A height of 7.7m based on average height of tanks from Reference 9 is chosen; A vertical vent, a vent diameter of 0.076 m (Reference 40), a velocity of 0.01 m/sec, and a temperature of 293°K (ambient) are used.

### I. Emissions

Plant-specific emissions of naphthalene from the production of 1- and 2-naphthalenesulfonic acid were calculated on the basis of total naphthalene consumption. It is assumed that 0.034% of total naphthalene consumed as end-use chemicals is lost to atmosphere (based on Reference 14 estimate that a maximum 0.07% of naphthalene produced is lost to the environment and 48% of that amount is lost to atmosphere). This gross estimating procedure is used because of the lack of usable plant-specific information. Based on: (1) 0.034% of total naphthalene consumed (315 Gg, Reference 3) is lost to air and (2) 7% of total naphthalene consumption is from production of surface active agents (Reference 3), total naphthalene emissions from production of surface active agents are calculated as:

 $0.07 \times 0.00034 \times 315 \text{ Gg} = 0.0075 \text{ Gg}$ 

= 7.5 Mg

1. <u>1-naphthalenesulfonic acid (1-NSA) production</u> - Naphthalene emissions from 1-NSA production are calculated by multiplying the above total (7.41 Mg) by 15%, the relative percentage of 1-NSA in surface active agent compounds (estimate based on Reference 34):

$$0.15 \times 7.5 = 1.1 \text{ Mg}$$

This total was apportioned among the nine 1-NSA producers to obtain a plant-specific estimate of 123 kg per plant. One-third of the plant total (41 kg) was assigned each to process, storage, and fugitive emissions.

2. 2-naphthalenesulfonic acid (2-NSA) production - Naphthalene emissions from 2-NSA production are calculated by multiplying the total emissions from NSA production (7.41 Mg) by 85%, the relative percentage of 2-NSA in surface active agent compounds (Reference 34):

$$0.85 \times 7.41 = 6.3 \text{ Mg}$$

This total was apportioned among the six 2-NSA producers to derive a plant-specific estimate of 1,050 kg per plant. One-third of the plant total (350 kg each) was assigned to process, storage, and fugitive emissions.

### A.9 MOTH REPELLANT END USE

A. SIC Code

Reference 1.

B. Plant Name

Plant 1 - Morflex, Inc. (formerly Ciba-Geigy Corp.), Greensboro, NC (Reference 31).

Plant 2 - Kincaid Enterprises, Inc., Nitro, WV (Reference 31).

West Virginia Air Pollution Control Commission reports no information on Plant 2 and that the plant may no longer be in operation or not using naphthalene in the production of moth repellant (Reference 35).

### C. Latitude/Longitude

Based on conversion of zip codes from U.S. Postal Service Zip Code Directory to UTM coordinates using computer program from the Office of Toxic Substances.

D. Urban

Plants are assumed to be located in an urban area.

E. City, State

Reference 31.

# F. Emissions

Plant 1 - No information was available on Morflex, Inc. from the North Carolina Department of Natural Resources permit files to indicate that the plant is manufacturing moth repellant.

It is assumed that if the plant produced moth repellant from naphthalene, emissions from production and handling of moth repellant would be included in estimates for production of naphthalene because the product is made directly from the production of naphthalene as a solid

flake, powder, or ball, and is repackaged as a consumer product at another facility (Reference 10, p. 46). It is assumed that the Morflex facility only repackages the product that is already manufactured in a crystallized form by one of the naphthalene producers. Therefore, no emissions of naphthalene are expected from Morflex.

<u>Plant 2</u> - Based on information from the West Virginia Air Pollution Control Commission, no emissions of naphthalene are estimated from Kincaid Enterprises (References 35 and 42).

# A.10 MISCELLANEOUS ORGANIC CHEMICALS END USE

No plant-specific information was available on miscellaneous chemicals except one, RSA Corporation, Ardsley, New York, which produces 1-bromonaphthalene.

# A. SIC Code

Reference 1.

### B. Plant Name

The following organic chemicals are classified as miscellaneous in terms of naphthalene end use:

	Source Category/Chemical	Plant Name/Location	Refer- ence
1.	1-naphthol	Union Carbide, Institute, WV (Emissions included in carbary) production)	4 9
2.	1-naphthylamine	Sigma Chemical Co., St. Louis, MO	31
3.	1,2,3,4-tetrahydronaphthalene (tetralin)	DuPont, Deepwater, NJ Union Carbide, Institute, WV (Emissions included in carbaryl production)	4 4 9
4.	decahydronaphthalene (decalin)	DuPont, Deepwater, NJ	4
5.	1-naphthaleneacetic acid	Greenwood Chemical, Greenwood, VA (No longer in operation) Union Carbide, Ambler, PA	4 36 4
6.	1-bromonaphthalene	RSA Corp., Ardsley, NY	4

7.	1-methylnaphthalene	Chemical Exchange Industries, Houston, TX	4
8.	methylnaphthalene .	Koppers, Follansbee, WV Crowley Chemical, Kent, OH Crowley Chemical, Oklahoma City, OK	4 4 4
9.	1-naphthaleneacetamide	Greenwood Chemical, Greenwood, VA (No longer in operation)	4 36
10.	nitronaphthalenesulfonic acids	Ciba-Geigy, Toms River, NJ	4
11.	naptalam	Uniroyal, Gastonia, NC	4

### C. Latitude/Longitude

Based on conversion of zip codes from Reference 4 and U.S. Postal Service Zip Code Directory to UTM coordinates using computer program from Office of Toxic Substances.

### D. Urban

All plants are assumed to be located in urban areas.

# E. City/State

References 4 and 31.

### F. Emission Type

Reported as process (P), fugitive (F), and storage (S) emissions.

# G. Stack Number

Corresponds to an emission point, either process, fugitive, or storage.

# H. Stack Parameters

1. <u>Process emissions</u> - Unless a specific stack height is known, the average of stack heights, 13 m, is used, Reference 9; specific stack heights were available from some of the New Jersey plants (Reference 32) and from RSA Corporation (Reference 37).

Vents are vertical and a stack diameter of 0.15 m is used (average of stack diameters from Reference 9). Stack diameter for RSA Corp. is from Reference 37.

A stack velocity of 6.3 m/sec is used based on average velocity from Reference 9. If stack velocities are known for specific plants, they are based on velocities from References 32 and 37.

A stack temperature of 320°K is used based on average temperatures for process stacks from Reference 9. Stack temperature for RSA Corporation-is from Reference 37.

- 2. Fugitive emissions A release height of 3 m, crosssectional downwash area of  $200 \text{ m} \times 100 \text{ m}$  for large plants,  $50 \text{ m} \times 100 \text{ m}$  for mediumsized plants, and  $50 \text{ m} \times 25 \text{ m}$  for small plants. Horizontal vents are assumed. A velocity of 0.01 m/sec and a temperature of  $293^{\circ}\text{K}$  (ambient) are assumed.
- 3. Storage emissions A height of 7.7 m is used based on average height of tanks from Reference 9. PES assumes venting is vertical, a vent diameter of 0.076 (Reference 40), a velocity of 0.01 m/sec, and a

temperature of 293°K (ambient).

### I. Emissions

Except for RSA Corp., plant-specific emissions of naphthalene from miscellaneous organic chemical production were calculated on the basis of total naphthalene consumption. (RSA Corporation reported emissions as "trace," which means <0.001 lb/hr.) For other plants, it is assumed that 0.034% of total naphthalene consumed as end-use chemicals is lost to atmosphere (based on Reference 14 estimate that a maximum of 0.07% of naphthalene produced is lost to the environment and 48% of that amount is lost to atmosphere). This gross estimating procedure is used because of the lack of usable or no plant-specific information.

Based on (1) 0.034% of total naphthalene consumed (315 Gg, Reference 3) is lost to air and (2) 2% of total naphthalene is from production of miscellaneous organic chemicals (Reference 3), total naphthalene emissions from production of miscellaneous organic chemicals is calculated as:

 $0.02 \times 0.00034 \times 315 \text{ Gg} = 0.0021 \text{ Gg}$ 

= 2.1 Mg

This total was divided among all plants for which no specific emission was available (2.1 Mg  $\pm$  14 plants = 150 kg each plant). One-third of the total plant estimate was assigned each to process, storage, and fugitive emissions (50 kg each).

Only storage emissions of methylnaphthalene were estimated for Crowley Chemicals, Kent, OH, and Oklahoma City, OK, since no chemical production occurs at either facility (References 38 and 39).

Emissions from 1-naphthol production at Union Carbide, Institute, WV, are included in naphthalene emissions from carbaryl production (Reference 7) (see Section A.5).

Table A-2 presents the modeling parameters for naphthalene production. After completion of the modeling, a review of the emission estimating procedures resulted in revised emission estimates. Overall emissions for the production category increased 0.4 percent, from 52,960 kg/yr to 53,200 kg/yr. Total fugitive emissions increased from 1,560 kg/yr to 2,180 kg/yr. Process emissions decreased from 47,200 kg/yr to 46,900 kg/yr. Storage emissions decreased from 4,200 kg/yr to 4,170 kg/yr. EPA determined that additional modeling was not necessary.

Record	update	pollutant	source_cat			plant_name		longitude		
1	10/28/86	Naphthalene	Coke by-product	1	3312 .	Empire Coke	331425	873011		Holt
- 2	18/28/86			1			0	0	0	
3	10/28/86			1			0	0	0	
4	10/28/86			5		Republic Steel	340046	869238	0	Gadsden
5	10/28/86			٤			0	0	0	
6	10/28/86			2			0	0	0	•
7	10/28/86			3		National Steel	384140	900742	0	Granite City
8	10/28/86			3			0	0	0	
9	10/28/86			3			0	8	0	
10	10/28/85			4		Interlake	413922	873732	0	-
11	10/28/86			4			0		8	
12	10/28/86			4			0	_	0	
13	10/28/86			5		Indiana Gas & Chem.	392648	872347		Terre Haute
14	10/28/86			5			Ø		0	
15	10/28/86			5			0		_	
16	10/28/86			6		u.S. Steel	413655	872003		Gary
17	10/28/86			6			0	0	_	
18	10/28/86			6			Ø	_	-	
19	10/28/86			7		Rouge Steel Co.	421819	830940	0	Dearborne
20	10/28/86			7			Ø	0	9	
21	10/28/86			7			0	_	_	
22	10/28/86			8		National Steel	421516	830743	0	Detroit
23	10/28/86			8			0	, 0	0	İ
24	10/28/86			a			0		_	
25	10/28/86			9	1	Bethlehem Steel	403651	752113	0	Bethlehem
26	10/28/86	,		9			9	. 0		1
27	10/28/66	•		. 9	<b>)</b>		8	ı e		•
28	10/28/86			10	ŀ	Chattanooga Coke & 8	350216	851811	0	Chattanooga
29	10/28/86	•		16	<b>i</b>		0	. 6		)
30	10/28/86			10	i .		0	. 6		1
31	10/28/86			11		Lone Star Steel	325459	944257	. 6	Lone Star
32				11			Ø	ı lê	ı e	1
33	10/28/86			11	•		0	e	e	1
34	10/28/86		•	18	2	J&∟ Steel	402534	795747		Pittsburgh
35	18/26/86			18	2		ď	) (	۱ و	)
36	10/28/86			18	2		8	. 8		)

A-2

Table A-1. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM COKE BY-PRODUCT RECOVERY PLANTS (concluded)

Record# plant_name state type stack_num height area vent_type diameter velocity		15510ns
1 Empire Coke AL P 1 4.30 0.00 0 0.160 2.930	367 <b>0.000</b> 3	33 <b>0. 000</b>
F 1 3.00 4875.00 1 0.000 0.010 7	2937 0.000 - 3	330.000
3 S 1 12.30 0.00 0 0.076 0.010		330.000
4 Republic Steel AL P 1 1.00 0.00 0 0.160 2.930	367 0.000 17	700.000
5 F 1 3.00 10000.00 1 0.000 0.010	293 0.000 17	700.000
6 5 1 12.30 0.00 0 0.076 0.010	293 0.000 17	700,000
7 National Steel IL P 1 4.30 0.00 6 0.160 2.930	367 0.000 10	000.000
8 F 1 3.00 10000.00 1 0.000 0.010	293 0.000 10	880.666
g S 1 12.30 0.00 0 0.076 0.010	293 0.000 10	000.000
10 Interlake IL P 1 4.30 0.00 0 0.160 2.930	367 0.000 10	000.000
11 F 1 3.00 10000.00 1 0.000 0.010	293 0.000 10	000.000
12 S 1 12.30 0.00 0 0.076 0.010	293 0.000 10	000.000
13 Indiana Gas & Chem. IN P 1 4.30 0.00 0 0.160 2.930	367 0.000	330.000
14 F 1 3.00 4875.00 1 0.000 0.010	293 0.000	330.000
15 5 1 12.30 0.00 0 0.076 0.010		330.000
16 U.S. Steel IN P 1 4.30 0.00 0 0.160 2.930		000.000
17 F 1 3.00 28000.00 1 0.000 0.010		000.000
18 5 1 12.30 0.00 0 0.076 0.010		000.000
19 Rouge Steel Co. MI P 1 4.30 0.00 0 0.160 2.930		600.000
20 F 1 3.00 10000.00 1 0.000 0.010	293 0.000 1	600.000
21 5 1 12.30 0.00 0 0.076 0.010	293 0.000 1	600.000
22 National Steel MI P 1 4.30 0.00 0 0.160 2.930	367 0.000 2	700.000
23 F 1 3.00 20000.00 1 0.000 0.010		700.000
24 5 1 12.30 0.00 0 0.076 0.010		700.000
25 Bethlehem Steel PA P 1 4.30 0.00 0 0.160 2.930		300.000
26 F 1 3.00 20000.00 1 0.000 0.010		300.000
27 S 1 12.30 0.00 0 0.076 0.010		300.000
28 Chattanooga Coke & C TN P 1 4.30 0.00 0 0.160 2.930		330.000
29 F 1 3.00 4875.00 1 0.000 0.010		330.000
30 5 1 12.30 0.00 0 0.076 0.010		330.000
31 Lone Star Steel TX P 1 4.30 0.00 0 0.160 2.930		000.000
32 F 1 3.00 10000.00 1 0.000 0.010		000.000
33 5 1 12.30 0.00 0 0.076 0.010		000.000
34 J & L Steel PA P 1 4.36 8.66 6 6.168 2.936		300.000
35 F 1 3.90 20000.00 1 0.000 0.010		300.000
36 5 1 12.30 <b>0.00 0</b> 0.076 <b>0</b> .010	293 0.000 3	300.000

Table A-2. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM NAPHTHALENE PRODUCTION

8 10/28/86 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	<b>Re</b> cord <b>*</b>	update	pollutant	source_cat		plant_numb	sic_code	plant_name	latitude	longitude	urban	city
1 10/28/86	i	10/28/86	Nahothalene	Naonthalene	arod.	1	2865	Allied Chemical Co.	383016	823942	•	Ironton,
4 10/28/86	5	10/26/86				1			8	0	9	
5 10/28/86	3	10/28/86				i			0	8	0	
6 10/28/86 7 10/28/66 3 2869 E.I. duPont de Nem. 291550 951248 0 Chocolate Bay 8 10/28/86 3 3 8 0 0 0 0 9 10/28/86 3 0 0 0 0 10 10/28/86 4 2865 Koppers Company, Inc 402013 803620 0 Follansbee 11 10/28/86 4 2865 Koppers Company, Inc 402013 803620 0 Follansbee 12 10/28/86 4 0 0 0 0 0 13 10/28/86 4 0 0 0 0 0 14 10/28/86 4 0 0 0 0 0 15 10/28/86 4 0 0 0 0 0 16 10/28/86 4 0 0 0 0 0 17 10/28/86 5 2869 Texaco Chemical 393507 753744 0 Delaware City 19 10/28/86	4	18/28/86				5	2869	Chemical Exchange	294515	950100	0	Baytown
7 10/28/86 3 2869 E.I. duPont de Nem. 291550 951248 0 Chocolate Bay 8 10/28/86 3 0 0 0 9 10/28/86 3 0 0 0 10 10/28/86 4 2865 Koppers Company, Inc 402013 803620 8 Follansbee 11 10/28/86 4 0 0 0 12 10/28/86 4 0 0 0 13 10/28/86 4 0 0 0 14 10/28/86 4 0 0 0 15 10/28/86 4 0 0 0 16 10/28/86 4 0 0 0 17 10/28/86 4 0 0 0 18 10/28/86 5 2869 Texaco Chemical 393507 753744 0 Delaware City 19 10/28/86 5 0 0 0 0 0	5	10/28/86				2			0	0	0	
8 10/28/86 3 0 0 0 0 0 0 0 9 10/28/86 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	6	10/28/86				5			0	0	0	
9 10/28/86 3 4 2865 Koppers Company, Inc 402013 803620 6 Follansbee 11 10/28/86 4 2865 Koppers Company, Inc 402013 803620 6 Follansbee 11 10/28/86 4 0 0 0 0 13 10/28/86 4 0 0 0 0 14 10/28/86 4 0 0 0 0 15 10/28/86 4 0 0 0 0 16 10/28/86 4 0 0 0 0 17 10/28/86 4 0 0 0 0 18 10/28/86 5 2869 Texaco Chemical 393507 753744 6 Delaware City 19 10/28/86 5 0 0 0 0 0	7	10/28/86				3	2869	E.I. duPont de Nem.	291550	951248	0	Chocolate Bayou
10 10/28/86	8	10/28/86				3			0	0	0	ı
11       10/28/86       4       8       6       6         12       10/28/86       4       0       0       0         13       10/28/86       4       0       0       0         14       10/28/86       4       0       0       0         15       10/28/86       4       0       0       0         16       10/28/86       4       0       0       0         17       10/28/86       4       0       0       0         18       10/28/86       5       2869       Texaco Chemical       393507       753744       0       Delaware City         19       10/28/86       5       0       0       0       0	9	10/28/86				3			8	0	0	
12 10/28/86	10	10/28/86				4	2865	Koppers Company, Inc	402013	803620	9	Follansbee
13       10/28/86       4       0       0       0         14       10/28/86       4       0       0       0         15       10/28/86       4       0       0       0         16       10/28/86       4       0       0       0         17       10/28/86       4       0       0       0         18       10/28/86       5       2869       Texaco Chemical       393507       753744       0       Delaware City         19       10/28/86       5       0       0       0       0	11	10/28/86				4			8	0	0	
14       10/28/86       4       0       0       0         15       10/28/86       4       0       0       0         16       10/28/86       4       0       0       0         17       10/28/86       4       0       0       0         18       10/28/86       5       2869       Texaco Chemical       393507       753744       0       Delaware City         19       10/28/86       5       0       0       0       0	12	10/28/86				4			Ø	0	0	
15 10/28/86 4 0 0 0 0 16 16 10/28/86 4 0 0 0 0 17 10/28/86 4 0 0 0 0 0 0 0 0 18 10/28/86 5 2869 Texaco Chemical 393507 753744 0 Delaware City 19 10/28/86 5 0 0 0 0 0	13	10/28/86				4			0	0	0	
16 10/28/86 4 0 0 0 0 0 17 10/28/86 4 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	14	10/28/86				4			0	0	0	
17 10/28/86 4 0 0 0 0 0 18 10/28/86 5 2869 Texaco Chemical 393507 753744 0 Delaware City 19 10/28/86 5 0 0 0	15	10/28/86				4			0	0	0	
18 10/28/86 5 2869 Texaco Chemical 393507 753744 6 Delaware City 19 10/28/86 5 0 0 0	16	10/28/86				. 4			0	Ø	0	
19 10/28/86 5 0 0 6	17	10/28/86				4			0	8	0	
	18	10/28/86				5	2869	Texaco Chemical	393507	753744	0	Delaware City
	19	10/28/86				5			0	0	0	
£W 10/28/86 5 0 0 0	ڪَ0	10/28/86				5			9	0	0	
21 10/08/86 6 2869. Ashland Chemical 382736 823818 0 Ashland	21	10/08/86				6	2869.	Ashland Chemical	382736	823818	0	Ashland
22 10/06/86 7 2865 U.S.S. Chemicals 401736 795230 0 Clairton	22	10/06/86				7	2865	U.S.S. Chemicals	401736	795230	0	Clairton
23 10/08/65 8 2865 U.S.S. Chemicals 413600 872006 0 Gary	23	10/08/85				8	2865	U.S.S. Chemicals	413600	872006	0	Gary
24 10/08/86 9 2865 Koppers Company, Inc 415100 874742 0 Stickney	24	10/08/86				9	2865	Koppers Company, Inc	415100	874742	0	Stickney

Table A-2. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM NAPHTHALENE PRODUCTION (concluded)

Record#	plant_name	state	type stack_nu	118	height	area	vent_type	diameter	velocity	temp	ew_wax	emissions
1	Allied Chemical Co.	OH	P	1	13.00	0.00	0	<b>0.</b> 150	6.300	320	0.00 <del>0</del>	82 <b>00. 000</b>
2	,		F	1	3.00	20000.00	1	0.000	0.010	293	0.000	2 <b>98. 866</b>
3	1		5	i	7.60	0.00	0	<b>0.0</b> 76	0.010	293	0.000	780.000
4	Chemical Exchange	TX	P	1	13.00	0.00	9	0.150	6.300	320	0.000	3400.000
5	•		F	1	3.00	20000.00	1	ø. 000	0.010	293	0.000	120.000
Ĝ			S	1	7.60	0.00	0	0.076	0.010	293	0.000	320.000
7	E.I. duPont de Nem.	TX	P	1	13.00	0.00	8	0.150	6.300	320	0.000	9800.000
8			F	1	3.00	20000.00	1	0.000	0.010	293	0.000	340.000
9			S	1	7.68	0.00	0	0.076	0.010	293	0.000	940.000
10	Koppers Company, Inc	WV	P	1	13.00	0.00	0	0.150	6.300	320	0.000	19300.000
11			F	i	3.00	20000.00	1	0.000	0.010	293	0.000	580.000
12			S	1	6.70	0.00	0	0.076	8.010	293	0.668	160.000
13			S	2	7.60	0.00	0	0.076	0.010	293	0.000	170.000
14			S	3	10.90	0.00	0	0.076	0.010	293	0.000	261.000
15			5	4	9. 10	0.00	8	0.076	0.010	293	0.000	277.000
16			S	5	6.10	0.00	0	0.076	0.010	293	0.000	356.000
17			S	6	12.80	0.00	8	<b>0.0</b> 76	0.010	293	0.000	316.000
18	Texaco Chemical	DE	p	i	13.00	0.00	0	0.150	6.300	320	0.000	6500.000
19			F	1	3.00	20000.00	1	0.600	0.010	293	0.000	230.000
20			S	1	7.60	0.00	Ø	0.076	0.010	293	0.000	620.000
21	Ashiand Chemical	кү		0	0.00	0.00	0	0.006	0.000	0	0.000	0.008
25	U.S.S. Chemicals	PA		0	0.00	0.00	0	0.000	0.000	0	0.000	0.000
23	U.S.S. Chemicals	IN		0	0. 00	0.00	9	0.000	0.000	0.	0.000	0.000
24	Koppers Company, Inc	IL		Ò	0.00	0.00	8	0. 800	9. 666	ø	0.000	0.000

# Table A-3. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM PHTHALIC ANHYDRIDE PRODUCTION

Record#	upcate	pollutant	source_cat	plant_numb	S1C_Code	plant_name		latitude	longitude	urban (	city
1	10/08/86	Nachthalene	Phthalic Anyhdride	1	2869	Koppers Co.	Inc.	402136	800700	0	Bridgeville
5	10/08/86			2		Monsanto Co.		394886	752100	8 1	Bridgeport
3	10/08/86			• 3		Koppers Co.	Inc.	415100	874742	0	Stickney
4	10/28/86			3				Ø	0	Ø	
5	10/28/86			3				0	0	9	

Record#	olant_name	state	type stac	k_num	height	area v	ent_type	diameter	velocity	temp	<b>ew_ma</b> x	emissions
1	Koppers Co. Inc.	PA		0	Ø. 00	0.00	0	0.000	0.000	Ö	0.000	8.008
è	Monsanto Co.	ĹŃ		Ø	0.00	0.00	0	0.000	0.000	0	0.000	0.000
3	Koopers Co. Inc.	1L	ρ	1	0.00	0.00	0	0.000	0.000	0	0.606	0.000
4			F	1	3.00	20000.00	1	0.000	0.010	293	0.000	8470.000
5			S	1	9.80	0.90	0	0.076	0.010	293	0.000	46300.000

Table A-4. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM CARBAMATE INSECTICIDES PRODUCTION

Record#	update	pollutant	source_cat	plant_numb	sic_code	plant_nam	æ		latitude	longitude	urban	city
1	10/14/86	Naonthalene	Carbaryl Prod.	1	2879	Union Car	rbide (	Corp.	382258	814625	0	Institute
- 2			·	1					0	0	0	
3				1					8	0	0	
4				1					0	0	0	
5	10/14/86	•		1					0	8	0	
6				1					0	0	Ø	
7	10/14/86			1					0	0	0	
B				1					Ø	0	Ø	
9				-1					0	9	0	
10	10/28/66			i					Ø	0	Ø	
11	10/14/86			1					0	0	0	
12				1	•				0	0	0	
13	10/14/86			2		Union Car	ebide		383400	901500	9	St. Louis

Recora#	plant name	state type	stack_num	neight	area	vent_type	dlameter	velocity	temp	em_max	emissions
1	Union Carbide Corp.		1	12.20	0.00	Ø	0.150	1.200	339	0.000	686.000
ء ء		ρ	. 5	16.80	0.00	0	0.300	14.400	313	0.000	571.000
3		ą	3	4.60	0.00	Ø	0.250	0.220	313	0.000	72.000
4	•	p	4	15.20	0.00	0	0.040	2.400	261	0.000	71.000
5		ρ	5	13.70	0.00	Ø	0.100	19.800	313	0.000	1.300
6		p	6	15.20	0.00	0	0.037	0.910	323	0.000	0.820
7		Ē	7	3.00	20000.00	1	0.000	0.010	293	0.000	1250.000
A		S	8	12.20	0.00	0	0.076	0.010	293	0.000	1831.000
9		5	9	11.00	0.00	0	0.076	0.010	293	0.000	6.000
10		ŝ	10	3.00	0.00	Ø	0.076	0.010	293	0.000	7.670
11		5	11	9.10	0.00	0	0.076	0.010	293	0.000	43.200
12		S	12	3.40	0.00	ě	0.076	0.010	293	0.000	17.300
13	Union Carolde	MÜ	ð	0. 00	0.00	0	<b>8.0</b> 88	8. 900	0	0.000	6. 606

# Table A-5. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM 2-NAPHTHOL PRODUCTION

Record# update pollutant

source cat

plant\_numb sic\_code plant\_name

latitude longitude urban city

1 10/08/86 Napthalene

Beta-maphthol prod.

1 2869 American Cyanamid Co 392048 811912

0 Willow Island

state type stack\_num height area vent\_type diameter velocity temp emissions

Record# plant\_name 1 American Cyanamid Co WV

0.00

9.000

8.000

0.000

Record#	uodate	pollutant	source cat		plant_numb	sic_code	olant_name	latitude	longitude	urban	city
1		Naonthalene	_	tanning ag	1	2869	Diamond Shamrock	405018	740542	9	Carlstadt
	10/28/86		_,		1			0	0	0	
<u>۔</u> 3	10/28/86				1			Ø	Ø	0	
-	10/28/86				ءِ		Rohm & Haas Co.	395954	750400	0	Philadelphia
4	10/28/86				2			9	8	9	·
5					د			à	à	0	
6	10/28/86				2		Morflex, Inc.	360518	795324	_	Greensboro
7	10/28/86				3		MOTTER, INC.	206210	7 35524	a	G/ CE113001 0
8	10/28/86				3	i		U	_	•	
9	10/28/86				3			0	Ø	0	
10	10/28/86				4		Georgia Pacific Corp	484548	1222900	9	Bellingham
11	10/28/86				4			0	8	0	
12	10/28/86				4	ı		8	0	0	
	10/28/86				5		Diamond Snamrock	340048	851518	0	Cedartown
13	•						Didnord Briam CER	a a	0	9	
14	10/28/86				5	1		Ø	0		
15	10/28/86				5	,		Ø	0	0	

Recora#	plant_name	type	stack num	height	area v	ent_type	diameter	velocity	temo	<b>e</b> m_wax	emissions
1	Diamond Shamrock	۾ َ	1	13.00	0.00	Ø	0.150	6.300	320	0.000	430.000
- خ		F	1	3.00	20000.00	1	0.000	0.010	293	0.000	430.080
3		S	1	7.70	0.00	0	0.076	0.010	293	0.000	430.000
4	Ronm & Haas Co.	P	1 .	13.00	0.00	Ø	0.150	6.300	320	0.000	430.000
5		F	1	3.00	20000.00	1	0.000	0.010	293	0.000	430.000
6		S	1	7.70	Ø. ØØ	8	0.076	0.010	293	0.000	430.000
7	Morflex. Inc.	p	i	13.00	0.00	ø	0.150	6.300	320	0. 000	430.000
ŝ		Ê	1	3.00	20000.00	1	0.000	0.010	293	0. 000	430.000
9		ŝ	1	7.70	0.00	9	0.076	0.010	293	0.000	430. 600
10	Georgia Pacific Corp	Þ	1	13.00	0.00	0	0.150	6.300	320	0.000	430.000
11	ocornia ractite one	Ė.	1	3.00	20000.00	1	0.000	0.010	293	0.000	430, 000
12		ģ	1	7.70	0.00	è	0.076	0.010	293	0.000	430.000
13	Diamond Shamrock	ρ	1	13.08	Ø. ØØ	0	0.150	6.300	320	0.000	430.000
14	Diamond Pilaminek	Ē	1	3.00	20000.00	1	0.000	0.013		8.000	430,000
17		, G	1	7.78	0.00	ō	0.076	0.010	293	3. 888	430.000

Table A-7. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM PRODUCTION OF SURFACE ACTIVE AGENTS -- 1-NAPHTHALENESULFONIC ACID

Record	undate	pollutant	source_cat	plant_numb	SIC_CODE	plant_name	latitude	longitude	urban	city
. 1	10/14/86	Naphthalene	1-map.sulfonic acid	1	2843	American Cyanamid	403800	741500	0	Linden
2	10/14/86			1			0	0	0	
3	10/14/86			i			0	8	0	
4	10/14/86			٤		Ciba-Geigy Corp	395254	741048	0	Toms River.
5	10/14/86			2			0	0	0	
6	10/14/86			5			•	0	0	
7	10/14/86			3		DeSoto, Inc.	324448	972000	0	Fort Worth
8	10/14/86			3			8	9	8	
9	10/14/86			3			0	8	8	
10	10/14/86			4		Diamond Shamrock	405018	740542	0	Carlstadt
11	10/14/86			4			9	0	0	
12	10/14/86			4			0	0	Ø	
13	10/14/86			5		Diamond Shamrock	340048	851518	0	Cedartown
14	10/14/86			5			0	0	Ø	
15	10/14/86		J	5			0	0	8	
16	10/14/86			6		E.I. duPont de Nem.	394100	752924	0	Deepwater
17	10/14/86			6	•		. 0	0	0	
18	10/14/86			6			0	Ø	0	-
19	10/14/86			7		EmKay Chem. Co.	403912	741130	8	Elizabeth
20	10/14/86			7			0	0	0	
. 21	10/14/86			7			8	0	8	
55	10/14/86			8		Morflex, Inc.	360518	795324	0	Greensboro
23	10/14/86			8			0	8	8	
24	10/14/86			8			0	0	0	
25	10/14/86			9		Georgia Pacific	484548	1222900	0	Bellingham
26	10/14/86			9			0	Ø	0	
27	10/14/66			9			•			

Table A-7. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM PRODUCTION OF SURFACE ACTIVE AGENTS -- 1-NAPHTHALENESULFONIC ACID (concluded)

Record#	olant name	state	type s	stack_num	height	area	vent_type	diameter	velocity	temb	ew_wax	emissions
1	American Cyanamid	NJ	p	- 1	19.80	0.00	Ũ	0.150	17.200	320	0.000	41.000
غ .	range and a year.		F	1	3.00	20000.00	1	0.000	0.010	293	0.000	41.000
3			S	1	7.70	0.00	Ø	0.076	0.010	293	0.000	41.000
4	Ciba-Geigy Corp	NĴ	p	1	13.00	0.00	Ø	0.150	6.300	320	0.000	41.000
5	Ciba Cciay Co. 5		F	1	3.00	20000.00	1	0.000	0.018	293	0.000	41.000
6			S	1	7.70	0.00	0	0.076	0.010	293	0.000	41.000
7	DeSoto, Inc.	TX	p	1	13.00	0.00	Ø	0.150	6.300	320	0.000	41.000
ŝ	DEBOVO, TIME		F	1	3.00	5000.00	1	0.000	0.010	293	0.000	41.000
9			S	1	7.70	0.00	0	0.076	0.010	293	0.000	41.000
18	Diamond Shaprock	NJ	P	1	3.00	0.00	0	0.150	6.300	320	0.000	41.000
11	D10110110 D110111		F	1	3.00	20000.00	1	8. 888	0.010	293	0.000	41.000
12			S	1	7.70	0.00	0	0.076	0.010	293	0.000	41.000
13	Diamond Shamrock	GA	p	1	13.00	0.00	Ø	0.150	34.000	320	0.000	41.000
14			F	1	3.00	20000.00	1	0.000	0.010	293	0.000	41.000
15			Š	1	7.70	0.00	0	0.076	0.010	293	0.000	41.000
16	E.I. duPont de Nem.	ΝĴ	P	1	15.80	0.00	0	0.150	0.170	320	9.000	41.000
17		***	F	1	3.00	20000.00	1	0.000	0.010	293	0.000	41.000
18			S	1	7.70	0.00	9	0.076	0.010	293	0.000	41.000
19	Emkay Chem. Co.	NJ	p	1	13.00	0.00	0	0.150	6.300	320	0.000	41.000
20	zania, znami		F	i	3.00	5000.00	1	0.000	0.010	293	0.000	41.000
21			S	1	7.70	0.00	Û	0.076	0.010	293	0.000	41.000
55	Morflex, Inc.	NC	p	1	13.00	0.00	0	0.150	5.300	320	0.000	41.000
23			F	1	3.00	20000.00	1	0.000	0.010	293	0.000	41.000
24			S	1	7.70	0.00	Ø	0.076	0.010	293	0.000	41.000
25	Georgia Pacific	ЫĀ	ρ	1	13.00	0.00		0.150	6.300	320	0.000	41.000
26	HEN. 2-4 . HES	••	F	1	3.00	20000.00		0.000	0.010	293	0.000	41.000
27			5	1	7.70	0.00	0	0.076	0.010	293	0.008	41.000

# Table A-8. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM PRODUCTION OF SURFACE ACTIVE AGENTS -- 2-NAPHTHALENESULFONIC ACID

Kecord#	update	pollutant	source_cat	plant_numb	sic_code	plant_name	latitude	longitude	urban	city
1	10/15/86	Naphthalene	2-map.sulfonic acid	1	2843	Allied Corp.	394818	752712	0	Claymont
5	10/15/86			1			0	0	ø	•
3	10/15/86			1			0	0	6	
4	10/14/86			ž	2843	American Cyanamid Co	392830	812748	0	Marietta
5	10/15/86			2		•	ø	0	Ø	
6	10/15/86			2			0	Ø	8	
7	10/15/86			3	2810	American Cyanamid	403800	741500	0	Linden
8	10/15/86			3		,	0	0	0	
9	10/15/86			3			0	0	Й	
10	10/15/86			4	2843	DeSoto, Inc.	324448	972000	9	Fort Worth
11	10/15/86			4			Ú	0	Ø	
12	10/15/86			4			À	0	À	
13	10/15/86			5	2843	E. I. duPont de Nem.	394100	752924	ñ	Deepwater
14	10/15/86			5			0	0	9	accpiiose.
15	10/15/86			5				9	a	
16	10/15/86			6	2843	EmKay Chemical Co.	403912	741130	a	Elizabeth
17	10/15/86			6			ù		û	
18	10/15/86			6			Ä	. 0	ù	

Table A-8. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM PRODUCTION OF SURFACE ACTIVE AGENTS -- 2-NAPHTHALENESULFONIC ACID (concluded)

Record#	plant_name	state	type	stack_num	height	area	vent_type	diameter	velocity	temp	em_max	emissions
1	Allied Corp.	DE	p	1	13.00	0.00	Ú	<b>0.</b> 150	6. 300	320	0.000	350.000
ء ء			F	1	3.00	20000.00	1	0.000	0.010	293	v. 000	350.000
3			S	1	7.70	0.00	0	0.076	0.010	293	0.000	350.000
4	American Cyanamid Co	OH	p	1	13.00	0.00	0	0.150	6.300	320	0.000	350.000
5	FREE TEAM OF AMERICA		F	1	3.00	20000.00	1	0.000	0.010	293	0.600	350.000
6			S	1	7.70	0.00	•	0.076	0.010	293	ø. 000	350.000
7	American Cyanamid	NJ	ρ	1	19.80	0.00	0	0.150	17.200	320	0.000	350 <b>. 60</b> 6
A	ranci ican by annual		F	1	3.00	20000.00	1	0.000	0.010	293	0.000	350.000
9			S	1	7.70	0.00	Û	0.076	Ø. 01v	<b>ط93</b>	u. 000	350.000
10	DeSoto, Inc.	TX	ρ	1	13.00	0.00	0	0.150	6.300	320	0.000	350.000
11	pedovoj Tile:		F	1	3.00	5000.00		0.000	9.010	293	0.000	350.000
12			S	1	7.70	0.00		0.076	0.010	293	0.000	350.000
13	E.I. duPont de Nem.	NJ	p	1	15.80	8.00		0.150	0.170	320	U. 00U	350.000
14	C. I. Odrone de nem	110	F	1	3.00	20000.00		0.000	0.010		0.000	350.000
15			S	1	7.70	0.00		0.076	0.016		0.000	350.000
16	EmKay Chemical Co.	NJ	ρ	1	13.00	0.00		0.150	6.300	320	0.000	350.000
17	Empay Chemical Co.	110	F	. 1	3.00	5000.00		8.000	0.010		0.000	350.000
17			S	i	7.70	9.00		0.076	0.010		Ø. <del>80</del> 0	350.000

Table A-9. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM PRODUCTION OF MOTH REPELLANT

Record# update poilutant

source\_cat

plant\_numb sic\_coce plant\_name

latitude longitude urban city

	10/14/66 Naonthalene 10/14/66 10/14/66	Мо	th Recei	lant		1 2879 1 1	Morflex.	inc.	8: <b>6</b> 666 & & &		24 Ø G Ø & Ø Ø	r <mark>eenbo</mark> ro
4	1 1					خ	Kincaid	Enterorises	382524	8150	50 0 N	itro
3					<b>.</b>					****	02 121	001051545
Record#	plant_name	state	type sta	CK_YIUM	perčut		verit_type	01ameter	velocity		em_max	emissions
1	Morflex, inc.	NŪ	بَ	ē	ø. 38	ű. Øð	1 3	d. 638	d. 000	Ø	865.5	8. 233
2	1		F	è	હે. છેહે	0.00	12)	0.000	0.000	Ø	0.00C	0. &&&
3			ŝ	Ø	0.00	0.00	Ø	0.600	0.000	6	0.000	0.020
4	Kincaid Enterprises	wV		Ø	0.00	0.00	0	0.000	0.000	Ø	0.000	0.000

Georgian e	.⊤.ate	politiant	scurde_pat	clart_numb_sic_code	D.art_nade	latituce	respirace	erbak bity
		Neumonalera	\201712.		urion Cambide como	فكككف	#146£	@ Institute
	12 / 13 / 61		1-Naonthylamine	easa s	Sigma Chemical Co.	383742	901318	Ø St. ⊥ouis
	.ā.25/3c			<u> -</u>		Ċ	ð	3
	12/20/23			à	i	è	Ø	Ŵ.
	.1/_8/50		1234- atranvenchas.	a-28c9	I audort de New.	394188	/52524	& Deedwater
	12/33/3E			3		3	ù	ò
	.1, I3/3E			ۮٙ		ę	Ø.	ř
	12/26/82		iddy-Tetramycronap.	4 2879	union Carbice Corb	361536	812342	Ø institute
	.012875£			4		Ē	r,	2
	10/38/86			7		Ž.	Ŷ.	Z.
	16/23/38		Decanyoninabnu tawaka	၌ ခိုရစစ	E. I. Carono de New.	394100	752924	ð Deesmater
	.0/28/66			Cn		Ý	Ø	હ
	18, 18, 56			5		Ž)	õ	ð
	14/18/85		Nabacetic acid	£ 2879	Greenwood Chew. Co.	386315	764612	0 Greenwood
	10/18/58		Natacetic acid	7 2879	urion Carbiae Corp.	406560	/±13c4	
	30/85/56			7		Ŋ	ĕ	
	نَفُ لَيْنَاءُهُ.			7		نَ	ŷ	ð
	12,26/85		1-Bromonachthalena	8 2865	R.S.A. Corp.	404204	735:15	<b>Ø</b> Arcsiey
	10/22/58			à		ċ	ų.	ζ:
	10/08/63			ċ		ť	ð	Ž.
	. දී / දිනි / ප්ර		retrylesstralere	ālijā E	Kobbans Co., inc.	4020.3	ಪ0.36ಪ0	Ø Follanspææ
	10,12/20			Ŝ		Ò	Ø.	ઠે
	.∂/£6 d6			Ė		ů	Ž.	Ĵ
	10/28/68		Tetrv.rashthalenë	E385 &1	Erowley Chemical	418912	812136	Ø Kent
	.@/26/Sz			ئ د		Õ	Ů	<b>ೆ</b>
	.0/18/86			75		ş	Ø	<b>L</b> i
	10/26/ca		Methylhadhthalane	11 2065	Unowiey Chemical Co.	252936	9730lc	w Uklahopa Cit,
	17/33/26			11		Ş	Ø.	Ž:
	.ø/ _ŝ/ ŭ€			±1		ů	õ	ø
	10/23/23		hein/lraphinalene	12 2869	Enemical Exchange	294515	956,68	0 mouston
	10/25/56			12		Ù	ø	ô
	12/21/20			1Ē		Č	Ċ	ð
	12/22/28		as. adetawice	ı3 zá79	Greenwood Chemica.	<b>38€3</b> 1€		
	.2/32/61		inhad, adetamide	14 2879	umian Carbide	426366	75.324	Ø Auszer
	.6'12' â			. <b>+</b>		ů	ě	ž
	12 13/03			14		Ž	Ē	•
	16/20/05		Niinchapusuutonie ac	ເວີ ພຣີໄຊ	lipa-balqy £ora.	ಎ∄5ಪ್ ⊣	741414	
	.2725.55			.5		è		
	iv Lata			ıů		ď.	રો	
			iš Jaiši	.c ±ê7a	chitive. Mi.	38,554	à.1e5↔	W Bastinia
		-				ť	v.	\$ <sup>2</sup>

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# Table A-10. MODELING PARAMETERS FOR NAPHTHALENE EMISSIONS FROM PRODUCTION OF MISCELLANEOUS ORGANIC CHEMICALS (concluded)

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3e21124	liå": rä é	Stat	E Tyle 9	etack_4UM	seight		verit_type			temo	€01_11&×	EM.55lon5
	ur John Lar ot de lúcir d	₩Ý		€	છે. છેલે	l. cd	J	ને હેર્દે છ	ú. 880	Ø	d. (dd	6.000
ê	Elgha Osemica. Do.	23	Ě	ì	13.00	2.03	Ø.	ð. 152	6.300	320	0.000	50.030
3			£	1	3.00	1250.00	1	ò. 00ò	v. 210	293	0. 000	58. 828
4			S	<u>:</u>	7.70	હે. હેહે	Ø.	ð. 676	0.610	293	હ. હેહેહે	50.200
É	č.i. cu⊬ont ce vem.	\_	÷	1	15.60	ð. 20	G	Ø. 150	ð. 17¢	320	0.000	50.600
5			Ē	<u>:</u>	3.28	20000.00	1	Ø. £02	0.010	293	ð. <i>8</i> 80	50. 200
7			ā		7.70	છે. જહે	Ð	0.076	0.013	293	ð. 630	
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# APPENDIX B

PROCEDURES FOR ESTIMATING NAPHTHALENE EMISSIONS FROM COKE BY-PRODUCT RECOVERY PLANTS

### MEMORANDUM

October 7, 1986

TO: Bob Lucas, EPA:ESED:CPB

FROM: David Cole, PES, Inc. 560

THRU: Ken Meardon, PES, Inc. LDW

SUBJECT: Procedures for Estimating Naphthalene Emissions from Coke

By-Product Recovery Plants (EPA Contract No. 68-02-3887,

Assignment 43)

This memorandum describes two procedures for estimating naphthalene emisions from coke by-product recovery plants. The first method uses coke and coal tar production figures coupled with a coal tar materials balance to derive a plant-wide naphthalene emission factor. The second method is based on a process-specific approach that is derived from limited data from one coke by-product recovery plant. Following the descriptions of these methods, an example calculation is presented to estimate naphthalene emissions from a specific plant. Emissions are calculated by using each method as a basis for comparison.

### Method 1: Development of a Plant-wide Naphthalene Emission Factor

A plant-wide naphthalene emission factor is developed based on a material balance of a representative coke by-product recovery plant and the amount of naphthalene estimated in coal tar production. A naphthalene emission factor is needed on a "kilogram (kg) of naphthalene per megagram (Mg) of coke produced" basis because coke production rates are available for each coke by-product plant. To derive this factor, PES used the following procedure:

1. Estimate annual coal tar production based on (1) the amount of naphthalene in coal tar produced (1978 estimate) and (2) the weight percent of naphthalene in dry coal tar:

1978 coal-tar naphthalene production = 230,000 Mg (Reference 1) Average Weight % naphthalene of dry tar (U.S.) = 8.80% (Reference 2)

Coal Tar Production =  $\frac{230,000 \text{ Mg}}{0.088}$  = 2.614 Tg

2. Estimate relative amount of coal tar produced per megagram of coke from material balance of a representative coke by-product recovery plant:

380 Mg Coal Tar = 0.05156 Mg Coal Tar per Mg Coke (Reference 3)

3. Estimate annual coke production based on (1) and (2) above:

 $\frac{2.614 \text{ Tg coal tar}}{0.05156 \text{ Mg coal tar/Mg coke}} = 50.7 \text{ Tg coke production, U.S.}$  (1978 estimate)

Note: This estimate approximates 1979 U.S. coke production figure (48.0 Tg) from Reference 4.

4. Calculate naphthalene emission factor from estimate of total naphthalene emissions to atmosphere from coal tar production (Reference 1) and total U.S. coke production from (3) above:

300 Mg naphthalene = 5.92 Mg naphthalene per Tg coke produced, or 0.00592 kg naphthalene per Mg coke produced

# Method 2: Development of a Process-Specific Emission Estimation Procedure

Eight specific naphthalene emission sources have been identified at coke oven by-product recovery plants. Naphthalene emission factors are developed as described below for most of these sources based on limited data from a screening study at one coke by-product plant:

### 1. Coke Oven Doors

A naphthalene emission factor of 0.73 g/hr/oven is reported in Reference 1, based on EPA estimates (1977).

### 2. Tar Processing

### a. Decanting

Based on estimate of 4.1 g/Mg coal for emissions of polynuclear aromatic compounds (PNA) (Reference 3, p. 4) of which the major component is naphthalene (Reference 1, p. 28) (PES estimates 70%), and based on ratio of 1.42 Mg coal to 1 Mg coke (Reference 3), the following naphthalene emission factor is calculated:

 $0.70 \times 4.1g/Mg \text{ coal} \times 1.42 \text{ Mg coal} = 4.1 \text{ g naphthalene}$ Mg coke per Mg coke produced

# b. Dewatering/storage

Naphthalene emissions are negligible based on total PNA compound estimates for this source (Reference 3, p. 4)

# 3. Final Cooler Unit

No air emissions of naphthalene are expected since the unit is a closed system (Reference 5, p. 3-32).

# 4. Naphthalene Separation Tank

This step involves the separation of naphthalene from water by gravity separation (indirect water final cooling process), in open basins. Therefore, fugitive emissions of naphthalene are expected. A total vapor rate of 33.8 vapor per sm³ was measured directly above the tank surface in a screening study (Reference 3, p. 93-94), but no vent stream was at a rate sufficient to be measured. The total exposed surface area was about 1000 ft², but the actual surface exposed to the wind by the naphthalene slurry was not known nor was the rate of entrained air flow in the tank available. Consequently, because of the lack of data to quantify naphthalene, no emission factor was developed from the naphthalene separation tank. Subjectively, however, the odor of naphthalene in this area was reported to be quite strong.

# 5. Naphthalene\_processing (Drying/Melting)

Each drying tank may have a vent stack which extends about 5m above the tank. From Reference 3 (pp. 95-96), the vent rate from the tank from one plant was estimated to be 2.9 sm³ vapor/Mg coke by measuring the rate of air entering a hatch of a tank due to the chimney effect. A naphthalene concentration of 533 g/sm³ was found, or 1.56 kg naphthalene per Mg coke. Since this concentration represented about twice the plant's total naphthalene production, the sample was not representative of the average emission rate (Reference 3, p. 95, 99). However, assuming a worst-case and for the lack of other data, naphthalene emissions can be estimated to be the following:

 $533 \text{ y/sm}^3 \times 2.9 \text{ sm}^3/\text{Mg} \text{ coke} = 1546 \text{ g/Mg} \text{ coke}$ 

# 6. Tar Storage Tanks (containing naphthalene)

A VOC emission factor of 281 g/Mg coke production is based on Reference 5, p. 7-5, for tar storage. Assuming that the percentage of naphthalene in the primary coke tar storage tank is between 18 to 32 percent (PES assumes 25% for calculating emission factors) from Reference 6, and applying that percentage to the VOC emission factor, then the naphthalene emission factor can be estimated to be:  $0.25 \times 281 \text{g/Mg}$  coke = 70.25 g/Mg coke

### 7. Naphthalene Storage Tanks

No throughput data are available for naphthalene storage tanks at coke by-product recovery plants. If data were available, then the fixed-roof tank equations from EPA Publication AP-42 for calculating breathing and working losses could be applied, assuming 96% of contents of tank is naphthalene (Reference 6).

# 8. Equipment Leaks

Equipment leaks of naphthalene are assumed to originate from exhausters, pump seals, valves, relief valves, sampling connections, and open-ended lines. VOC emission factors from coke by-product plants (Reference 5, p. 3-43) are used to approximate naphthalene emissions. Naphthalene constitutes about 96% of crude naphthalene produced and 70% of coal tar produced. Assuming the naphthalene concentration increases as the coke by-products are recovered (which is certainly the case when refining the naphthalene), PES has assumed that naphthalene emissions throughout the plant represent 75% of total VOC fugitive emissions. Number of pieces of equipment per model plant is based on number of units in Reference 5, p. 6-13.

# Example Calculation of Plant-Specific and Nationwide Emissions of Naphthalene

# I. USS-Fairfield Coke Plant

Naphthalene emissions from the USS-Fairfield coke plant in Fairfield, Alabama, were calculated based on each of the above methods for comparison. Specific data from this plant (e.g., number of ovens) are used in the calculations when available.

Using Method 1, the naphthalene emissions are calculated as follows:

$$\frac{\text{0.00592 kg naphthalene}}{\text{Mg coke}} \times 4324 \frac{\text{Mg coke}}{\text{day}} \times 365 \frac{\text{days}}{\text{yr}} \times \frac{1 \text{ Mg}}{1 \times 10^3 \text{kg}}$$

= 9.34 Mg/yr.

Using Method 2, the naphthalene emissions are calculated as follows:

# 1. Coke Oven Doors

$$0.73g$$
 x 337 ovens x 8760 hr x 1 Mg = 2.16 Mg/yr yr 1 x 10<sup>6</sup>g

# 2. Tar Decanting

4.1 g naphthalene/Mg coke x 4324 Mg coke/day x 365 
$$\frac{\text{day}}{\text{yr}}$$
 x  $\frac{1 \text{ Mg}}{1 \times 10^6 \text{g}}$  = 6.47 Mg/yr

# 3. Naphthalene processing

1,546 g/Mg coke x 4324 Mg coke/day x 365 
$$\frac{\text{day}}{\text{yr}}$$
 x  $\frac{1 \text{ Mg}}{1 \text{ x } 10^{6} \text{ g}}$  = 2,440 Mg/yr

### 4. Tar Storage Tanks

70.25 g/Mg coke x 4324 Mg coke/day x 365 
$$\frac{\text{day}}{\text{yr}}$$
 x  $\frac{1 \text{ Mg}}{1 \times 10^{6} \text{g}}$  = 111 Mg/yr

# 5. Naphthalene Storage Tanks

None - all naphthalene is stored as a component of coal tar in tar storage tanks. Emissions included in (4) above.

# 6. Equipment Leaks

### Pump Seals

The Fairfield plant reports 12 single mechanical seal pumps in various service. All pumps are assumed to convey naphthalene, which is assumed to be 75 percent of VOC stream.

Pump seal emissions are based on VOC emission factor of 2.7 kg/source/day (Reference 5, p. 3-43):

9 pumps x 0.75 x 2.7 kg VOC/pump/day x 365  $\frac{\text{days}}{\text{yr}}$  = 6,652 kg/yr = 6.7 Mg/yr

# Valves

Assume total of 105 valves (Reference 5, p. 6-13); 75% of VOC is naphthalene:

105 valves x 0.75 x 0.26 kg VOC/valve/day x 365  $\frac{\text{days}}{\text{yr}}$  = 7.5 Mg/yr

# Relief Valves

Assume 5 relief valves (Reference 5, p. 6-13), 75% of VOC is naphthalene:

5 relief valves x 0.75 x 3.9 kg VOC/relief valve/day x 365 <u>days</u> yr

- = 5338 kg/yr
- = 5.3 Mg/yr

# Sampling connections

Assume 10 sampling connections (Reference 5, p. 6-13), 75% of VOC is naphthalene:

10 sampling connections x 0.75 x 0.36 kg VOC/sampling connection/day x 365  $\frac{\text{days}}{\text{yr}}$  = 986 kg/yr = 1.0 Mg/yr

### Open-ended lines

Assume 22 open-ended lines, (Reference 5, p. 6-13), 75% of VOC is naphthalene:

22 open-ended lines x 0.75 x 0.055 kg VOC/open-ended line/day x 365  $\frac{\text{days}}{\text{yr}}$  = 0.33 Mg/yr

### Exhausters

Assume 6 exhausters, 75% of VOC is naphthalene:

6 exhausters x 0.75 x 1.2 kg VOC/exhauster/day x 365  $\frac{\text{days}}{\text{yr}}$  = 1971 kg/yr

# = 2 Mg/yr naphthalene

Therefore, equipment leaks of naphthalene at the plant total about 23 Mg/yr.

Total naphthalene emissions from the Fairfield plant = 2,583 Mg/yr.

# II. Nationwide Naphthalene Emissions from Coke By-Product Plants

Total nationwide estimate may be calculated by each method as follows:

# Method 1:

$$\frac{\text{0.00592 kg naphthalene}}{\text{Mg coke}} \times \text{51,377} \frac{\text{Mg coke nationwide}}{\text{day}} \times$$

$$365 \frac{\text{days}}{\text{yr}} \times \frac{1 \text{ Mg}}{1 \times 10^3 \text{ kg}} = 111 \text{ Mg/yr}.$$

# Method 2:

Using all of the above emission factors for the emission sources described in Method 2, nationwide totals are the following:

Source	Nationwide Estimate, Mg/yr
Coke Oven Doors Tar Decanting Naphthalene Processing Tar Storage Tanks Equipment Leaks	28.2 76.9 28,991 1,313 540.7 <sup>a</sup>
Total =	30,949.8 Mg/yr (with naphthalene processing)
or	1,958.8 Mg/yr (without naphthalene processing)

### Summary and Conclusions

Emissions of naphthalene from the Fairfield plant based on Method 1 total about 9.34 Mg/yr compared to 2,583 Mg/yr for Method 2. Even subtracting out the naphthalene processing emissions (which are obviously overstated), the total naphthalene emissions from the plant based on Method 2 are 143 Mg.

afrom Reference 5, calculation of nationwide equipment leaks was based on a model plant approach in which the percent naphthalene in VOC (75%) was multiplied by the appropriate VOC emission factor, the number of pieces of equipment per model plant, and the total number of model plants based on coke production.

The nationwide estimates of naphthalene from coke by-product plants calculated above are much higher than two other nationwide estimates found in the literature (i.e., 34 and 40 Mg/yr from total naphthalene production, References 1 and 8, respectively). Process-specific emissions derived from Method 2 are based in most cases on total organics or vapor emissions due to the fact that naphthalene was difficult, or impractical to sample, particularly when naphthalene processing tanks were sampled. In addition, the relative percentage of naphthalene in a VOC stream is difficult to quantify in the case of equipment leaks because naphthalene is prevalent throughout most of the coke by-product plant. Therefore, process-specific emissions are based on data and assumptions that may overstate emissions. Since both plant-specific and nationwide emissions from Method 1 more closely approximate the estimates found in the literature than Method 2, Method 1 appears to be a more reasonable procedure for quantifying naphthalene emissions from coke by-product plants.

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