SAIC-87/1036

EVALUATION OF POTENTIAL TOXIC AIR CONTAMINANTS
PHASE I

EXECUTIVE SUMMARY

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DISCLAIMER

1.0
INTRODUCTION

1.1 PURPOSE AND OBJECTIVES OF THE STUDY

Regulatory agencies at all levels have in recent years been exploring means to reduce public exposure to "toxic" or "hazardous" air pollutants. Section 39655 of California Assembly Bill 1807 (known as the "Tanner Bill"), defines a "toxic air contaminant" as:

> "an air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health."

The Tanner Bill requires the ARB and the California Department of Health Services to give priority to the evaluation and regulation of substances "based on factors related to the risk of harm to public health, amount or potential amount of emissions, manner of usage of the substance in California, persistence in the atmosphere, and ambient concentrations in the community." In 1984, the ARB staff divided candidate toxic air contaminants into two major classes. "Level 1" compounds are those for which sufficient information exists to initiate a full health effects evaluation. Level 2 compounds are those which the ARB considers to be of "potential concern in California." They require additional documentation to determine whether further health effects assessment is needed. In keeping with the ARB's responsibilities under A.B. 1807, the emphasis of the Board's research is to be upon emissions and atmospheric concentrations, rather than upon health effects per se. Table 1.1-1 lists the Level 2 potential toxic air contaminants as originally defined by the ARB.

In order to determine which, if any, of the Level 2 potential toxic air contaminants merit further consideration under the Tanner Bill process, the ARB is conducting a two-phased research program, of which the present study comprises Phase I. The overall goals of Phase I were to obtain as much information as possible from available sources, to identify data gaps, and to plan more detailed activities, such as source testing, for Phase II. The

Table 1.1-1

ORIGINAL LIST OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

Acetaldehyde
Acrolein
Acrylonitrile
Allyl Chloride
Benzyl Chloride
Chlorobenzene(s)
Chloroprene
Cresols
p-Dichlorobenzene
Dialkyl Nitrosamines
1,4-Dioxane
Epichlorohydrin
Glycol Ethers
Hexachlorocyclopentadiene
Maleic Anhydride
Manganese
Methyl Bromide
Mercury
Nitrobenzene(s)
Nitrosomorpholine
Phenol(s)
Phosgene
Propylene Oxide
Vinylidene Chloride
Xylenes

specific objectives of the present study were:

- To evaluate the potential of listing Level 2 compounds as toxic air contaminants in accordance with the criteria listed in Section 39605 et seq. of the California Health and Safety Code; and
- To identify data deficiencies, provide missing data, and report where such data are not available.

Of the seven issues which the ARB must address in preparing a regulatory report under Section 38665 of the Health and Safety Code, the following three were of concern in this study:

- The rate and extent of present and anticipated future emissions and estimated levels of human exposure;
- The stability, persistence, transformation products, dispersion potential, and other physical and chemical characteristics of the substance when present in the ambient air; and
- The categories, numbers, and relative contribution of present or anticipated sources of the substance, including mobile, industrial, agricultural and natural sources.

Several of the original list of Level 2 compounds, such as dialkyl nitrosamines, comprise a large number of individual species. In order to keep the scope of the study manageable, specific compounds were chosen for each of the chemical classes on the basis of preliminary knowledge about their presence in ambient air in California. Table 1.1-2 shows the 45 species decided upon by Science Applications International Corporation (SAIC) and the ARB. The categories "chlorobenzene(s)" and "para-dichlorobenzene" were changed to "monochlorobenzene" and "chlorobenzenes," the latter consisting of those chlorinated benzenes which were most volatile and likely to be present in California.

1.2 OUTLINE OF THE RESEARCH

Research under this contract was conducted by SAIC between July 1985 and September 1986. It was suspected early in the project that only a few of the Level 2 compounds were likely to be produced in California.

Table 1.1-2

FINAL LIST OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

- Acetaldehyde
- Acrolein
- Acrylonitrile
- Allyl Chloride
- Benzyl Chloride
- Monochlorobenzene
- Chloroprene
- Cresols
    - ortho-cresol
    - meta-cresol
    - para-cresol
- Chlorobenzenes
    - o-dichlorobenzene
    - p-dichlorobenzene
    - 1,2,4-trichlorobenzene
    - 1,3,5-trichlorobenzene
- Dialkyl Nitrosamines
    - N-dimethylnitrosamine
    - N-diethylnitrosamine
    - N-methylethylnitrosamine
- 1,4-Dioxane
- Epichlorohydrin
- Glycol Ethers
    - Ethylene glycol monomethyl ether
    - Ethylene glycol monoethyl ether
    - Ethylene glycol monobutyl ether
- Hexachlorocyclopentadiene
- Maleic Anhydride
- Manganese
    - Elemental manganese
    - Manganese oxide (MnO)
    - Manganese dioxide (MnO_2)
    - Manganese sulfate ($MnSO_4$)
    - Manganese (II, III) oxide (Mn_3O_4)
    - Methylcyclopentadienyl manganese tricarbonyl (MMT)
- Methyl Bromide
- Mercury (elemental)
- Nitrobenzene
- Nitrosomorpholine
- Phenols
    - Phenol
    - 2-nitrophenol
    - 4-nitrophenol
    - 3-nitro-2-hydroxytoluene
    - 5-nitro-2-hydroxytoluene
- Phosgene
- Propylene Oxide
- Vinylidene Chloride
- Xylenes
    - ortho-xylene
    - meta-xylene
    - para-xylene

Nevertheless, considerable effort was devoted to identifying manufacturers and confirming that none had facilities in the state. "Known" California producers were also contacted to verify that they continued to manufacture Level 2 compounds.

We next turned our attention to the potential industrial uses of the compounds. An online data base search, as well as review of several chemical compound compendia, identified major uses of the Level 2 toxic air contaminants. Since many of the compounds have a dozen or more uses, identifying and contacting industrial users was much more difficult and time consuming than identifying producers.

Emission inventories for most of the Level 2 toxic air contaminants had been prepared by the South Coast and Bay Area Air Quality Management Districts, and by the U.S. Environmental Protection Agency (EPA). Staff of the EPA's Pollutant Assessment Branch in Research Triangle Park, NC provided us with additional information on several of the compounds. These previously compiled inventories were reviewed critically.

Finally, where no inventory data were available, we attempted to estimate emissions of several of the Level 2 compounds. Except for certain types of combustion sources, emission factors were not readily available. In some cases, such as emissions of manganese from sewage sludge combustion, we developed emission factors from reported experimental data.

Given the large number and variety of the Level 2 compounds, it was necessary to explore several avenues of research simultaneously. In general, relevant information on a given compound was obtained from more than one source. In keeping with the limited scope of Phase I of this program, we relied heavily on existing information. Wherever possible, however, we independently verified data through direct contacts with chemical producers and users. In addition, some heretofore unavailable information was obtained by SAIC.

While SAIC conducted the emissions research, Daniel Grosjean and Associates (DGA), collected data on ambient concentrations of the Level 2 potential toxic air contaminants and reviewed atmospheric formation and removal processes. Information obtained by SAIC and DGA was placed into 25 compound dossiers, which are presented as "stand-alone" chapters in the final report. Compounds were then ranked for suitability for Phase II research, and a program of field testing, surveys, modeling and laboratory experimentation was devised.

1.3 ESTIMATION OF CALIFORNIA USE AND EMISSIONS

1.3.1 Identification of Producers and Users of Level 2 Compounds

Potential use and emissions were placed into four categories. Direct production was defined as deliberate manufacture or refining. Indirect or incidental production includes the unintentional synthesis or release of a compound during production or processing of something else, and formation or release of compounds during combustion. (A third form of indirect production, atmospheric synthesis, is discussed in Section 1.4.) Emissions can also occur during industrial use, which includes use of a compound as a feedstock for other products, incorporation of a compound into a product without altering it chemically, or direct use as a solvent. Finally, several of the Level 2 compounds, such as glycol ethers, are found in consumer products, and may be emitted during use thereof. The following approaches were used to identify producers and users of Level 2 compounds in California.

Online Data Base Searches. SAIC searched the online data bases Toxicology Data Bank (TDB), Chemical Industry Notes (CIN), Thomas Register Online, and PTS U.S. Time Series for information on producers and users of the Level 2 compounds.

Letters to Producers. We used chemical industry directories and product catalogs to identify 196 U.S. chemical manufacturers and formulators who produce products for which Level 2 compounds are feedstocks and/or ingredients. Each firm was sent a letter asking whether it had any manufacturing plants in California and whether the compound(s) of interest were indeed used in the state. Plant capacity data were also requested.

Organic Chemical Producers Data Base Survey. The EPA's OCPDB was searched to identify all facilities having a California address and likely to produce or use Level 2 compounds. This search identified 54 California facilities, in which 10 of the compounds of interest could potentially be produced or used. SAIC contacted these facilities by telephone, and those which acknowledged producing or using a Level 2 compound were sent letters requesting a written confirmation and additional data on production capacity, production, and feedstock use.

U.S. Bureau of Mines. A mercury specialist at the U.S. Bureau of Mines provided SAIC with a computer listing of the names and addresses of 10 California firms which had reported consumption or processing of mercury in the past few years. Attempts were made to contact all of these firms.

1.3.2 Emission Estimation

1.3.2.1 Review of Existing Emission Inventories

Several existing California toxic air pollutant emission inventories were critically reviewed; in many cases, listed facilities were contacted to verify their use of the compounds of interest, and emission calculations were checked for validity and accuracy. Inventories included the following:

ARB Statewide Emission Inventory. SAIC requested the ARB's Emission Inventory Branch to search the emission inventory for combinations of standard industrial classification (SIC) code and source classification code (SCC) likely to be met by facilities in which certain Level 2 compounds are produced or used as feedstocks.

South Coast Air Quality Management District Inventory. This point source compilation, which included 8 Level 2 compounds, is based upon a 1983 survey of 1,606 facilities in the District's Automated Equipment Information System having equipment categories in which certain toxic air contaminants were believed likely to be used. Emissions were estimated by respondents and/or calculated by the District. A supplemental document shows emissions by SIC code for each pollutant and displays point sources on a gridded map of the South Coast Air Basin.

Bay Area Air Quality Management District Study. In 1984 and 1985, the Bay Area Air Quality Management District (BAAQMD) surveyed all facilities having District permits, except for gasoline dispensing facilities and dry cleaners, to determine purchase, use and disposal of 50 organic compounds, including all the Level 2 compounds except glycol ethers. Usage values were converted by BAAQMD staff into emission estimates. The report includes a breakdown of point sources and emissions for each chemical, and a list of sources and toxic substances by three-digit SIC code. Area sources were not included in the inventory.

EPA Region IX Compilation. In 1985 a contractor compiled source-specific data on 51 chemicals, including 14 Level 2 compounds and compound groups, for EPA Region IX. Much or most of the information was obtained by contacting project officers in EPA's Pollutant Assessment Branch (PAB) in Research Triangle Park, NC and then reviewing unpublished data and recently published reports. The compilation includes relevant source categories; specific sources and/or plant names and locations; relevant air pollution control district; emissions from processing, storage and fugitive sources; origin of emission estimates; modeled ambient concentrations, and risks.

1.3.2.2 Indirect Source and Consumer Product Emissions

Information on mobile source emission factors for, and activity levels of, acetaldehyde, acrolein, manganese and dialkyl nitrosamines was obtained primarily through a literature review and contacts with relevant governmental agencies. In addition, the U.S. Environmental Protection Agency's Office of Mobile Source Air Pollution Control in Cincinnati, OH and its Atmospheric Science Research Laboratory in Research Triangle Park, NC provided us with internal reports and other unpublished data on mobile source emissions tests. Information on stationary combustion sources was obtained through a literature review and from the EPA's Office of Air Quality Planning and Standards, Pollutant Assessment Branch, Research Triangle Park, NC.

Emissions of glycol ethers and ortho-xylene from applications of paints and coatings were estimated by apportioning national use data to California on the basis of population, housing units, and other factors. National para-dichlorobenzene emissions from use in mothballs and space deodorants were apportioned by population. Product formulation data were too variable to permit estimation of consumer product emissions in California of other Level 2 potential toxic air contaminants.

1.4 REVIEW OF ATMOSPHERIC CONCENTRATIONS AND CHEMISTRY

1.4.1 Atmospheric Concentrations

The literature was searched for California data on ambient concentrations of Level 2 potential toxic air contaminants. Information found was critically reviewed before being included in the report. For compounds never measured in California, ambient data for other locations were obtained in order to establish a range of likely concentrations in the State.

1.4.2 Atmospheric Formation and Removal

The Level 2 potential toxic air contaminants under study include a wide variety of compounds whose persistence in the atmosphere may be controlled by a number of reaction pathways. Many of these compounds had not been studied before, and there was little or no information concerning their rates of reaction in the atmosphere and the corresponding reaction products. For these compounds, estimates were made upon the basis of available data for compounds having similar structure, using structure-reactivity relationships (SRRs) for the relevant atmospheric reactions. For each compound, we identified reactions and chemical species that are important in atmospheric formation and removal, explored corresponding reaction mechanisms, and identified likely reaction products.

1.5 SELECTION OF COMPOUNDS FOR PHASE II

Compounds were first ranked according to amount of emissions, uncertainty in emissions, and uncertainty in ambient concentration data.

Seven compounds rated significantly higher than the others, and were tentatively designated as the "highest priority" group; others were placed into "secondary priority," "lower priority," and "elimination" groups. All compounds were then rated as to their atmospheric persistence, existence of measurement data for California, and toxicity of degradation products.

Compounds for which at least some California ambient concentration data are available, which form in the atmosphere, and which have high atmospheric persistence or toxic degradation products, were "promoted" from the secondary and lower priority groups resulting from the first ranking step.

2.0

FINDINGS AND CONCLUSIONS

2.1 CALIFORNIA PRODUCTION, USE AND EMISSIONS

Table 2.1-1 summarizes the information obtained through this project on the types of sources of Level 2 potential toxic air contaminants, estimates of the statewide emissions of the compounds, and the uncertainties in the emission estimates. Specific data on each Level 2 compound and compound group are as follows.

2.1.1 Acetaldehyde

No acetaldehyde is produced or used as an industrial feedstock in California. Acetaldehyde is produced and emitted through a variety of combustion sources, including automobiles (1,400 - 2,500 tons/yr), trucks (1,800 - 4,800 tons/yr), aircraft (230 tons/yr), electric power plants (120 tons/yr), oil refining (1,200 tons/yr), industrial and residential fossil fuel use (1,300 tons/yr), wood combustion (1,700 tons/yr), tobacco smoke (36 tons/yr) and coffee roasting (0.1 - 1 ton/yr). Some acetaldehyde may be present in acetone and in other consumer products, but emissions from these sources are likely to be negligible when compared with indirect production. Statewide emissions are estimated to be 7,800 - 12,000 tons/yr. This figure is fairly uncertain, given the scarcity of data on emission factors for combustion sources.

2.1.2 Acrolein

No acrolein is produced or used as an industrial feedstock in California. Acrolein is produced and emitted through a variety of combustion sources, including automobiles (270 - 760 tons/yr), trucks (585 - 2,370 tons/yr), aircraft (50 tons/yr), electric power plants (27 tons/yr), oil refining (260 tons/yr), industrial and residential fossil fuel use (290 tons/yr), wood combustion (300 tons/yr), tobacco smoke (50 tons/yr) and coffee roasting (0.1 - 1 ton/yr). Acrolein is not present in consumer products. Statewide emissions are estimated to be 1,800 - 4,100 tons/yr.

Table 2.1-1

SOURCES AND EMISSIONS OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS IN CALIFORNIA

	Produced in CA	Indirect Sources[a]	Industrial Use	Consumer Use	Emissions (Tons/yr) Low	High	Uncertainty in Emissions
Acetaldehyde	No	SC,M	No	Low	7,800	12,000	High
Acrolein	No	SC,M	No	No	1,800	4,100	High
Acrylonitrile	No	No	Wide	No	0	3	High
Allyl Chloride	No	No	Narrow	No	0	1	High
Benzyl Chloride	No	No	Narrow	Low?	1	1	High
Monochlorobenzene	No	SC	Wide	Wide?	2	?	High
Chloroprene	No	No	No	No	None		Low
Cresols	Yes	No	Wide	Wide	870	870	High
Chlorobenzenes	No	No?	Wide	Wide	3,000	3,000	High
Dialkyl Nitrosamines	No	SC,M	No	No	Unknown		High
1,4-Dioxane	No	No	Wide	Low	200	600	Medium
Epichlorohydrin	No	No	Narrow	Low	0	1	High
Glycol Ethers	No	No	Wide	Wide	12,400	13,850	Medium
Hexachlorocyclopentadiene	No	No	No	No	None		High
Maleic Anhydride	No	No	Narrow	No	8	8	High
Manganese	No	SC,M	Wide	Low?	56	84	High
Methyl Bromide	No	No	Wide	Low	3,500	?	Medium
Mercury	Small	SC,Geoth	Wide	Wide	1	2	High
Nitrobenzenes	No	No	Narrow	Unknown	Unknown		High
Nitrosomorpholine	No	No	Low?	Low?	Unknown		High
Phenol	Yes	SC,M	Narrow	Low	514	514	Medium
Phosgene	No	No	No	No	None		High
Propylene Oxide	No	No	Narrow	Low?	160	160	Medium
Vinylidene Chloride	No	No	Narrow	No	4	4	Medium
Xylenes	No?	No	Wide	Wide	32,500	32,500	Medium

[a] SC = stationary combustion source, M = mobile source, Geoth = geothermal power plants.

This figure is fairly uncertain, given the scarcity of data on emission factors for combustion sources.

2.1.3 Acrylonitrile

No acrylonitrile is produced in California. According to inventories developed by the Bay Area and South Coast air quality management districts, about 2.8 tons per year are emitted from use of the compound to manufacture acrylonitrile-butadiene-styrene (ABS) and acrylic resins at about 30 facilities; however, information obtained in this project indicates that the statewide total may actually be as low as 0.4 ton. There are no consumer uses, and there is no evidence for a significant release of acrylonitrile from finished ABS and acrylic resins.

2.1.4 Allyl Chloride

No allyl chloride is produced in California. The only potential source of allyl chloride emissions in the state is from manufacture of phenol-formaldehyde resins at one location in Los Angeles County. Our emission estimate of less than 0.25 ton per year is highly uncertain.

2.1.5 Benzyl Chloride

Benzyl chloride is not produced in California. Outgassing of benzyl chloride trapped as a contaminant in PVC which contained butyl benzyl phthalate (a plasticizer) has been reported in the literature. Only one U.S. PVC manufacturer reported using benzyl phthalate plasticizers, however, so emissions from this source are likely to be negligible. Benzyl chloride is not used directly in any consumer products.

2.1.6 Monochlorobenzene

No monochlorobenzene is produced in California. The compound has been identified in a variety of settings known to be present in California, although the locations and amounts of emissions cannot be determined from available data. Potential sources are as follows.

(1) About 1.7 tons per year of chlorobenzene are emitted by wastewater treatment plants in California.

(2) Chlorobenzene has numerous industrial uses, including the manufacture of adhesives, paints, polishes, waxes, resins, drugs, and perfumes. The extent of monochlorobenzene use in these applications in California is unknown.

(3) Chlorobenzene is a solvent/carrier in the herbicide Lasso^{TM}. Information on the monochlorobenzene content of Lasso formulations used in California is proprietary and cannot be reported.

(4) Other consumer uses are parts degreasing, solvent for gloss rwhite butyrate lacquer, and solvent for certain types of adhesives. Again, it is not known to what extent products with mronochlorobenzene are used in California.

2.1.7 Chloroprene

Chloroprene is only used captively in the manufacture of neoprene rubber outside California. It is highly unlikely to be present in California.

2.1.8 Cresols

PMC Specialties Group, Inc., the sole manufacturer of cresols and cresylic acids in California, was estimated to have emitted 17 tons of cresol in 1978; a more recent estimate cannot be reported without revealing proprietary data. The likely California industrial end-uses for cresols and cresylic acids are manufacture of tri-cresylic phosphate and cresyl diphenol phospate, production of phenolic resins, use as a solvent for wire hanger enamel, manufacture of pesticides, and use as an ore flotation agent. We estimate that over 714 tons of cresols are released to the atmosphere annually due to these industrial activities. Disinfectant/cleaning compounds are the major cresol-containing consumer products; others include metal degreasing agents, inks, and some paint removers. We estimate that approximately 137 tons/yr of cresols are emitted from consumer products. Total cresol emissions in the state are about 900 tons per year.

2.1.9 Chlorobenzenes

(1) None of the chlorobenzenes reviewed in this study, ortho-dichlorobenzene (o-DCB), para-dichlorobenzene (p-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB), and 1,3,5-trichlorobenzene (1,3,5-TCB) is manufactured in California, although p-DCB is isolated at one plant from a crude mixture of dichlorobenzenes.

(2) There is limited evidence that p-DCB may form as a byproduct of carbon tetrachloride (CT) manufacturing; it could therefore be present in vent releases from a CT plant in Pittsburg. Chlorination of drinking water is not a significant source of chlorinated benzenes. Formation of chlorobenzenes during wastewater treatment has been reported in the literature, but has not been confirmed by recent studies. Various chlorinated benzenes may also be products of metabolism and degradation of the insecticide lindane.

(3) The chlorobenzenes are used in a variety of industrial settings. We found no evidence that o-DCB is used in California as a feedstock for chloroaniline compounds or ?rrtoluene diisocyanate. It is possible that it is used industrially as a coolant for magnetic coils, heat transfer medium, degreasing agent, and solvent, although the extent of this o-DCB use in the state is unknown. Para-dichlorobenzene is isolated from a mixture of dichlorobenzenes at a facility in Irwindale. A published, but highly uncertain, estimate of emissions from this facility is 3.85 tons per year. PDCB has

several other industrial uses, including pesticide manufacturing, but none appears to be significant in California. The two trichlorobenzenes investigated are also used industrially as pesticide intermediates and solvents, but we could find no information on the extent of their use in California.

(4) Para-dichlorobenzene is a major constituent of moth control blocks and room deodorants. California emissions from these consumer products are estimated to be 3,000 tons per year. It is also used, to an unknown extent, as a direct pesticide and soil fumigant.

2.1.10 Dialkyl Nitrosamines

None of the three dialkyl nitrosamine compounds of interest, dimethyl nitrosamine (DMN), diethyl nitrosamine (DEN), and methylethyl nitrosamine, is produced in California. Nitrosamines may form in the atmosphere from reactions with secondary and tertiary amines. They have been found in some industrial processes, high explosives, livestock and poultry manure, animal rendering plants, and leather tanneries. Amine precursors are used in the preparation of rubber accelerators, pharmaceuticals, herbicides, fungicides, and insecticides, and in the leather tanning industry. DMN is used as an industrial solvent, antioxidant, solvent in the fiber and plastics industry, and in lubricants and condensers. DEN has been used as a gasoline and lubricant additive. Alkyl amines emitted by motor vehicles are unlikely to be significant precursors for dialkyl nitrosamines. The amounts of dialkyl nitrosamines emitted to the atmosphere and formed there are not presently known.

2.1.11 1,4-Dioxane

No 1,4-dioxane is produced, used as a feedstock, or released as a byproduct of any manufacturing process in California. The main use of the compound is as a reaction inhibitor in methyl chloroform (1,1,1-trichloroethane). Although there is some discrepancy among different estimates of methyl chloroform use in the state, corresponding 1,4-dioxane emissions are probably between about 200 and 600 tons per year.

2.1.12 Epichlorohydrin

Epichlorohydrin is not produced in California. No facilities for its primary industrial use, manufacturing of epoxy resins and synthetic glycerin, are located in the state. Less than 0.1 ton/year of epichlorohydrin emissions occur from various other manufacturing uses in the San Francisco Bay and South Coast air basins. Consumer products containing epichlorohydrin include paints, varnishes, lacquers, nail enamels, and pesticides. Emissions from use of these products is unknown but likely small.

2.1.13 Glycol Ethers

Glycol ethers are neither produced in California, nor likely to form as industrial byproducts or products of combustion. A variety of industrial formulations, such as fuel additives, protective coatings, printing inks, and leather dyes, contain glycol ethers as solvents. Consumer products which may contain glycol ethers include gasoline, brake fluids, insecticides, detergents, cosmetics, adhesives, and liquid household cleaners. Direct industrial use accounts for over 4,950 tons/yr of ethylene glycol monobutyl ether, and over 5,750 tons/yr of ethylene glycol monoethyl ether. Approximately 200 tons/yr of ethylene glycol monoethyl ether are released by direct industrial use, but we are unable to estimate industrial and consumer emissions from products which contain this compound. Annual California emissions of these three glycol ethers from industrial uses is approximately 11,000-12,450 tons/yr. Annual emissions from consumer products are 1,450 tons. Thus, total California emissions of these glycol ethers is between 12,400 and 13,850 tons/yr.

2.1.14 Hexachlorocyclopentadiene

It is highly unlikely that hexachlorocyclopentadiene is emitted into the California ambient air. The only manufacturer neither produces the compound in California nor ships it into the state. The only industrial uses are as intermediates in the manufacturing of flame retardants and chlorinated hydrocarbon pesticides which does not appears to take place in California.

2.1.15 Maleic Anhydride

Maleic anhydride is not produced in California. The only potential sources of maleic anhydride emissions in California are unsaturated polyester resin and alkyd resin manufacturing plants. Inventoried emissions from these facilities are about 8.0 tons per year. This value is highly uncertain, given the lack of established emission factors.

2.1.16 Manganese

(1) Manganese is not produced in California.

(2) The primary industrial use of manganese is as an additive to strengthen and harden iron and steel products, although minor uses exist in copper, nickel, and aluminum alloys and in production of carbon-zinc dry cell batteries. We estimate that emissions from steel production are 0.18 - 5.9 tons/yr and those from cast iron production are about 0.2 - 0.52 ton/yr.

(3) Between 9 and 30 tons/yr of manganese are estimated to be emitted by automotive exhaust, due to the presence of manganese in gasoline. Use of methylcyclopentadienyl manganese tricarbonyl (MMT) as an octane booster contributes another 46 tons per year. Mn is being considered as an additive to diesel fuels to help purge and regenerate ceramic particulate trap filters in diesel engines.

(4) Assuming that all manganese present in fuel oil is emitted, we estimate that up to 0.09 ton/yr of Mn is emitted by residual fuel oil combustion in California. Coal combustion contributes another 1.0 to 1.6 tons/yr.

(5) A rough estimate of manganese emitted from sludge incineration in the state is 0.01 ton/yr.

(6) Manganese sulfate and manganous oxide are used in soil conditioners. The extent of production of airborne manganese from this source is not known. In addition, soil and road dust make an unknown contribution to ambient levels.

(7) Total statewide manganese emissions accounted for in this review are about 56 to 84 tons/yr.

2.1.17 Methyl Bromide

Methyl bromide is neither manufactured nor produced indirectly in California. Potentially large amounts of the compound may be produced biologically in the ocean off the California coast, although this remains unconfirmed at present. It is not known to what extent the chemical is used industrially as a methylating or wool degreasing agent or disinfectant. However, industrial emissions are likely to be minor compared to the 3,500 tons per year of methyl bromide which are released through use of the compound as a soil fumigant in California. Methyl bromide may also be released through its use in special purpose fire extinguishers.

2.1.18 Mercury

Estimates of elemental mercury emissions from all identified sources in California are quite uncertain but likely to be small. One California mine produces mercury in conjunction with gold. Emissions from associated ore processing are about 0.12 ton/yr. The main indirect sources of mercury include municipal sewage sludge incineration, geothermal power production, and fossil fuel combustion. Releases from these sources are estimated to be 0.07, 0.3 - 0.4, and 0.09 - 0.9 ton/yr, respectively, for a total of 0.4 - 1.4 tons/yr. A lower bound for industrial emissions, which occur from mainly from use of mercury in instrument manufacturing, electroplating and used battery reclamation, is about 0.24 ton/yr. Unknown amounts of mercury may be released from use of consumer products and from dental amalgams. It is unlikely that total emissions in the State exceed 2 tons/yr.

2.1.19 Nitrobenzene

Nitrobenzene is not directly produced in California. Its industrial use in the state, chiefly in electronics manufacturing, is unknown but does not appear to be major. Consumers may be exposed to small amounts of nitrobenzene from a variety of products such as shoe polish, floor polish, metal polish, some soaps, perfume, and leather dressings.

2.1.20 Nitrosomorpholine

Nitrosomorpholine is not deliberately produced or used; it is believed to form in the atmosphere from the nighttime reaction of nitrous acid with morpholine. Morpholine is not produced in California. The main uses for the compound are as an ingredient in rubber accelerators, corrosion inhibitors, optical brighteners, waxes and polishes. The only significant sources of morpholine emissions in California are likely to be from the use of corrosion inhibitors and waxes and polishes. No recent data on these uses were available. Using old and highly uncertain data, we estimate that a maximum of 1.1 MM lb of morpholine were released in California in 1978. If all of this were converted to nitrosomorpholine by atmospheric reaction, then production would be about 700 tons per year. Most of this atmospherically generated nitrosomorpholine would be rapidly removed by photolysis, and would not accumulate in the atmosphere during daytime.

Work settings where elevated concentrations of nitrosomorpholine could occur are rubber tire manufacturing and leather tanning. New car interiors are another localized source of nitrosomorpholine. A variety of consumer products may contain small amounts of morpholine, but are unlikely to be used in large enough quantities at one location to produce measurable concentrations of nitrosomorpholine.

2.1.21 Phenols

Emissions from the only phenol producing facility in California, which is in Santa Fe Springs, are approximately 1.2 tons/yr. Indirect sources of phenol emissions include automobile exhaust (about 222 tons/yr) and wood combustion (276 tons/yr). Emissions from volatilization from wastewater are probably negligible. The only industrial use of phenol in the state is the production of phenol-formaldehyde resins by at least 7 facilities. We estimate that 15 tons/yr of phenol are released from these sites. Total California phenol emissions are approximately 514 tons/yr.

2.1.22 Phosgene

Phosgene is not produced, used, or directly emitted to the atmosphere in California. Trichloroethylene and other chlorinated hydrocarbons are its major precursors for atmospheric formation.

2.1.23 Propylene Oxide

Propylene oxide (PO) is not produced in California. Statewide emissions of PO are estimated to be about 160 tons per year, largely from one source in San Diego County. Some additional emissions may occur through consumer use of paints and coating containing PO as a stabilizer and evaporation of residual PO used in food processing. All available emission estimates are highly uncertain.

2.1.24 Vinylidene Chloride

The only likely sources of vinylidene chloride (VDC) emissions in California are manufacture of VDC copolymers and releases from wastewater treatment processes. Emissions from these sources in the San Francisco Bay area are about 3.2 - 3.5 tons/yr. Emissions in the rest of the state are about 0.6 ton/yr, for a total of 3.8 - 4.1 tons/yr.

2.1.25 Xylenes

(1) No manufacturers of isolated mixed xylenes are located in California; we do not presently know whether non-isolated xylenes are produced in the state.

(2) No manufacturing plants in California use individual xylene isomers as feedstocks.

(3) Emissions from industrial formulation of xylene-containing products; use of paints, coatings and adhesives; and direct use of xylenes as solvents are about 14,900 tons/yr. This value exceeds considerably the combined total of estimates developed by the Bay Area and South Coast air quality management districts; however, these districts' inventories may have ignored emissions from use of xylene-containing industrial paints and coatings. In any event, industrial emissions are uncertain.

(4) Use of nonindustrial paints and coatings and other consumer products accounts for about 1,370 tons/yr of xylene emissions.

(5) Automotive-related uses, which include evaporation from automobiles, evaporation from gasoline marketing, and automotive exhaust gases, account for another 16,200 tons/yr.

(6) Total annual California xylene emissions are approximately 32,500 tons.

2.2 AMBIENT CONCENTRATIONS IN CALIFORNIA

Table 2.2-1 summarizes the results of the review of ambient concentration data. Some of our principal findings are:

Table 2.2-1

SUMMARY OF AMBIENT GAS-PHASE CONCENTRATION DATA FOR CALIFORNIA

Level 2 Compound	California Concentrations	Dates	Size of Data Base	Comments
Acetaldehyde	3 - 39 ppb	1980-1981	Extensive	
Acrolein	Up to 14 ppb	1961-1968	Limited	Means 4 - 7 ppb in CA
Acrylonitrile	No data	-	None	Mean 12 ppb, max 110 ppb near sources in other states
Allyl Chloride	No data	-	None	
Benzyl Chloride	No data	-	None	
Monochlorobenzene	Up to 21 ppb	1979-1981	Limited	Means 0.004 - 3.4 ppb in CA; concentrations vary widely among investigators; some discrepancies within data sets
Chloroprene	No data	-	None	
Cresols	Up to 29 ppb	1979	14 samples	O-cresol measured near point source at 1 point (mean = 6.0 ppb); no CA data for m- or p-cresol; in OR, mean ambient o-cresol 0.016 ppb, m+p-cresol 0.03 ppb
Chlorobenzenes				
o-DCB	Up to 310 ppt	1979-1983	Limited	Means 13 - 130 ppt; higher values may have been near sources; some discrepancies within data sets; higher values in U.S. urban areas outside CA
m-DCB	Up to 150 ppt	1983	Limited	Means 4 - 77 ppt; higher values may have been near sources; some discrepancies within data sets; higher values in U.S. urban areas outside CA

Table 2.2-1 (Continued)

SUMMARY OF AMBIENT GAS-PHASE CONCENTRATION DATA FOR CALIFORNIA

Level 2 Compound	California Concentrations	Dates	Size of Data Base	Comments
Chlorobenzenes (continued)				
p-DCB	No data	-	None	
Dialkyl Nitrosamines	0 - 160 ppt	1978	Limited	Data for dimethylnitrosamine only; means 0 - 31 ppt in 15 cities in South Coast Air Basin
Dimethylnitrosamine	20 - 360 ppt	1978	One set	Dimethylnitrosamine in Contra Costa County
1,4-Dioxane	No data	-	None	
Epichlorohydrin	No data	-	None	
Glycol Ethers	No data	-	None	
Hexachlorocyclopentadiene	No data	-	None	
Maleic Anhydride	No data	-	None	
Manganese	10 to 110 ng/m^3	1970-1974	Extensive	No recent (>1980) sampling data available
Methyl Bromide	Up to 1300 ppt	1982-1984	Extensive	Means of 5 - 250 ppt reported for various urban areas; most readings in ARB network in South Coast Air Basin < detection limit of 200 ppt
Mercury	Up to 50 ng/m^3	1968-1986	Limited	High values near sources; urban levels are 3 - 4 ng/m^3.
Nitrobenzenes	No data	-	None	Means up to 0.37 ppb and maximum of 2.8 ppb measured outside CA, 1977-1978
Nitrosomorpholine	No data	-	None	Up to 500 ppt in new car interiors

Table 2.2-1 (Continued)

SUMMARY OF AMBIENT GAS-PHASE CONCENTRATION DATA FOR CALIFORNIA

Level 2 Compound	California Concentrations	Dates	Size of Data Base	Comments
Phenol	Up to 87 ppb	1979	One set	Measured near point source; mean 17 ppb; urban means outside CA are 0.1 - 0.55 ppb phenol and 0.004 ppb 2-nitrophenol
Phosgene	Up to 61 ppt	1976	Limited	Means 16.5 - 40 ppt in 3 urban, 1 rural location
Propylene Oxide	No data	-	None	
Vinylidene Chloride	Up to 24.4 ppt	1981-1984	Limited	ARB monitoring network in South Coast Air Basin finds no values above detection limit of 100 ppt
Xylenes	Up to 45 ppb	1968-1984	Extensive[a]	Most CA urban values 3 - 20 ppb; no data for northern CA

[a] Data are extensive for southern California only.

(1) No data were found on concentrations of acrylonitrile, allyl chloride, benzyl chloride, chloroprene, m-cresol, p-cresol, dialkyl nitrosamines other than dimethylnitrosamine, p-dichlorobenzene, trichlorobenzenes, 1,4-dioxane, epichlorohydrin, glycol ethers, hexachlorocyclopentadiene, maleic anhydride, nitrobenzenes, nitrosomorpholine, or propylene oxide in the ambient air of California.

(2) An extensive California ambient air data base exists for acetaldehyde, methyl bromide, and xylenes.

(3) Limited information, generally from fewer than 10 sets of sampling data, was available for acrolein, monochlorobenzene, o-cresol, o-dichlorobenzene, m-dichlorobenzene, dimethylnitrosamine, mercury, phenol, phosgene, and vinylidene chloride.

(4) Reported concentrations of acetaldehyde, acrolein, monochlorobenzene, cresols, phenol, and xylenes are generally in the range of 20 to a few hundred parts per billion (ppb). Dichlorobenzenes, dialkyl nitrosamines, methyl bromide, phosgene, and vinylidene chloride, in contrast, are present in the range of about 10 to several hundred parts per trillion (ppt).

(5) The geographical coverage of the existing ambient data is quite limited; the great majority of reported California measurements were made in the South Coast Air Basin.

(6) The data for acrolein, dimethylnitrosamine, and phosgene were collected before 1978 and may be different if measured today, given changes in the nature and strengths of many sources of precursors to atmospheric formation of these compounds.

(7) Ambient data reported for o-cresol, o-dichlorobenzene, m-dichlorobenzene, mercury, and phenol were obtained near point sources of these compounds. General ambient levels of these compounds are expected to be much lower, i.e. 1 ppb or less.

2.3 ATMOSPHERIC CHEMISTRY

2.3.1 In-Situ Formation of Level 2 Compounds

Table 2.3-1 shows which of the Level 2 potential toxic air contaminants are likely to form in the atmosphere, and identifies their precursors. The findings of our investigation of atmospheric formation processes may be summarized as follows.

(1) Atmospheric formation, through reaction of the hydroxyl radical (OH) with chloroethenes and chloromethanes, is probably the only source of ambient phosgene in California.

(2) Atmospheric reactions are probably responsible for a significant fraction of the acetaldehyde and cresols observed in the atmosphere in the South Coast Air Basin and, perhaps, in other urban areas of California.

(3) Theoretical considerations and laboratory evidence suggest that acrolein, monochlorobenzene and other chlorobenzenes, dialkyl nitrosamines, maleic anhydride, elemental mercury, nitrobenzenes, nitrosomorpholine, and phenol may form in the atmosphere; however, ambient concentration data are insufficient to determine the existence and importance of these reactions.

(4) It is interesting to note that some Level 1 toxic air contaminants (benzene, chloroform, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethene) are precursors for Level 2 compounds; control of the former could therefore result in reduced atmospheric formation

Table 2.3-1

IN-SITU FORMATION OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

	Atmospheric Reaction Precursors	Importance of In-Situ Formation
Acetaldehyde	O_3, OH and all methyl paraffins; OH + some paraffins; aromatics; cresols; propylene oxide	Major (50-200 tons/day in SCAB)
Acrolein	OH, O_3 + dienes (e.g. butadiene)	Unknown
Acrylonitrile	None	-
Allyl Chloride	None	-
Benzyl Chloride	None	-
Monochlorobenzene	Benzene, Cl (only near source)	Unknown
Chloroprene	None	None
Cresols	OH + toluene	Major (3,650-16,790 tons/yr)
Chlorobenzenes	Benzene, Cl (only near source)	Unknown
Dialkyl Nitrosamines	HONO + amines (dark) OH + amines (daytime)	Unknown Unknown
1,4-Dioxane	None	None
Epichlorohydrin	None[a]	None
Glycol Ethers	None	None
Hexachlorocyclopentadiene	None	None
Maleic Anhydride	OH + benzene, toluene, o-xylene[b]	
Manganese	None	None
Methyl Bromide	None	None
Mercury	Dimethyl mercury (daytime)	Unknown
Nitrobenzenes	OH + benzene	Important?
Nitrosomorpholine	Morpholine + HO, NO_x	Unknown
Phenols	OH + Benzene	Unknown
Phosgene	Halocarbons[c]	Only source
Propylene Oxide	None[d]	None
Vinylidene Chloride	None	None
Xylenes	None	None

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[a] Epichlorohydrin may form by reaction of atomic oxygen with allyl chloride, but this reaction is not expected to be important in ambient air.

[b] Formation of maleic anhydride from these precursors may occur, but has not been fully documented.

[c] Precursors, in decreasing order of importance, are trichloroethylene, 1,1-dichloroethane, 1,1,1-trichloroethane, methylene chloride, tetrachloroethylene (perchloroethylene), and chloroform.

[d] Propylene oxide may form by reaction of atomic oxygen with propene, but this reaction is not expected to be important in ambient air.

of the latter.

(5) Certain Level 2 potential toxic air contaminants (o-cresol, propylene oxide, nitrobenzene, phenol, and vinylidene chloride) may also be precursors for other Level 2 compounds.

2.3.2 Atmospheric Removal

2.3.2.1 Estimation of Reaction Rates

(1) The most important reactions in the atmosphere include photolysis (dissociation of a molecule upon exposure to sunlight), reaction with ozone (O_3), reaction with the hydroxyl radical (OH), and reaction with the nitrate radical (NO_3). The role of each reaction in the removal of each pollutant was investigated.

(2) Measured rate constants were available for only 11 organic-OH reactions, 10 organic-O_3 reactions (of which 9 are negligible for atmospheric removal), and 8 organic-NO_3 reactions (of which 3 are negligible), for a total of 29 reactions.

(3) Using measured ionization potentials and SRRs, rate constants could be estimated for another 63 reactions.

(4) Using estimated ionization potentials and SRRs, rate constants were estimated for all of the remaining reactions of interest, except for those undergone by the dialkyl nitrosamines; however, since nitrosamines photolyze rapidly in sunlight, the lack of OH, O_3 and NO_3 reaction data was not critical.

2.3.2.2 Removal Mechanisms and Products

Table 2.3-2 shows, for each Level 2 compound and compound class, the relative importance of the four main removal mechanisms, along with the observed or predicted reaction products. Note that many of the reaction

Table 2.3-2

ATMOSPHERIC REMOVAL OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

	Removal Mechanisms[a]				Atmospheric Reaction Products
	$h\nu$	OH	O_3	NO_3	
Acetaldehyde	*	*	-	-	Formaldehyde, peroxyacetyl nitrate (PAN)
Acrolein	+	*	+	+	Formaldehyde, glyoxal, formic acid, glyoxylic acid
Acrylonitrile	-	*	-	-	Formaldehyde, formyl cyanide, HCN
Allyl Chloride	-	*	+	+	Formaldehyde, chloroacetaldehyde, chloro-PAN, formic acid, chloroacetic acid
Benzyl Chloride	-	*	-	-	Peroxybenzoyl nitrate (PBzN), nitrobenzyl chloride, chlorocresols, chlorinated dicarbonyls
Monochlorobenzene	-	*	-	-	Chlorophenol, nitrochlorobenzene, chlorinated dicarbonyls
Chloroprene	-	+	+	+	Acyl chlorides (ClCOCHO, ClCOCOOH), formaldehyde
Cresols	-	*	-	+	OH: nitrocresols, pyruvic acid, PAN; NO_3: nitric acid formed at night
Chlorobenzenes	?	+	-	-	Chlorophenol, nitrochlorobenzene, chlorinated dicarbonyls
Dialkyl Nitrosamines	*	-	-	-	Nitramines, aldehydes, amides
1,4-Dioxane	-	*	-	-	Formaldehyde, CO, CO_2
Epichlorohydrin	-	*	-	-	Formaldehyde, chloroacetaldehyde, chloro-PAN
Glycol Ethers	-	*	-	-	Large number of hydroxy and alkoxy acids, aldehydes, and acetates
Hexachlorocyclopentadiene	?	+	+	+	Oxalyl chloride and other chlorinated products

Table 2.3-2 (Continued)

ATMOSPHERIC REMOVAL OF LEVEL 2 POTENTIAL TOXIC AIR CONTAMINANTS

	Removal Mechanisms[a]				Atmospheric Reaction Products
	$h\nu$	OH	O_3	NO_3	
Maleic Anhydride	-	+	+	?	Dicarbonyls, CO, CO_2, HO_2
Manganese	-	-	-	-	Washout is main removal mechanism
Methyl Bromide	-	*	-	-	Very slow; deposition and upward diffusion are main removal mechanisms
Mercury	-	-	-	-	Washout is main removal mechanism
Nitrobenzenes	-	*	-	-	3-nitrophenol, dinitrobenzene, aliphatic dicarbonyls, phenol
Nitrosomorpholine	*	-	-	-	Nitramines, aldehydes, amides
Phenols	-	+	-	+	Nitrophenols, glyoxal, glyoxylic acid, nitrocresols
Phosgene	-	-	-	-	Very slow; deposition and upward diffusion are main removal mechanisms
Propylene Oxide	-	*	-	-	Formaldehyde, acetaldehyde, CO, PAN
Vinylidene Chloride	-	*	-	-	Formaldehyde, phosgene, formyl chloride (minor), chloroacetyl chloride (?)
Xylenes	-	*	-	-	CO, formaldehyde, glyoxal, methylglyoxal, biacetyl, PAN, methylbenzyl nitrate, tolualdehyde, nitro-xylene isomers, dimethyl phenol isomers, others

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[a] Symbols denote importance of photolysis ($h\nu$) reaction, with the hydroxyl radical (OH), reaction with ozone (O_3), and nighttime reaction with NO_3:

* = predominant mechanism
\+ = mechanism plays some role in removal
\- = mechanism unimportant in ambient atmosphere
? = possible mechanism

products are the result of secondary reactions occurring after initial removal of the Level 2 compound of interest; since many of these secondary products are of environmental importance, they have been included in the discussion. The results of our evaluation of atmospheric removal mechanisms are as follows.

(1) For 15 of the Level 2 compounds and compound classes, reaction with OH is clearly the predominant removal mechanism; OH is also important in the removal of another 5 compounds.

(2) Photolysis is the most significant removal mechanism for the dialkyl nitrosamines and nitrosomorpholine, and is important in removing acetaldehyde and acrolein. Its role in removing hexachlorocyclopentadiene is expected, but unconfirmed.

(3) There appear to be no significant chemical removal mechanisms for manganese, mercury, methyl bromide, or phosgene; they leave the troposphere chiefly through diffusion to the stratosphere, washout, and dry deposition.

(4) Ozone reactions do not predominate for any of the Level 2 compounds, although they are important for acrolein, allyl chloride, chloroprene, hexachlorocyclopentadiene, and maleic anhydride.

(5) Reaction with NO_3, which is expected to be important for acrolein, allyl chloride, chloroprene, cresols, hexachlorocyclopentadiene, and phenols, predominates only at night, in the absence of competition from photolysis, OH and O_3.

(6) Formaldehyde, which is a Level 1 toxic air contaminant, is an expected reaction product for 10 of the Level 2 compounds.

(7) Several Level 2 potential toxic air contaminants, including acetaldehyde, nitro- and dinitro-cresols, maleic anhydride,

nitrophenols, and phosgene, are predicted to form from the chemical removal of other Level 2 compounds.

(8) Other compounds, which are not presently designated as potential toxic air contaminants, but which are nevertheless of health concern, result from the reaction of Level 2 compounds; these include chloroacetaldehyde, formyl cyanide, hydrogen cyanide, nitramines, oxalyl chloride, peroxyacyl nitrates (PAN) and chloro-PAN, and peroxybenzoyl nitrate (PBzN).

2.3.3 Atmospheric Residence Time

Figure 2.3-1 shows the atmospheric half life, in days, of each of the Level 2 compounds and compound classes, assuming the presence of 10^6 molecules cm^{-3} of OH. From this figure, and other information obtained as part of this study, we may conclude the following:

(1) The most reactive compounds are the dialkyl nitrosamines and nitrosomorpholine, which are removed by photolysis within one or two hours.

(2) The remaining Level 2 compounds may be divided into four groups, on the basis of their reactivity with OH. The shortest-lived group, with half-lives of about 2 to 20 hours, includes acetaldehyde, acrolein, allyl chloride, chloroprene, cresols, 1,4-dioxane, glycol ethers, hexachlorocyclopentadiene, maleic anhydride, phenols, vinylidene chloride, and xylenes.

(3) The second most-reactive group with respect to OH includes acrylonitrile, benzyl chloride, chlorobenzenes, epichlorohydrin, and propylene oxide; their half-lives are several days.

(4) The third group, with half-lives of several weeks, includes the nitrophenols and nitrocresols.

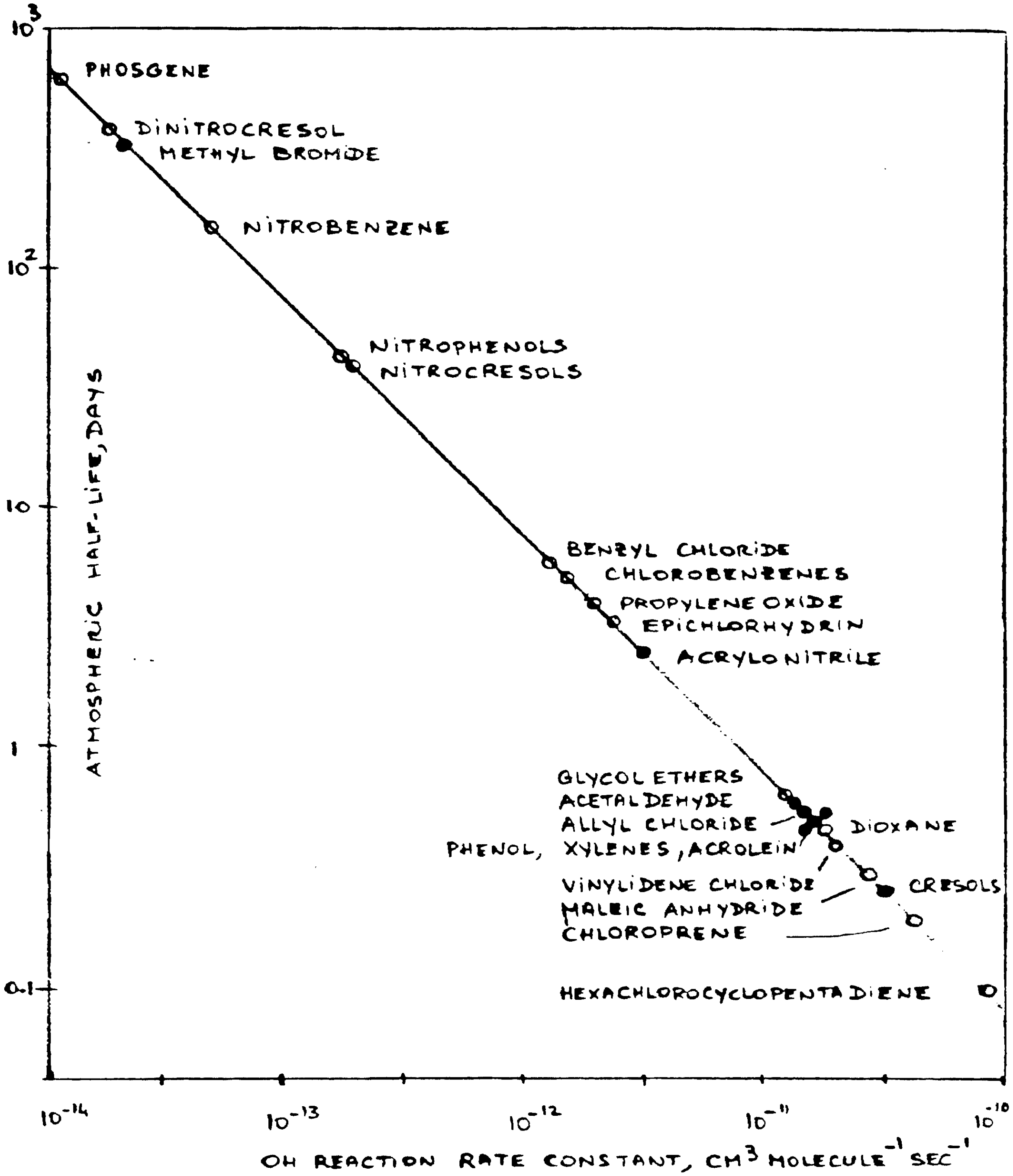

Figure 2.3-1. Atmospheric Removal of Level 2 Compounds by Reaction with OH for OH = 10^6 molecules cm^{-3}. Dark Circles are Measured OH Reaction Rate Constants. Open Circles are Rate Constants Estimated from SRR.

(5) Phosgene, dinitrocresol, methyl bromide, and nitrobenzene are the least chemically reactive in the atmosphere. In the absence of diffusion to the stratosphere, washout by rain, and dry deposition, the half lives of these compounds would be about 8 to 20 months.

(6) Although the atmospheric persistence of most of the Level 2 potential toxic air contaminants is controlled by their reaction with OH, nighttime reaction with NO_3 can dominate in some instances; for example, the half-lives of cresols, hexachlorocyclopentadiene, and phenol, in the presence of 50 ppt of NO_3, would be about 10 minutes.

2.4 SELECTION OF COMPOUNDS FOR PHASE II

(1) On the basis of California use and emissions, uncertainty in emissions, and uncertainty in ambient concentration data, the following compounds were assigned highest priority: acetaldehyde, acrolein, chlorobenzenes, glycol ethers, monochlorobenzene, methyl bromide, and xylenes. Secondary priority was given to cresols, 1,4-dioxane, phenols, and propylene oxide.

(2) On the basis of their high atmospheric persistence or toxic degradation products, we "promoted" cresols, dialkyl nitrosamines, phenols and phosgene from lower groups to the highest priority group. Vinylidene chloride, which has been documented in California ambient air, was not promoted, since it has low persistence in the atmosphere and is not a major precursor for ambient phosgene.

(3) The final list of compounds highly recommended for Phase II investigation includes acetaldehyde, acrolein, monochlorobenzene, cresols, chlorobenzenes, dialkyl nitrosamines, glycol ethers, methyl bromide, phenols, phosgene, and xylenes.

3.0
RECOMMENDATIONS

3.1 COMPOUNDS RECOMMENDED FOR PHASE II

We recommend that the following 11 Level 2 compounds and compound groups be investigated further in Phase II:

- Acetaldehyde
- Acrolein
- Monochlorobenzene
- Cresols
- Chlorobenzenes
- Dialkyl nitrosamines
- Glycol ethers
- Methyl bromide
- Phenols
- Phosgene
- Xylenes

If resources permit, then the following compounds should be included in Phase II:

- 1,4-Dioxane
- Propylene oxide

Compounds which probably do not require further investigation as potential toxic air contaminants in California include:

- Acrylonitrile
- Allyl chloride
- Benzyl chloride
- Epichlorohydrin
- Maleic anhydride
- Manganese
- Mercury

- Nitrobenzenes
- Nitrosomorpholine
- Vinylidene chloride

Finally, the following compounds are not recommended for further investigation:

- Chloroprene
- Hexachlorocyclopentadiene

3.2 EMISSIONS CHARACTERIZATION

(1) Acetaldehyde, phenols, and xylenes should be added to the set of compounds to be investigated in the upcoming ARB program, "Measurement of Selected Toxic Substances from Gasoline-Powered Light-Duty Vehicles."

(2) Source tests of stationary fossil fuel combustion sources, including industrial and domestic boilers and heaters, should be conducted to develop improved emission factors for acetaldehyde and acrolein.

(3) Source tests should also be conducted at the following facilities:

- PPG Industries, Inc., Irwindale (to determine o,p-dichlorobenzene emissions from production);
- PMC Specialties Group, Inc., Santa Fe Springs (to determine cresol emissions from production);
- Sandia National Laboratory and one or two other cresol users (to develop improved emission factors);
- Feedlots and leather tanneries (to develop emission factors for amine precursors of dialkyl nitrosamines);
- Niklor Chemical Company, Long Beach (to develop emission factors for methyl bromide packaging);

- Stapleton Spence Packing, San Jose (to develop emission factors for use of methyl bromide in food processing); and

- Marine waters off central and southern coasts (to determine the potential for emissions of methyl bromide from biogenic sources)

(4) Industrial surveys should be conducted to obtain information on purchase, incorporation into products, use of formulations, recycling, disposal, and existence and effectiveness of emission control for the following compounds and industries:

- Monochlorobenzene and other chlorinated benzenes (manufacturers of adhesives, paints, polishes, waxes, pharmaceuticals and perfumes, dyes, insecticides, and herbicides);

- Cresols (manufacturer of coated fabrics, metal household furniture, plastics materials and resins, polishes, paints, agricultural chemicals, and industrial machinery; and wood preservers);

- Amine precursors to dialkyl nitrosamines (leather tanneries, users of synthetic cutting fluids);

- Glycol ethers (a wide variety of industries);

- Phenols (electronics, computer manufacturing, and several other industries in the Bay Area and South Coast air basins); and

- Xylenes (a wide variety of industries)

(5) The extent of use of consumer products which contain recommended Level 2 potential toxic air contaminants, including chlorinated benzenes in pesticides, cresols in disinfectants and cleaning products and glycol ethers and xylenes in a variety of products, needs to be determined.

3.3 AMBIENT SAMPLING

(1) An areawide sampling program should be conducted for acrolein, monochlorobenzene, o-dichlorobenzene, p-dichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, o-, m- and p-cresol, dimethyl nitrosamine, diethyl nitrosamine, methyl

ethyl nitrosamine, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, phenols, and phosgene.

(2) Recommended methods for collecting and analyzing ambient samples of these compounds are shown in Table 3.3-1.

(3) We recommend collection of hourly, diurnal, and 24-hour samples at at least three locations in each of the major air basins, during at least two seasons. The sampling locations should be away from major point sources, and should be representative of public exposure.

(4) Urban "street canyon" sampling of Level 2 potential toxic air contaminants which are believed to be present in automobile and truck exhaust, including acetaldehyde, acrolein, dialkyl nitrosamines, phenols, and xylenes, should be conducted to determine whether drivers and pedestrians are exposed to significantly higher levels of the compounds of interest than would be inferred from the results of the areawide sampling.

(5) Phase II should also include sampling around known point sources of chlorobenzenes, cresols, methyl bromide, and phenols, to ascertain whether population exposure in the neighborhood of the source was significantly higher than elsewhere in the general area; this type of sampling could also be used in conjunction with modeling to "back-calculate" emission rates and therefore confirm emission estimates obtained through source testing or mass balance calculations.

3.4 MODELING

(1) Short-term (i.e. 1-hour, 8-hour or 24-hour) and long-term (annual average) concentrations around selected point sources should be determined by atmospheric dispersion modeling under worst-case meteorological scenarios in order to assess the

Table 3.3-1

SAMPLING AND ANALYTICAL METHODS FOR MEASURING HIGHEST-PRIORITY LEVEL 2 COMPOUNDS AND COMPOUND CLASSES IN AMBIENT AIR

Compound	Sampling/Analysis Method	Minimum Detectable Concentration ($\mu g/m^3$)	Typical Sampling Volume (Liters)
Acetaldehyde	DNPH-impinger collection/HPLC	<2 - <5	30 - 60
	DNPH-SepPak C18 collection/HPLC	<2	100
Acrolein	DNPH-impinger collection/HPLC	NA[a]	NA[a]
	DNPH-SepPak C18 collection/HPLC	<0.7[b]	100
Chlorobenzenes	Tenax-GC collection/GC/MS	0.01 - 0.05	100
Cresols	Tenax-GC collection/GC/MS	NA	NA
Glycol Ethers	Charcoal Tube collection/GC/MS	200 - 500	NA
Methyl Bromide	CMS collection/GC/MS	0.0 - 0.8	25
Phenols	Tenax-GC collection/GC/MS	NA	NA
Phosgene	GC/ECD[c]	4[d]	NA
Secondary and Tertiary Amines	Silica Gel collection/GC/MS	NA	NA
TCE/PERC	CMS collection/GC/MS	0.01 - 0.2	100
Xylenes	Tenax-GC collection/GC/MS	0.008 - 0.04	130

[a] NA = Not available.

[b] Estimated value.

[c] Information on sampling methods was unavailable in cited references.

[d] Detection limit without preconcentration.

potential for significant population exposure.

(2) Basin-wide modeling, using generic point and area emission sources, should be used to identify areas of high potential ambient concentrations.

(3) We recommend the Industrial Source Complex Short-Term model for the short-term modeling and the Climatological Dispersion Model for the annual average modeling.

3.5 LABORATORY STUDIES OF ATMOSPHERIC REACTIVITY

(1) Atmospheric formation and removal processes should be evaluated using small Teflon outdoor chambers and experimental protocols recommended by the U.S. Environmental Protection Agency.

(2) Experiments should include the following (although all may not apply to some compounds):

- A control run, with only the Level 2 compound in pure air in the dark;
- A photolysis run, involving sunlight irradiation of the Level 2 compound in pure air;
- An ozone reaction run, with mixtures of ozone and the Level 2 compound in pure air in the dark;
- A hydroxyl radical run, with sunlight-irradiated mixtures of oxides of nitrogen and the Level 2 compound in pure air; and
- A nitrate radical run, involving mixtures of ozone, nitrogen dioxide, and the Level 2 compound in pure air in the dark.

(3) Table 3.4-1 lists the recommended laboratory studies for each of the Level 2 potential toxic air contaminants to be investigated in Phase II.

Table 3.5-1

RECOMMENDED LABORATORY STUDIES OF LEVEL 2 COMPOUNDS

	Processes to be Studied	
Level 2 Compound	Atmospheric Formation	Atmospheric Removal
Acetaldehyde	Large, many HC precursors	Has been extensively studied
Acrolein	OH + diene (e.g. butadiene)	OH, O_3, fast; NO_3
Chlorobenzene	None	OH, slow
Glycol ethers	None	OH, rapid
Cresols (ortho, meta, para)	From toluene + OH; emphasis on isomer	OH, NO_3, rapid; emphasis on p-cresol and m-cresol
Phenol and nitrophenols	OH + benzene, slow; OH + phenol (nitrophenols), fast	OH, NO_3, slow (nitrophenols) to fast (phenol)
Xylenes	None	OH, fast
Phosgene	From selected chlorinated hydrocarbons	None
Methyl bromide[a]	None	None
Nitrosamines	From amines	Photolysis, fast

[a] No laboratory studies planned for this compound.