FINAL REPORT

EMISSIONS OF VOLATILE AND POTENTIALLY TOXIC ORGANIC COMPOUNDS FROM SEWAGE TREATMENT PLANTS AND COLLECTION SYSTEMS

by

Daniel P.Y. Chang
Edward D. Schroeder
Richard L. Corsi

Department of Civil Engineering
University of California, Davis

Submitted to the California Air Resources
Board in fulfillment of Contract No. A5-127-32
(July 1987)

DISCLAIMER

"THE STATEMENTS AND CONCLUSIONS IN THIS REPORT ARE THOSE OF THE CONTRACTOR AND NOT NECESSARILY THOSE OF THE CALIFORNIA AIR RESOURCES BOARD. THE MENTION OF COMMERICAL PRODUCTS, THEIR SOURCE OR THEIR USE IN CONNECTION WITH MATERIAL REPORTED HEREIN IS NOT TO BE CONSTRUED AS EITHER AN ACTUAL OR IMPLIED ENDORSEMENT OF SUCH PRODUCTS."

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACRONYMS

AC	Adsorption Capacity (to activated carbon)
ADL	Above Detection Limit
BDL	Below Detection Limit
BOD	Biochemical Oxygen Demand
BOD5	5 day Biochemical Oxygen Demand
BODu	Ultimate Biochemical Oxygen Demand
CARB	California Air Resources Board
CFR	Code of Federal Regulations
CFSTR	Continuous Flow Stirred-Tank Reactor
COD	Chemical Oxygen Demand
CSDLAC	County Sanitation Districts of Los Angeles County
DAF	Dissolved Air Flotation
DSE	Domestic Sewage Exclusion
EPA	Environmental Protection Agency
FR	Federal Register
GAC	Granular Activated Carbon
HTP	Hyperion Treatment Plant
IU	Industrial User
IUPAC	International Union of Pure and Applied Chemists
JWPCP	Joint Water Pollution Control Plant
MGD	Million Gallons per Day
MLSS	Mixed Liqour Suspended Solids
MUD	Municipal Utility District
MWTP	Municipal Wastewater Treatment Plant
NEEDS	A Report to EPA concerning the needs of MWTPs
NPDES	National Pollution Discharge Elimination System

NPP	National Pretreatment Program
OCSD	Orange County Sanitation District
ORT	Odor Removal Tower
PAC	Powdered Activated Carbon
PAR	Pretreatment Annual Report
PCE	Perchloroethylene
PFR	Plug-Flow Reactor
POTW	Publicly-Owned Treatment Work
PTOC	Potentially Toxic Organic Compound (assumed volatile)
RBC	Rotating Biological Contactor
RCRA	Resource Conservation and Recovery Act
RFP	Request For Proposals
RWQCB	Regional Water Quality Control Board
STP	Sewage Treatment Plant
SWRCB	State Water Resources Control Board (California)
TCA	1,1,1 Trichloroethane
TCE	Trichloroethylene
TEST	Toxic Emissions during Sewage Treatment (a model)
THM	Trihalomethane
TSS	Total Suspended Solids
VOC	Volatile Organic Compound
WAS	Waste Activated Sludge
WEST	Worst-case Emissions during Sewage Treatment (a model)
WWTF	Wastewater Treatment Facility
WWTP	Wastewater Treatment Plant

ACKNOWLEDGEMENTS

This study could not have been completed without several individuals and organizations who provided us with necessary data, technical information, data management assistance, and assistance with preparation of the final report. Foremost, the authors wish to thank the staff of the California Air Resources Board (CARB), particularly Mr. Joseph Pantalone, for their comments and the cooperative working relationship that they offered throughout this study. We also thank the CARB for funding this study in its entirety.

We would like to thank the following individuals for their cooperation, and for expending their time and energy to provide us with information and data required to complete this study: Keith Silva and Vicky Choy (EPA Region IX); Paul Johnston, James Kassel, Don Owens, Herb Deardorff, and Don Anderson (California Water Resources Control Board); Eric Hsiang (Water Quality Control Board, Region 2); Angela Charpentier (Water Quality Control Board, Region 3); Earle Hartling, Robert Horvath, and Norman Ackerman (Los Angeles County Sanitation District); Richard von Langen (Orange County Sanitation District); Helen Farnham (Sunnyvale WWTF); Ron Linden (Sacramento Regional Wastewater Treatment Plant); Mark Niver (City of San Jose Department of Water Pollution Control); Frank Wada (Hyperion Treatment Plant); Joseph Damas, Jr. (East Bay MUD WWTF); Walter Kanopka (Point Loma Treatment Plant); Steven Medberry (City of San Francisco); and Michael Porter and John Woods (South Coast Air Quality Management District).

The following individuals were kind enough to assist us during our visits of the noted wastewater treatment facilities: Ron Linden (Sacramento Regional Wastewater Treatment Plant); Charles Turner (City of Bakersfield Wastewater Treatment Plant); Ross Caballero (Joint Water Pollution Control Plant); Frank Wada and Sam Cheng (Hyperion Treatment Plant); Anderson Dill (Fresno Regional Wastewater Treatment Facility #1); Roy Stevens (Sunnyvale WWTF); Mark Niver (San Jose-Santa Clara Water Pollution Control Plant); and Joseph Dames, Jr., A. Greenberg, and Mr. Frye (East Bay MUD WWTF).

Ms. Qingzeng Qiu provided valuable technical assistance with regard to modeling. Finally, the authors would like to acknowledge and thank Michael Hom and Mike Fong for excellent data base management, and Barbara Nichols and Virginia Roy for their patience and efficiency during the preparation of this manuscript.

ABSTRACT

Publicly-owned treatment works (POTWs) are a source of potentially toxic organic compound (PTOC) emissions for which limited data are available. This study was commissioned by the California Air Resources Board (CARB) in order to assess the potential for PTOC emissions from municipal wastewater treatment plants (MWTPs) and collection systems throughout California. The fates of 16 PTOCs were reviewed in terms of volatilization, biodegradation, and adsorption to solids and biomass as the primary removal mechanisms from wastewater. For the compounds that were studied, it was concluded that volatilization is the dominant removal mechanism in MWTPs. However, the paucity of existing data regarding the occurrence and distribution of PTOCs in collection systems made it impossible to estimate emissions from those sources. A methodology was developed to predict PTOC emissions from 589 MWTPs in California. A limited but growing data base was used along with extrapolation methods to estimate speciated PTOC emissions from MWTPs on statewide, county-by-county, and plant-by-plant bases. The results indicated that approximately 800 tons per year (tpy) of total PTOCs were emitted from MWTPs throughout California. Toluene and methylene chloride dominated the total PTOC emissions. Each was estimated to have been emitted in excess of 200 tpy. A small number of the 589 MWTPs were identified as having accounted for a large fraction of the total PTOC emissions. Furthermore, a comparison of PTOC emissions from two large MWTPs in the South Coast Air Basin (SCAB) suggested that emissions of some PTOCs from those sources were comparable to, and possibly greater than, emissions from the largest known point sources in the SCAB. Finally, specific MWTPs and treatment processes were recommended for future source sampling, and areas that will require future research in order to reduce the uncertainties in emissions estimates were identified.

1. INTRODUCTION

Recent concerns regarding human exposure to potentially toxic organic compounds (PTOCs) and the role that PTOCs play in the formation of photochemical air pollution have necessitated a review of PTOC emission sources. Municipal wastewater treatment plants (MWTPs) are a source of PTOC emissions for which limited data are available. This document reports the findings of a study to assess the potential for PTOC emissions from publicly-owned treatment works (POTWs) in California.

Specific Objectives

The work objectives that were specified in the Request for Proposals (RFP), issued by the California Air Resources Board (CARB), are summarized below.

1. Conduct a literature search to obtain information regarding emissions of PTOCs from POTWs. The PTOCs to consider include acrylonitrile, benzene, bromodichloromethane, carbon tetrachloride, chlorobenzene, chloroform, dibromochloromethane, 1,1-dichloroethylene, 1,2-dichloroethane, ethylbenzene, methylene chloride, perchloroethylene, toluene, 1,1,1-trichloroethane, trichloroethylene, and vinyl chloride.

2. Develop and/or refine models for estimating emissions of the 16 PTOCs from POTWs.

3. Complete a county-by-county inventory of POTWs in California and rank them by capacity.

4. Estimate the quantity and ultimate method of disposal of sludge and solid refuse recovered by MWTPs in California.

5. Estimate the fraction of each PTOC that adsorbs to sludge.

6. Using the models and methods described above, complete county-by-county and statewide emission estimates for methane and non-methane hydrocarbons, and total and speciated PTOCs. The level of confidence associated with the estimates will also be addressed.

7. Include a comprehensive description of all data bases used in the compilation of the emissions inventory, and indicate explicitly which data were taken from each data base.

8. Prepare a final report which describes, in detail, the projected PTOC emissions, as well as the models and methods used to arrive at those projections. A discussion of data acquisition techniques, mathematical calculations, uncertainties in estimates, and recommendations for future sampling are to be included.

In addition to the objectives specified in the RFP, the following additional tasks were completed as it was felt that the resulting information would be useful to the staff of the CARB during future emission studies.

1. For emission inventory purposes, the location (latitude and longitude) of every MWTP in the state of California were obtained.

2. In addition to the methodology applied to estimate the total emissions from each POTW, treated as individual point sources, a model was developed to estimate emissions from specific wastewater treatment processes. With knowledge of the individual process locations, the model will allow for greater spatial resolution with respect to emissions estimates based upon entire MWTPs. The process-specific model can be used with standard Gaussian dispersion models to predict downwind concentrations. The detailed emissions model is the subject of Appendix H of this report.

3. During the course of this study, it became evident that the quantity of trihalomethanes (THMs) formed in MWTPs is often greater, as a result of chlorination practices in the MWTP, than that received in the influent to the MWTP. Thus, a review of the factors affecting THM formation, potential precursors, and evidence of THM formation in California is included.

A combination of a lack of existing sample data on total methane and non-methane hydrocarbon emissions or a suitable surrogate, prevented us from making reliable estimates of those emissions. That objective was not accomplished.

Scope

Many organic compounds can be found in the influent to MWTPs. However, because of the limited time and resources associated with this contract, a manageable list of 16 PTOCs was selected for review as requested in the RFP. Although many other potentially toxic organic compounds exist, throughout the remainder of this report, the term "PTOCs" will refer to the subset comprised of those 16 compounds noted previously.

The contract did not provide for actual field sampling for the PTOCs. Thus, the completion of those objectives involving quantitative estimates of PTOCs required the use of existing data bases. Unfortunately, existing data bases are incomplete with respect to PTOC mass loadings into MWTPs. In addition, those facilities that have sampled for PTOCs typically sample on a very infrequent basis (e.g., 4 days per year). The existing data base is expected to improve in the following years, as the Environmental Protection Agency's (EPA) Pretreatment Program takes full effect. Data bases that were employed in this study will be described in detail in a later section.

Information regarding the monitoring of PTOCs in sewer lines is virtually non-existent. At this time it is not possible to predict emissions from collection systems. However, the factors that affect emissions from collection systems are described in this report, and past sampling efforts are reviewed.

Organization of the Report

It was assumed that the readers of this report may not have a complete understanding of wastewater treatment or the important characteristics of those PTOCs that are commonly discharged to wastewater collection systems. Thus, Sections 2 and 3 provide brief overviews of wastewater treatment systems, common terminology associated with the field of wastewater treatment, and a description of the characteristics, sources, and occurrences of the PTOCs selected for review. A glossary (Appendix A) and a list of acronyms (page vi) used in the report are provided as well as both chemical and common names, structural formulas and important physico-chemical parameters of the PTOCs (Tables 1 and 5).

The fate of PTOCs in collection systems and MWTPs is reviewed in Section 4. The results of data analyses completed to predict the importance of removal mechanisms other than volatilization are also presented. Previous studies regarding volatile emissions from wastewater to the atmosphere are described.

A presentation of emissions estimation techniques, limitations, and assumptions is included in Section 5. A discussion of uncertainties based upon sampling procedures, analysis techniques, and estimation methods is also included.

A complete analysis of predicted PTOC emissions is provided in Section 6. Emissions estimates are provided on a county-by-county and statewide basis. Reference is made to a data base, provided to the CARB on magnetic recording media, which provides emissions estimates for every MWTP in California. Special attention is given to those counties which contribute significant emissions to the statewide total.

In Sections 7 and 8, conclusions are drawn regarding the significance of volatilization as a PTOC removal mechanism in POTWs, and recommendations are forwarded for future studies and source sampling, respectively.

A process-specific model is described in Appendix H of this report. A theoretical development is provided, along with a description of required model inputs. An interactive FORTRAN program has been written and provided to the CARB along with example applications.

2. PUBLICLY-OWNED TREATMENT WORKS AND WASTEWATER TREATMENT

This section provides a brief overview of POTWs and wastewater treatment facilities. The reader is referred to the glossary in Appendix A, as needed, for further descriptions and definitions associated with municipal wastewater treatment. A number of texts and public documents with detailed descriptions of wastewater treatment and associated processes are listed in the Supplemental Readings.

Wastewater systems that are referred to as publicly-owned treatment works (POTWs) are defined by section 212 of the Clean Water Act (33 U.S.C. 1292). For the purposes of this study, a POTW is defined as a system that is owned by a public entity, and which conveys wastewater to or from a municipal wastewater treatment plant (MWTP). As shown in Figure 1, this includes the wastewater collection system, wastewater and sludge treatment facilities, and effluent, sludge disposal, or outfall, systems.

The wastewater collection system is typically composed of an extensive network of sewerage piping used to convey wastewater discharged by users of the POTW. Collection systems vary in type and length. Collection systems are considered to be either combined or separate. In combined systems, storm water and wastewater are conveyed through the same system. Conversely, in separate systems wastewater is segregated from stormwater, leading to more uniform seasonal flows. Most systems in California are of the separate type. The collection system length for some large POTWs, such as the County Sanitation Districts of Los Angeles County, are on the order of thousands of miles!

Users of POTWs can be classified into many categories. Most commonly, users are classified as residential, commercial, or industrial (see Glossary for definitions). Other users may include institutions such as hospitals, prisons, and educational facilities. Potentially toxic organic compounds are most often discharged by industrial users (IUs), but the contribution from residential, commercial, and institutional users may also be significant. Specific sources of PTOCs are addressed in detail in Section 3.

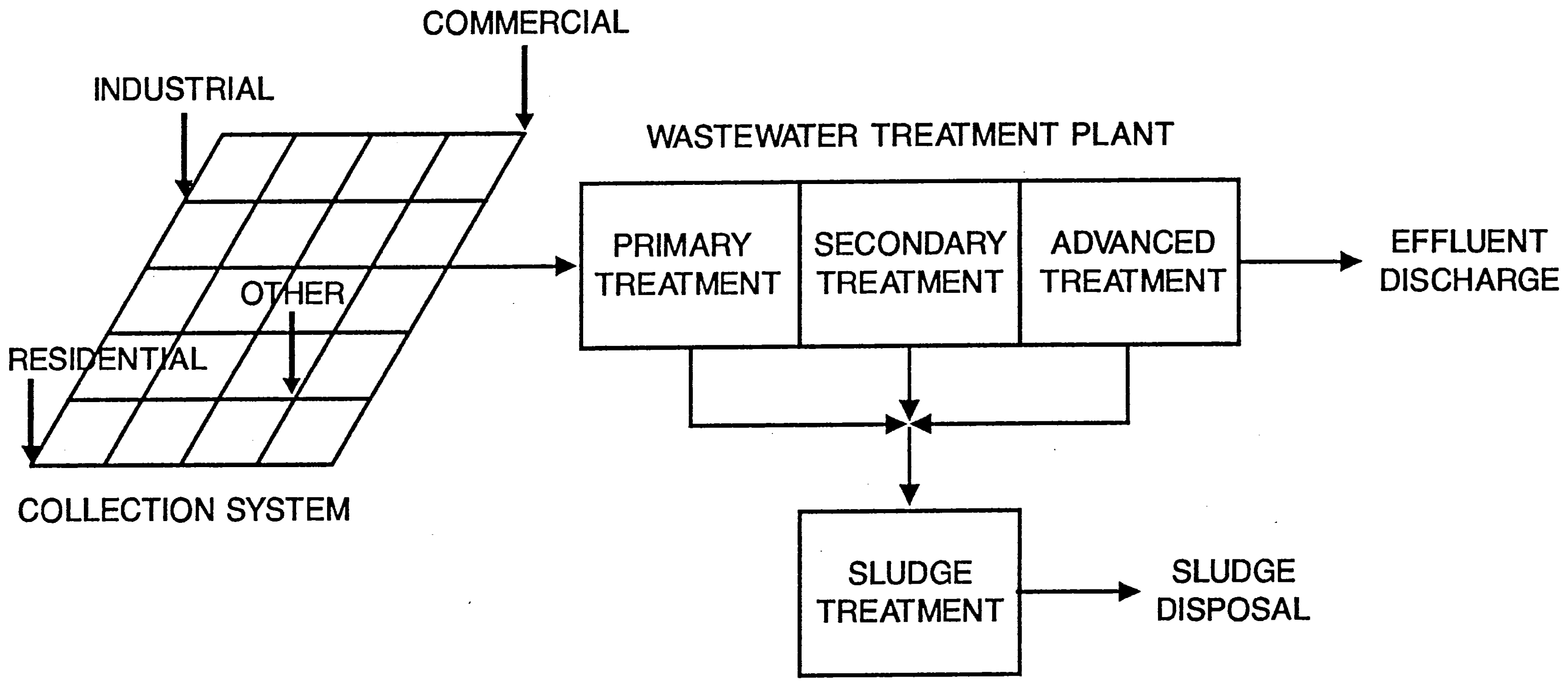


Figure 1: Simplified Representation of a POTW

Municipal wastewater treatment plants are composed of processes to treat both the incoming wastewater and solids separated from the wastewater or that are generated during biological treatment. Wastewater treatment processes are typically categorized as primary, secondary, or advanced treatment. Primary treatment may include the use of bar screens, comminuters, grit chambers, and primary clarifiers. While not all MWTPs employ secondary treatment, it is common practice in large facilities and those facilities that discharge to potentially sensitive receiving waters. Secondary treatment typically includes biological treatment such as activated sludge systems, trickling filters, oxidation ponds, rotating biological contactors, overland flow, and marsh systems. Advanced, or tertiary, treatment systems may include filtration units, biological nitrification systems, stripping towers, and the use of activated carbon adsorption systems. Chlorination is often employed as a treatment step to disinfect treated wastewater before it is dis-charged to a receiving water. Dechlorination of the effluent using sulfur dioxide commonly follows disinfection.

Receiving systems for effluent discharge vary considerably, and are highly dependent upon the geographic location of the POTW. For instance, effluent from MWTPs in the Central Valley region of California are typically discharged to surface receiving waters, usually rivers or smaller surface waters that flow into rivers. Effluent is also employed for restrictive agricultural uses, or may be disposed of to the atmosphere from evaporation ponds, or to the groundwater using percolation ponds. In Los Angeles and Orange counties, as well as all along the California coast, a large fraction of municipal effluent is discharged to the ocean. Finally, many large MWTPs in the South and East San Francisco Bay regions discharge final effluent directly to San Francisco Bay.

Sludge is collected during primary and secondary treatment, and sometimes during advanced treatment. Secondary and advanced treatment sludges are typically thickened, and combined sludges are commonly stabilized using anaerobic digestion. The combined, digested sludge is dewatered by centrifuge, belt press, or drying beds, before ultimate disposal to a landfill. Incineration, composting, and discharge to the ocean are also currently employed as disposal processes.

3. POTENTIALLY TOXIC ORGANIC COMPOUNDS OF INTEREST

Compounds and Characteristics

The potentially toxic organic compounds, as well as several of their important physico-chemical characteristics, are shown in Table 1. Names approved by the International Union of Pure and Applied Chemists (IUPAC) are provided under the heading of chemical name. Common synonyms are also provided. The relatively low solubility, and high vapor pressures for most of the PTOCs under consideration indicate their tendency toward volatilization.

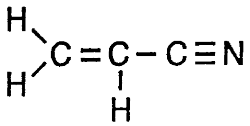
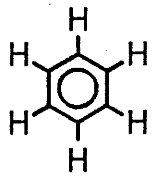
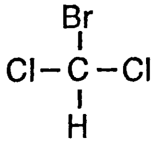
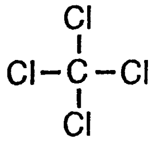
Sources

As was indicated in Section 2, several types of users discharge to POTWs. Those classified as residential, commercial, or industrial may be broken down further according to the specific source. Tables 2 and 3 are provided to indicate typical uses of PTOCs, and to list those sources that have been known to discharge significant amounts of PTOCs to POTWs.

Pretreatment Requirements

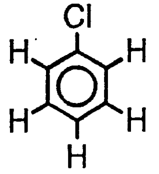
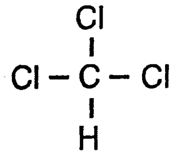
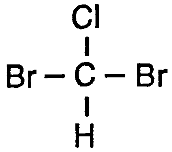
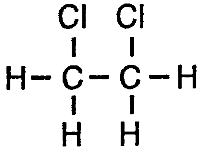
On June 26, 1978, the EPA issued regulations for a National Pretreatment Program (NPP). Revised regulations (Appendix B) became effective on March 30, 1981. The NPP was established to protect POTWs and their surrounding environments from the adverse effects associated with the discharge of hazardous and/or toxic wastes to the POTW's wastewater system. In particular, it was desired to protect biological treatment systems from interferences and failures, to minimize the potential for the pass-through of toxic wastes in the MWTP effluent, to prevent the contamination of municipal sludge, and to reduce the exposure of workers to chemical hazards. The NPP is the primary mechanism for achieving such objectives. It has gained increased importance in that role following the Domestic Sewage Exclusion (DSE) enacted under

Table 1A : POTENTIALLY TOXIC ORGANIC COMPOUNDS

Chemical Name	Synonyms	Chemical Structure	Molecular Weight g/g-mole	Solubility mg/l	Vapor Pressure (mmHg)	Boiling Point (°C)	Henry's Law Constant (X1000) (atm-m^3/mol)
2- Propenenitrile	Acrylonitrile Vinyl cyanide		53.06	73500	100^2	77.3	0.067^1
Benzene			78.11	1800	76	80.1	5.55
Bromodichloro-methane		 $Cl-\overset{Br}{\underset{H}{C}}-Cl$	163.83	–	50	90.0	2.12
Tetrachloromethane	Carbon tetra-chloride	 $Cl-\overset{Cl}{\underset{Cl}{C}}-Cl$	153.84	785	90	76.5	30.2

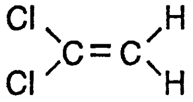
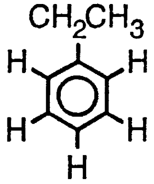
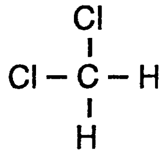
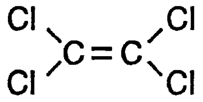
Solubility and vapor pressure at 20°C except (1) = 15°C, (2) = 23°C, (3) = 25°C
Henry's Law constants at 25°C except (1) = 15°C
References: Mackay et al. (1979), Nicholson et al. (1984), USEPA (1983), Verschueren (1977), CRC (1977)

Table 1B : POTENTIALLY TOXIC ORGANIC COMPOUNDS

Chemical Name	Synonyms	Chemical Structure	Molecular Weight g/g-mole	Solubility mg/l	Vapor Pressure (mmHg)	Boiling Point (°C)	Henry's Law Constant (X1000) (atm-m^3/mol)
Chlorobenzene	Phenyl chloride		112.56	500	8.8	132.0	3.93
Trichloromethane	Chloroform	 $\mathrm{Cl-\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}-Cl}$	119.38	8000	160	61.7	3.39
Chlorodibromo-methane	Dibromochloro-methane	 $\mathrm{Br-\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}-Br}$	208.29	–	15	122.0	0.78
1,2 Dichloroethane	Ethylene dichloride	 $\mathrm{H-\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}-\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}-H}$	98.96	8690	61	83.5	1.1

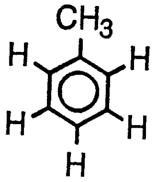
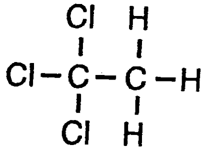
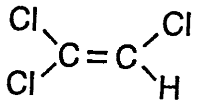
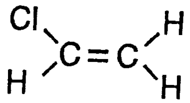
Solubility and vapor pressure at 20°C except (1) = 15°C, (2) = 23°C, (3) = 25°C
Henry's Law constants at 25°C except (1) = 15°C
References: Mackay et al. (1979), Nicholson et al. (1984), USEPA (1983), Verschueren (1977), CRC (1977)

Table 1C : POTENTIALLY TOXIC ORGANIC COMPOUNDS

Chemical Name	Synonyms	Chemical Structure	Molecular Weight g/g-mole	Solubility mg/l	Vapor Pressure (mmHg)	Boiling Point (°C)	Henry's Law Constant (X1000) (atm-m^3/mol)
1,1 Dichloroethylene	Vinylidene chloride		96.94	400	500	37.0	15.0
Ethylbenzene			106.16	152	7	136.0	6.4
Dichloromethane	Methylene chloride	 $\mathrm{Cl-\overset{Cl}{\underset{H}{C}}-H}$	84.94	20000	349	39.8	3.19
Tetrachloroethene	Perchloroethylene (PCE)		165.83	150^2	14	121.0	28.7

Solubility and vapor pressure at 20°C except (1) = 15°C, (2) = 23°C, (3) = 25°C
Henry's Law constants at 25°C except (1) = 15°C
References: Mackay et al. (1979), Nicholson et al. (1984), USEPA (1983), Verschueren (1977), CRC (1977)

Table 1D : POTENTIALLY TOXIC ORGANIC COMPOUNDS

Chemical Name	Synonyms	Chemical Structure	Molecular Weight g/g-mole	Solubility mg/l	Vapor Pressure (mmHg)	Boiling Point (°C)	Henry's Law Constant (X1000) (atm-m^3/mol)
Methyl benzene	Toluene		92.13	515	22	110.8	5.93
1,1,1 Trichloroethane	Methyl chloroform	 $Cl-\underset{Cl}{\overset{Cl}{C}}-\underset{H}{\overset{H}{C}}-H$	133.41	4400	100	74.1	4.92
Trichloroethene	Trichloro-ethylene (TCE)		131.39	1100^3	58	87.0	11.7
Chloroethene	Vinyl chloride		62.50	1^3	2660^3	-13.4	36.0

Solubility and vapor pressure at 20°C except (1) = 15°C, (2) = 23°C, (3) = 25°C
Henry's Law constants at 25°C except (1) = 15°C
References: Mackay et al. (1979), Nicholson et al. (1984), USEPA (1983), Verschueren (1977), CRC (1977)

Table 2: Common Uses of PTOCs

Compound	Uses
Acrylonitrile	production of resins and fibers; modifier for natural polymers; stored grain fumigant,
Benzene	fuel additive; solvent (waxes, resins, oils, etc.).
Carbon tetrachloride	solvent (oils, fats, lacquers, rubber waxes, resins); insecticide; drying agent for spark plugs.
Chlorobenzene	solvent in insecticide and herbicide formulation; solvent for paints; auto parts degreaser; heat transfer medium; manufacture of phenol.
Chloroform	solvent (oil, rubber, alkaloids, waxes, resin); cleansing agent; soil fumigant; solvent for pharmaceuticals.
1,1 Dichloroethylene	intermediate in the production of vinylidene polymer plastics.
Ethylbenzene	resin solvent; conversion to styrene monomer.
1,2 Dichloroethane	solvent (fats, oils, gums, waxes, resins, rubber); extract for tobacco; manufacture of acetyl cellulose.
Methylene chloride	solvent for cellulose acetate; solvent in food processing; degreasing agent; cleansing agent; paint stripping; fire extinguisher compounds; beer flavoring from hops; extraction of caffeine from coffee; metal degreaser; solvent in textile processing.
Perchloroethylene	solvent in dry cleaning; solvent in textile processing; metal degreaser.
Toluene	solvent (paints, lacquers, gums, resins); extraction of principles from plants; gasoline additive; production of benzene, dyes, and explosives.
1,1,1 Trichloroethane	cold-type metal cleaning; cleaning of plastic molds; aerosol formulation.
Trichloroethylene	solvent (fats, waxes, resins, oils, rubber, paints, cellulose esters, ethers, varnishes); degreasing agent; dry cleaning.
Vinyl chloride	refrigerant; direct production of polyvinyl chloride.

References: Merck Index (1983), USEPA (1986).

Table 3: Common Sources of PTOCs

Compounds	Sources
Acrylonitrile	production of resins and acrylic fiber.
Benzene	metal finishing; non-ferrous metals; organic chemicals, plastics, and synthetics industries; pharmaceuticals; manufacturing (dyes, artificial leather, linoleum, varnishes, lacquers, paints); motor vehicle services.
Bromodichloromethane	non-ferrous metals; organic chemicals, plastics, and synthetics industries; chlorinated drinking water.
Carbon tetrachloride	adhesives industry; metal finishing; organic chemicals, plastics, and synthetics industries; pharmaceuticals; food processing; fluorocarbon production.
Chlorobenzene	organic chemicals, plastics, and synthetics industries; pharmaceuticals; motor vehicle services.
Chlorodibromomethane	chlorinated drinking water.
Chloroform	adhesives industry; aluminum forming; leather tanning and finishing; pulp, paper, and fiberboard manufacture; organic chemicals, plastics, and synthetics industries; pharmaceuticals; rubber industry; chlorinated drinking water.
1,1 Dichloroethylene	metal finishing.
Ethylbenzene	adhesives industry; production of electrical products; organic chemicals, plastics, and synthethics industries; leather tanning and finishing; metal finishing; motor vehicle services; pharmaceuticals.
Methylene chloride	adhesives industry; aluminum forming; production of electrical products; leather tanning and finishing; non-ferrous metals; organic chemicals, plastics, and synthetics industries; pharmaceuticals; wood finishing; motor vehicle services; food processing; photographic chemicals.
Perchloroethylene	copper forming; metal finishing; textile mills; non-ferrous metals; organic chemicals, plastics, and synthetics industries; dry cleaners; wood finishing.

section 1004 (27) of the Resource Conservation and Recovery Act (RCRA). The DSE provides that a hazardous waste, when mixed with domestic sewage, is no longer considered to be hazardous according to RCRA definitions. Thus, POTWs that receive such waste are not subject to RCRA treatment, storage and disposal facility requirements. A recent report describes the philosophy behind and the suspected impacts of the DSE (USEPA, 1986).

General pretreatment regulations (listed in 40 CFR 403) require that any POTW, or POTWs operated by the same authority, with a combined design flow of greater than 5 million gallons per day (MGD) must establish a pretreatment program. Furthermore, that program is to be a condition of the POTW's National Pollutant Discharge Elimination System (NPDES) permit. If a POTW has a design flow of less than 5 MGD, it may be required to establish a pretreatment program if nondomestic users discharge wastes that cause interferences or upsets, contamination of sludge, NPDES permit violations, or if the users are subject to pretreatment standards. In the State of California, over 100 MWTPs exist within POTWs that are required to establish Pretreatment programs. Those MWTPs account for approximately 90% of the total municipal wastewater that is treated in California. A summary of California POTWs that have fully-established, or that are developing, pretreatment programs is provided in Appendix C.

To implement an effective pretreatment program, a POTW must have the ability to:

1. identify and evaluate its nondomestic users,

2. operate under a legal authority that will enable it to apply and enforce the requirements of the General Pretreatment Regulations (Appendix B),

3. characterize discharges to its treatment system and establish sufficiently protective local effluent limits,

4. monitor industrial users to determine compliance and noncompliance,

5. provide funds, equipment, and personnel,

6. properly administer and manage its pretreatment program.

A comprehensive review of pretreatment program approval and implementation procedures can be found in the EPA's "Guidance Manual for POTW Pretreatment Program Development," (Hanmer et al., 1983).

Two types of standards are used to control pollutant discharges to POTWs. The first, "prohibited discharge standards", applies to all commercial and industrial establishments which discharge to POTWs. Prohibited standards restrict the discharge of pollutants that create a fire or explosion hazard in sewers or treatment works, are corrosive (pH < 5.0), obstruct flow, upset treatment processes, or increase the temperature of the wastewater entering the plant to above 40°C. "Categorical standards" apply to industrial and commercial discharges in 25 industrial categories ("categorical industries"), and are intended to restrict the discharge of 126 priority pollutants, including all of the 16 PTOCs.

As part of their pretreatment programs, POTWs in California report to the appropriate Regional Water Quality Control Board (RWQCB) and to the Region IX office of the EPA. The State Water Resources Control Board (SWRCB) also maintains copies of a large percentage of the reports. In general, quarterly reports document the monitoring of industrial and commercial users, violations, and enforcement activities. Summaries of nondomestic users, user additions, and user losses are also common. Annual reports typically document the overall treatment characteristics of MWTPs within the POTW. These include monitoring results for conventional pollutant parameters such as biochemical oxygen demand (BOD), total suspended solids (TSS), and oil and grease, as well as hydraulic loading characteristics, and the results of any sampling for priority pollutants in the influent, effluent, and sludge streams. This data source on PTOCs will become extremely valuable in future years. However, because of the recent implementation of the National Pretreatment Program, measurements for those MWTPs that have sampled for PTOCs are typically limited to the past one or two years.

4. THE FATE OF POTENTIALLY TOXIC ORGANIC COMPOUNDS IN PUBLICLY-OWNED TREATMENT WORKS

Within a wastewater collection and treatment system PTOCs may be removed, transformed, generated or simply transported through the system unchanged. Five primary mechanisms are involved: (1) volatile emissions, (2) degradation, (3) adsorption to sludge, (4) pass-through (i.e., passage through the entire system), and (5) generation as a result of chlorination or as byproducts of degradation of precursor compounds. Furthermore, these mechanisms are not mutually exclusive, as competition and simultaneous action can be significant.

A schematic summary of the mechanisms which affect PTOCs in POTWs is provided in Figure 2. As indicated, volatile emissions can occur throughout the collection and treatment system. Degradation, particularly through biological activity (biodegradation), can also occur throughout most of the system. Adsorption to sludge occurs during primary, secondary, and advanced treatment. Pass-through is reflected in a total system removal efficiency of less than 100%, and the subsequent discharge of PTOC residuals to the final receiving system. Finally, PTOCs may be generated via the degradation of other PTOCs, or by the formation of trihalomethanes (THMs) during and after chlorination.

The mechanisms described above are discussed in greater detail in the remainder of this section. This section has been included to summarize the extent of existing knowledge about the fate of priority pollutants during wastewater collection and treatment. The importance of adsorption to sludge, biodegradation, pass-through, and formation during chlorination are also illustrated by presenting selected results of this study. Quantitative estimates of the extent of volatile emissions are described in greater detail in Section 6.

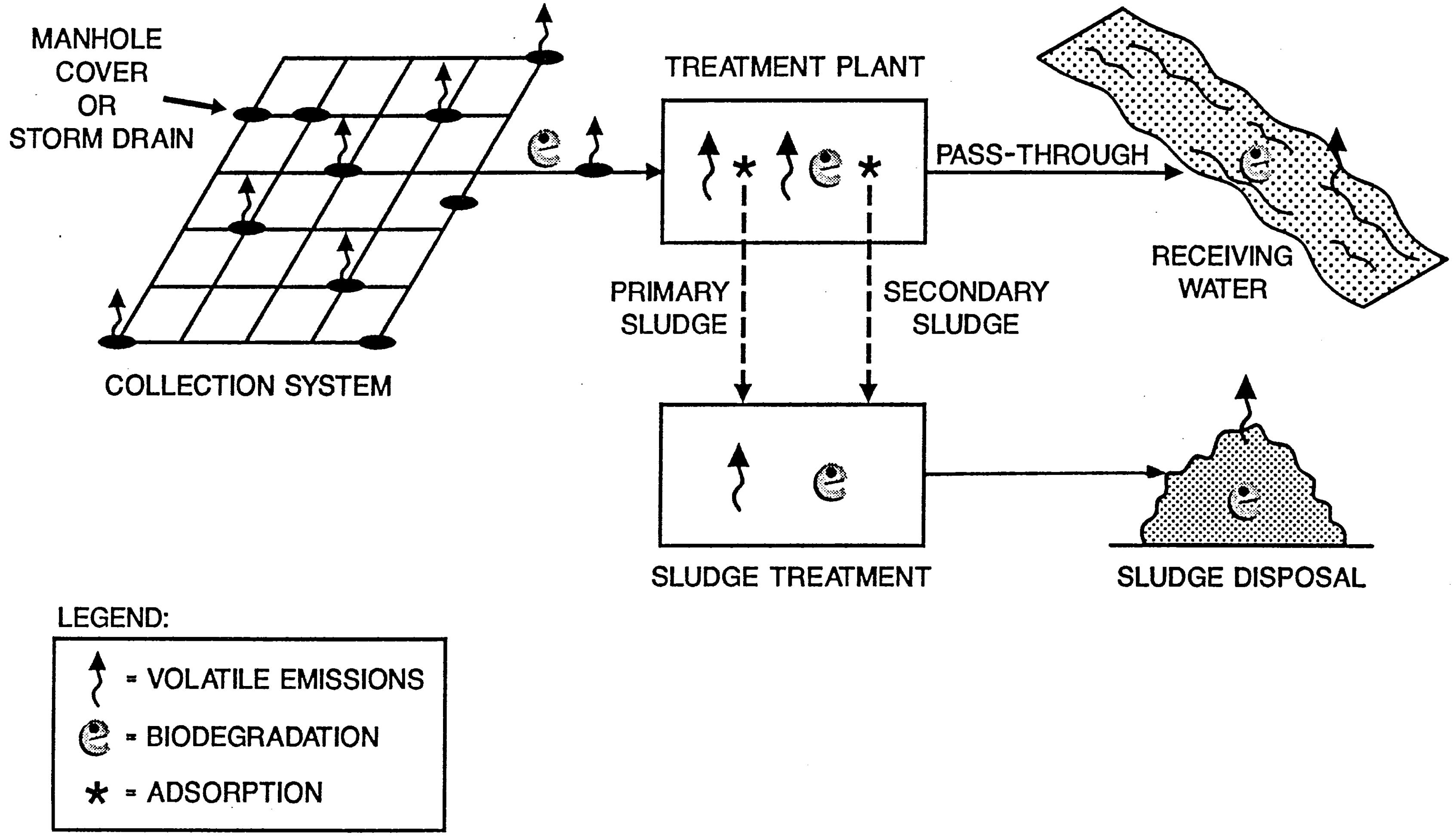


Figure 2: The Fate of PTOCs in POTWs

Removal From Collection Systems

Organic compounds may be removed from the aqueous phase in the collection system by adsorption to particles, biodegradation, exfiltration, pass-through to the treatment facility, or volatilization. Past studies have focused upon material balances at points of entry to the collection system and discharge to the wastewater treatment facility. Few measurements of gas phase concentrations and air exchange with the atmosphere have been made. Thus, the relative significance of the removal mechanisms in collection systems is not well understood at this time. However, based upon past studies using a shallow stream desorption model, volatile organic compounds appear to desorb rapidly to the gas phase in sewers (USEPA, 1986). These results indicate that emissions from collection systems to the ambient atmosphere are potentially significant with respect to the other removal mechanisms. Due to the paucity of experimental data on the topics of adsorption, biodegradation, and exfiltration in collection systems, those mechanisms will not be addressed here. Pass-through to the treatment system will be addressed in Section 6, and appear as MWTP influent mass loadings. Thus, this subsection will only address the existing knowledge regarding volatilization from collection systems.

In addition to the competition among removal mechanisms, several factors can affect the volatile emissions of PTOCs from collection systems. Those factors include the physico-chemical characteristics and concentrations of the PTOCs, flowrate and system geometry as they affect turbulence, effective interfacial area, headspace volume in the sewer line, and ventilation of the collection system (USEPA, 1986; Matthews, 1975). The latter is believed to be very important, as the characteristics of air exchange between the sewer line and the ambient atmosphere are significantly different depending upon the type of system. For instance, in combined storm and sanitary sewers, air exchange occurs at manhole covers and storm drains. However, storm drains are not employed for separate sanitary sewer systems. Thus, it is expected that of the two types of collection systems, combined systems are more conducive to volatile losses of PTOCs. Unlike many older

astern United States, most cities in Cali
y sewers. One exception is the city and
combined systems are still in use.

eported the occurrence and emissions of
on systems. In part, this is due to the
an be both a physically difficult and dan
to conduct sampling. However, recent stu
urrences in collection system atmospheres
to the potential magnitudes of PTOC emiss
as (1981) observed high levels of many po
ove wastewater in interceptor sewers. A
effort indicated that volatilization
ounted for significant losses of PTOCs
a (Frederick, 1985).

nitoring for PTOCs in California collect
ver, studies were recently completed th
of several PTOCs in trunk lines in Sunnyva
tington Park (Los Angeles County). Partia
summarized in Table 4. Because of a la
flowrates, emissions from the Sunnyvale an
d not be projected.

that volatile emissions of PTOCs from col
icant, particularly in sewer lines servin
tablishments which discharge large quanti
se emissions may be of greatest concer
sewers are employed. However, high con
of separate systems indicates that they
es of PTOC emissions. Unfortunately, the
a does not allow for meaningful emission
ere future studies would be of great value
ssociated with the relative significance
mission sources.

municipalities in the Eastern United States, most cities in California employ separate sanitary sewers. One exception is the city and county of San Francisco, where combined systems are still in use.

Few studies have reported the occurrence and emissions of PTOCs from wastewater collection systems. In part, this is due to the fact that collection systems can be both a physically difficult and dangerous environment in which to conduct sampling. However, recent studies of organic compound occurrences in collection system atmospheres have afforded some insight as to the potential magnitudes of PTOC emissions from those sources. Lucas (1981) observed high levels of many pollutants in the headspace above wastewater in interceptor sewers. A combined modeling/monitoring effort indicated that volatilization from sewer lines may have accounted for significant losses of PTOCs from a large POTW in Philadelphia (Frederick, 1985).

Reported results of monitoring for PTOCs in California collection systems are scarce. However, studies were recently completed that document the concentration of several PTOCs in trunk lines in Sunnyvale (Santa Clara County) and Huntington Park (Los Angeles County). Partial results of those studies are summarized in Table 4. Because of a lack of data on the ventilation flowrates, emissions from the Sunnyvale and Huntington Park systems could not be projected.

In summary, it appears that volatile emissions of PTOCs from collection systems may be significant, particularly in sewer lines serving industrial and commercial establishments which discharge large quantities of PTOCs to POTWs. Those emissions may be of greatest concern where combined sanitary/storm sewers are employed. However, high concentrations in the atmosphere of separate systems indicates that they may also be significant sources of PTOC emissions. Unfortunately, the lack of existing sample data does not allow for meaningful emission estimates. This is an area where future studies would be of great value to reduce the uncertainties associated with the relative significance of collection systems as PTOC emission sources.

Table 4: PTOC Concentrations in Collection System Atmospheres.

Compound	Gas Concentration (ppb)	
	Sunnyvale[1]	Huntington Park[2]
Benzene	4.9	4600
Ethylbenzene	2.9	NR
Methylene chloride	36.4	NR
Perchloroethylene	NR	4300
Toluene	35.6	5800
1,1,1 Trichloroethane	NR	60000

NR = Not reported.
Sunnyvale values based on the average of 5 samples.
Huntington Park values based on a single bulb sample.

(1) Dixon and Bremen (1984).
(2) Porter (1986).

Volatilization Within Wastewater Treatment Plants

The purpose of this subsection of the report is to provide the reader with background material regarding past efforts to measure volatile PTOC emissions from wastewater treatment processes. Results from laboratory and field tests are reviewed.

Measurements completed to assess the relative importance of volatilization as a chemical removal mechanism appear to be sensitive to the experimental arrangement. For instance, analyses completed in the laboratory tend to predict that volatilization is not as important in biological reactors as would be indicated by pilot plant and field studies. Possible reasons for the discrepancies include such factors as differences in the acclimation of organisms and unmeasured losses from pilot or bench-scale equipment.

Lawson and Siegrist (1981) studied the relative importance of volatilization and biodegradation in bench-scale biological reactors. They found that biodegradation dominated volatilization for acrylonitrile, toluene, and 1,2-dichloroethane. The latter was found to have the highest percent volatilized (10%) during the experiments. Kincannon et al. (1983) observed similar results for acrylonitrile, methylene chloride, and benzene in the laboratory. However, volatilization was found to be complete (100%) for 1,1,1-trichloroethane and 1,2-dichloroethane. The fate of toxic organic compounds in activated sludge and integrated powdered activated carbon (PAC) systems were recently investigated in the laboratory (Weber et al., 1983; Weber et al., 1986). After a certain concentration of PAC addition was exceeded, the ratio of volatilization to biodegradation was observed to decrease significantly. The ratio of biodegradation to volatilization losses typically exceeded 3:1 for the PTOCs that were studied.

Field studies have been conducted in order to assess the relative significance of PTOC emissions during wastewater treatment, and to categorize treatment processes according to their relative significance with respect to emissions from other treatment processes.

The fate of toluene in an organic chemical wastewater facility was studied (Berglund et al., 1985). It was observed that 10-15% of the toluene volatilized during primary treatment, 25-35% volatilized from an equalization basin, and 10-34% was removed by volatilization in aeration basins. This exemplifies the fact that while aerated secondary treatment may be very efficient at stripping PTOCs to the atmosphere, a significant amount of the PTOCs may be removed by volatilization before ever reaching secondary treatment. A recent report to Congress (USEPA, 1986) described various processes from which volatilization can be expected to occur. In addition to aeration basins, other processes included flumes, grit chambers, sumps, equalization basins, pH adjustment stations, nutrient addition stations, clarifiers, oxidation basins, open storage tanks, wastewater transfer lines, pipes, and ditches.

The report to Congress (USEPA, 1986) also noted the importance of acclimation of the secondary treatment system with respect to volatile emissions. Volatile losses from unacclimated activated sludge systems were typically observed to be greater than 80% for VOCs. However, the degree of volatilization was significantly reduced, as low as 25% for benzene, ethylbenzene, and toluene, within acclimated systems.

While most studies have focused upon emissions from activated sludge systems, some studies have also indicated the potential for emissions from other wastewater processes. Jenkins et al. (1980) suggested that volatile losses accounted for the high removal efficiencies of chloroform (78.9-98.3%) and toluene (95.7-100%) during overland flow treatment. Biodegradation and adsorption were addressed and it was found that neither could account for the observed losses. However, overland flow systems are currently rare in the state of California.

The California Air Resources Board (1985) recently conducted source tests at two large MWTPs in California. Based upon the concentrations of specific PTOCs in or above individual treatment processes, it would appear that emissions from grit chambers, digester tanks, and aerated channels are potentially significant with respect to emissions from other processes. Concentrations of vinyl chloride, toluene, and 1,1-dichloroethylene were much greater in digester gases than in the other processes that were sampled. However, the high concentrations do not necessarily result in high emissions, as digester gases are most often flared or combusted to generate power. The PTOCs are expected to be efficiently destroyed during those processes. Emissions can, however, occur through out-breathing pressure-relief valves or around the skirt of floating roof digesters.

In summary, there are limitations to the generalizations that can be made based upon previous monitoring studies. Laboratory studies to predict the fate of PTOCs in wastewater are usually completed under conditions that are not typical of those found in the field. While they may be valuable in assessing the relative affinities of various PTOCs for specific removal pathways, the results can not be accurately extrapolated to field conditions. Field studies are the most valuable for obtaining direct measurements of PTOC removal. However, the lack of existing data based upon similar studies makes it difficult to generalize about the fate of PTOCs in MWTPs. More complete studies of PTOC concentrations, in both the liquid and gas phases, and off-gas flowrates at individual treatment processes would be desirable.

Removal in the Sludge Stream

Chemical contaminants can adsorb at the solution/air interfaces of non-viable suspended solids or biomass. Furthermore, sorption can occur with uptake into biomass. Because almost all of the literature regarding the removal of organic compounds in sludge streams refers to adsorptive processes, in this report, the mechanism for removal in the sludge stream will be referred to as adsorption.

Adsorption to suspended solids can occur during primary treatment, with subsequent removal in the primary sludge stream. Some fraction of the suspended solids pass through to secondary treatment, as does the remaining contaminant mass which is not adsorbed to solids. Some of the adsorbed contaminant is removed from the system as pass-through in the effluent stream and via sludge wastage (secondary sludge removal). However, a significant amount is typically recycled. This leads to a potential for accumulation on biomass, as noted in the literature for benzene, ethylbenzene, and chlorobenzene (USEPA, 1982). Accumulation might also be the explanation for detection of PTOCs in sludge, when they were not detected in the influent stream (Feiler, 1979; USEPA, 1982).

After a compound is adsorbed to biomass and removed in the sludge stream, it can be biodegraded to a chemical of lesser concern. However, transformation or formation of other chemicals of concern can also occur. An example would be reductive dechlorination during anaerobic digestion, whereby chlorine atoms are removed from a molecule leading to a compound with fewer chlorine atoms.

An adsorbed PTOC also has the potential to be desorbed and volatilized to the atmosphere during one of several stages of sludge treatment. For instance, dissolved air flotation is used to thicken sludge. This is an aerated process which might be conducive to desorption and stripping. Also, drying processes and sludge composting expose large amounts of surface area of the sludge to the atmosphere. Sludge is commonly disposed of to landfills, where desorption, degradation, leaching, and volatilization of adsorbed contaminants can occur. Volatile emissions and groundwater contamination as a result of sludge disposal practices at landfills is a growing concern.

Several factors which affect a compound's affinity for adsorption to sludge have been described in the literature. They include the presence of other compounds which compete for adsorption sites, electrolytes, oils and greases, and the presence of sorbents (USEPA, 1986). Strier and Gallup (1983) analyzed priority pollutants grouped according to their physico-chemical properties. They concluded that the physico-chemical parameters that favor adsorption are a low water solubility, high partition coefficient, high molar volume, low Henry's law constant, low oxidizability, and low chemical reactivity. The contribution of the wastewater matrix has also been reviewed (Strier and Gallup, 1983). A lack of emulsifiers and a high dissolved salt content both tend to reduce solubility thereby increasing the tendency for adsorption. High total suspended solids, which serve as additional adsorption sites, also promote adsorption. The presence of a light oily phase provides a means by which contaminants may partition out of liquid water before being adsorbed to the surface of solids, leading to decreased adsorption. Finally, since adsorption is usually an exothermic process, low temperatures are expected to increase the amount of adsorption.

Two physico-chemical parameters which have been used to compare relative affinities for adsorption are the log of the octanol/water partition coefficient (log(Kow)) and the activated carbon adsorption capacity (AC) (Dixon and Bremen, 1984). Table 5 shows log(Kow) and AC values for the 16 PTOCs. It has been observed that if the log(Kow) is greater than 3.5, a compound is significantly hydrophobic and adsorptive on solid organic matter such as mixed liquor suspended solids (MLSS) and sludge. The highest log(Kow) value for the PTOCs is 3.15 for ethylbenzene. It has also been noted that the relative adsorption of organics on biomass is similar to that for activated carbon, but with the value of AC typically an order of magnitude lower (Dixon and Bremen, 1984). Thus, in terms of log(Kow) and AC, ethylbenzene, chlorobenzene, and perchloroethylene would be expected to have a greater affinity for adsorption than other PTOCs. Vinyl chloride and methylene chloride would be expected to have a relatively low affinity for adsorption.

A set of categories to estimate partition coefficients (fraction removed in sludge stream) was developed based upon a compound's octanol/water partition coefficient, Henry's law constant and analyses of sludge samples obtained from 50 POTWs (USEPA, 1986). The categories and average partition coefficients are shown in Table 6. The criteria for grouping the compounds is given in the column headings. None of the PTOCs of interest to this study fell into group A. Aromatic PTOCs (benzene, chlorobenzene, ethylbenzene, toluene) fell into group B, as did 1,1,1-trichloroethane. Other PTOCs with partition coefficients greater than 0.1 and falling into group C included bromodichloromethane,

Table 5: PTOC Adsorption Parameters

Compound	Log (Kow)	AC (mg/g)
Acrylonitrile	-0.14	1.4
Benzene	2.13	1.0
Bromodichloromethane	1.88	7.9
Carbon tetrachloride	2.64	11.
Chlorobenzene	2.84	91.
Chloroform	1.97	2.6
Dibromochloromethane	2.09	4.8
1,1 Dichloroethylene	1.48	4.9
Ethylbenzene	3.15	53.
1,2 Dichloroethane	1.48	3.6
Methylene chloride	1.25	1.3
Perchloroethylene	2.88	51.
Toluene	2.69	26.
1,1,1 Trichloroethane	2.17	2.5
Trichloroethylene	2.29	28.
Vinyl chloride	0.60	--

Log(Kow) = Logarithm (base 10) of the octanol/water partition coefficient (dimensionless).

AC = Activated carbon adsorption capacity at neutral pH and a PTOC concentration of 1 mg/L.

References: USEPA (1980), USEPA (1983).

Table 6: Partition Coefficients for Adsorption to Sludge

Group	Log(Kow)	K_H(x1000) (atm-cu.m/mole)	Partition Coefficient
A	> 4	< 1	0.366
B	2 - 4	1 - 10	0.149
C	< 2	1 - 10	0.1395
D	< 2	< 1	0.10
E	> 4	1 - 2	0.0895
F	2 - 4	< 1	0.079
G	2 - 4	> 10	0.035
H	< 2	> 10	0.0075

Group numbers (A-H) were adopted for this study.

Log(Kow) = Logarithm (base 10) of the octanol/water partition coefficient (dimensionless).

K_H = Henry's law constant.

Partition coefficient = fraction partitioned to sludge.

Reference: USEPA (1986).

chloroform, 1,2-dichloroethane and methylene chloride. Acrylonitrile fell into group D, dibromochloromethane into group F, and carbon tetrachloride, perchloroethylene, and trichloroethylene into group G. The only PTOCs in group H were 1,1-dichloroethylene and vinyl chloride.

Several recent studies have addressed the analysis of organic contaminants in sludge (Bell and Tsezos, 1986; Lawson and Seigrist, 1981; Schröder, 1986). However, there are difficulties associated with the measurements of contaminants in sludge, particularly for volatile organic compounds. Volatilization can occur prior to or during sampling. Preservation of samples against degradation during sample transport, and analysis in a complex matrix pose additional problems. Furthermore, physical adsorption is often a reversible process, and contaminants can return to the aqueous phase (Bell and Tsezos, 1986).

Despite the difficulties noted, laboratory studies have been valuable in assessing the relative affinities of different chemicals for adsorption and have led to an improved understanding of how adsorption might be affected by changes in sludge and wastewater treatment systems. Biosorption was found to be negligible compared to volatilization and biodegradation for several PTOCs studied in the laboratory (Kincannon and Stover, 1983). Those observations were made for benzene, chlorobenzene, ethylbenzene, 1,2-dichloroethane, methylene chloride, toluene, and 1,1,1-trichloroethane. However, in pilot plant studies Schröder (1986) observed a significant quantity of chloroform, trichloroethylene, and chlorobenzene in sludge.

The removal of PTOCs by adsorption at primary clarifiers and activated sludge tanks was reviewed (Dixon and Bremen, 1984). The results observed for PTOCs are summarized in Table 7. It is obvious that adsorption during primary treatment was much more significant than adsorption to biomass during biological treatment. This is not surprising, as volatile stripping occurs during aerated secondary treatment. As indicated by the grouping shown in Table 6, partitioning to sludge was relatively high for benzene, chlorobenzene, ethylbenzene, and toluene. However, the trichloroethylene result shown in Table 7 is inconsistent with

Table 7: A Comparison of Adsorption to Primary and Secondary Sludge

Compound	% Adsorption to Primary Sludge	% Adsorption to Secondary Sludge
Benzene	15.6	0.09
Carbon tetrachloride	0.08	0.16
Chlorobenzene	10.6	0.03
Chloroform	0.52	0.23
Ethylbenzene	33.3	0.25
Methylene chloride	3.2	0.04
Toluene	9.4	0.06
Trichloroethylene	17.5	0.09

References: Dixon and Bremen (1984).

its grouping shown in Table 6. The reasons for the discrepancy between observed and predicted behavior were not given.

The most comprehensive contaminant mass flow analysis in MWTPs to date was completed as part of an EPA sponsored "50 POTW Study" (USEPA, 1982). An analysis of the raw mass flow data provided in that report was completed to study the significance of adsorption as a PTOC removal mechanism. The results are shown in Table 8. Toluene was found to be the PTOC most effectively removed in sludge streams, with an average removal of 9.7%. The values in Table 8 represent total removal from all sludge streams. With the exceptions of methylene chloride and chlorobenzene, the percent removal in sludge was less than 5% for the other PTOCs. The surprisingly high results for methylene chloride might be an artifact because of its use in laboratories as a solvent, and the subsequent possibility of contamination during analysis. The possibility for significant contamination is increased since the concentrations of PTOCs in sludge are often near the detection limits.

Biodegradation

Of the four primary removal mechanisms (volatilization, adsorption, biodegradation, pass-through), biodegradation is the most complex and difficult to resolve in terms of its significance with respect to the other mechanisms. This subsection is provided to describe the extent of existing knowledge regarding biodegradation, especially as it relates to PTOCs in wastewater. An overview of biodegradation and where it occurs in MWTPs is included. Factors which are known to affect biodegradation are reviewed. Actual measurements of biodegradation are discussed along with the uncertainties and limitations of such techniques. The objective of the discussion is to provide the reader with background regarding the relative biodegradability of the PTOCs, a realization of the complexity of the biodegradation process, and an understanding of the important factors which can affect the extent of biodegradation.

Table 8: PTOC Removal in Sludge Streams

Compound	# of Plants	% Removed
Toluene	44	9.7
Methylene chloride	41	8.0
Chlorobenzene	6	5.1
Carbon tetrachloride	6	4.3
Perchloroethylene	43	4.1
Trichloroethylene	44	4.1
Ethylbenzene	38	4.0
Vinyl chloride	7	1.3
1,2 Dichloroethane	10	1.1
Benzene	26	1.0
Chloroform	37	0.7
1,1,1 Trichloroethane	38	0.7
Bromodichloromethane	3	0.
1,1 Dichloroethylene	11	0.
Dibromochloromethane	0	-

% Removed indicates total removal from all sludge streams.

Microorganisms that are responsible for the breakdown of organic contaminants are characterized by a high degree of variation in their biological nature. Although the principal microorganisms are bacteria, many diverse types exist. These have been summarized elsewhere (Tchobanoglous and Schroeder, 1985). The organisms have been classified as aerobic, anaerobic, and facultative. The former require oxygen for survival and reproduction. Anaerobic bacteria are adversely affected by the presence of oxygen, and facultative bacteria are able to grow in both aerobic and anaerobic environments. Because of the wide variety of microorganisms that occur in nature and the open characteristics of treatment processes, a continual innoculation can be expected in any biological wastewater treatment process. An important result is that the species best able to compete under a set of physical and chemical conditions will predominate.

A commonly utilized aerobic biological system is the activated sludge process (AS). The majority of AS units employ air to provide the oxygen to sustain the biomass of the system, in which case the aeration basins are typically open to the atmosphere. Less typical are covered, pure-oxygen systems. Additional aerobic systems include trickling filters, rotating biological contactors, overland flow systems, and oxidation ponds. Descriptions of such systems have been given elsewhere (Tchobanoglous and Schroeder, 1985).

A method of characterizing biological treatment process performance is degradation efficiency; defined as the ratio of contaminant concentration leaving the system to the contaminant concentration entering the system. The degradation efficiency of a biological system is affected by the degree of acclimation of the system. Acclimation is characterized by a lag period during which time little or no degradation takes place (Skow, 1982). The delay is thought to be caused by two phenomena (Skow, 1982). The first involves the selection of appropriate biological species that are capable of assimilating the contaminant, in which case the lag period is due to an initial phase of exponential population growth of that microorganism. The second phenomenon involves the adaptation of microorganisms through the induction of enzymes that facilitate degradation. The acclimation period has been noted to vary from hours to weeks depending upon the contaminant, microbial population, and the medium (Skow, 1982). The length of the acclimation period can have a significant affect on the relative importance of biodegradation, adsorption, and volatilization. For instance, if a system is unacclimated, a highly volatile contaminant may volatilize long before biodegradation can compete as a removal mechanism. This is exemplified by results that have been compiled by the EPA, as shown in Table 9 (Frederick, 1985). The results were developed from pilot plant studies. They show that unacclimated systems were characterized by greater volatilization than were acclimated systems. Similar results were observed by Patterson and Kodukala (1981).

The ability of a system to acclimate and remain acclimated is very sensitive to deviations from steady-state conditions (Blackburn et al., 1985). However, PTOC mass loadings in influent streams are typically characterized by a high degree of variability. In addition, it has been noted that the actual magnitude of the contaminant concentration is significant (Alexander, 1973). For instance, if the concentration is too low, biodegradation will be limited because of a lack of sufficient stimulus to initiate an enzymatic response (Alexander, 1973). There is additional evidence that compounds which are usually degradable can be persistent at low concentrations (Digeronimo et al., 1979; Jannasch, 1967). This may be significant for the PTOCs, since many studies to quantify the degree of biodegradation were completed at PTOC concentrations above 10 mg/L, while typical concentrations in the influent to MWTPs are less than 10 µg/L.

A complete assimilation and examination of existing biodegradation data, across individual classes of compounds, has not been effectively completed. Thus, the variables which control rates of biodegradation are not well understood. However, several general observations have been made regarding the factors that affect the degree of biodegradation. These can be classified as substrate-related, organism-related and environment-related.

Table 9: The Effects of Acclimation on Stripping and Biodegradation

Compound	Fraction Stripped		Fraction Biodegraded	
	Acclim.	Unacclim.	Acclim.	Unacclim.
Benzene	0.25	0.80	0.74	0.18
Carbon tetrachloride	0.80	0.90	0.07	0.
Chlorobenzene	0.30	0.50	0.55	0.35
Chloroform	0.70	0.90	0.28	0.08
1,1 Dichloroethylene	0.80	0.90	0.20	0.10
Ethylbenzene	0.25	0.80	0.69	0.14
1,2 Dichloroethane	0.50	0.90	0.45	0.05
Perchloroethylene	0.50	0.80	0.47	0.17
Toluene	0.25	0.80	0.47	0.
1,1,1 Trichloroethane	0.80	0.90	0.19	0.14
Trichloroethylene	0.70	0.80	0.24	0.14
Vinyl chloride	0.90	0.95	0.08	0.03

Reference: USEPA (1986).

Much of the work that has addressed the effects of substrate characteristics has focused upon the solubility of organic compounds (Strier and Gallup, 1983). It has been observed that biodegradation is facilitated for compounds with intermediate solubilities in water, or log(Kow) values between 1.5 and 3.5 (Skow, 1982; Strier and Gallup, 1983). This range corresponds to all of the PTOCs with the exception of 1,1-dichloroethylene, 1,2-dichloroethane, methylene chloride, and vinyl chloride, all of which have log(Kow) values less than 1.5. As noted previously, the contaminant concentration is also an important factor since low concentrations may not be sufficient to initiate the biodegradation process. Also, high concentrations of toxic organic compounds may lead to deleterious "shock-loading" of the biological system (Allen et al., 1985).

Other substrate-related factors can be subclassified under chemical structure. However, the relationships among biodegradation and such factors are not universally agreed upon. It has been observed that biodegradation decreases as the degree of halogenation of a compound increases, and that more than one chloro or nitro group substituted on a benzene ring tends to reduce a compound's degradability (USEPA, 1986).

Because of the complexity of viable systems, the significance of organism-related factors are even less well understood than substrate-related factors. A review of organism-related factors is beyond the scope of this study.

Environment-related factors which have been observed to increase biodegradation include the presence of emulsifiers, low non-viable suspended solids concentrations, and pH values in the range of 6 to 9 (Strier and Gallup, 1983). Higher temperatures, a sufficient dissolved oxygen concentration, the availability of co-metabolites serving as food for biota, and sufficient reaction and solid retention times have all been observed to assist biodegradation (Allen et al., 1985; Strier and Gallup, 1983; USEPA, 1986).

Competing reaction mechanisms can also be significant with respect to the degree of biodegradation. The relationship between biodegradation and volatilization is complicated because many of the factors that affect one mechanism also affect the other.

Most of the measurements made to quantify biodegradation are completed by differencing (i.e., subtracting adsorption and volatile losses from the total removal) after the completion of laboratory or pilot scale experiments. However, difficulties often exist in measuring and/or controlling volatile losses. Thus, inflated biodegradation rates exist in the literature as volatilization losses are mistakenly taken to be degradation losses (Lawson and Siegrist, 1981; Schröder, 1986). Significant test-to-test variabilities in measured biodegradation rates have been observed, as some tests provide a better environment for degradation than others. Such difficulties should be kept in mind before attempting to extrapolate from laboratory, or pilot scale, results to actual field conditions. The factors mentioned previously are likely to be quite different in an actual wastewater treatment facility.

Using bench-scale activated sludge systems, Blackburn et al. (1985) found that biodegradation accounted for 67-70% of the removal of toluene. For acrylonitrile, methylene chloride, and benzene, Kincannon et al. (1984) observed that biodegradation accounted for 100%, 93%, and 84% of the total removal, respectively, in continuous flow biological reactors. However, 1,1,1-trichloroethane was found to completely volatilize. In similar systems, greater than 98% of the removal of acrylonitrile and toluene was attributed to biodegradation (Lawson and Siegrist, 1981). In a completely acclimated bench-scale activated sludge system, biodegradation was observed to account for between 78 and 84% of the total removal of benzene, toluene, ethylbenzene, and chlorobenzene (Weber et al., 1986). However, conditions in all of the experiments were greatly simplified with respect to typical field conditions.

The discussion to this point has dealt primarily with aerobic systems. However, based upon limited digester gas sample data (California Air Resources Board, 1985) and typical PTOC concentrations in the influent stream, it appears that vinyl chloride is produced during anaerobic digestion. The source of the vinyl chloride could be the result of simultaneous removal of a chlorine and a hydrogen atom from a precursor compound, such as 1,2-dichloroethane, with subsequent formation of vinyl chloride. Alternatively, successive substitution of chlorine by hydrogen atoms on compounds such as perchloroethylene might explain the occurrence of vinyl chloride. The sequential dehalogenation of chlorinated ethenes to form vinyl chloride in groundwater environments has been observed (Barrio-Lage et al., 1986). A recent study also indicated that chlorinated organics form as a result of the Purifax process due to the addition of chlorine gas to stabilize sludge (Pincince and Fournier, 1984).

It is safe to say that little is known regarding the biodegradability of PTOCs, or the relative importance of biodegradation with respect to the other removal mechanisms. A better understanding of PTOC biodegradation (e.g., acclimation) would improve our understanding of the extent of volatilization during wastewater treatment. Modification of wastewater treatment processes to increase biodegradation rates might be a useful control technique to reduce volatile losses of PTOCs, and is an area where further research is warranted.

Formation

During the course of literature and data review for this study, it became apparent that halogenated organics form as a result of chlorination during wastewater treatment. It was observed that THMs formed during wastewater treatment in amounts greater than were initially present in the influent streams of MWTPs. This was particularly true for chloroform, and less significant for bromodichloromethane and dibromochloromethane. A detailed review of THM formation is provided in Appendix D. Factors which affect THM formation are described there, along with potential precursors and important reaction mechanisms. Post-chlorination emissions are also discussed. Only a cursory review is provided here.

To study the potential for the formation of chloroform, MWTPs that post-chlorinate on a continuous basis were separated from those that do not regularly chlorinate. In the latter case, the ratio of chloroform concentration in the effluent stream to concentrations in the influent stream (Ce/Ci) was always less than 1. This reflects a net average removal of chloroform. However, for those plants that do post-chlorinate, the value of Ce/Ci was often greater than unity, and as high as 12.7. The data are clearly suggestive of chloroform formation as a result of chlorination. It would also be expected that Ce/Ci would be much greater if the influent concentration was replaced by the chloroform concentration immediately prior to chlorination, since much of the chloroform entering a MWTP in the influent stream would be removed during treatment prior to post-chlorination. This pattern of removal followed by higher Ce/Ci ratios was observed during the 50 POTW study (EPA, 1982).

Pass-through

Up to this point, the removal of PTOCs during wastewater treatment has been described in terms of volatilization, adsorption, and biodegradation. That portion of the PTOC mass which is not removed in the MWTP is discharged in the effluent stream. The same removal mechanisms that operate in a treatment plant continue to act in a receiving water. However, conditions are typically less favorable to biodegradation than in treatment systems designed to induce biological degradation, and less solid surface area is typically available for adsorption. Therefore, it is conceivable that volatilization could account for an even larger percentage of the fate of PTOCs which are discharged than occurs within MWTPs. For the purposes of this study, calculated removal efficiencies and volatile emission estimates do not include emissions associated with pass-through.

Average total percent removals (100% - % pass-through) for 12 PTOCs are shown in Table 10. Acrylonitrile was not observed above its detection limits in either the 50 POTW study or this study. In many MWTPs, the effluent concentrations of THMs were much greater than the cor-

Table 10: Average Total Removal Efficiencies for PTOCs

Compound	No. of Plants 50 POTW	No. of Plants Calif.	Average Removal Efficiency (%) 50 POTW	Average Removal Efficiency (%) Calif.	Standard Deviation (%) 50 POTW	Standard Deviation (%) Calif.
Benzene	21	13	80.9	72.1	29.8	34.6
Carbon tetrachloride	2	3	76.5	94.7	16.3	8.4
Chlorobenzene	7	3	99.8	86.7	0.4	23.1
1,1 Dichloroethylene	7	8	63.7	76.8	44.7	31.3
Ethylbenzene	38	20	87.1	84.0	29.0	28.9
1,2 Dichloroethane	8	6	64.1	96.7	45.3	3.7
Methylene chloride	49	29	49.0	64.6	32.2	26.3
Perchloroethylene	45	35	79.0	79.0	25.7	28.9
Toluene	48	39	92.1	86.4	13.9	23.5
1,1,1 Trichloroethane	42	27	86.7	79.5	22.8	23.8
Trichloroethylene	46	23	88.3	83.1	20.3	23.5
Vinyl chloride	3	0	95.7	--	3.8	--

responding influent concentrations. Thus it was not possible to compute meaningful removal efficiencies for the THMs.

It is common for influent concentrations to be above detection limits (ADL) and effluent concentrations to be below detection limits (BDL). One technique to handle such data is to assume a total percent removal of 100%. This assumption is relatively accurate for PTOCs that are found in concentrations several times greater than their detection limits (e.g., toluene). However, uncertainties associated with such an assumption increase for PTOCs that are present at concentrations that are only slightly above their detection limits (e.g., 1,2-dichloroethane). Therefore, an influent concentration to effluent detection limit ratio of three was arbitrarily chosen as the criterion for using such data in computing average removal efficiencies. The average percent removals for PTOCs other than the THMs were typically found to be in the range of 75-95%. The exception was methylene chloride which had a significantly lower percent removal based upon both the 50 POTW study and the data collected for this study.

Differences in the type and degree of treatment account for some of the variance of the data presented in Table 10. For instance, if volatilization was the most important removal mechanism, MWTPs that utilized aerated secondary treatment were likely to have high total removals. Additional removal would be expected due to biodegradation. The results shown in Table 10 reflect average removal rates without regard to the type or degree of treatment. For MWTPs which employ only primary treatment, the average percent removals are likely to be lower than those shown in Table 10.

Summary

In this section, the fate of PTOCs in both wastewater collection and treatment systems was addressed. For collection systems it was found that the potential exists for significant emissions, but a lack of existing sample data does not allow for meaningful emissions estimates.

It is believed that this is one source which deserves further attention in order to reduce the uncertainties associated with the relative significance of emissions.

Wastewater treatment processes were reviewed in terms of volatilization, adsorption, biodegradation, and pass-through as PTOC removal mechanisms. The formation of trihalomethanes was also discussed. Mechanisms were described in terms of existing laboratory, pilot plant, and field studies. From a limited data set, some general observations were made.

Adsorption and removal in sludge streams typically accounted for less than 10% of the incoming mass of any PTOC. In addition, the total fraction removed in sludge streams is greater in primary sludge than in waste-activated sludge. Although many of the PTOCs have been observed to biodegrade during simplified laboratory analyses, little is known regarding the biodegradation of PTOCs during treatment in actual municipal wastewater treatment plants. The most important factor can be defined as the degree of acclimation of the microbial population to the PTOC of interest. Based upon current knowledge of the acclimation process, it is concluded that requirements for the acclimation to PTOCs usually remain unsatisfied in MWTPs. If that is true, studies have indicated that the percent degraded during conventional activated sludge treatment would be typically less than 20%. One possible exception would be chlorobenzene (% biodegraded = 35%).

Based upon PTOC concentrations in the influent and effluent streams of MWTPs throughout California, it was clear that chloroform formed as a result of chlorine disinfection. In addition, the degree of formation was often significant with respect to chloroform mass loadings in the influent stream.

The overall removal efficiency of PTOCs during wastewater treatment was estimated to be, on the average, between 75% and 95%. Exceptions (lower than 75%) included the trihalomethanes which can form as a result of chlorination, and methylene chloride. For most of the PTOCs, the remaining 5% to 25% were discharged in the effluent stream. The ultimate fate following discharge was expected to be volatilization.

Based upon the observations discussed above, a large fraction of PTOCs that enter a MWTP are expected to be removed via volatile losses.

5. EMISSIONS ESTIMATION METHODS AND DATA QUALITY AND AVAILABILITY

In this section, methods used to estimate PTOC losses from wastewater due to volatilization and adsorption to sludge are described. A discussion of the corresponding assumptions and limitations, and an analysis of the data available for use in the estimation methods was also included. This was done in order to provide the reader with an understanding of typical sampling and analysis techniques that are used to measure PTOC concentrations in influent and effluent streams, as well as to indicate the extent and representativeness of the data collected for MWTPs in California.

Emissions Estimates

The uncontrolled emission rate, "E_m", of a specific PTOC, "m", from a MWTP can be expressed as a fraction of the average total removal of "m" such that

$$E_m = (f_m/n) \sum_{j=1}^{n} (C_{m,i,j}-C_{m,e,j})Q_j, \qquad (1)$$

where "f_m" is an average stripping factor for PTOC "m" ($0 < fm < 1$), "n" is the number of sampling periods, "Q_j" is the average wastewater flowrate during sampling period "j", and "$C_{m,i,j}$" and "$C_{m,e,j}$" are the concentrations of PTOC "m" in the influent and effluent streams, respectively, during sampling period "j". Of course, all parameters should have consistent units, or should be converted to the desired units. The worst-case emission estimate is based upon a value of "f_m" equal to unity. Because this study focussed upon the potential for PTOC emissions, worst-case, uncontrolled, emission estimates were computed.

If "$C_{m,i,j}$" and "$C_{m,e,j}$" are replaced by flow-weighted, average values, "$C_{m,i}$" and "$C_{m,e}$", respectively, Equation 1 can be rewritten as

$$E_m = f_m (C_{m,i} - C_{m,e})Q, \qquad (2)$$

where "Q" is the flowrate averaged over all sample periods.

Equation 2 can be applied if concentrations are known in both the influent and effluent streams. For MWTPs in which effluent data are not available, the worst-case emission rate can be estimated by

$$E_m = b_m f_m (C_{m,i} - C_{m,e})Q, \tag{3}$$

where "b_m" is an average total removal efficiency for PTOC "m". Equation 3 is also useful for estimating the emissions of trihalomethanes. For THMs, Equation 2 is not suitable as formation during treatment causes an increase in "$C_{m,e}$" and a corresponding decrease in the estimated emission rate. However, Equation 3 does not account for volatile emissions which can occur following the formation of THMs. For this study, values for "b_m" were based upon the total removal efficiencies shown in Table 10. A value of $b_m = 0.9$ was chosen for the THMs, based upon removal efficiencies for similar compounds. While Equation 2 is preferred to Equation 3, it should be noted that only four of the fifty-one MWTPs for which data were gathered did not submit effluent data. Those four facilities accounted for only one percent of the total municipal wastewater treated in California. The most significant effect of the use of Equation 3 was on the estimate of chloroform emissions. While the worst-case assumption was conservative with respect to emissions estimates, it was partially offset by not accounting for volatile emissions of the chloroform that were generated as a result of chlorination. The formation of bromodichloromethane and dibromochloromethane was relatively insignificant with respect to chloroform and was ignored.

Twenty-three percent of the municipal wastewater in California was treated by MWTPs for which no concentration data were obtained. Several methods were examined to extrapolate emissions estimates to those MWTPs. The simplest was to assume average statewide concentrations at those MWTPs without data. However, the coefficient of variation (cv) for specific PTOCs taken over all MWTPs with available data was typically greater than a factor of three. Using such an approach would tend to overestimate emissions in less-industrialized regions, and underestimate emissions in heavily industrialized regions. A second approach was to maintain a statewide analysis while attempting to correlate concentrations with available parameters. However, normalizing the PTOC concentrations by total suspended solids, total phenols, phenol (acids), cyanide, and fractional industrial flow all failed to significantly reduce the cvs with respect to the non-normalized cvs. A more successful approach was to partition the MWTPs with existing data into geographic regions where similar mixes of industrial users discharge to POTWs. This approach led to decreases in the cvs for most of the PTOCs in nearly every region. In addition, normalizing by the fraction of flow accounted for by industrial users further reduced the cvs. After comparing other methods of correlation with distinct geographic regions, the industrial flow approach was adopted, as it appeared to be superior to the other methods that were studied. The counties that were grouped into specific regions for analysis are indicated in Figure 3.

For MWTPs that did not treat industrial flows and for which data were missing, extrapolation was completed by analyzing corresponding facilities for which data were available, i.e., which had no industrial flow contribution. Average PTOC concentrations from those facilities were assumed to apply to all facilities without industrial flow contributions.

The significance of extrapolation, on a county-by-county basis is indicated in Table 11 which shows the percent of total wastewater that is accounted for by MWTPs with existing concentration data. The contribution of extrapolated emissions, on a percent flow basis, was much smaller in the populated, industrialized counties where PTOC mass loadings to POTWs were relatively high. A larger percentage of the extrapolated emissions estimates were needed in rural, nonindustrialized counties with relatively lower total emissions.

The approach described above was used to estimate emissions from approximately 600 MWTPs in California. Estimates for individual MWTPs were summed to predict county-by-county and statewide emissions on a speciated and total PTOC basis. This was accomplished through the use of a program, WEST (Worst-case Emissions during Sewage Treatment), which was developed for this study, and coded in FORTRAN 77. WEST (Appendix

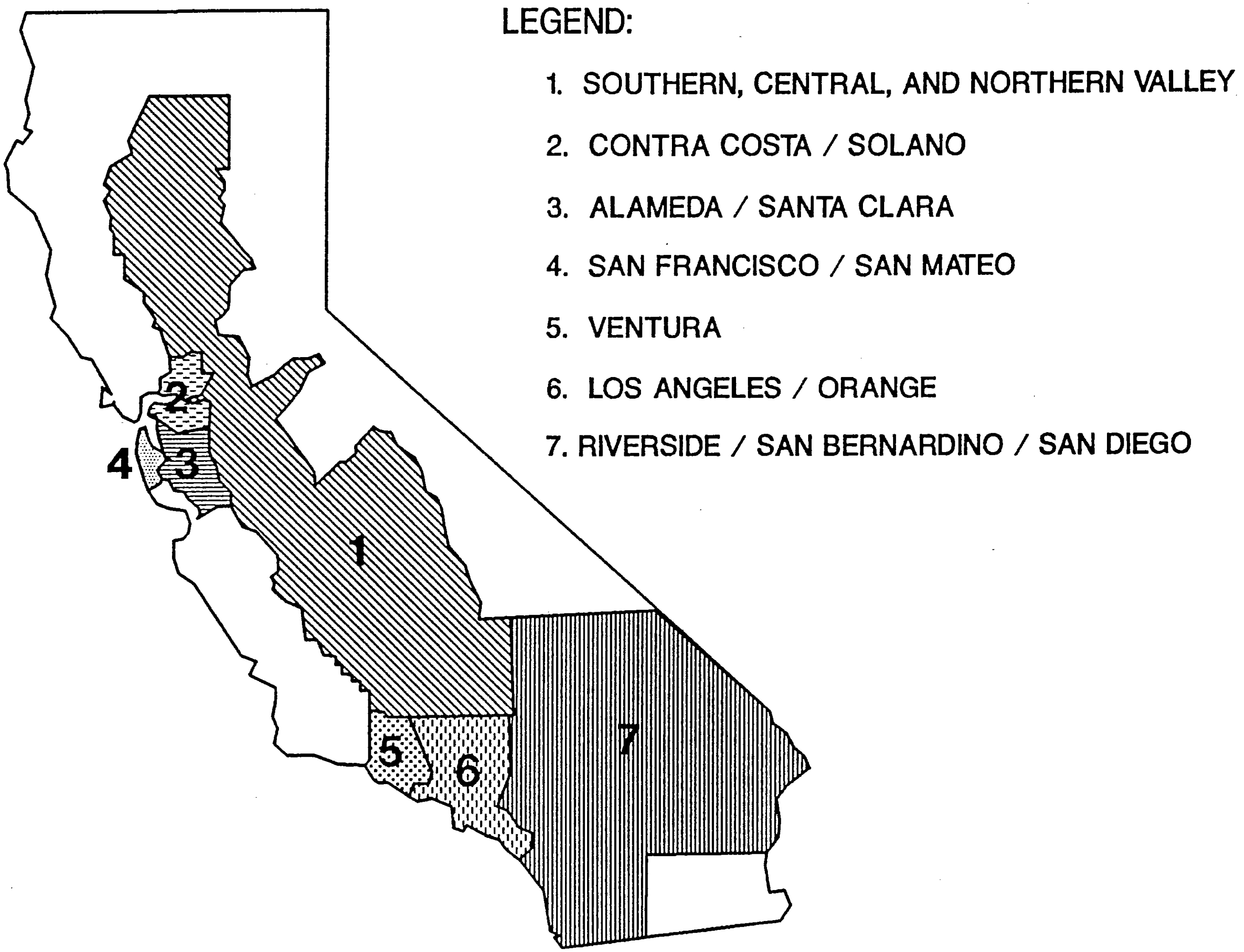


Figure 3: Data Extrapolation Regions

Table 11: Percent of Flow Accounted for by MWTPs with Data

County	Total Flow[1] (MGD)	Percent of Flow Accounted for by MWTPs with Data
Alameda	124	97 %
Contra Costa	72	93
Fresno	51	82
Kern	36	51
Los Angeles	984	93
Marin	21	21
Merced	13	37
Monterey	24	62
Orange	278	92
Riverside	58	42
Sacramento	127	99
San Diego	184	86
San Francisco	115	99
San Joaquin	56	81
San Luis Obispo	11	36
San Mateo	60	59
Santa Clara	175	99
Santa Cruz	21	39
Solano	29	81
Sonoma	23	14
Ventura	49	56
All others	650	0
Statewide	2800	78

(1) Based upon annual averages from 1983 to 1986, and NEEDS data.

E) draws upon flowrate and concentration data stored in an external file (COUNTY.DAT).

Sludge Generation Estimates

Two methods for estimating sludge generation were compared. One method of extrapolation (method 1) was to normalize the existing sludge generation data by the wastewater flowrate, and analyze those facilities without data in terms of their known flowrates. This method was crude, as it did not account for the actual solids loading into the MWTP, or the degree of treatment. Total suspended solids (TSS) information was usually available for most of the MWTPs. Therefore, a second method (method 2) to estimate sludge generation was

$$S_g = (S_i - S_e)Q, \tag{4}$$

where "S_g" is the amount of sludge generated (mass/time), "Q" is the average wastewater flowrate, and "S_i" and "S_e" are the total suspended solids concentrations in the influent and effluent streams, respectively. If effluent TSS values were not available, an average percent reduction of 80-90% was assumed. Since effluent concentrations of less than 50 mg/l were typical, the error incurred in doing so was small. Method 2 is believed to be more appropriate than method 1, as it accounted for the actual solids loadings to individual MWTPs. However, for comparative purposes both methods were applied in this study. Influent TSS concentrations were extracted from a data base (NEEDS) maintained by the California Water Resources Control Board. In order of priority, flowrate data were obtained from direct contacts with POTWs, reviews of Pretreatment Annual Reports, and dry weather flow data available in the NEEDS survey.

Estimating the Removal of PTOCs in Sludge

The amount of each PTOC that was removed in sludge streams was estimated on a county-by-county and statewide basis. This was completed by summing removal rates, "S_m", at individual treatment facilities. The value of "S_m" was estimated as the product of the mass loading in the influent stream and the appropriate partition coefficient as listed in Table 8. The resulting equation was

$$S_m = K_m C_{m,i} Q, \qquad (5)$$

where "S_m" is the amount (mass/time) of PTOC "m" removed in the sludge streams of a specific MWTP, "K_m" is the partition coefficient (fraction of incoming mass of PTOC "m" that is removed in sludge), and "Q" and "$C_{m,i}$" are as defined previously.

Data Quality and Availability: PTOC Sampling Procedures

A generally approved method for PTOC sample collection has not been established. Subsequently, collection methods vary among MWTPs in California. For instance, some MWTPs use containers with a top surface open to the atmosphere to sample the influent and effluent streams. Samples are typically transferred immediately to teflon-lined capped glass vials with no observable air space in the vial. Other MWTPs proceed further to minimize exposure to air by utilizing a closed container with a tube attached for siphoning wastewater samples into the container. The tube opening is then sealed prior to removing the sample container from the wastewater stream. Sludge samples are commonly taken as a single "scoop" before being sealed in a container.

Sampling locations also vary among the MWTPs. Some treatment plants sample influent streams in the collection system before the wastewater ever reaches the headworks, while others sample at, or slightly downstream of, the headworks. Effluent streams are most often sampled after chlorination, but some are sampled prior to dechlorination. A few MWTPs report concentrations in the effluent stream at the point of ultimate discharge, which can exist miles from the actual treatment plant. In the latter case, volatile losses in the outfall line may further reduce concentrations, and the additional reaction time for those facilities that chlorinate may act to increase THM concentrations in the effluent stream.

Temporal requirements are an important part of sampling. For influent, effluent, and sludge streams, such requirements have been outlined in the Federal Register (FR) (1981). The FR states that the data collected shall be representative of seasonal and yearly conditions, as well as of similar quantity and quality as normal influent and effluent flows. In addition, twelve samples are to be taken at approximately equal intervals during the course of each annual period of plant operation. Representative samples must be taken into account for both workdays and non-workdays.

Requirements were also established for sampling procedures based upon both composite and grab samples. For composite samples, influent and effluent data must be obtained through 24-hour samples which are proportioned by flow. Either discrete or continuous sampling is allowed. However, for discrete sampling at least twelve samples are recommended for compositing. These must be flow-proportioned either by varying the volume of each aliquot, or the time interval between each aliquot. Aliquots used for the collection of volatile pollutants must be combined immediately prior to analysis.

The effects of lag time (hydraulic retention time) in an MWTP may lead to influent and effluent samples which do not correspond to the same wastewater "parcels". However, for continuous sampling over a 24-hour period, the FR states that "effluent sample collection need not be delayed to compensate for hydraulic retention unless the POTW elects to include retention time compensation or unless the Approval Authority requires retention time compensation." Furthermore, if retention time is required to be taken into account it is required "to be based on a 24-hour average daily flow value." The average daily flow corresponds to the average flow during the same month of the previous year.

When composite samples are not feasible, grab sampling may be necessary. Here, grab sample refers to an individual sample collected over a time period of less than fifteen minutes. Retention time should be taken into account whenever grab samples are used.

According to the FR (1981), composite sludge samples should be taken during the same period as the influent and effluent samples. Each composite sample must contain a minimum of twelve discrete samples taken over a 24-hour period. If necessary, grab samples may also be taken.

In MWTPs in California, influent and effluent samples are typically drawn during the same 24-hour period, without accounting for the hydraulic retention time. In most cases, eight grab samples are taken, once every three hours, and composited immediately prior to analysis.

The frequency between 24-hour composite/grab sampling for volatile priority pollutants varies significantly from plant to plant. For instance, the Point Loma Wastewater Treatment Plant in San Diego reports average influent and effluent concentrations for all volatile priority pollutants on a once per month basis. Other facilities sample on a quarterly, or wet season/dry season basis. Due to the infancy of the EPA's National Pretreatment Program (NPP), volatile priority pollutant sampling extends back only one or two years for most POTWs, and some relatively large POTWs have yet to sample for such pollutants.

Sampling for PTOCs in sludge streams is not as common as in influent and effluent streams. Many of the MWTPs in California have not sampled sludge streams for volatile priority pollutants, and the data from those which have are not of great value to adsorption studies because of sampling location. Sludge "scoops" are usually taken from digested and partially or fully dewatered sludge. Volatilization, transformation, and degradation during digestion, and volatilization during dewatering make it impossible to predict the actual mass removal in untreated (raw) sludge.

Sample Analysis Techniques

The EPA has specified a maximum time period, between the sampling and analysis of most volatile priority pollutants, of fourteen days. Many POTWs must contract with a private laboratory having a gas chromatograph (GC) or GC/mass spectrometer (GC/MS) capabilities to analyze the wastewater samples. However, several major POTWs (e.g., County Sanitation Districts of Los Angeles County, City of Los Angeles, East

Bay MUD, and the Sacramento Regional Wastewater Treatment Plant) have laboratories which carry out the analyses.

The majority of POTWs in California, and private laboratories contracted by POTWs, utilize EPA method 624 for the analysis of influent and effluent samples. Detection limits for this method are listed in Table 12. However, the method detection limit for specific wastewaters may differ from those listed in Table 12 depending upon the nature of interferences in the sample matrix. Method 624 is a purge-and-trap technique which utilizes mass spectrometry as the detection method.

A recent study of the analysis methods for volatile compounds revealed intra-laboratory and inter-laboratory differences in results for duplicate samples analyzed using method 624 (Gurka, 1984). The intra-laboratory study revealed differences generally less than 30%, with a range of 5% to 300% depending on the compound. The inter-laboratory differences were characterized by the same range, with differences typically less than 70%. The highest variabilities were reported for compounds that are common background contaminants in laboratories (i.e., methylene chloride, 1,2 dichloroethane, and chloroform). In the same study, it was observed that problems exist in retaining volatile priority pollutants on solid samples, such as POTW sludge matrices.

The preceding discussion exemplifies the fact that uncertainties in the data exist due to sampling and analysis techniques. The intra-laboratory study suggested that such inaccuracies can lead to overestimates or underestimates of concentration by as much as a factor of three.

Data Sources

Several sources of data were investigated as part of this study. It is easiest to describe those sources in terms of data categorized as concentration, flow, and other treatment characteristics (e.g., treatment train). The former two types of data were needed to complete mass flow estimates in influent, and effluent streams. The latter was re-

Table 12: Typical Detection Limits for the PTOCs

	Detection Limits (µg/L)	
Compound	EPA Method 624	Range (Data Survey)
Acrylonitrile	-	1.0 - 100
Benzene	4.4	0.1 - 5
Bromodichloromethane	2.2	0.1 - 2
Carbon tetrachloride	2.8	0.1 - 3
Chlorobenzene	6.0	0.1 - 5
Chloroform	1.6	0.1 - 2
Dibromochloromethane	3.1	0.1 - 3
1,1 Dichloroethylene	2.8	0.1 - 3
Ethylbenzene	7.2	0.1 - 6
1,2 Dichloroethane	2.8	0.1 - 3
Methylene chloride	2.8	0.1 - 4
Perchloroethylene	4.1	0.1 - 4
Toluene	6.0	0.1 - 6
1,1,1 Trichloroethane	3.8	0.1 - 4
Trichloroethylene	1.9	0.1 - 2
Vinyl chloride	2.0	0.1 - 5

quired to complete more refined analyses of individual treatment plants (Appendix H).

Concentration data

As a preliminary step in attempting to obtain concentration data, each of the nine Regional Water Quality Control Boards (RWQCBs) were contacted. While it was not possible for most of the RWQCBs to supply summaries of PTOC measurements at POTWs within their respective region, most of the RWQCBs were cooperative in assisting with the study. They were able to provide lists of the appropriate contacts at each of the POTWs within their region. Through such initial contacts it became apparent that many of the POTWs that sample for volatile priority pollutants summarize and submit sample results in their Pretreatment Annual Reports (PARs) and/or NPDES reports.

PAR and NPDES reports are maintained by the individual POTWs that are required to complete such reports, as well as their respective RWQCB. In addition, the Region IX Office of the EPA, and the State Water Resources Control Board (SWRCB), maintain copies of the reports for POTWs throughout California. A list of the POTWs that are required to submit PAR reports is provided in Appendix C. To obtain data from those reports, visits to the SWRCB and the EPA Regional office were made. This proved to be valuable, as some of the reports which had yet to be obtained by either the SWRCB or the EPA had been received by the other.

While most of the reports that were reviewed (> 100) contained sample information for some priority pollutants, a majority did not contain information for volatile priority pollutants. Furthermore, the degree of data that were submitted by those POTWs that did sample varied from influent/effluent/sludge streams to concentrations in only one or two of those streams. Many POTWs reported concentrations on a quarterly basis, while some reported sample measurements taken only once in a calendar year. Less sample data were available for sludge streams than for influent and effluent streams. Nearly all of the samples that were reported corresponded to sampling completed during 1985. Some extended into the first two quarters of 1986, while a few data sets extended back to 1984. Due to the infancy of the National Pretreatment Program, and relatively recent concerns regarding the fate of VOCs during wastewater treatment, a large fraction of the POTWs have completed only one or two years of sampling for volatile priority pollutants. The existing data base will grow and will become a valuable resource in the coming years.

Several major POTWs did not include sample data for volatile priority pollutants in their PAR reports, or their PAR reports were not found at the SWRCB or the EPA. For this reason, a follow-up survey was completed by telephone, letters of request, and plant visits. The response was generally positive, with most of the POTWs promptly responding to our requests. The direct survey actually accounted for data at MWTPs that represented a higher percentage of the municipal wastewater treated in California than did the data compiled through analyses of the PAR reports. The extent of the concentration data base will be discussed in the following subsection.

Flow data

Hydraulic loading data were typically provided in the PARs. Influent flowrates were commonly provided on an average annual basis. However, some POTWs submitted average monthly or average wet season and dry season flows, and several POTWs reported flows that occurred during the period that concentration sampling was completed. Flowrate data were also obtained as a result of the survey described for concentration data. Average dry-weather flows were provided by the SWRCB via the NEEDS data base that was completed for the EPA. The NEEDS data base (hereafter referred to simply as the NEEDS) consists of information regarding the characteristics of municipal wastewater collection and treatment systems. It was completed in order to assess the future needs of POTWs in terms of federal assistance. However, the data contained in the NEEDS suffers from uncertainties due to the following reasons:

1. Many of the quantitative values are based upon engineering estimates rather than historical data.

2. Some of the information in the NEEDS is outdated (e.g., not updated since 1978-82). The SWRCB is currently in the process of completing a partial update.

3. For some of the MWTPs, no historical or estimated values are provided.

Because of these limitations, data from the NEEDS were used on a low-priority basis (i.e., only if data could not be obtained from more reliable sources).

Other treatment characteristics

Other treatment characteristics refers primarily to MWTP treatment trains, and more detailed information regarding specific treatment processes. For the largest MWTPs in California, this information was obtained by contacting the appropriate individuals at either the MWTP or the POTW. Information was generally available concerning plant layouts and process specifications. For smaller MWTPs, treatment train data were extracted from the NEEDS and then compiled as described in the following subsection. A cross-check of treatment train information contained in the NEEDS with information provided by the MWTPs revealed that the NEEDS was fairly accurate with respect to MWTP treatment characteristics. However, because much of the information in the NEEDs has not been updated for several years, recent modifications to MWTPs are often not accounted for in the NEEDS data base.

Data Base Compilation

Data from the sources described in the previous subsection were compiled and maintained on mini and microcomputers in the Department of Civil Engineering at the University of California at Davis. The minicomputer was used for computational analyses of the larger data sets. A commercial data base software package was used to maintain data for reporting purposes on the microcomputer. The data base structure is described in detail in Appendix F. The remainder of this subsection describes the extent and nature of data that were obtained for each of the categories listed previously.

Concentration data

A summary of the MWTPs from which concentration data were compiled is provided in Table 13. The MWTPs listed in Table 13 represent less than 10%, by number, of the MWTPs in California. However, they account for 77% of the total municipal wastewater that is treated in California. Those with both influent and effluent data account for greater than 76%. Those with only influent data account for 1%. Table 13 also indicates that, even for the largest MWTPs in California, a very limited amount of data exists regarding mass loadings of PTOCs. As noted previously, the frequency of sampling for PTOCs is low, and for many of the MWTPs it was non-existent until the past one or two years. The data compiled for this study are representative of the extent of existing concentration data, but must be interpreted cautiously. Table 11 indicates the percent of total flow, on a county-by-county basis, that is accounted for by MWTPs with either influent data alone, or concentration data in both the influent and effluent streams.

Flow data

Flow data were obtained for every MWTP in the NEEDS data base. For the major POTWs, the NEEDS data were supplemented with more recent (e.g., 1985) flow data. Existing wastewater flowrates were maintained in a manner that allowed for NEEDS dry weather flowrates to be separated from the other flow values.

Other treatment characteristics

Treatment train information was obtained for all of the MWTPs in the NEEDS. Major MWTPs (> 25 MGD) were contacted directly to obtain plant specifications and treatment process information. The NEEDS

Table 13a: A Summary of MWTPs with Existing Concentration Data[1]

Facility Name	County	Number of Sample Days Influent	 Effluent	Code[2]
Alvarado (Union City)	Alameda	1	1	A
East Bay MUD (Oakland)	"	6	3	D
Hayward	"	1	3	B
Livermore	"	3	3	A
Oro Loma (Castro Valley)	"	1	2	B
San Leandro	"	1	4	B
C. Contra Costa (Martinez)	Contra Costa	1	4	B
Delta Diablo (Pittsburg)	"	2	5	B
Richmond/San Pablo	"	1	1	A
Fresno	Fresno	1	1	A
Selma/Kingsburg/Fowler	"	1	0	-
Bakersfield #2	Kern	1	1	A
Bakersfield #3	"	1	1	A
Hyperion (El Segundo)	Los Angeles	5	5[a]	D
JWPCP (Carson)	"	2	1	C
Long Beach	"	2	1	C
Los Coyotes (Cerritos)	"	2	1	C
Pomona	"	2	1	C
San Jose Creek (Whittier)	"	2	1	C
Saugus-Newhall	"	2	1	C
Valencia	"	2	1	C
Whittier Narrows (El Monte)	"	2	1	C
Ignacio	Marin	1	2	B
Novato	"	1	2	B
Merced	Merced	3	3	E
Monterey/Salinas[b]	Monterey	1	1	A
Irvine Ranch	Orange	1	1	A
OCSD #1	"	3	12[c]	B
OCSD #2	"	3	12[c]	B
Riverside	Riverside	1	1	A
Sacramento Regional	Sacramento	9	9	A
Encina Joint Powers (Carlsbad)[d]	San Diego	1	0	-

Table 13b: A Summary of MWTPs with Existing Concentration Data[1]

Facility Name	County	Number of Sample Days Influent	Number of Sample Days Effluent	Code[2]
Point Loma (San Diego)	San Diego	18	18	A
Richmond-Sunset	San Francisco	2	2	A
Southeast/Northpoint	"	2	2	A
Stockton Regional	San Joaquin	2	2	A
San Luis Obispo	San Luis Obispo	1	1	E
San Francisco Int'l Airport[e]	San Mateo	1	1	A
Burlingame	"	1	4	B
South Bayside (Redwood City)	"	2	2	A
South San Fran-San Bruno	"	1	1	A
Gilroy	Santa Clara	2	0	-
Palo Alto WWTF	"	2	2	A
San Jose-Santa Clara	"	6	9	B
Sunnyvale	"	4	4	A
Watsonville	Santa Cruz	1	0	-
Fairfield-Suison	Solano	1	5	B
Vallejo	"	1	2	B
Petaluma	Sonoma	1	4	B
Hill Canyon (Thousand Oaks)	Ventura	2	2	A
Oxnard	"	1	1	A

(1) Based upon data that were collected from Pretreatment Annual Reports and POTW survey.

(2) A = influent and effluent data correspond to same day; B = all influent data have corresponding effluent data from the same day, but additional effluent data exists; C = all effluent data have corresponding influent data from the same day, but additional influent data exists; D = some, but not all, of the influent and effluent data correspond to the same day; E = influent and effluent data do <u>not</u> correspond to the same day.

(a) At 5 mile effluent outfall.
(b) Blended influent from Monterey, Salinas #1, and 4 smaller MWTPs. Monterey and Salinas #1 WWTFs made up greater than 70% of the total flow.
(c) Combined effluent from OCSD #1 and OCSD # 2.
(d) Data from sampling completed in 1978.
(e) Includes an industrial wastewater treatment plant, and a water quality control plant.

information, with minor adjustments for some of the larger MWTPs, was compiled as a separate data set so that those facilities with specific treatment processes or configurations could be easily identified.

Assumptions and Limitations

This subsection is provided in order to describe the assumptions and limitations regarding the use of the compiled data. The discussion is of fundamental importance with respect to assessing the representativeness and uncertainties associated with estimated removal and emission rates. Those rates will be discussed in Section 6. Again, data is addressed in terms of concentration, flow, and other treatment characteristics.

Concentration

In the following sections, emissions and mass removal estimates will be presented in units which suggest a long-term basis (i.e., tons/year). In making such estimates, it was assumed that the limited data which are available are representative of "typical" concentration and flow conditions. In reality, quantitative estimates based upon a small number of samples drawn during discrete sampling periods may not be representative of the long-term average.

One limitation to the existing data is that most of the MWTPs did not account for hydraulic retention time when concentrations were measured in both the influent and effluent streams. This, coupled with uncertainties in analysis techniques, may be the reason that for a few MWTPs the non-THM PTOC concentrations in the effluent stream were greater than those in the influent stream. For lack of a better approach, the effects of hydraulic retention time were neglected, and non-THM effluent concentrations were assumed to be equal to influent concentrations when they were actually reported to be greater than the influent concentrations.

Another assumption was made regarding the treatment of concentrations that were listed as below detection limit (BDL). Such concentrations were assumed to be zero. In terms of concentrations in the effluent stream, such an assumption is conservative with respect to emissions estimates. The opposite is true for the influent stream. However, at major MWTPs in industrialized regions such as the South Coast Air Basin (SCAB) most of the PTOC concentrations in influent streams were well above detection limits, so that the BDL=0 assumption should not lead to underestimates of emission rates. The PTOCs that were least likely to be affected by the BDL=0 assumption were those that were frequently detected, and at concentrations well above the detectable limit. Chloroform, methylene chloride, perchloroethylene, and toluene satisfied these requirements.

The BDL=0 assumption also had varying degrees of significance depending upon the specific PTOC detection limit. For instance, although acrylonitrile was not detected by any MWTP that sampled for it, its detection limit was quite high (1-100 µg/L) with respect to the other PTOCs.

Flow data

Many of the POTWs that supplied volatile priority pollutant measurements did not provide corresponding flowrates. However, the use of annual average flowrates was found to be sufficient for this study. Throughout most of the state, temporal variations in wastewater flow were much less significant than those in PTOC concentrations.

For those treatment facilities for which 1985 annual average flowrates were not readily available, the NEEDS dry weather flow data were applied.

Most of the hydraulic flow data were available only for the influent stream. For lack of a more appropriate approach, it was assumed that the average flowrate in the effluent stream was equal to the average influent flow. This neglects losses due to evaporation which may be significant during warm weather in MWTPs that employ ponds with large surface-to-volume ratios.

Although several uncertainties in the use of flow data were noted above, such uncertainties were small with respect to those for concentration data.

Other treatment characteristics

Except for special characteristics (e.g., fractional secondary treatment) treatment trains were not considered in preliminary emissions estimates. They are important for more refined emissions modeling (Appendix H). However, for the largest MWTPs in industrialized regions, up-to-date treatment train and process specifications were obtained directly from the MWTP or corresponding POTW.

Summary of Uncertainties

The uncertainties in emissions or total removal rates stem from a number of factors. These include losses arising from sampling techniques, variabilities in the results obtained using existing analysis techniques, lack of a sufficient data base to confidently extrapolate to typical or representative conditions in individual MWTPs, and the necessity to extrapolate to MWTPs without existing PTOC loading data. A qualitative summary can be completed based upon the concepts described above to alert the reader of uncertainties in the estimates reported in Section 6. Semi-quantitative estimates are more difficult to make. However, the concepts described above were used along with best engineering judgement (BEJ) to compile a qualitative and semi-quantitative summary of the uncertainties associated with the emissions estimates described in Section 6. That summary is provided in the remainder of this subsection.

Sampling techniques: Whenever dealing with volatile compounds, one must be aware of the potential for volatile losses during sample collection, preservation, and analysis. Unfortunately, such losses could not be quantified from the existing data as they were highly dependent upon the sampling approach and devices used, as well as the degree of care taken in handling the samples. After reviewing the procedures that were used in order to obtain concentrations in the influent and effluent streams, it is the authors' judgement that the relative significance of losses during sampling, transport and preservation before analysis were small in comparison to uncertainties in other factors described below.

Analysis techniques: As noted previously, comparison studies of laboratories conducting VOC analyses have indicated that limitations in current analytical techniques can lead to uncertainties as high as a factor of three for PTOCs that are commonly found in laboratory environments, e.g., methylene chloride. The limited information on intra-laboratory errors suggested that the majority of VOC analyses were within about 30%. Differences formed from influent and effluent concentrations would result in somewhat larger error bounds, the closer the difference between influent and effluent concentrations, the larger the relative error, but the absolute error would tend to decrease. Thus, we believe that the larger sources of emissions, which had a larger contribution and significance to the emission inventory, should have had a smaller error associated with them. Similarly, for the inter-laboratory comparisons typical errors for VOC analyses were less than about 70%, and one would anticipate smaller errors with increasing sample concentrations. Thus, based upon the PTOCs involved in the lab study and experience with other VOCs, we believe a typical range of uncertainty resulting from the chemical analyses should be less than 100% (a factor of two).

Temporal variations in data: The historical data available for individual MWTPs were limited either by the number of days, or sampling periods, during which PTOC samples were drawn. The assumption that the existing data is representative of typical flow and concentration, i.e., mass loading, conditions was an additional source of uncertainty in the emission estimates. Hourly variations in wastewater flowrates were accounted for by most POTWs, since flow-proportioned composite samples were common. Flow variations over longer time periods were not significant at most MWTPs. For the largest MWTPs in California, recent annual average flowrates were available. For others, flows corresponding to the PTOC sampling periods were available, and concentrations were weighted accordingly in order to better represent average mass loadings. For smaller MWTPs that were not directly contacted and that did not submit PAR reports, average dry-weather flow data from the NEEDS data base were used. On the average, NEEDs flows were found to underestimate more recent annual average flowrates by approximately 20%. The differences could be caused by the out-dated nature of the NEEDS data, as well as higher flowrates due to infiltration during wet seasons which are not accounted for by the NEEDS. The overall uncertainties in wastewater flowrates are not expected to exceed approximately 20% on an MWTP-by-MWTP basis, and should be even less on a county-by-county and statewide basis.

Temporal variations in PTOC concentration were expected to be much greater than those for flowrate. Estimating the uncertainties due to such variations was difficult because of a lack of historical data. Long-term reductions in the use and discharge of priority pollutants as a result of environmental regulations and programs such as the National Pretreatment Program could result in additional systematic errors in the emission estimates beyond those of day-to-day variability of industrial and commercial discharges. Furthermore, variations and uncertainties are expected to differ according to the specific PTOC. Table 14 summarizes temporal variations in the influent concentrations of the most commonly detected PTOCs, at three large MWTPs in California. Assuming normal distribution functions for the influent concentration, a 95% confidence limit would correspond to about a factor of three. (In reality, concentrations appeared to be more closely approximated by log-normal distributions.) These tentative uncertainty estimates were based upon a limited number of sample points at a small number of MWTPs. Given the amount of data available , a more sophisticated statistical analysis was not warranted. Additional, though smaller sources of errors were associated with temporal variation of effluent concentrations and lack of account of hydraulic retention time during some sampling. Insufficient data existed for quantification.

Extrapolation to MWTPs without data: Based upon a comparison of extrapolated results for MWTPs with existing data on total PTOC emis-

Table 14: Temporal Variation of PTOC Concentrations in Influent Streams

			Concentration (µg/l)			
				Extremes		
Facility/Compound	# of sample days	Sampling period	Average[1]	min	max	Coefficient of Variation
Point Loma WWTF		4/85 - 8/86				
Chloroform	18		7.3	<1.6	55.5	1.71
Perchloroethylene	18		7.8	<1	56	1.71
Toluene	18		51.3	<2	260	1.30
Sacramento Regional WWTF		5/83 - 5/86				
Chloroform	9		5.9	<1	12	0.98
Perchloroethylene	9		11.8	<2	31	1.08
Toluene	7		10.1	<2	45	1.60
East Bay MUD WWTF		9/84 - 6/86				
Chloroform	6		20.9	6	44	0.62
Perchloroethylene	6		122.5	<4.1	610	1.95
Toluene	6		37.6	18	52	0.34
Hyperion Treatment Plant		2/86 - 4/86				
Chloroform	5		21.4	16.2	24.7	0.16
Perchloroethylene	5		102.1	65.5	138	0.27
Toluene	5		151.8	49.7	425	1.03

(1) Values listed as below detection limit were assumed to be equal to zero.

sions against those without, differences as high as a factor of five were observed. For individual PTOCs, the differences could have been higher. However, the MWTPs that fell into the extrapolation category accounted for only 23% of the total municipal wastewater treated throughout California. Furthermore, most of those MWTPs were located in non-industrialized areas where large discharges of PTOCs were not expected. In the extrapolation procedure, this was accounted for by normalizing by the fraction of the total flow that originated from industrial dischargers. It should be noted that a partial survey of MWTPs and POTWs indicated that the method of classification of industrial and commercial dischargers was not uniform. Significant sources of emissions projected using extrapolated concentrations are identified in Section 6 of this report.

Although, overall uncertainties in emissions due to extrapolation may be relatively high for individual MWTPs, the uncertainties should not be as large on a regional or statewide basis. A county-by-county summary of the wastewater flowrate accounted for by MWTPs with concentration data was presented in Table 11. The information included in Table 11 also serves as an indicator of the extent of extrapolation in various counties.

Assuming worst-case conditions: From an emissions standpoint, "worst-case" refers to the condition in which the total removal of PTOCs in a MWTP is attributed entirely to volatilization. The existing literature suggested that the errors associated with such an assumption are probably small for volatile organic compounds (e.g., the PTOCs). The combined removal by adsorption and unacclimated biodegradation were typically reported to be less than 30% of the total compound removal. The removal decreased as the volatility of the PTOC increased and the degradability and affinity for adsorption decreased. In addition, errors in the emissions estimate vary according to the physical processes employed by individual MWTPs. For primary treatment facilities biodegradation would be insignificant and the assumption of volatilization as the only removal mechanism would be better than for facilities which employ biological treatment.

Assuming uncontrolled emissions: Some MWTPs that utilized covered treatment processes attempted to treat off-gases, primarily to reduce emissions of odorous gases such as hydrogen sulfide. The efficiency of the off-gas control devices for removing gaseous PTOCs has not been determined. Although the number of MWTPs that treat off-gases was small, probably less that 10, the effects of efficient off-gas treatment could be significant as some of the larger MWTPs utilize off gas control devices.

Removal efficiencies: For those MWTPs with influent-only or no data, Equation 3 was used to estimate emissions. Values had to be selected for the overall removal efficiency factor "b_m". For this study, average values of "b_m" were calculated based upon the MWTPs with existing influent and effluent data. The efficiencies were typically high (> 80%), and were probably conservative for many primary treatment facilities for which extrapolation was required. On an individual MWTP basis, it is the authors' collective judgement that the removal efficiencies led to overestimates as high as a factor of two, and underestimates as great as 25%. However, only 24% of the total municipal wastewater discharged in California fell into that category.

Overall uncertainty: As was illustrated by the previous discussion, the uncertainties in emissions estimates were a function of many factors. Those factors included whether or not the uncertainties were based upon estimated emissions at individual MWTPs, or on a regional or statewide basis, the degree and quality of data available for individual MWTPs, and the method used to estimate emissions (i.e., direct estimate from existing data, or extrapolation). Because of such diverse factors, the prescription of overall uncertainties in estimated emissions must be based upon best engineering judgement which incorporates as much of the existing quantitative information as possible. As some facilities are characterized by a larger historical data base than others, ranges of the uncertainty for individual MWTPs are presented in Table 15. In addition, the degree of uncertainty associated with emissions varied from MWTP-to-MWTP and from PTOC-to-PTOC, while the data base used for extrapolation varied from county-to-county. A range of factors from two to

Table 15: Estimated Uncertainties in Emissions Estimates[1]

Category	Within a Factor of[2]
Individual Treatment Facilities:	
influent and effluent data	2 - 5
influent data only	2 - 5+
extrapolation	5 - 10
County-by-County	2 - 10
Statewide	2 - 4

(1) Based upon "best engineering judgement"

(2) Ranges account for differences in the extent of historical data from individual MWTPs and/or different uncertainties for different PTOCs.

ten is estimated for counties. Those counties at the lower end of the range include Alameda, Contra Costa, Los Angeles, Orange, Sacramento, San Francisco, and Santa Clara. In those counties, the degree of extrapolation was low, as MWTPs with both influent and effluent data accounted for a large fraction of the county's wastewater discharge. The statewide uncertainty factor range is based upon the fact that most of the emissions in California occurred in those counties mentioned above. A range is given, as uncertainties vary according to the specific PTOC. PTOCs at the lower end of the range include perchloroethylene, toluene, and 1,1,1 trichloroethane. The PTOCs at the upper end of the range include bromodichloromethane, carbon tetrachloride, chlorobenzene, chloroform, dibromochloromethane, 1,1 dichloroethylene, 1,1 dichloroethane, methylene chloride, and vinyl chloride. These observations were based upon the frequency and magnitude of detected concentrations, the potential for emissions that were not accounted for from the formation of THMs during chlorination, and other sources of errors (e.g., analytical techniques) noted for individual PTOCs as previously described.

The trend in uncertainty of the estimates was such that the larger the emissions, both by PTOC and by individual source, the smaller the uncertainty, i.e., closer to a factor of two. The largest contributors to the uncertainty being the temporal variation of influent loadings in those cases. With increased data availability expected as a result of recent reporting requirements, the uncertainty in future estimates should be reduced.

6. RESULTS and DISCUSSION

Emissions estimates are presented in this section based upon Equations 2 and 3 of Section 5. The estimates represent a "worst-case" scenario in the sense that the difference between the mass of PTOCs entering the MWTP in the influent and leaving in the effluent was assumed to completely volatilize. The estimates do not account for adsorption to sludge, biodegradation within the plant, nor the possible presence of control devices on off-gas streams. In spite of those limitations, it is felt that the estimates provide a good approximation to the potential levels of emissions from MWTPs in California given the available data, and are an improvement over estimates previously reported (Dixon and Bremen, 1984). The format of the presentation is such that a successively more detailed breakdown of the emissions is provided, first on a statewide basis, followed by county-by-county and individual MWTP analyses. Thus, the reader can easily trace statewide emissions to the most significant counties, and the county-wide emissions to the MWTPs which were the most significant sources of either speciated or total PTOC emissions. Estimates of sludge generation and the removal of PTOCs in sludge streams are also presented on a statewide and county-by-county basis. These are followed by a discussion of the results. Conclusions and recommendations are provided in Sections 7 and 8.

Statewide Emissions

On an annual basis an estimated 803 tons of the 16 PTOCs were emitted from MWTPs throughout California during the period roughly corresponding to 1983 to 1985. If emissions of THMs, formed as a result of chlorination, as well as emissions of PTOCs that pass through the treatment system were to be taken into account, that total would have risen to approximately 1400 tons/year (tpy). For scaling purposes, those PTOCs with emissions less than 10 tpy are shown in Figure 4 while those with emissions of greater than or equal to 10 tpy are shown in Figure 5.

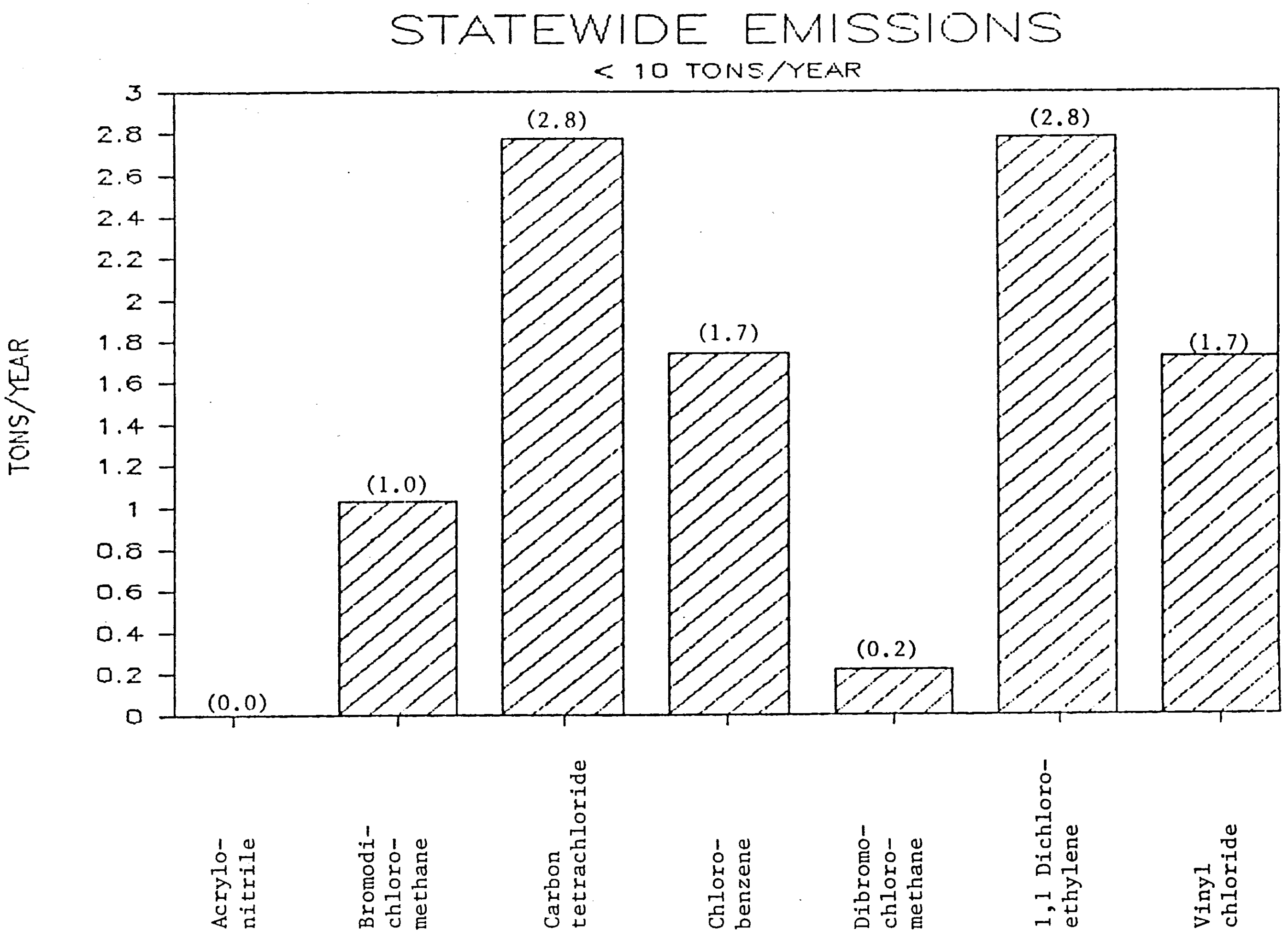


Figure 4: Statewide Emissions of PTOCs Totalling Less Than 10 tpy. Values in parenthesis above bars are emissions in tpy.

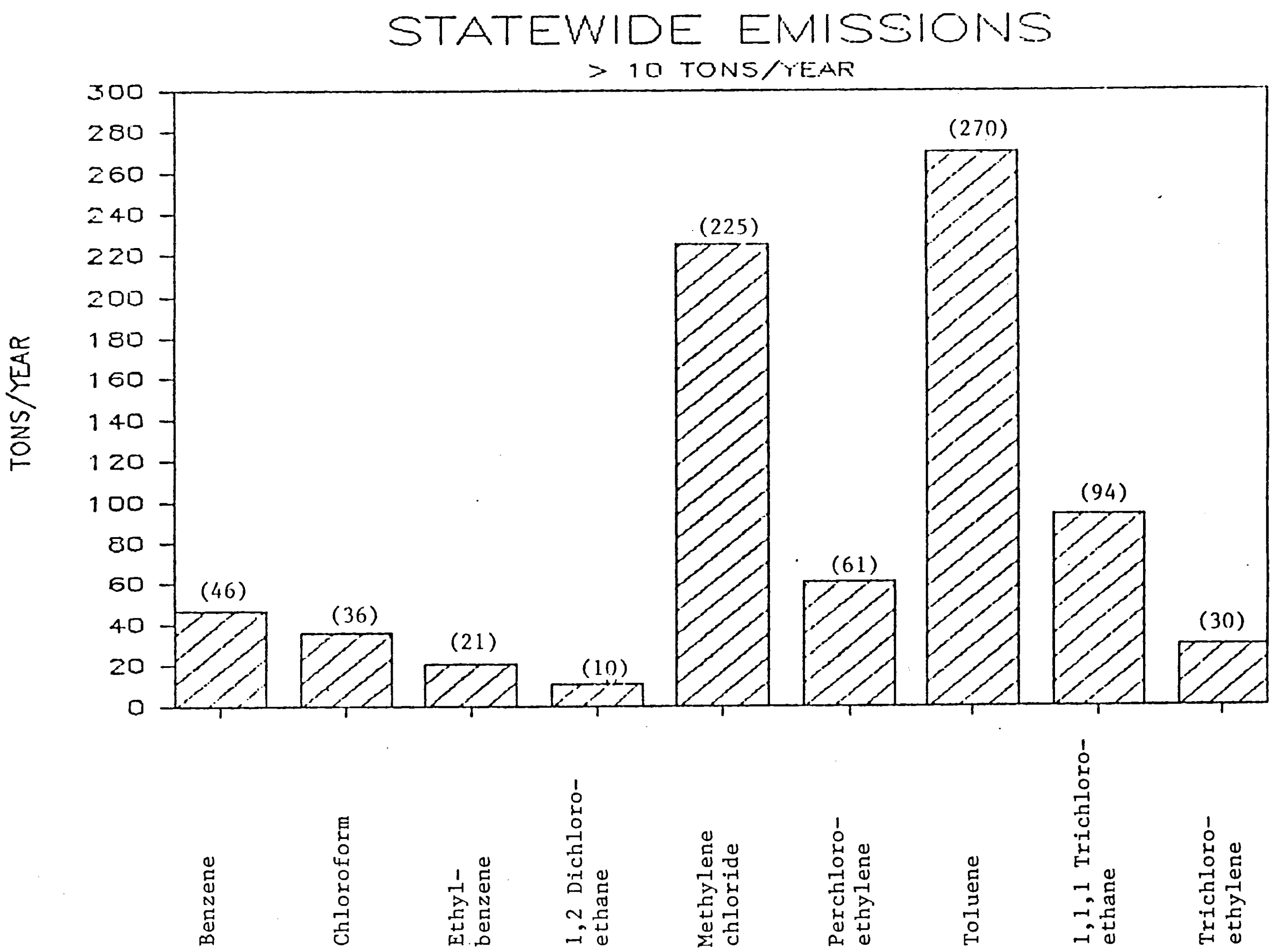


Figure 5: Statewide Emissions of PTOCs Totalling Greater Than 10 tpy. Values in parenthesis above bars are emissions in tpy.

The zero emissions estimate for acrylonitrile was based on the fact that acrylonitrile was never detected at any of the MWTPs for which existing concentration data were obtained. However, detection limits for acrylonitrile were typically much higher (10-100 µg/L) than those for the other PTOCs. It is possible that acrylonitrile could have been discharged and emitted without detection. Based upon a flow-weighted average detection limit of 30 µg/L, acrylonitrile emissions could have been as high as 140 tpy. However, knowledge of its limited uses and sources (Tables 2 and 3), and the fact that it went undetected consistently, suggests that there were very low emissions of acrylonitrile from MWTPs in California.

The estimated emissions for bromodichloromethane and dibromochloromethane would have been higher if THM formation had been considered. For instance, at a number of MWTPs, one or both of those PTOCs were detected in the effluent stream but not in the influent stream. While accounting for the formation resulting from chlorination would have increased the estimated emissions of both PTOCs by a factor of approximately two, the statewide emissions for each would have remained relatively low.

A review of past data at MWTPs in Los Angeles County suggested that carbon tetrachloride emissions from MWTPs have decreased significantly (greater than an order of magnitude) during the past decade, as the use of carbon tetrachloride has been severely restricted. The estimate reported here reflects the newer data.

It is possible that emissions of both 1,1 dichloroethylene and vinyl chloride have been underestimated, as the estimates did not account for their formation as a result of the degradation of more halogenated compounds, particularly during anaerobic digestion. A lack of existing data made it impossible to estimate such emissions. This is an area where future measurements could prove to be valuable.

The estimated emissions for chloroform may be low for the same reasons listed previously for bromodichloromethane and dibromochloromethane. If THM formation had been taken into account, the estimated statewide emissions of chloroform would have been approximately 50 tpy. The increase is lower than a factor of two, because a large percentage of the chloroform emissions were attributed to MWTPs that did not chlorinate on a regular basis. The two PTOCs with emissions estimated to be greater than 200 tpy were methylene chloride and toluene. The combined emissions for those two PTOCs accounted for greater than 62% of the total mass emissions of all PTOCs.

County-By-County Emissions

The ten counties with the highest total PTOC emissions are shown in Figure 6. The total and speciated PTOC emissions for each of the 58 counties in California are listed in Table 16. The ten counties shown in Figure 6 accounted for 93% of the total PTOC emissions throughout the state. Los Angeles County alone accounted for 59% of those emissions. Thirty-seven counties individually contributed less than 1.0 tpy to the statewide emission total. Of the ten counties shown in Figure 6, Los Angeles, San Diego and Stanislaus counties require additional comments to clarify the nature of uncertainties in the estimates.

In San Diego County, high emissions (47 tpy) were estimated from the Encina Joint Powers WWTF in Carlsbad. However, that estimate was based upon data collected in 1978, when very high concentrations of methylene chloride and 1,1,1 trichloroethane were observed in the influent stream. Based upon reductions in influent concentrations observed in other MWTP data over the same period, emissions from the Encina Joint Powers WWTF, and San Diego County, were likely to have been over-estimated.

Emissions in Stanislaus County were based entirely upon extrapolation from other MWTPs in the Central Valley. Large "industrial flow" contributions were reported at the Modesto and Riverbank treatment facilities and resulted in most of the estimated emissions for that county. It was not known whether the "industrial flows" were represen-

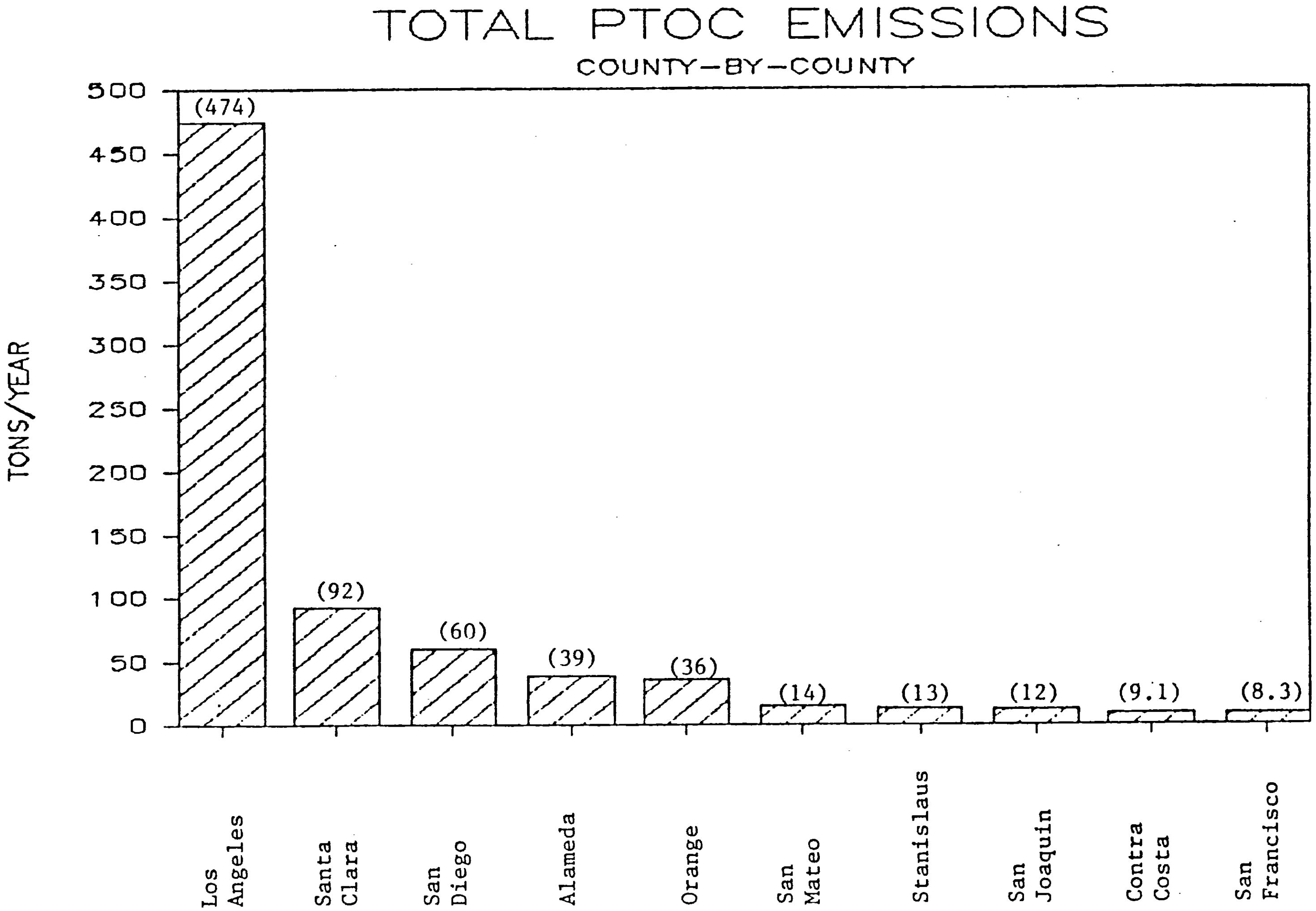


Figure 6: PTOC Emissions from the 10 Counties with the Highest Emissions. Values in parenthesis above bars are emissions in tpy.

Table 16a: County-By-County Emissions

COUNTY NAME	TOTAL EMISSIONS (TONS/YEAR)	INDIVIDUAL PTOC EMISSIONS (TONS/YEAR)				
		(2)	(3)	(4)	(5)	(6)
Los Angeles	473.53	41.44	0.22	0.93	0.34	13.32
Santa Clara	92.30	0.00	0.00	0.00	0.00	3.13
San Diego	59.77	0.30	0.37	0.00	0.00	0.82
Alameda	38.86	1.24	0.18	1.84	0.00	0.35
Orange	35.70	1.24	0.04	0.00	0.00	1.36
San Mateo	14.20	0.04	0.03	0.00	1.34	1.85
Stanislaus	13.03	0.00	0.00	0.00	0.02	0.95
San Joaquin	11.85	0.00	0.00	0.00	0.00	0.52
Contra Costa	9.06	0.14	0.00	0.00	0.00	3.68
San Francisco	8.28	0.67	0.00	0.00	0.00	0.83
Sacramento	6.93	0.00	0.00	0.00	0.00	1.23
San Bernardino	5.93	0.26	0.09	0.00	0.00	0.64
Fresno	5.85	0.00	0.00	0.00	0.02	0.22
Solano	3.30	0.07	0.00	0.00	0.00	1.42
Ventura	2.95	0.84	0.04	0.00	0.00	0.78
Tulare	2.62	0.00	0.00	0.00	0.00	0.26
Yolo	2.41	0.01	0.00	0.00	0.00	0.28
Merced	2.26	0.00	0.00	0.00	0.00	0.18
Riverside	1.90	0.07	0.01	0.00	0.00	0.47
Santa Barbara	1.11	0.02	0.01	0.00	0.00	0.43
Kern	1.08	0.00	0.00	0.00	0.00	0.20
Sutter	0.89	0.00	0.00	0.00	0.00	0.07
Monterey	0.88	0.01	0.00	0.00	0.00	0.23
Sonoma	0.85	0.01	0.00	0.00	0.00	0.31
Marin	0.70	0.02	0.00	0.00	0.00	0.26
Santa Cruz	0.65	0.01	0.00	0.00	0.00	0.26
Kings	0.47	0.00	0.00	0.00	0.00	0.04
Humboldt	0.39	0.01	0.00	0.00	0.00	0.15
Imperial	0.38	0.00	0.00	0.00	0.00	0.11
San Luis Obispo	0.38	0.01	0.00	0.00	0.00	0.17
Shasta	0.37	0.01	0.00	0.00	0.00	0.14
Napa	0.34	0.01	0.00	0.00	0.00	0.13
Butte	0.33	0.00	0.00	0.00	0.00	0.07
Placer	0.31	0.01	0.00	0.00	0.00	0.12
El Dorado	0.30	0.00	0.00	0.00	0.00	0.12
San Benito	0.28	0.00	0.00	0.00	0.00	0.11
Nevada	0.23	0.00	0.00	0.00	0.00	0.09
Madera	0.22	0.00	0.00	0.00	0.00	0.02
Mendocino	0.18	0.00	0.00	0.00	0.00	0.07
Tehama	0.16	0.00	0.00	0.00	0.00	0.03
Lake	0.16	0.00	0.00	0.00	0.00	0.06
Glenn	0.14	0.00	0.00	0.00	0.00	0.02
Siskiyou	0.13	0.00	0.00	0.00	0.00	0.05
Tuolumne	0.13	0.00	0.00	0.00	0.00	0.05
Yuba	0.12	0.00	0.00	0.00	0.00	0.05
Plumas	0.11	0.00	0.00	0.00	0.00	0.04
Inyo	0.08	0.00	0.00	0.00	0.00	0.03
Colusa	0.08	0.00	0.00	0.00	0.00	0.01
Mono	0.08	0.00	0.00	0.00	0.00	0.03
Lassen	0.05	0.00	0.00	0.00	0.00	0.02
Del Norte	0.05	0.00	0.00	0.00	0.00	0.02
Amador	0.04	0.00	0.00	0.00	0.00	0.02
Calavaras	0.03	0.00	0.00	0.00	0.00	0.01
Mariposa	0.02	0.00	0.00	0.00	0.00	0.01
Trinity	0.01	0.00	0.00	0.00	0.00	0.00
Modoc	0.01	0.00	0.00	0.00	0.00	0.01
Sierra	0.00	0.00	0.00	0.00	0.00	0.00
Alpine	0.00	0.00	0.00	0.00	0.00	0.00

(2) Benzene
(3) Bromodichloromethane
(4) Carbon tetrachloride
(5) Chlorobenzene
(6) Chloroform

Table 16b: County-By-County Emissions

COUNTY	EMISSIONS INDIVIDUAL PTOCS (TONS/YEAR) (7)	(8)	(9)	(10)	(11)	(12)	(13)
Los Angeles	0.05	0.34	15.40	8.19	136.48	19.62	191.36
Santa Clara	0.00	0.00	0.04	0.00	42.75	8.33	32.65
San Diego	0.00	0.00	2.20	0.01	14.06	1.03	4.94
Alameda	0.07	1.24	0.13	0.00	4.34	14.19	7.21
Orange	0.00	0.00	0.18	0.14	14.43	1.69	8.75
San Mateo	0.00	0.90	0.55	1.89	2.64	1.78	1.40
Stanislaus	0.00	0.08	0.27	0.00	0.71	2.95	2.71
San Joaquin	0.00	0.01	0.03	0.00	0.08	2.40	7.59
Contra Costa	0.00	0.00	0.06	0.02	3.30	0.81	0.71
San Francisco	0.00	0.00	0.45	0.00	0.82	0.00	2.47
Sacramento	0.00	0.00	0.00	0.00	0.87	2.08	2.16
San Bernardino	0.00	0.00	0.63	0.00	0.95	0.44	2.56
Fresno	0.00	0.06	0.09	0.00	0.31	0.56	0.87
Solano	0.00	0.00	0.05	0.01	0.69	0.45	0.40
Ventura	0.03	0.07	0.03	0.00	0.05	0.48	0.13
Tulare	0.00	0.02	0.05	0.00	0.17	0.57	0.53
Yolo	0.00	0.01	0.05	0.00	0.17	0.51	0.48
Merced	0.00	0.01	0.08	0.00	0.13	0.57	0.43
Riverside	0.00	0.00	0.12	0.01	0.32	0.15	0.58
Santa Barbara	0.01	0.00	0.01	0.01	0.19	0.14	0.17
Kern	0.00	0.00	0.05	0.00	0.08	0.29	0.23
Sutter	0.00	0.01	0.02	0.00	0.05	0.20	0.18
Monterey	0.00	0.00	0.00	0.00	0.17	0.25	0.10
Sonoma	0.00	0.00	0.01	0.01	0.14	0.14	0.14
Marin	0.00	0.00	0.01	0.01	0.12	0.08	0.12
Santa Cruz	0.00	0.00	0.01	0.01	0.09	0.11	0.09
Kings	0.00	0.00	0.01	0.00	0.03	0.10	0.09
Humboldt	0.00	0.00	0.00	0.00	0.07	0.05	0.06
Imperial	0.00	0.00	0.01	0.00	0.05	0.06	0.06
San Luis Obispo	0.01	0.00	0.01	0.00	0.06	0.04	0.05
Shasta	0.00	0.00	0.00	0.00	0.06	0.05	0.05
Napa	0.00	0.00	0.00	0.00	0.06	0.04	0.05
Butte	0.00	0.00	0.01	0.00	0.04	0.06	0.06
Placer	0.00	0.00	0.00	0.00	0.05	0.04	0.05
El Dorado	0.00	0.00	0.00	0.00	0.05	0.04	0.04
San Benito	0.00	0.00	0.00	0.00	0.05	0.04	0.04
Nevada	0.00	0.00	0.00	0.00	0.04	0.03	0.03
Madera	0.00	0.00	0.00	0.00	0.01	0.05	0.04
Mendocino	0.00	0.00	0.00	0.00	0.03	0.02	0.03
Tehama	0.00	0.00	0.00	0.00	0.01	0.03	0.03
Lake	0.00	0.00	0.00	0.00	0.03	0.02	0.02
Glenn	0.00	0.00	0.00	0.00	0.01	0.03	0.03
Siskiyou	0.00	0.00	0.00	0.00	0.02	0.02	0.02
Tuolumne	0.00	0.00	0.00	0.00	0.02	0.02	0.02
Yuba	0.00	0.00	0.00	0.00	0.02	0.02	0.02
Plumas	0.00	0.00	0.00	0.00	0.02	0.01	0.02
Inyo	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Colusa	0.00	0.00	0.00	0.00	0.01	0.02	0.02
Mono	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Lassen	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Del Norte	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Amador	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Calavaras	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mariposa	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Trinity	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Modoc	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sierra	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Alpine	0.00	0.00	0.00	0.00	0.00	0.00	0.00

(7)	Dibromochloromethane
(8)	1,1 Dichloroethylene
(9)	Ethylbenzene
(10)	1,2 Dichloroethane
(11)	Methylene chloride
(12)	Perchloroethylene
(13)	Toluene

Table 16c: County-By-County Emissions

	EMISSIONS INDIVIDUAL PTOCS (TONS/YEAR)		
COUNTY	(14)	(15)	(16)
Los Angeles	35.95	8.18	1.72
Santa Clara	2.64	2.76	0.00
San Diego	36.01	0.03	0.00
Alameda	6.54	1.54	0.00
Orange	6.87	1.00	0.00
San Mateo	1.10	0.67	0.00
Stanislaus	0.64	4.69	0.00
San Joaquin	0.07	1.14	0.00
Contra Costa	0.24	0.10	0.00
San Francisco	1.02	2.02	0.00
Sacramento	0.29	0.30	0.00
San Bernardino	0.31	0.04	0.00
Fresno	0.40	3.30	0.00
Solano	0.09	0.13	0.00
Ventura	0.46	0.03	0.00
Tulare	0.13	0.88	0.00
Yolo	0.12	0.76	0.00
Merced	0.11	0.74	0.00
Riverside	0.11	0.06	0.00
Santa Barbara	0.07	0.05	0.00
Kern	0.04	0.18	0.00
Sutter	0.04	0.32	0.00
Monterey	0.11	0.02	0.00
Sonoma	0.05	0.04	0.00
Marin	0.04	0.03	0.00
Santa Cruz	0.05	0.02	0.00
Kings	0.02	0.16	0.00
Humboldt	0.03	0.02	0.00
Imperial	0.02	0.05	0.00
San Luis Obispo	0.02	0.01	0.00
Shasta	0.02	0.02	0.00
Napa	0.02	0.02	0.00
Butte	0.02	0.07	0.00
Placer	0.02	0.01	0.00
El Dorado	0.02	0.01	0.00
San Benito	0.02	0.01	0.00
Nevada	0.01	0.01	0.00
Madera	0.01	0.07	0.00
Mendocino	0.01	0.01	0.00
Tehama	0.01	0.04	0.00
Lake	0.01	0.01	0.00
Glenn	0.01	0.04	0.00
Siskiyou	0.01	0.01	0.00
Tuolumne	0.01	0.01	0.00
Yuba	0.01	0.01	0.00
Plumas	0.01	0.01	0.00
Inyo	0.01	0.00	0.00
Colusa	0.00	0.02	0.00
Mono	0.00	0.00	0.00
Lassen	0.00	0.00	0.00
Del Norte	0.00	0.00	0.00
Amador	0.00	0.00	0.00
Calavaras	0.00	0.00	0.00
Mariposa	0.00	0.00	0.00
Trinity	0.00	0.00	0.00
Modoc	0.00	0.00	0.00
Sierra	0.00	0.00	0.00
Alpine	0.00	0.00	0.00

(14) 1,1,1 Trichloroethane
(15) Trichloroethylene
(16) Vinyl chloride

tative of "industrial flows" at MWTPs in the Central Valley for which data were available.

Several of the PTOCs were emitted in relatively small quantities on a county-by-county basis. For instance, the maximum county-wide emissions of bromodichloromethane, chlorobenzene, dibromochloromethane, and 1,1-dichloroethylene were each less than 1.5 tpy.

Los Angeles County was responsible for large fractions of the statewide emissions of other PTOCs. In particular, Los Angeles County accounted for 100% and 89% of the vinyl chloride and benzene emissions, respectively. It also accounted for greater than 70% of the emissions of ethylbenzene, 1,2 dichloroethane, and toluene, and greater than 50% of the statewide emissions of methylene chloride. Two large plants contributed the majority of the estimated potential emissions. As will be subsequently discussed, the controlled emissions from one of those plants could be substantially lower.

With the exception of Los Angeles County, only a few other counties contributed large fractions of individual PTOCs to the statewide total. For instance, Alameda County accounted for 67% and 43% of the statewide emissions of carbon tetrachloride and 1,1 dichloroethylene, respectively. In addition, 77% of the chlorobenzene emitted by MWTPs in California was emitted in San Mateo County.

MWTP-By-MWTP Emissions

The MWTPs with total PTOC emissions of greater than 2.0 tpy were ranked according to total PTOC emissions, and are listed in Table 17. Twenty-nine MWTPs emitted greater than 2.0 tpy of total PTOCs. Of those 29 treatment facilities, 8 were located in Los Angeles County. The emissions estimates for those facilities noted with asterisks were based upon extrapolation techniques described in Section 5 and were characterized by a greater degree of uncertainty than most of the other facilities listed in Table 17.

Table 17a: Plant-By-Plant Emissions

			INDIVIDUAL PTOC EMISSIONS (TONS/YEAR)	
PLANT NAME	TOTAL EMISSIONS (TONS/YEAR)	(2)	(3)	(4)
Joint WPCP	296.09	29.55	0.00	0.00
Hyperion WWTF	112.32	8.50	0.17	0.87
San Jose/Santa Clara WPCP	58.67	0.00	0.00	0.00
Encina Joint Powers STP	46.94	0.00	0.00	0.00
* Terminal Island WWTF	29.75	1.34	0.03	0.02
Palo Alto WWTF	29.14	0.00	0.00	0.00
East Bay MUD WWTF	25.07	1.21	0.18	0.00
OCSD WWTF No. 2	20.42	1.07	0.00	0.00
Los Coyotes WRP	14.82	1.54	0.00	0.03
OCSD WWTF No. 1	13.26	0.13	0.02	0.00
Pt Loma WWTF	11.41	0.25	0.35	0.00
Stockton Reg. WWTF	10.35	0.00	0.00	0.00
Hayward WWTF	10.10	0.00	0.00	1.84
South Bayside WWTP	8.66	0.00	0.03	0.00
Southeast/North Point	7.56	0.64	0.00	0.00
Sacto Reg WWTF	6.87	0.00	0.00	0.00
* Modesto WWTF	6.71	0.00	0.00	0.00
* L.A. Glendale WWRP	5.46	0.25	0.01	0.00
Richmond/San Pablo WWTF	5.30	0.05	0.00	0.00
Sunnyvale WWTF	4.37	0.00	0.00	0.00
* Chino Basin Reg TP #1	3.93	0.18	0.06	0.00
* Riverbank WWTF	3.85	0.00	0.00	0.00
Fresno WWTF	3.78	0.00	0.00	0.00
* Burbank WWRF	3.19	0.14	0.00	0.00
San Francisco Intnl. Airp	3.07	0.03	0.00	0.00
Pomona WRP	2.50	0.00	0.00	0.00
Whittier Narrows WRP	2.42	0.03	0.00	0.00
San Leandro WWTF	2.17	0.00	0.00	0.00
Central Contra Costa WWTF	2.01	0.06	0.00	0.00

* = emissions based upon extrapolation

(2) Benzene
(3) Bromodichloromethane
(4) Carbon tetrachloride

Table 17b: Plant-By-Plant Emissions

	INDIVIDUAL PTOC EMISSIONS (TONS/YEAR)					
PLANT NAME	(5)	(6)	(7)	(8)	(9)	(10)
Joint WPCP	0.00	2.63	0.00	0.00	3.99	0.00
Hyperion WWTF	0.32	6.57	0.03	0.19	8.87	7.70
San Jose/Santa Clara WPCP	0.00	1.73	0.00	0.00	0.00	0.00
Encina Joint Powers STP	0.00	0.12	0.00	0.00	0.00	0.00
* Terminal Island WWTF	0.01	2.17	0.01	0.08	1.44	0.32
Palo Alto WWTF	0.00	0.97	0.00	0.00	0.00	0.00
East Bay MUD WWTF	0.00	0.04	0.05	0.00	0.00	0.00
OCSD WWTF No. 2	0.00	0.48	0.00	0.00	0.11	0.03
Los Coyotes WRP	0.00	0.48	0.00	0.00	0.47	0.02
OCSD WWTF No. 1	0.00	0.33	0.00	0.00	0.02	0.06
Pt Loma WWTF	0.00	0.42	0.00	0.00	2.09	0.00
Stockton Reg. WWTF	0.00	0.41	0.00	0.00	0.00	0.00
Hayward WWTF	0.00	0.19	0.00	1.24	0.06	0.00
South Bayside WWTP	1.33	1.47	0.00	0.90	0.47	1.86
Southeast/North Point	0.00	0.43	0.00	0.00	0.44	0.00
Sacto Reg WWTF	0.00	1.22	0.00	0.00	0.00	0.00
* Modesto WWTF	0.01	0.48	0.00	0.04	0.14	0.00
* L.A. Glendale WWRP	0.00	0.40	0.00	0.02	0.26	0.06
Richmond/San Pablo WWTF	0.00	3.05	0.00	0.00	0.00	0.00
Sunnyvale WWTF	0.00	0.38	0.00	0.00	0.04	0.00
* Chino Basin Reg TP #1	0.00	0.34	0.00	0.00	0.45	0.00
* Riverbank WWTF	0.01	0.27	0.00	0.03	0.08	0.00
Fresno WWTF	0.02	0.03	0.00	0.05	0.05	0.00
* Burbank WWRF	0.00	0.23	0.00	0.01	0.15	0.03
San Francisco Intnl. Airp	0.00	0.05	0.00	0.00	0.01	0.02
Pomona WRP	0.00	0.01	0.00	0.03	0.00	0.00
Whittier Narrows WRP	0.00	0.01	0.00	0.01	0.03	0.02
San Leandro WWTF	0.00	0.03	0.00	0.00	0.01	0.00
Central Contra Costa WWTF	0.00	0.00	0.00	0.00	0.00	0.00

* = emissions based upon extrapolation

(5) Chlorobenzene
(6) Chloroform
(7) Dibromochloromethane
(8) 1,1 Dichloroethylene
(9) Ethylbenzene
(10) 1,2 Dichloroethane

Table 17c: Plant-By-Plant Emissions

	INDIVIDUAL PTOC EMISSIONS (TONS/YEAR)					
PLANT NAME	(11)	(12)	(13)	(14)	(15)	(16)
Joint WPCP	120.93	5.86	124.76	5.47	2.46	0.44
Hyperion WWTF	5.00	4.37	48.73	15.62	4.37	1.01
San Jose/Santa Clara WPCP	18.65	7.32	28.29	0.72	1.97	0.00
Encina Joint Powers STP	11.44	0.00	0.00	35.37	0.00	0.00
* Terminal Island WWTF	5.70	4.66	7.82	5.21	0.75	0.19
Palo Alto WWTF	22.18	0.26	3.69	1.59	0.45	0.00
East Bay MUD WWTF	3.97	13.13	4.60	0.68	1.20	0.00
OCSD WWTF No. 2	7.25	0.96	5.48	4.30	0.73	0.00
Los Coyotes WRP	1.25	1.44	6.05	3.49	0.04	0.00
OCSD WWTF No. 1	6.84	0.44	2.88	2.32	0.22	0.00
Pt Loma WWTF	2.38	0.90	4.45	0.56	0.00	0.00
Stockton Reg. WWTF	0.00	2.06	7.28	0.00	0.60	0.00
Hayward WWTF	0.00	0.72	0.20	5.59	0.26	0.00
South Bayside WWTP	0.00	1.08	0.74	0.39	0.38	0.00
Southeast/North Point	0.82	0.00	2.46	1.02	1.75	0.00
Sacto Reg WWTF	0.86	2.07	2.15	0.29	0.29	0.00
* Modesto WWTF	0.36	1.53	1.40	0.33	2.43	0.00
* L.A. Glendale WWRP	1.05	0.86	1.44	0.96	0.14	0.04
Richmond/San Pablo WWTF	1.64	0.16	0.30	0.07	0.03	0.00
Sunnyvale WWTF	1.90	0.73	0.65	0.33	0.33	0.00
* Chino Basin Reg TP #1	0.62	0.28	1.78	0.20	0.01	0.00
* Riverbank WWTF	0.21	0.88	0.80	0.19	1.39	0.00
Fresno WWTF	0.20	0.00	0.48	0.31	2.65	0.00
* Burbank WWRF	0.61	0.50	0.84	0.56	0.08	0.02
San Francisco Intnl. Airp	2.37	0.02	0.12	0.42	0.03	0.00
Pomona WRP	0.11	0.03	0.02	2.30	0.00	0.00
Whittier Narrows WRP	0.57	0.66	0.56	0.36	0.17	0.00
San Leandro WWTF	0.09	0.11	1.93	0.00	0.00	0.00
Central Contra Costa WWTF	1.21	0.41	0.19	0.13	0.00	0.00

* = emissions based upon extrapolation

(11) Methylene chloride
(12) Perchloroethylene
(13) Toluene
(14) 1,1,1 Trichloroethane
(15) Trichloroethylene
(16) Vinyl chloride

While Los Angeles County was responsible for 59% of the PTOC emissions statewide, two MWTPs were responsible for 86% of the emissions in Los Angeles County and 50% of the total PTOC emissions from MWTPs throughout the entire state. The total estimated emissions from the Joint Water Pollution Control Plant (JWPCP) were 296 tpy (uncontrolled), and the total emissions from the Hyperion Treatment Plant (HTP) were 112 tpy. It should be noted that the JWPCP is not a "typical" MWTP, as it utilizes a covered conveyance and primary treatment system with control devices on off-gas vents of processes ahead of the pure-oxygen aeration units used for secondary treatment. Other large pure-oxygen treatment facilities in California include the East Bay MUD WWTF, the Orange County Sanitation District Plant #2 (OCSD #2), and the Sacramento Regional WWTP. However, these are not believed to employ as extensive a set of air pollution control devices on vented gases.

The emissions from the JWPCP reported herein were inconsistent with emissions estimated by the staff of the County Sanitation Districts of Los Angeles County (CSDLAC). The CSDLAC completed gas-phase measurements at gas scrubbers installed principally for odor control, at primary treatment off-gas vents, at aerated channels, and at vents leading from the pure-oxygen biological reactors. Preliminary results of an ongoing study by the CSDLAC indicated that total emissions of 23 VOCs, including most of the PTOCs, were 150 lb/day (27 tpy) (Caballero, 1987). Most of those emissions were attributed to PTOCs. A large fraction (80%) of the emissions were detected after passage through off-gas scrubbers. PTOC emissions resulting from gases vented from the pure-oxygen system were particularly low (< 3 lb/day), which could possibly be attributed to the fact that surface oxygenation rather than submerged diffuser oxygenation was utilized. The order of magnitude difference in total emissions as observed by the CSDLAC and estimated for this study can possibly be explained by one or more of the following reasons:

1. The time periods during which the liquid and gas-phase samples were drawn did not coincide. It is possible that unusually high PTOC loadings

in the influent stream were experienced, although for the two 24 hour periods (12-6-85 and 5-14-86) for which data were available, the influent concentrations differed by only a factor of 2.6. By the same token, the gas-phase samples could have been drawn during a period characterized by unusually low PTOC mass loadings in the influent stream.

2. Scrubbers that were designed to reduce emissions of odorous gases (e.g., hydrogen sulfide) could have also been efficient at removing PTOCs. The off-gases from most of the aerated processes were passed through caustic scrubbers, activated carbon beds, or both. The authors do not believe that removal in caustic scrubbers could have accounted for an order-of-magnitude reduction in PTOC emissions. However, the PTOCs could have adsorbed in the activated carbon beds, thereby reducing emissions. Previous testing by the CSDLAC has indicated break-through times for the beds as low as two weeks for some of the PTOCs (Caballero, 1987). The activated carbon was being replaced with regenerated or virgin carbon at intervals of approximately four to six months. However, even following break-through, some fraction of the stripped PTOCs could continue to be removed. The extent of this removal is not known, and further research would be valuable in order to study the treatment of off-gases as a method for reducing PTOC emissions.

3. Although many processes were analyzed as part of the gas-sampling study, additional processes which were not considered could be sources of PTOC emissions. These included emissions after adsorption to solids (e.g., stripping in, and leakage from, digesters; volatilization during composting). However, as noted in Section 4 of this report, only a small fraction of the incoming PTOC mass is typically removed in sludge streams.

4. The "worst-case" assumption (i.e., all removal of PTOCs is by volatilization) might not be valid for pure-oxygen treatment facilities which, in comparison to conventional activated sludge systems, typically contact much less gas with the liquid phase. Because pass-through was accounted for by subtracting the effluent concentrations from the in-

fluent concentrations, the removal of PTOCs, if not by volatile losses, would be expected to result from adsorption and biodegradation. As noted above, adsorption was expected to be low, leaving only biodegradation to account for PTOC removals. Such a conclusion can not be verified at the present time. However, further studies are warranted in light of the potential significance with respect to reducing PTOC emissions during wastewater treatment.

The HTP is currently a partial secondary treatment facility. On the average, 300 MGD (75%) of the incoming wastewater is treated using only primary treatment processes. The remaining 100 MGD (25%) is treated using conventional activated sludge systems. Higher in-plant PTOC emissions would be expected if a larger percentage of the wastewater was subjected to aerated secondary treatment. Emissions from the HTP could change significantly, as the facility was scheduled to be modified to a pure-oxygen activated sludge plant by 1993. At that time, four 130 MGD pure-oxygen systems will go on-line. The overall effects of the modification on emissions can not be accurately predicted at this time. The added treatment could lead to either an increase or a decrease in PTOC emissions, depending upon the importance of biodegradation or installation of off-gas control systems. <u>In either case, a study of the PTOC emissions before and after the modifications would be valuable and would provide a better understanding of the role of such modifications on PTOC emissions.</u>

Other Los Angeles County treatment facilities that emitted greater than 15 tpy of total PTOCs were the Terminal Island Treatment Plant (30 tpy) and the Los Coyotes Water Reclamation Plant in Cerritos (15 tpy). Estimated emissions at the Terminal Island Treatment Plant were based upon extrapolation using data from other MWTPs in Los Angeles and Orange Counties. The high emissions estimates were a result of a large industrial flow contribution to the total wastewater flow.

Throughout the rest of California, other MWTPs with total PTOC emissions greater than 10 tpy included the San Jose/ Santa Clara WPCP (59 tpy) and the Palo Alto WWTF (29 tpy) in Santa Clara County, the East Bay MUD WWTF in Oakland (25 tpy) and the Hayward WWTF (10 tpy), each in Alameda County, the OCSD plants #2 (22 tpy) and #1 (13 tpy) in Huntington Beach and Fountain Valley, respectively, the Encina Joint Powers WWTF (47 tpy) and the Point Loma WWTF (11 tpy), each in San Diego County, and the Stockton Regional WWTF (10 tpy) in San Joaquin County. None of the emissions from those facilities were based upon extrapolation. The use of possibly outdated data for the Encina Joint Powers WWTF was discussed previously.

The combined benzene emissions from the JWPCP and the HTP accounted for 82% of the total benzene emissions from all MWTPs in the state (assuming no control systems). The third and fourth largest sources were also from Los Angeles County; the Los Coyotes WRP (1.5 tpy), and the Terminal Island Treatment Plant (1.3 tpy).

Ninety-eight percent of the statewide carbon tetrachloride emissions were accounted for by the Hayward WWTF (1.8 tpy) and the HTP (0.9 tpy).

Seventy-six percent of the statewide chlorobenzene emissions were emitted by the South Bayside WWTF in Redwood City.

The two largest sources of chloroform emissions were the HTP (6.6 tpy) and the Richmond/San Pablo WWTF (3.1 tpy). Recall that volatile losses after in-plant formation were not considered.

At 8.9 tpy, the HTP was the largest source of ethylbenzene emissions. The HTP also emitted 7.7 tpy of 1,2 dichloroethane.

The JWPCP was responsible for 89% (121 tpy) of the methylene chloride emissions in Los Angeles County (and 54% of the methylene chloride emissions statewide (assuming no control systems). Emissions of methylene chloride were also significant at the Palo Alto WWTF (22 tpy) and the San Jose-Santa Clara Water Pollution Control Plant (19 tpy).

Perchloroethylene emissions at the East Bay MUD WWTF (13 tpy) accounted for 52% of the total PTOC emissions from that plant. Other sources which emitted greater than 5.0 tpy were the San Jose/Santa Clara WPCP (7.3 tpy) and the JWPCP (5.9 tpy).

An estimated 46% of the toluene (uncontrolled) emitted by MWTPs in California was emitted by the JWPCP (125 tpy). The HTP added 49 tpy. The San Jose/Santa Clara WPCP added 28 tpy, and the Terminal Island Treatment Plant and the Stockton Regional WWTF each emitted greater than 7 tpy.

The largest sources of 1,1,1 trichloroethane emissions were the Encina Joint Powers WWTF (35 tpy), the HTP (16 tpy), the Hayward WWTF (5.6 tpy), and the JWPCP (5.5 tpy).

No single MWTP dominated in terms of trichloroethylene emissions. The largest sources were the HTP (4.4 tpy), the Fresno Regional WWTF #1 (2.7 tpy), the JWPCP (2.5 tpy), the Modesto WWTF (2.4 tpy), and the San Jose/Santa Clara WPCP (2.0 tpy).

Finally, emissions of vinyl chloride occurred only at MWTPs in Los Angeles County. The MWTPs included the HTP (1.0 tpy), the JWPCP (0.4 typ), and the Terminal Island Treatment Plant (0.2 tpy).

A data base which included speciated PTOC emissions from all of the MWTPs in California was provided to the CARB on floppy-disk in partial fulfillment of the contract which sponsored this report. It also included information regarding the locations and treatment characteristics of individual MWTPs throughout California. The data base is described in detail in Appendix F.

The Significance of MWTPs in the South Coast Air Basin

In the previous subsections, quantitative estimates of worst-case, uncontrolled, emissions of PTOCs were presented on a statewide, county-by-county, and MWTP-by-MWTP bases. For completeness, the significance of such emissions will be addressed. While a discussion of the significance of those emissions with respect to public health and/or photochemical oxidant formation was beyond the scope of this study, it was possible to compare the predicted emissions with known or predicted emissions from other sources. A well documented summary of the emissions of potentially toxic air contaminants exists for the South Coast Air Basin (SCAB) (Zwiacher et al., 1985). The report contains estimates of emissions from point sources (> 20 tpy) and combined area sources (< 20 tpy) throughout Los Angeles, Orange, Riverside, and San Bernardino Counties (the SCAB). Because such a summary exists, and because most of the predicted emissions from MWTPs in California occurred in the SCAB, that region was chosen for further analysis. It is important to note that the emissions report for the SCAB was updated as of 1984, and that MWTPs were not incorporated as emissions sources. Therefore, the emissions estimates completed for this study could be added to the existing emissions base.

In Table 18, emissions from all of the MWTPs in the South Coast Air Basin are compared with total emissions from other sources. From a basin-wide perspective, emissions of benzene, methylene chloride, perchloroethylene, 1,1,1 trichloroethane, and trichloroethylene from MWTPs were much less than emissions from other sources. However, emissions of toluene, chloroform, carbon tetrachloride, 1,2 dichloroethane, and vinyl chloride from MWTPs were comparable to other sources.

Predicted emissions from individual MWTPs, particularly the JWPCP, HTP, and the Terminal Island Treatment Plant, indicated that each facility could be a major source of some PTOCs with respect to other known point sources. As an example, in Table 19, emissions from the HTP are compared with emissions from the largest known sources of each PTOC in the SCAB.

The Significance of Emissions Following Wastewater Treatment

The emissions estimates presented in this section were based upon in-plant volatilization. However, at several major MWTPs, a significant quantity of PTOCs passed through the entire treatment train or were gen-

Table 18: A Comparison of Emissions from MWTPs and Other Sources in the South Coast Air Basin

Compounds	Emissions (tons/year)	
	MWTPs	Other Sources[1]
Benzene	43.	7983.
Carbon tetrachloride	0.9	3.
Chloroform	16.	negligible
1,2 Dichloroethane	8.3	12.5
Methylene chloride	152.	14304.
Perchloroethylene	22.	12756.
Toluene	203.	1010.
1,1,1 Trichloroethane	43.	16495.
Trichloroethylene	9.3	546.
Vinyl chloride	1.7	1.3

(1) From Zwiacher et al. (1985).

Table 19: A Comparison of Emissions from the Hyperion Treatment Plant and Large Point Sources in the South Coast Air Basin

	Emissions (tons/year)	
Compound	Hyperion	Largest Point Source[1]
Benzene	8.5	34.
Carbon tetrachloride	0.9	3.
Chloroform	6.6	<0.025
1,2 Dichloroethane	7.7	1.8
Methylene chloride	5.0	529.
Perchloroethylene	4.4	214.
Toluene	49.	103.
1,1,1 Trichloroethane	15.6	588.
Trichloroethylene	4.4	5.0
Vinyl chloride	1.0	1.3[2]

(1) From Zwiacher et al (1985).

(2) Combined emissions from three PVC producing facilities.

erated during the chlorination process. Those PTOCs were not accounted for in the emissions estimates. Ultimately, those PTOCs could have volatilized from either the effluent conveyance system or the receiving water to which they were discharged. In many cases it would have been inappropriate to add such emissions to the total emissions from a MWTP, as the point of discharge was often located several miles from the treatment facility. On a statewide basis, greater than 50% of the total wastewater treated by MWTPs is discharged directly to the Pacific Ocean. Furthermore, such MWTPs in the South Coast Air Basin and San Diego account for a large percentage of the total statewide loading of PTOCs in effluent streams. It should also be noted that the ultimate fate of PTOCs that are discharged to receiving waters, particularly to the ocean, is not well understood.

The quantity of PTOCs that annually pass-through a MWTP can be estimated. An analysis was completed using PTOC concentration data for the effluent streams of MWTPs in the largest, most industrialized counties. These included the five counties with the highest total PTOC emissions from MWTPs. The results are shown in Table 20. If one further assumes that volatilization was the ultimate fate of the PTOCs, "worst-case" emissions following treatment were nearly equal to those that occurred during treatment in Los Angeles County. In Orange County, the 94 tpy emitted from effluent streams would be a factor of 2.6 greater than emissions during treatment. In both San Diego County and Alameda County emissions from effluent streams were approximately 35% of the total in-plant emissions, and emissions from MWTPs in Santa Clara County were relatively small compared to emissions during treatment. The latter was due to strict discharge requirements for those facilities which discharged into the southern end of San Francisco Bay. Bearing in mind the above caveats, the statewide PTOC emissions would have risen from 803 tpy to approximately 1400 tpy.

Sludge Generation and PTOC Removal in Sludge Streams

Table 21 provides a list of counties ranked according to the total removal of all PTOCs by adsorption, sludge treatment, and sludge dispo-

Table 20: Worst-Case Emissions from Effluent Conveyance Systems and Receiving Waters

County	Total PTOC Emissions (tons/year)
Los Angeles	446
Orange	94
San Diego	20
Alameda	14
Santa Clara	7
Statewide	600

Table 21: PTOC Mass Removals in Sludge Streams

			Estimated Mass Removals in Sludge Streams (tons/year)											
County	Estimated Sludge Generation (1000 tons/yr)	Total PTOCs	BENZ	CTET	CBENZ	CFORM	EBENZ	DCA	METH	PERC	TOL	TCA	TCE	VIN
Los Angeles	243	58.60	0.85	0.05	0.05	0.18	1.70	0.10	18.50	4.00	32.20	0.50	0.49	0.02
Santa Clara	43	7.20	0.00	0.00	0.01	0.02	0.01	0.00	3.50	0.35	3.20	0.02	0.12	0.00
Orange	122	4.30	0.06	0.01	0.01	0.02	0.13	0.00	2.20	0.41	1.30	0.11	0.10	0.00
San Diego	54	2.80	0.01	0.00	0.00	0.01	0.12	0.00	1.30	0.08	1.00	0.25	0.00	0.00
Alameda	40	2.40	0.03	0.08	0.00	0.02	0.02	0.00	0.62	0.70	0.74	0.05	0.09	0.00
San Joaquin	17	0.91	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.10	0.74	0.00	0.05	0.00
Stanislaus	16	0.80	0.00	0.00	0.00	0.01	0.01	0.00	0.09	0.15	0.30	0.01	0.23	0.00
San Francicso	17	0.79	0.01	0.00	0.00	0.01	0.02	0.00	0.24	0.12	0.27	0.01	0.09	0.00
San Mateo	17	0.62	0.00	0.00	0.07	0.02	0.02	0.02	0.23	0.08	0.14	0.01	0.03	0.00
Contra Costa	21	0.50	0.00	0.00	0.00	0.03	0.01	0.00	0.34	0.04	0.07	0.00	0.01	0.00
Sacramento	24	0.47	0.00	0.00	0.00	0.01	0.00	0.00	0.12	0.11	0.21	0.00	0.01	0.00
San Bernardino	20	0.47	0.00	0.00	0.00	0.00	0.03	0.00	0.12	0.02	0.28	0.00	0.00	0.00
Fresno	13	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.07	0.09	0.00	0.19	0.00
Solano	9	0.21	0.00	0.00	0.00	0.01	0.00	0.00	0.10	0.03	0.05	0.00	0.01	0.00
Tulare	6	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.06	0.00	0.04	0.00
Merced	6	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.05	0.00	0.04	0.00
Yolo	6	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.05	0.00	0.04	0.00
Riverside	18	0.12	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.01	0.06	0.00	0.00	0.00
Monterey	8	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.01	0.02	0.00	0.00	0.00
Ventura	22	0.07	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.02	0.02	0.00	0.00	0.00
Kern	7	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.00	0.01	0.00
Santa Barbara	9	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.02	0.00	0.00	0.00
Sonoma	8	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.02	0.00	0.00	0.00
Sutter	2	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.00	0.02	0.00
All Others	47	0.29	0.01	0.01	0.01	0.05	0.02	0.01	0.08	0.02	0.06	0.02	0.04	0.01
Statewide	795	81.7	0.98	0.15	0.15	0.40	2.10	0.13	27.7	6.45	41.0	0.98	1.61	0.03

0.00 = <0.01

Where BENZ = benzene; CTET = carbon tetrachloride; CBENZ = chlorobenzene; CFORM = chloroform; EBENZ = ethylbenzene; DCA = 1,2 dichloroethane; METH = methylene chloride; PERC = perchloroethylene; TOL = toluene; TCA = 1,1,1 trichloroethane; TCE = trichloroethylene; and VIN = vinyl chloride.

sal. The estimated amount of sludge generated is shown, as are speciated PTOC removals. Negligible removals were assumed for acrylonitrile, bromodichloromethane, dibromochloromethane, and 1,1 dichloroethylene.

The estimated amount of sludge generated was based on the average of amounts obtained by using both the flow-correlation and total suspended solids approaches that were described in Section 5. The estimates were corrected for known values. The resultant estimate was 0.8 million dry tpy were generated. Los Angeles and Orange Counties accounted for 46% of that total.

The sum of PTOCs removed in sludge streams statewide was 81.7 tpy, with Los Angeles County accounting for 72% of the total.

Only four individual PTOCs were removed in quantities of more than 1.0 tpy for any given county. An estimated 1.7 tpy of ethylbenzene were removed in the sludges generated in Los Angeles County. Methylene chloride and toluene removals were both greater than 1.0 tpy in Los Angeles, Santa Clara, Orange, and San Diego Counties. Perchloroethylene removals in Los Angeles County were estimated to be 4.0 tpy. On a statewide basis, only toluene (41 tpy), methylene chloride (28 tpy), perchloroethylene (6.5 tpy), ethylbenzene (2.1 tpy), and trichloroethylene (1.6 tpy) were removed in sludge at quantities exceeding 1.0 tpy.

A large fraction of the sludge that was generated in California was placed in landfills. The Hyperion Treatment Plant has practiced sludge disposal to the ocean, but will soon convert to sludge incineration and removal to landfills. A small fraction of the total sludge generated in California was composted and utilized commercially as a soil amendment.

Finally, the PTOC removals in sludge could be subtracted from statewide and county emissions to arrive at new, less than worst-case, estimates for PTOC emissions. In most counties this would have led to less than a 10% reduction in the emissions estimates.