# EXECUTIVE SUMMARY

## Emissions of Volatile and Potentially Toxic Organic Compounds from Sewage Treatment Plants And Collection Systems

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# EXECUTIVE SUMMARY

## 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. Therefore a study to assess the potential for PTOC emissions from publicly-owned treatment works (POTWs) in California was commissioned by the California Air Resources Board. In its final form, this study included the following elements:

1. A literature search to obtain information regarding emissions of 16 volatile PTOCs from POTWs. The PTOCs considered included 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. Development of a procedure for estimating emissions of the 16 PTOCs from POTWs.

3. Completion of a county-by-county inventory and ranking of estimated emissions of the 16 PTOCs from 589 MWTPs in California.

4. Estimation of the quantity of sludge and the fraction of each of the 16 PTOCs removed in sludge streams.

5. Estimation of the level of confidence associated with the emissions inventory.

6. A description of all data bases used in the compilation of the emissions inventory.

7. The location (latitude and longitude) of every MWTP in the state of California.

8. Development of an interactive model to estimate emissions from specific wastewater treatment processes.

9. A review of the factors affecting trihalomethane (THM) formation, potential precursors, and evidence of THM formation in California.

10. Visits to a number of treatment plants to gather site specific data and to make recommendations regarding possible sampling sites.

## LITERATURE REVIEW

The literature review established that within a wastewater collection and treatment system PTOCs can be removed, transformed, generated, or simply transported through the system unchanged. Five primary mechanisms are involved: (1) removal by volatile emissions, (2) removal by chemical and/or biochemical degradation, (3) removal by adsorption to sludge, (4) pass-through (i.e., passage through the entire system without change), and (5) generation as degradation by-products of precursor compounds or as a result of reaction with chlorine added as a disinfectant. These mechanisms are not mutually exclusive. Competition and simultaneous action can be significant. A schematic summary of the mechanisms which affect PTOCs in POTWs is shown in Figure 2 (extracted from the report).

From the few available concentration measurements, it appeared that volatile emissions of PTOCs from collection systems are probably significant, particularly in sewer lines serving industrial and commercial establishments. Unfortunately, the paucity of existing sample data did not allow for meaningful emissions estimates from collection systems. This is an area where future studies would be of great value to reduce

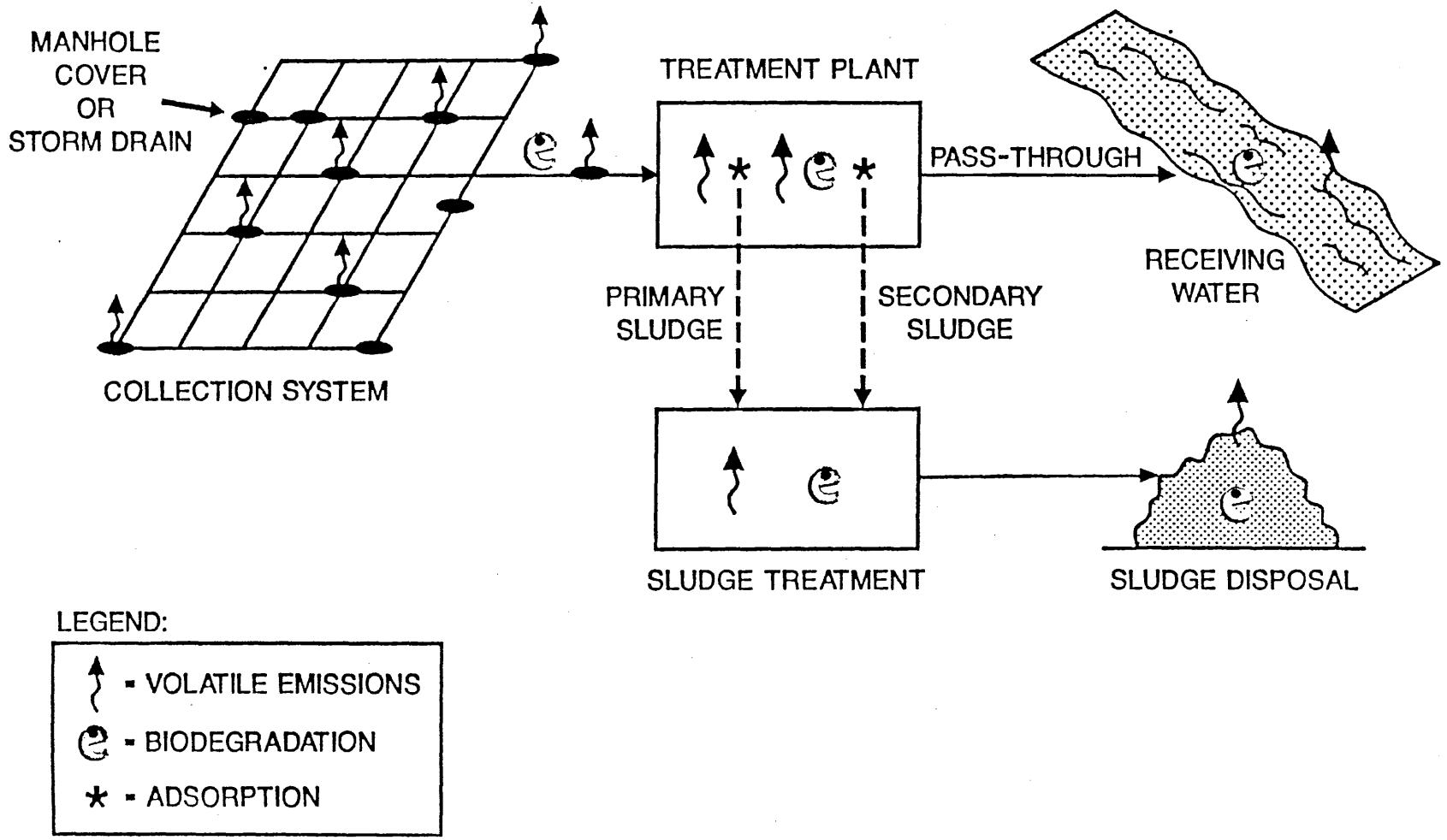


Figure 2: The Fate of PTOCs in POTWs

the uncertainties associated with the relative significance of collection systems as PTOC emission sources.

Wastewater treatment processes were reviewed in terms of the following removal mechanisms: volatilization, adsorption, biodegradation, and pass-through. The formation of trihalomethanes was also reviewed. It was concluded that while laboratory studies 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 of treatment plant emissions were the most valuable for obtaining direct measurements of PTOC removals in the plant. However, the lack of existing data for a wide variety of treatment train configurations made it difficult to generalize about the fate of PTOCs in MWTPs. Nevertheless, the following observations were noted:

1. The previous literature and expert opinion indicated that biodegradation of the volatile PTOCs under field conditions was unlikely to be a major removal pathway.

2. 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.

3. Adsorption and removal in sludge streams was typically found to account for less than 10% of the incoming mass of any PTOC.

4. 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.

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

## EMISSION ESTIMATE METHODS AND QUALITY

Several valuable sources of plant specific data were discovered. The primary source of data regarding hydraulic characteristics and PTOC concentrations in influent and effluent streams were the Pretreatment Annual Reports (PAR) required by recently instituted federal and state pretreatment programs. The number and length of sample records currently available is sparse, but will increase in future years. A somewhat older, but valuable source of MWTP treatment train configurations was the NEEDS data base (a study of future MWTP needs for federal assistance monies). With the availability of these data bases, it was decided that the best emission estimation method would be on a plant-by-plant basis for each MWTP in the state. However, even with the data bases noted above, it was necessary to contact several major MWTPs directly with requests for concentration and flow data.

Two basic methods were applied to estimate the emissions from MWTPs. The first was based upon a simple materials balance, i.e., the product of influent concentration and influent flowrate less the product of effluent concentration and effluent flowrate. Where the requisite data were not available, a second method was employed. This involved extrapolation of emissions corrected for flow, industrial flow contribution and geographic location. The extrapolation procedure was based on industry averages from plants having data and does not reflect the variability known to exist. Thus, extrapolated estimates indicate potential discharges rather than actual values. Both methods assumed the total in-plant volatilization of the 16 PTOCs which were not carried out with the plant effluent, and that no air pollution controls were applied. In that regard, the estimates represent "worst-case", potential emissions from a given MWTP. However, as discussed above, the error incurred by assuming complete volatilization was small and, with the possible exception of one major MWTP, effective air pollution controls for PTOCs were not applied by the MWTPs.

The quantities of sludge generated were obtained either from plant-reported values or by one of two extrapolation techniques. The first

extrapolation method involved applying average sludge generation quantities per unit of flow calculated from plants having data. The second technique involved use of plant-reported total suspended solids (TSS) reductions when available, or assuming a fractional TSS removal for those plants without effluent TSS data. The mass of the 16 volatile PTOCs associated with the sludge streams were estimated by applying partition coefficients, obtained from the literature, to the quantities of sludge generated. The fates of the PTOCs adsorbed to sludges were too diverse to permit an accurate assessment of their subsequent emission. However, to a degree, the quantities of PTOCs removed with the sludge were already taken into account by assuming "worst-case" emissions.

Best engineering judgement (BEJ) was employed to compile a qualitative and semi-quantitative summary of the uncertainties associated with the emissions estimates. These sources of uncertainty are detailed in Section 5 of the report. The uncertainty factors are summarized in Table 15 (extracted from the report). The trend in uncertainty of the estimates was such that the greater the emissions, both by PTOC and by individual source, the smaller the uncertainty, i.e., closer to a factor of two.

## EMISSIONS

### Statewide

On an annual basis, an estimated total of 803 tons of the 16 PTOCs were emitted from MWTPs throughout California. The estimate corresponds roughly to the period from 1983 to 1986. Although the magnitude of the estimated emissions is substantial, they are lower than an earlier estimate of emissions for some of the larger MWTPs by about a factor of seven.

For purposes of visual presentation, those PTOCs with emissions less than 10 tons per year (tpy) are shown in Figure 4 while those with emissions of greater than or equal to 10 tpy are shown in Figure 5

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.

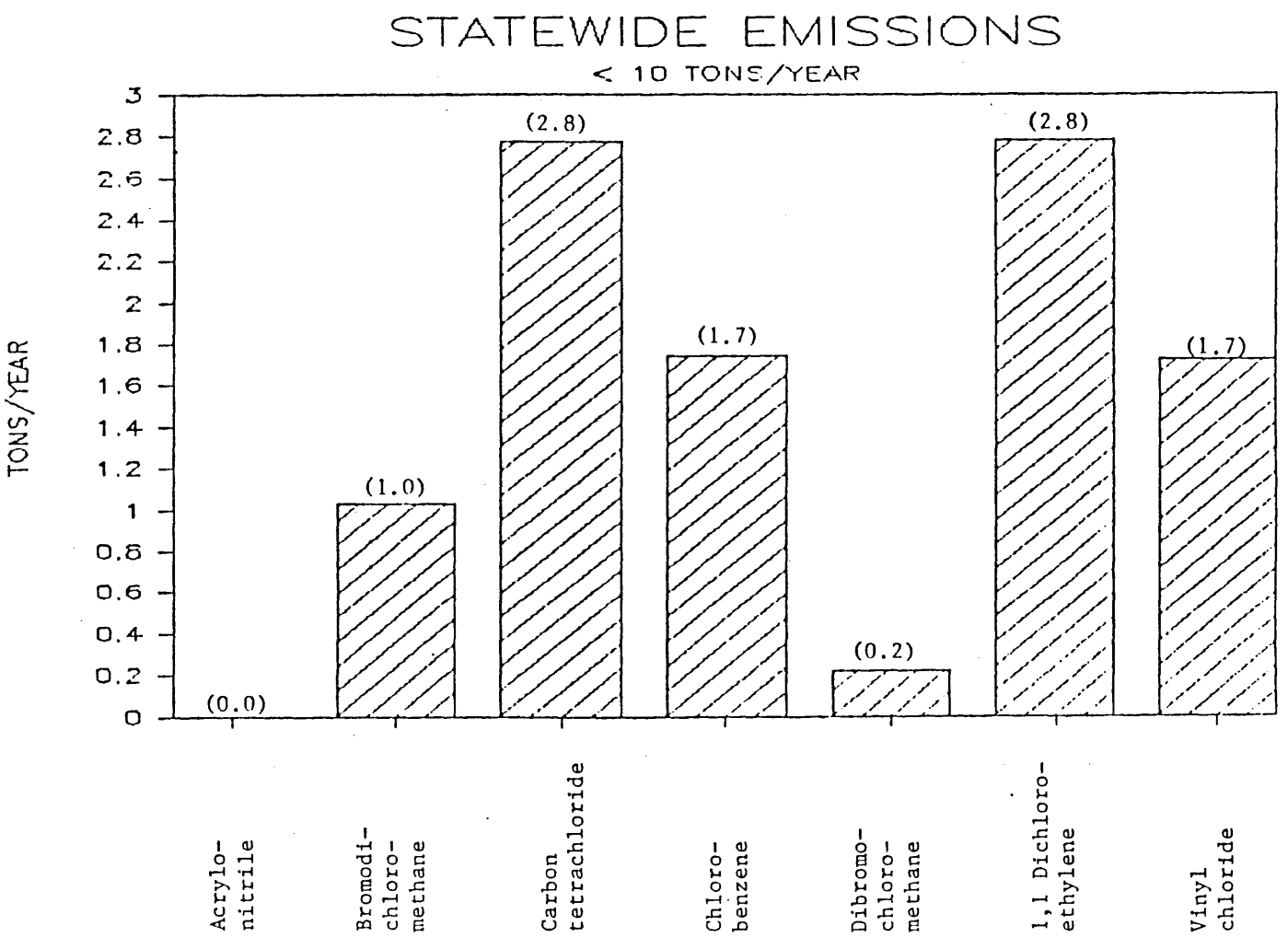


Figure 4: Statewide Emissions of PTOCs Totalling Less Than 10 tpy. Values in parenthesis above bars are emissions in tpy.

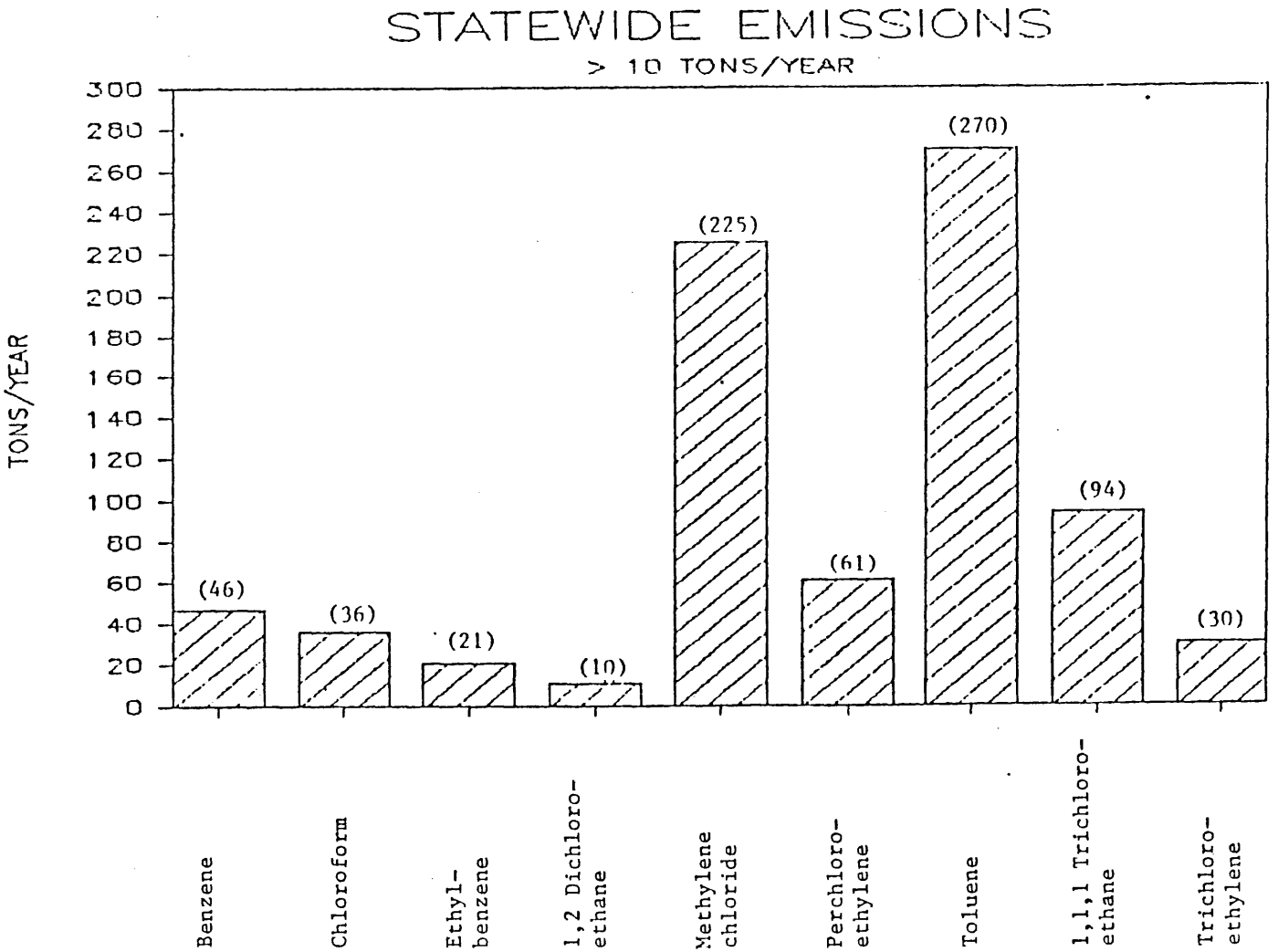


Figure 5: Statewide Emissions of PTOCs Totalling Greater Than 10 tpy. Values in parenthesis above bars are emissions in tpy.

(extracted from the report). A few brief comments regarding the estimates are in order here. Additional comments will be found in Section 6 of the report.

1. 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 more than 62% of the total mass emissions of all PTOCs.

2. 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 (1-100 µg/L) than those for the other PTOCs. It is possible, though unlikely, that acrylonitrile could have been discharged without detection.

3. If THM formation had been taken into account, the estimated statewide emissions of chloroform would have risen to approximately 50 tpy. The estimated emissions for bromodichloromethane and dibromochloromethane would have increased by a factor of approximately two, but the statewide emissions for either compound would have remained relatively low.

4. 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.

5. It is possible that emissions of both 1,1-dichloroethylene and vinyl chloride have been underestimated, as the methodology did not account for their possible formation as a result of the degradation of more highly halogenated compounds.

## County-By-County Emissions

The total and speciated PTOC emissions for each of the 58 counties in California are listed in Table 16 of the report. The ten counties

with the highest total PTOC emissions are shown in Figure 6 (extracted from the report). These ten counties 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. Los Angeles County requires additional comments to clarify uncertainties in the estimates.

While 59% of the statewide PTOC emissions were estimated to be in Los Angeles County, 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 was not a "typical" MWTP, as it utilized a covered conveyance and primary treatment system, with control devices on off-gas vents of processes upstream of the pure-oxygen aeration units. Preliminary results of an ongoing study by the County Sanitation Districts of Los Angeles County (CSDLAC) indicated that total emissions of 23 VOCs, including most of the PTOCs, were 150 lb/day (27 tpy), a factor of 10 lower than the current estimate. Further investigation of the efficiency of the control devices and methods of oxygen application employed by the JWPCP is warranted.

## The Significance of MWTPs in the South Coast Air Basin

A summary of the emissions of potentially toxic air contaminants exists for the South Coast Air Basin (SCAB). Because MWTPs were not incorporated as emissions sources, the emissions estimates completed for this study could be added to the existing emissions base. In Table 18 (extracted from the report), 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. How-

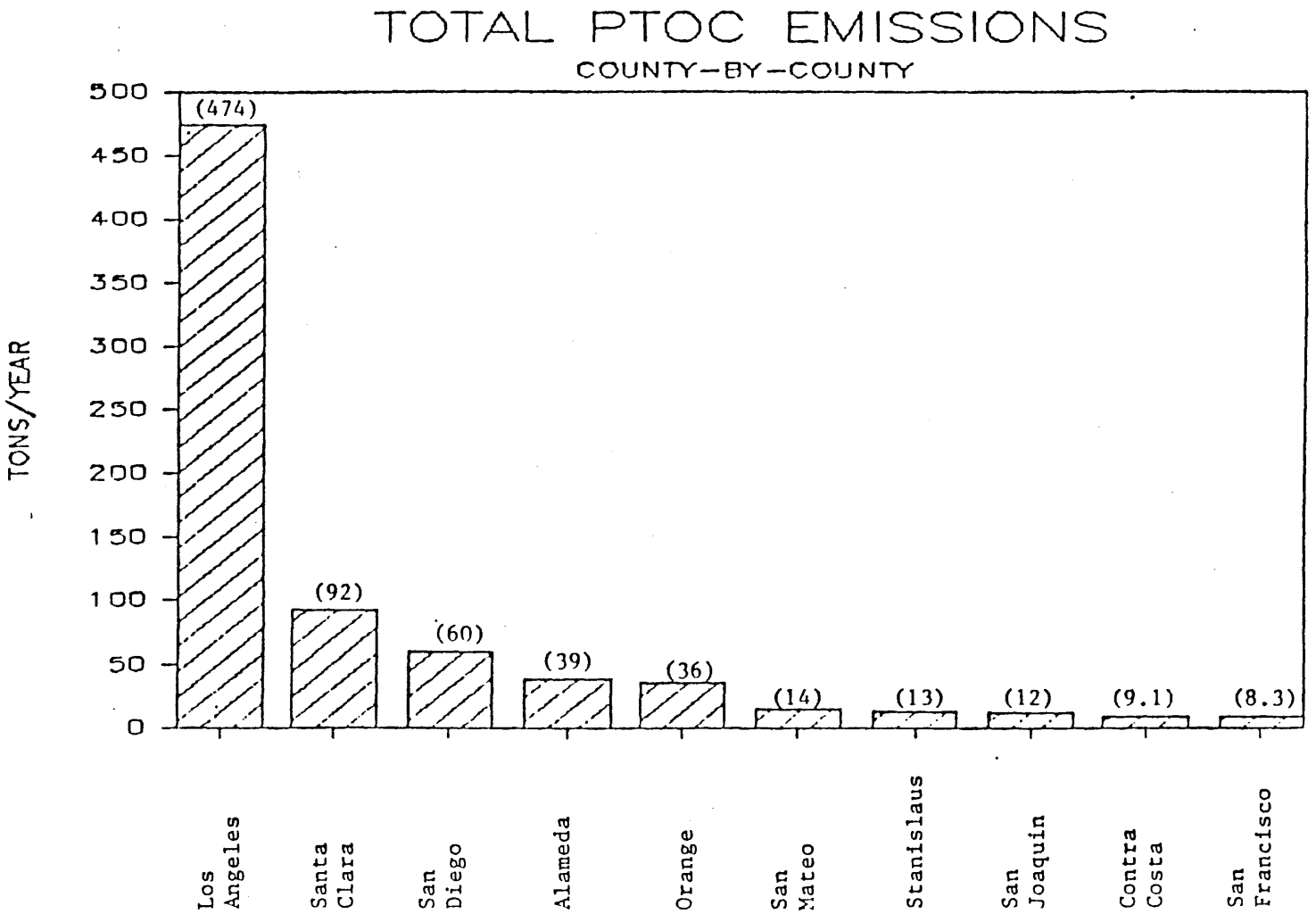


Figure 6: PTOC Emissions from the 10 Counties with the Highest Emissions. Values in parenthesis above bars are emissions in tpy.

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).

ever, emissions of toluene, chloroform, carbon tetrachloride, 1,2-dichloroethane, and vinyl chloride from MWTPs were significant with respect to other sources. As an example, in Table 19 (extracted from the report), emissions from the HTP are compared with emissions from the largest known point sources of each PTOC in the SCAB.

Pass-through

The emissions estimates of this study were based upon in-plant volatilization. However, at several major MWTPs, a significant quantity of PTOCs passed through the entire treatment system or were generated 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 an 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 was 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. Bearing in mind the above caveats, the statewide PTOC emissions would have risen from 803 tpy to approximately 1400 tpy. The results for the five counties with the highest total PTOC emissions are shown in Table 20 (extracted from the report).

## SLUDGE GENERATION AND PTOC REMOVAL IN SLUDGE STREAMS

The estimated amount of sludge generated was 0.8 million dry tpy. Los Angeles and Orange Counties accounted for 46% of that total. The sum of PTOCs removed in sludge streams statewide was 82 tpy, with Los

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

| Compound | Emissions (tons/year) 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.

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 |

Angeles County accounting for 72% of the total. 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.

## CONCLUSIONS

1. For volatile PTOCs the literature, expert opinion, and limited data favor removal from wastewater primarily by volatilization with a lesser amount being degraded or removed with sludge.

2. Little is known regarding the fate of PTOCs in collection systems or after discharge to a receiving water. However, the limited data available suggest that volatile emissions from collection systems could be significant with respect to emissions during wastewater treatment, depending upon the type of collection system, and the degree of "breathing" losses and degradation in the system.

3. PTOC data were collected for MWTPs that treated 77% of the municipal wastewater that was discharged to POTWs in California. Extrapolation techniques were studied and applied to account for the remaining 23%.

4. The uncertainties associated with emissions estimates were reviewed and estimated to be within a factor of two to four on a statewide basis, depending on the PTOC.

5. In recent years (1983-1986), an estimated 803 tons/year (tpy) of

PTOCs were emitted during wastewater treatment throughout California. A review of past data suggested that emissions of PTOCs from MWTPs have been reduced significantly during the past decade.

6. An additional 600 tpy of total PTOCs was discharged in the effluent streams of MWTPs throughout California. The fate of PTOCs in receiving waters was also uncertain, though for most surface receiving waters one would expect a high degree of volatilization and significant additional emissions of PTOCs. However, a large portion of treated effluent in California was being discharged to the ocean by submerged outfalls.

7. On a statewide basis, emissions were low (<3.0 tpy) for acrylonitrile, bromodichloromethane, carbon tetrachloride, chlorobenzene, dibromo-chloromethane, 1,1-dichloroethylene, and vinyl chloride. Emissions were relatively high (> 200 tpy) for methylene chloride and toluene. Emissions of benzene, chloroform, ethylbenzene, 1,2-dichloroethane, perchloroethylene, 1,1,1-trichloroethane, and trichloroethylene were in the range of 10 tpy to 100 tpy.

8. Total PTOC emissions from MWTPs were relatively low in most counties and from all but a few individual MWTPs. The regions of most significant emissions were the South Coast Air Basin and the region consisting of Alameda and Santa Clara Counties.

9. The Joint Water Pollution Control Plant (JWPCP) and the Hyperion Treatment Plant (HTP), both in Los Angeles County, appeared to be potentially significant sources of total and speciated PTOC emissions in comparison to existing point sources in the SCAB. However, the JWPCP utilized pure-oxygen activated sludge treatment with off-gas controls on many aerated processes. These control devices could have led to actual emissions that were significantly lower than the uncontrolled emissions estimated for this study.

10. Chlorination of wastewater led to significant increases in the concentration of chloroform in the effluent streams of those MWTPs that post-chlorinate. On a statewide basis, chlorination could have increased chloroform emissions from 36 tpy to approximately 50 tpy.

11. Large uncertainties continue to exist regarding several key elements associated with emissions from POTWs. However, in order to reduce uncertainties, to improve emissions estimates, and to gain a better understanding of the factors that affect the fate of PTOCs in POTWs, additional sampling and research is needed.

## RECOMMENDATIONS

1. Collection Systems: The largest source of uncertainty in total emissions estimates stems from the potential emissions from collection systems. To reduce the uncertainty, sampling should be undertaken in collection systems. Collection system air exchange ("breathing") rates with the atmosphere need to be measured to determine whether significant air exchange with the atmosphere occurs.

2. Emissions at MWTPs with Significant PTOC Loadings: The identification of treatment facilities with specific processes that should be considered for future sampling are listed at the end of Appendix G of the report.

3. Pure-Oxygen Activated Sludge Treatment: Several of the MWTPs that were ranked highly as individual sources of PTOC emissions utilized pure-oxygen activated sludge treatment. Because those systems were covered and employed lower gas-to-liquid volume ratios than conventional activated sludge treatment processes, reduced PTOC emissions would be expected from such systems and emissions could be more readily controlled. A field study of the stripping efficiencies of conventional and pure-oxygen systems would be valuable.

4. Biodegradation as an Emissions Control Technique: Biodegradation could become a feasible method for reducing PTOC emissions during secondary wastewater treatment. Research to study the factors that affect acclimation could lead to physical, chemical, or biological treatment

modifications, e.g., sequenced batch reactor operation, which would increase the relative fraction of PTOCs degraded while reducing the fraction volatilized.

5. Production of PTOCs During Digestion: Biodegradation, particularly during anaerobic digestion, can lead to the production of PTOCs through sequential dehalogenation of other halogenated compounds. Emissions of PTOCs from anaerobic digesters should be investigated through field sampling. Knowledge of the degradation/formation process could be improved through laboratory or pilot-scale studies.

6. Off-Gas Control Devices: Spray scrubbers and activated carbon filters are control devices sometimes used to treat off-gases from those MWTPs equipped with covered treatment processes. Field studies to investigate the efficiencies of those devices are warranted.

7. Formation of Trihalomethanes: The formation of chloroform during and after chlorination can occur at MWTPs. The results of this study indicated that chloroform formation could be significant, not only with respect to emissions of chloroform prior to chlorination, but also to other known sources of chloroform. Field studies and laboratory studies regarding the formation of trihalomethanes and possibly other chlorinated organics would be valuable in order to identify important precursor compounds. Methods to remove precursors prior to chlorination, or to modify disinfection processes could then lead to reductions in trihalomethane formation and emission.

8. Volatilization from Effluent Outfall and Receiving Waters: The results of this study indicated that approximately 600 tons/year of PTOCs were discharged in the effluent streams of MWTPs. The potential emissions of those PTOCs from effluent conveyance channels and from receiving waters was not well understood. A large fraction of the PTOCs were discharged to the ocean, however, little is known about the roles of chemical and biological reactions in the degradation of PTOCs in an ocean environment. Large quantities of sludge, with additional semivolatile PTOCs, have also been placed in the ocean. If sludge deposits

have built up, it is conceivable that anaerobic decomposition will occur (probably at greatly reduced rates in comparison to sludge digesters) and produce bulk gas releases which might rapidly transport PTOCs to the ocean surface. Additional research in these areas should be undertaken if it has not already been completed.