CALIFORNIA AIR RESOURCES BOARD

CONTRACT NO. A732-085
FINAL REPORT
AUGUST 1991

Emissions of Volatile and Potentially Toxic Organic Compounds from Wastewater Treatment Plants and Collection Systems (Phase II)

Volume 1:

Project Summaries

State of California
AIR RESOURCES BOARD
Research Division

EMISSIONS OF VOLATILE AND POTENTIALLY TOXIC ORGANIC COMPOUNDS FROM WASTEWATER TREATMENT PLANTS AND COLLECTION SYSTEMS (PHASE II)

VOLUME 1 - PROJECT SUMMARIES

Final Report
Contract No. A732-085

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August 1991

ABSTRACT

The objectives of the Phase II research project on emission
of potentially toxic organic compounds (PTOCs) from wastewater
treatment plants were fivefold: 1) assessment of the importance
of gaseous emissions from municipal wastewater collection
systems; 2) resolution of the discrepancy between the measured
and estimated emissions (Phase I) from the Joint Water Pollution
Control Plant (JWPCP) operated by the County Sanitation Districts
of Los Angeles County (CSDLAC); 3) determination of airborne
concentrations of PTOCs immediately downwind of an activated
sludge aeration process at the City of Los Angeles' Hyperion
Treatment Plant (HTP); 4) a modeling assessment of the effects of
transient loading on emissions during preliminary and primary
treatment at a typical municipal wastewater treatment plant
(MWTP); 5) a preliminary investigation of effects of chlorination
practices on haloform production. The results of those studies
are reported in four separate volumes. Volume 1, for which this
abstract was prepared, contains a summary of results from each
project; Volume 2 contains the discussion regarding the modeling
of collection system emissions; Volume 3 addresses methods
development and field sampling efforts at the JWPCP and HTP, data
on emissions from a mechanically ventilated sewer and results of
some preliminary haloform formation studies in wastewaters; and
Volume 4 discusses aspects of the emissions modeling problem.

DISCLAIMER

ACKNOWLEDGEMENTS

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LIST OF ACRONYMS

ACB - activated carbon bed
ARB - California Air Resources Board
CI - Central Interceptor of Sacramento County
CFSTR - Continuous flow stirred-tank reactor
CSDLAC - County Sanitation Districts of Los Angeles County
EBMUD - East Bay Municipal Utilities District
EMI - El Macero Interceptor
GC/MS -   Gas chromatography/Mass spectrometry
HTP - Hyperion Treatment Plant
JWPCP - Joint Water Pollution Control Plant
MGD - Million gallons per day
MLD - Monitoring and Laboratory Division
MWTP - municipal wastewater treatment plant
PTOC - Volatile and potentially toxic organic (inorganic)
     compounds - 16 selected in Phase I:
     ACY - 2-propenenitrile (acrylonitrile)
     BZ - benzene
     BDCM - bromodichloromethane
     CT - tetrachloromethane (carbon tetrachloride)
     ClBZ- chlorobenzene
     TCM - trichloromethane (chloroform)
     DBCM - chlorodibromomethane
     EDC - 1,2-dichloroethane
     DCE - 1,1-dichloroethene (vinylidene chloride)
     ETBZ - ethylbenzene
     DCM - dichloromethane
     PERC - tetrachloroethane
     TOL - methylbenzene (toluene)
     TCA - 1,1,1-trichloroethane (methyl chloroform)
     TCE - trichloroethene (trichloroethylene)
     VC - chloroethene (vinyl chloride)
     additional compounds identified by GC/MS
     DCB - dichlorobenzene isomers
     LIM - limonene
     NAPH - naphthalene
     UND - undecane
SRWTP - Sacramento Regional Wastewater Treatment Plant
T-BACT - Toxics best available control technology
TPD - Volumetric turnovers per day for specific sewer reach
TPY - Tons per year (English)
UCD - University of California, Davis - Civil Engineering
VOC - Volatile organic compound - for the purposes of this study
     any compound in the wastewater captured in an air sample
WCS - Wastewater Collection System

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30   22
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I. INTRODUCTION and BACKGROUND

In 1987, the Department of Civil Engineering of the University of California, Davis (UCD) submitted to the California Air Resources Board (ARB) a Final Report (#A5-127-32) on the first phase (Phase I) of a study of emissions of volatile and potentially toxic organic compounds (PTOC) from municipal wastewater treatment plants (MWTP). This effort employed a "pseudo-mass balance" (mass difference) procedure for estimating the emissions from California's MWTPs, based upon the existant and somewhat limited historical database on plant influent and effluent concentrations and flows. The methodology basically assumed that for the sixteen compounds of interest, no loss other than volatilization from the plant occurred. This assumption was justified in the Phase I report on the basis of a review of the literature dealing with sorption and biodegradability of the compounds of interest. It was recognized that the emissions estimate would likely be conservative, but on the basis of engineering judgement, was thought to be within a factor of 2 to 4 for the statewide inventory.

At the time the inventory was compiled (1986), it was known that a large discrepancy between measured and estimated emissions existed at one of the largest treatment plants in California, which consequently introduced considerable uncertainty into the statewide inventory. Furthermore, there was essentially no basis for estimating emissions from collection systems, questions were raised with regard to whether significantly elevated emissions could even be measured downwind of a treatment plant, and the magnitude of haloform formation from in-plant chlorination practices was unknown. For the above reasons, the ARB supported a follow-on study (Phase II) to reduce the uncertainties in the emissions estimate. This report deals with results of the Phase II study.

The projects undertaken during the Phase II study were largely guided by the recommendations of Phase I. In particular,

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the first major objective of the current study was the assessment of the importance of collection system emissions. A second major objective of the study was resolution of the discrepancy between the measured and estimated emissions (Phase I) from the Joint Water Pollution Control Plant (JWPCP) operated by the County Sanitation Districts of Los Angeles County (CSDLAC). This plant was estimated to be the largest single source of emissions of the total mass of sixteen PTOCs on the basis of the pseudo-mass balance. It was thought that either the sampling methodology or the presence of activated carbon bed (ACB) odor control units on vent streams of aerated processes at the JWPCP would provide an explanation for the differences. Thus the Phase II objectives were limited to comparison with the CSDLAC's method of sample collection and analysis, and to measurement of emissions from the ACB units. A third major objective undertaken was to determine whether measurable increases in ambient concentrations occurred downwind of a treatment plant. For that reason, the second largest treatment plant in California, the Hyperion Treatment Plant (HTP) operated by the City of Los Angeles, was studied. The HTP was selected because of its unique geometry and position relative to upwind emission sources. Development of the sampling methodology to be used at both the JWPCP and the HTP was carried out in northern California in conjunction with the staff of the East Bay Municipal Utilities District's (EBMUD) plant in Oakland, and with the assistance of the ARB's Monitoring and Laboratory Division (MLD). The preparatory sampling study was undertaken to compare multi-sorbent tube and Tedlar bag methodologies. A fourth objective included an emissions modeling study. The purpose of that effort was to determine the effects of transient loading observed at MWTPs on emissions. This represented an extension of the modeling carried out in Phase I which assumed steady-state liquid phase concentrations (TEST model). Preliminary and primary treatment processes (headworks, aerated grit chamber, primary sedimentation basin, aerated channel) of a MWTP were modeled in order to have a more accurate tool to assess the magnitude of emissions from specific processes. (Figure 1-1

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illustrates typical processes present at a MWTP.) Lastly, a
preliminary investigation of the possibility of haloform
formation as a result of wastewater chlorination practices was
undertaken.

The objectives of the Phase II study were quite distinct
from one another, and do not lend themselves to treatment in a
single monograph. For that reason this report has been broken
down into four volumes. First, a general "Introduction and
Background" are provided for the report, and is combined in a
single volume (1) with a "Summary" of all conclusions and
recommendations from the entire study. A separate volume (2) has
been written as a stand alone report on "Wastewater Collection
System Emissions." The third volume (3) combines the
experimental measurements of emissions at the JWPCP and HTP
treatment plants, methods development at the EBMUD, and reported
measurements of emissions from a mechanically ventilated
collection system. In addition, preliminary experiments dealing
with haloform formation as a result of raw wastewater
chlorination are discussed. Volume 3 is entitled "Wastewater
Treatment Plant Emissions - Experimental Phase," and can be read
as a stand-alone document. Lastly, Volume 4 deals with aspects
of modeling of "Preliminary and Primary Treatment Processes
Emissions," from a typically configured MWTP.

Schematic of Processes at a Typical POTW

Notes:
sludge — — —
gas – – –
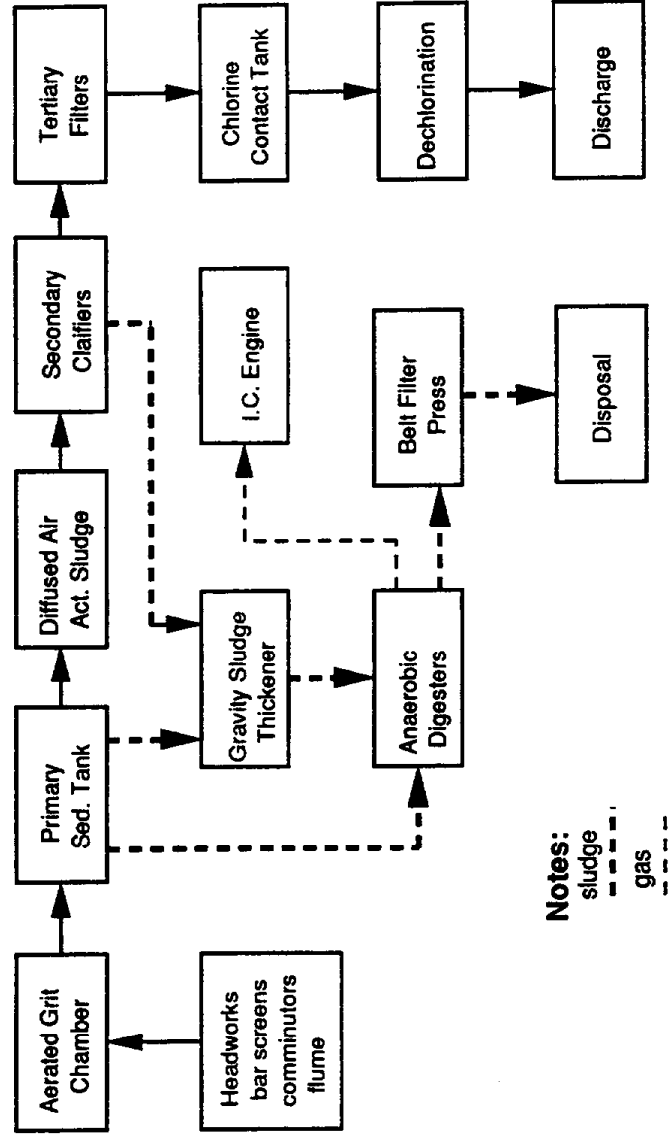
Figure 1-1. Schematic of POTW Treatment Train Illustrating Typical Processes

II. SUMMARY

A. VOL. 2 WASTEWATER COLLECTION SYSTEM STUDY

A major goal of the Phase II research program was an
improved understanding of the processes associated with VOC
emissions from wastewater collection systems (WCS). This
included an assessment of important factors that influence gas-
liquid partitioning from raw wastewater, and gas exchange between
the WCS and ambient atmospheres. Specific tasks undertaken were:
1) a computer-assisted literature review, 2) a theoretical (fluid
mechanical) assessment of gas ventilation associated with sewers,
3) a series of field experiments in operating sewers, 4)
development of a collection system model, based on results of
items 1 through 3, to assess the potential for VOC emissions over
a wide range of hypothetical scenarios, 5) application of the
model to a "typical" collection system from residence to
treatment plant for the purpose of estimating chloroform loss. A
summary of the findings from the collection system phase of the
research project follows.

Literature Review

Results of the literature review confirmed the earlier
findings that little work had been completed regarding the fate
(particularly gas-liquid partitioning) of VOCs in raw (untreated)
wastewater, or quantification of the mechanisms that affect gas
ventilation of WCS. Therefore there was almost no basis for
estimating collection system emissions.

Previous work sponsored by the USEPA (Levins, 1979)
indicated the major sources of specific VOCs to WCS, as well as
the average liquid-phase concentrations of some VOCs in
residential, commercial, and industrial sewers, and in the
influent streams of wastewater treatment plants. One important
observation from this data set was a significant reduction of
both the occurrence and concentration of trihalomethanes from tap

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water to residential sewers, suggesting significant volatile losses during residential activities, e.g. showers, and from building plumbing leading to a public sewer. (Note BDCM, TCM and BDCM concentrations in TAP and RES in Figure 1-2.) These results were later found to be consistent with modeling results undertaken as part of the present study. These findings suggest that conclusions regarding apportionment of sources of chloroform in an earlier ARB sponsored research effort (Rogozen, 1988) be re-examined. A second observation was the occurrence of highly volatile VOCs (e.g. carbon tetrachloride) in combined industrial sewers, with a complete absence of such compounds in treatment plant influents, suggesting significant removal of high volatility VOCs in a well-ventilated WCS. Losses of VOC from separated systems, the majority of sewers in California, would be lower.

Losses from the sewer can be thought of conceptually as a two step process: volatilization from the aqueous phase and ventilation of the gases from the sewer. A great deal of literature exists regarding hydrogen sulfide in sewers, with corresponding studies of oxygen transfer from sewer atmospheres to raw wastewater. Fortunately, because oxygen is a gas, hence highly volatile, theoretical estimates of the mass transfer rates of other VOCs out of the wastewater can be made based upon the amount of oxygen absorbed into the wastewater. As part of the experimental work on the sewers, predictions of oxygen transfer models were tested against measured volatilization rates.

Only two published works were identified whose intentions were to quantify the effects of natural ventilation mechanisms. Those studies were limited in the range of conditions that were addressed. Nevertheless, the factors which affect ventilation of a WCS had been identified as liquid drag, rise and fall of waste-water, eduction by wind blowing over building vents and manhole covers, barometric pressure gradients, differences in temperature between sewer and ambient atmospheres (buoyancy effects), and

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AVERAGE CONCENTRATIONS OF VOCs

IN SEWERS

AQUEOUS CONC. [µg/L]

30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0

Bz BDCM CT MCBz TCM DBCM DCA

COMPOUND

TAP RES COM IND INF
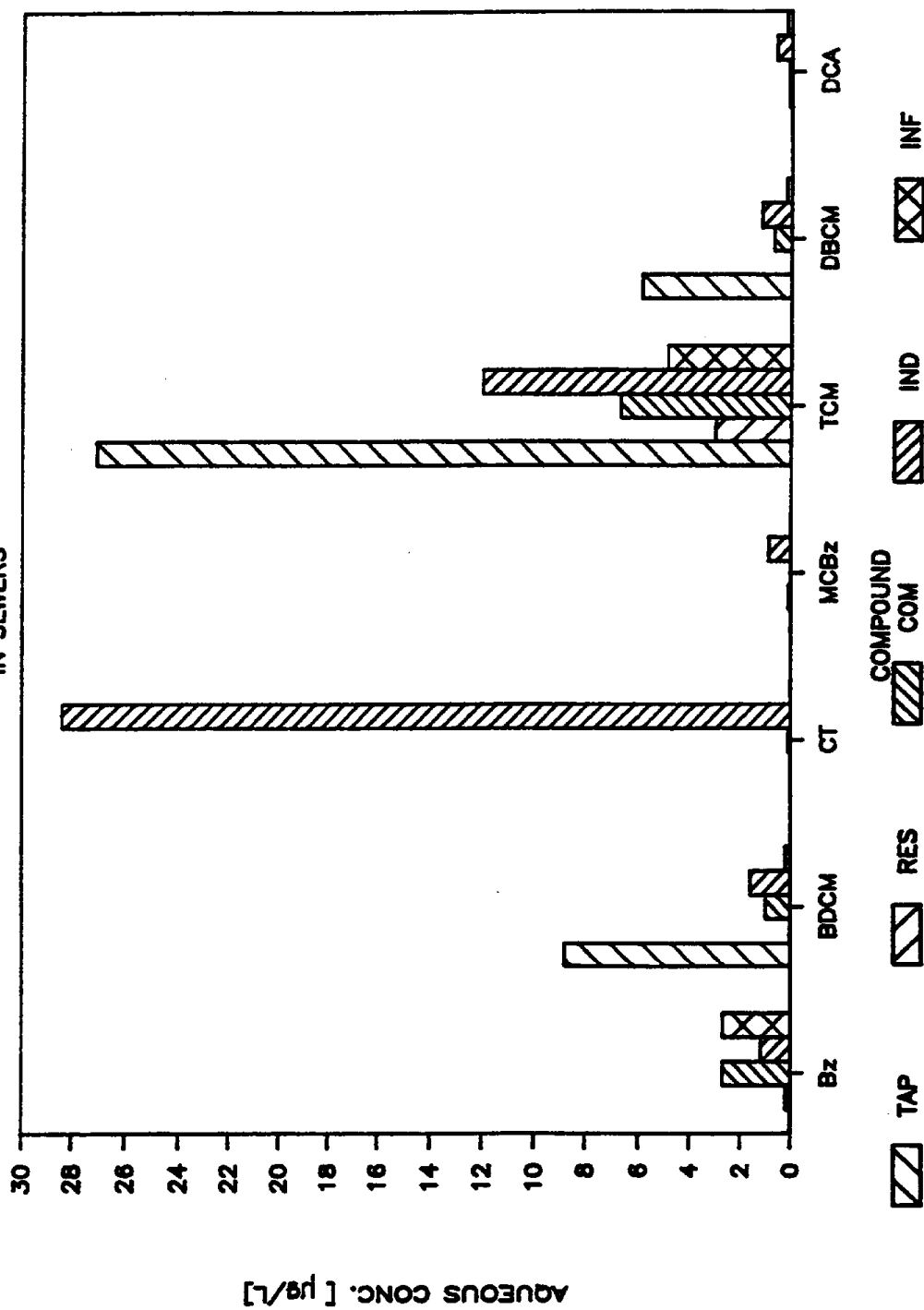
Figure 1-2. Average Aqueous Concentrations of VOCs in Sewers (Adapted from Levins, 1979).

changes in barometric pressure. (Barometric "pumping" was calculated to be minor).

Assessment of Gas Ventilation Associated with Sewers

A theoretical assessment of the ventilation mechanisms noted previously was completed by application of fluid mechanics principles to several hypothetical WCS configurations. Important conclusions were as follows:

1. Given the complexity of most collection systems, it is impossible to accurately calculate actual ventilation rates and gas flow patterns. For a specific sewer reach, release of an inert tracer can be used to estimate gas flow rates.

2. For combined sanitary/storm sewers, gas ventilation rates are likely to be high, and a simplifying assumption of infinite dilution (zero VOC concentration above wastewater) is often valid for emission estimation purposes.

3. For small diameter sewers with many vents, gas velocities should be relatively high. Examples include residential areas with many house vents. For such systems, infinite dilution can be assumed without significant loss of accuracy in emissions estimates.

4. For mid-to-large diameter sewers, particularly sanitary interceptors, gas velocity will be low relative to wastewater velocity. An assumption of infinite dilution is not valid except where forced-ventilation is applied.

5. Under conditions of relatively low resistance to ambient air inflow and sewer gas exhaust, liquid drag can induce maximum mean gas velocities of up to 0.2 m/s. Actual gas velocities in sanitary sewers are expected to be on the order of 0.04-0.2 m/s for small pipes (e.g., 0.25 m i.d.), 0.003-0.2 m/s for mid-size pipes (e.g., 1.0 m i.d.), and 0.005-0.18 m/s for large pipes (e.g., 2.5 m i.d.).

6. Based on typical wastewater depth changes in a WCS, rise and fall of wastewater establishes a lower bound on ventilation rates when other factors are unimportant. "Breathing" of the collection system can induce gas velocities on the same order as liquid drag for larger pipes, and approximately an order of magnitude lower than liquid drag for smaller pipes.

7. Barometric pumping is insignificant as a ventilation mechanism.

8. An assumption of infinite ventilation can significantly overestimate VOC emissions under conditions of low ventilation and/or for VOCs with low Henry's law constants. However, such an assumption may be valid and lead to a reduction in modeling complexity for compounds with high Henry's law constants and/or conditions of high ventilation. The latter condition of high ventilation rate should exist in combined sanitary/storm sewers, or in residential areas because of building vents or small collectors with many openings between the sewer and ambient atmospheres.

Experiments in Operating Sewers

Tracer experiments were completed in operating sewers in the City of Davis and County of Sacramento. Deuterated chloroform was injected into wastewater below one manhole and sampled from both liquid and gas phases at a downstream manhole. Samples were analyzed using GC/MSD, and results were used to back-calculate mass transfer coefficients between raw wastewater and the overlying sewer atmosphere. The two systems selected for study allowed for a wide variation in transfer coefficients. The resulting transfer coefficients were compared to estimates based on application of several oxygen transfer models (adjusted for differences between oxygen and chloroform) given inputs associated with conditions observed during field experiments (e.g., wastewater flow rate, depth of flow, temperature of wastewater).

A major conclusion stemming from field experiments is that existing models developed to describe oxygen absorption to either clean water or untreated wastewater can be adjusted to predict mass transfer coefficients for VOCs in wastewater. A model developed by Parkhurst and Pomeroy (1972), which was based upon oxygen transfer experiments in operating sewers, required no adjustment to account for differences between clean water and wastewater. It was found to be the most appropriate model in the literature based on a comparison of model results and experimental data. A clean water reaeration model attributed to

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O'Connor and Dobbins (1958) was found to yield the lowest coefficient of variation for the ratio of predicted to experimental transfer coefficients, but required application of an empirically determined average "alpha factor" (ratio of wastewater to clean water transfer coefficients) of 0.24.

Computational Modeling

A two-phase finite-volume model was developed to predict VOC partitioning and emissions from a WCS based on imposed gas ventilation rates and flow patterns. Mass was conserved in both the liquid and gas phases. The link between phases was interfacial partitioning as defined by the Parkhurst-Pomeroy model during uniform flow conditions, and an oxygen transfer model (adjusted for VOCs) developed by Nakasone (1986) for flow over drops (e.g., drops into pump station wet wells, drop manholes). The model was applied to several thousand hypothetical scenarios (combinations of influencing factors), and led to the following conclusions:

1. For large interceptors flowing with relative depths of greater than 0.5 and with small channel slopes, VOC removal for discharges which occur within 10 kilometers of a treatment plant are likely to be small relative to emissions at a plant of uncovered design. For the large interceptors, emissions are enhanced at shallower depths of flow or high ventilation rates (e.g., caused by blowers at headworks of a treatment plant). However, even at infinite ventilation, relative losses are likely to be low (e.g., less than 10%) for VOCs with Henry's law constant less than 0.5.

2. Discharge of VOCs to smaller interceptors located five kilometers or more from a treatment plant can lead to emissions comparable to those at the treatment facility. This is particularly true during periods of low wastewater flow, high ventilation flow rates, or for VOCs with high Henry's law constant.

3. If VOCs are discharged well upstream of wastewater treatment facilities and traverse building laterals and many smaller reaches with steep channel slopes prior to reaching an interceptor, cumulative emissions of VOCs are likely to be greater than those observed at a downstream treatment plant. This is true even for lower volatility compounds

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such as chloroform, and is particularly true for VOCs which are degraded during wastewater treatment (e.g., benzene and toluene).

4. Extensive relative removal (greater than 50% of the total collection system loss) of a VOC is likely to occur following potable water discharge to building laterals leading to street sewers. Model predicted chloroform loss during a typical 13 km, "residence-to-plant" scenario was approximately 23%. (See Figure 1-2A.)

5. Relative removal from short reaches of sewer (i.e., less than two kilometers) with moderate to low channel slopes (i.e., less than 0.005 m/m) should not exceed 50% unless absolute depth of flow is very low (i.e., less than 0.2 m), even with moderately high ventilation rates.

6. Rapid VOC accumulation in sewer atmospheres can lead to low VOC losses from drops, unless high ventilation rates are present (e.g., forced ventilation at wet wells).

7. For a given mass discharge of VOC, total emissions can be substantially higher during periods of low flow in comparison to periods of high flow. Thus, to control emissions from collection systems, discharges from known sources of VOCs should be limited during periods of low flow. This finding may require reassessment by POTWs of the impacts of current practices that encourage industrial discharges at night for the purpose of flow equalization, especially if buoyancy-induced ventilation is likely.

8. Elevated wastewater temperature (e.g., 40 $^{\circ}$C as opposed to 20 $^{\circ}$C) significantly increases VOC emissions (by up to a factor of nearly two) by increasing a VOC's mass transfer coefficient and Henry's law constant, as well as by increasing buoyancy-driven ventilation.

9. Little is known regarding competing removal mechanisms in sewers. A wide range of first-order decay constants was applied for aerobic and anaerobic biodegradation. Results indicated relatively small impacts on total VOC emission reductions (less than 14% reduction at high rate constants) over a two kilometer sewer reach.

10) Data supplied by a POTW regarding sewer vent emissions (presented in Volume 3) reinforces the notion that significant emissions can and do occur in specific instances from vent points along a sewer system. Although these emissions represent a small portion of the total quantity of compound carried by the collection system, they can lead to locally elevated ambient concentrations.

Sewer Model Schematic Diagram
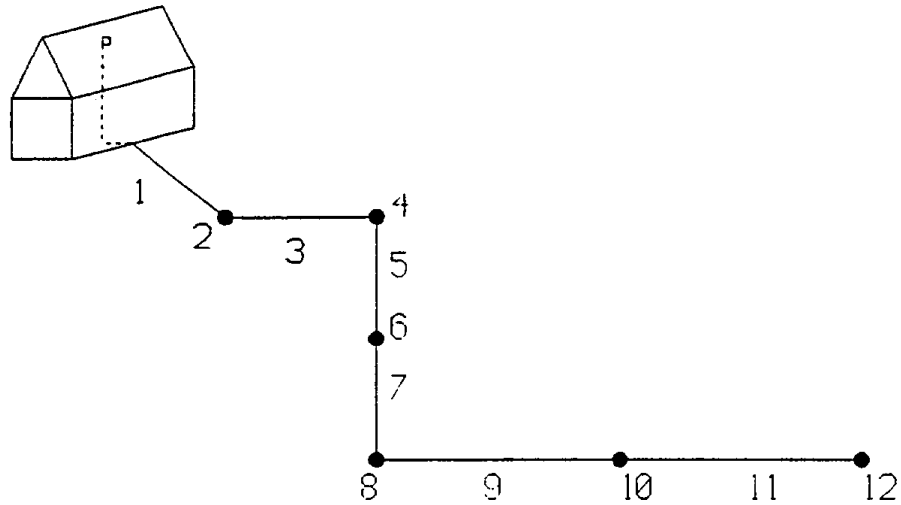
Sewer Model Concentration Distribution

Concentrations at end of Segment
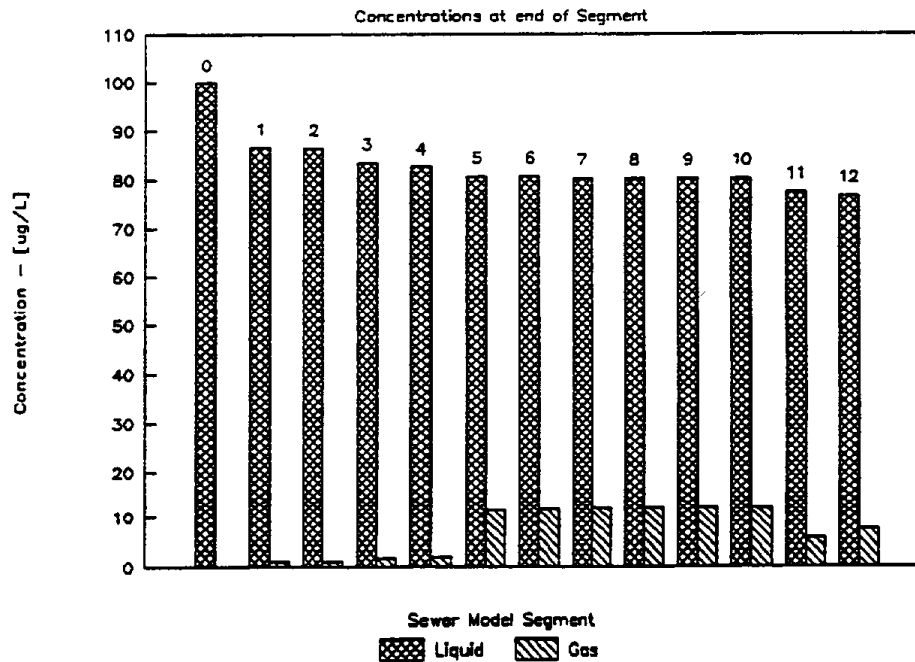
Figure 1-2A. Model Predicted Chloroform Loss from a Typical
13 km Sewer Reach.

Recommendations for Future Research

For accurate system-specific emission estimates, data
regarding mass loadings from all major dischargers, time profiles
of wastewater flows in various segments of the system, detailed
information on physical characteristics of the system, and
information regarding wastewater temperature would be required.
Even then, a lack of information or ability to reliably estimate
ventilation flow rates in various portions of a system could
negate the accuracy of such a data-intensive effort. Thus, it
may be more appropriate to concentrate on evaluation of a few
major dischargers and associated reach-by-reach emissions
estimates, and/or analysis of potentially elevated emission
points (outlined in full report). The following recommendations
for research are not directed solely to the air regulatory
agencies, but also for the purpose of improving the knowledge
base associated with VOC emissions from wastewater collection
systems in general:

1. An emphasis should be placed on identifying major
dischargers of toxic VOCs to sewers, quantifying mass
release of speciated VOCs from those dischargers. Such
information is needed for developing source control
strategies. Subsequently, quantification of physical
characteristics of the discharge pipe, connection to a
public sewer, and characteristics of the sewer from point-
of-discharge to a downstream treatment facility can lead to
an estimate of the emission rates from the collection system
to the ambient air.

2. Field experiments should be completed to evaluate gas-
liquid partitioning at areas of agitated wastewater that
were not studied directly during this study. Areas of
potentially high transfer rates include drops, transitional
junctions of two reaches, and areas of changing slope
(particularly from steep to lower channel slope).

3. Additional experiments are needed to develop a means of
easily predicting gas ventilation rates from sewers.
Preliminary experiments completed for this study suggested
the possibility of employing routine gas-phase oxygen
measurements to estimate ventilation flows for individual
sewer reaches. Used in conjunction with a model of mass
transfer in a sewer, such as the one used in this study, it
may be feasible to back-calculate the ventilation rate.

4. Wastewater collection systems, particularly segments associated with residential areas and commercial laundries should be considered for inventories of chloroform emissions. Studies of in-home and in-sewer formation of chloroform following the use and discharge of chlorine bleaches are also recommended. Such studies could reduce the uncertainty of an earlier chloroform inventory which discounted the importance of collection system losses.

5. On the basis of the collection system study and the monitoring and modeling results, innovative, enforceable rules need to be developed to encourage upstream source control that prevents both the escape of pollutants to the atmosphere from the collection system as well as at the treatment plant. It is suggested by the authors that such rules allow credits for source reductions in a conceptually similar manner to "bubbling" rules.

6. Based upon the quantities of PTOCs conveyed through major wastewater collection systems, it is conceivable that ex-filtration of liquid from the collection system represents a source of groundwater contamination. Water pollution control agencies may want to determine the significance of collection systems as potential contaminant sources.

B. VOL. 3 EMISSIONS MEASUREMENTS

Two additional goals of the Phase II study were a) the resolution of the discrepancy between the CSDLAC measurements of the JWPCP's emissions and the pseudo-mass balance estimate of the JWPCP's emissions during Phase I, and b) determination of whether measurable increases in ambient concentration could be observed across a treatment plant. Before field measurements were made a method validation study of the sorbent tube sampling technique was conducted in collaboration with the EBMUD. Subsequently, measurements of concentrations of PTOCs into and out of activated carbon bed (ACB) odor control units at the CSDLAC/JWPCP were undertaken. Ambient concentrations of PTOCs were also measured downwind from the activated sludge aeration basins at the HTP during two field sampling efforts. Measurements of emissions from a mechanically ventilated sewer were also provided by a POTW. Lastly, preliminary measurements of haloform formation in chlorinated raw wastewaters were obtained in one of the County of Sacramento's sewers, and from laboratory chlorination experiments of raw wastewaters.

EBMUD Sorbent Tube Validation Study

Both the UCD sampling team and the East Bay Municipal Utilities District (EBMUD) staff had selected multi-sorbent tube sample collection (modified VOST) over Tedlar® bag sampling. Although successful use of multi-sorbent tube sampling had been reported for incinerator (James, et al., 1986), indoor air (Hodgson et al., 1986), and ambient air sampling (Anonymous, 1986), to our knowledge, no method validation studies had been performed for wastewater treatment plant emission streams. In such an environment, high humidity and strong oxidizing (chlorine) or reducing agents (sulfides) can be present. A collaborative sampling effort was undertaken to gather data that could be used to validate the modified volatile organic sampling train (MVOST) method.

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Side-by-side sampling was conducted on both an emission source (pure-oxygen reactor vent) and from gas standards. Sorbent tube samples (TENAX-TA/Ambersorb) were collected by EBMUD staff in accordance with their MVOST protocol (Appendix A, Modified Method 0030; EBMUD, 1989). Samples were analyzed by the EBMUD (a certified wastewater lab) by thermal desorption into a GC/MS. The UCD team collected Tedlar bag samples using ARB Method 201 and samples were returned to the ARB's Monitoring and Laboratory Division for analysis by GC/ECD for chlorinated species. The results of the multi-sorbent tube and bag sampling comparison were favorable, with the multi-sorbent tubes yielding slightly higher recoveries for most compounds, especially for the compound with the highest boiling point, PERC (approximately 50% greater recovery, b.p. 121 $^\circ$C). Because of artifacts produced during the UCD sampling effort at the JWPCP using the TENAX-TA/Ambersorb tubes, additional laboratory studies were conducted to compare commercially prepared TENAX-TA/Ambersorb tubes (T.R. Associates) with Carbopak/Carbosieve$^\circledR$ tubes (Supelco). In our hands, the latter multi-sorbent tubes exhibited lower blank backgrounds and reduced tube-to-tube variability.

Emissions Study of Activated Carbon Adsorbers at the JWPCP

The UCD sampling team conducted emission studies at the JWPCP treatment facility in three stages. The first study (Stage I) involved the sampling of a large number of compounds, including benzene, immediately upstream and downstream from a freshly recharged activated carbon bed (ACB) used for odor control (DS-4) and additional units which had been in service for periods of at least several months, DS-5 and DS-28. This study was carried out for comparison with the earlier findings of the CSDLAC regarding ACB breakthrough and emissions. The temporal variation of ACB collection efficiency was followed over a period of about one and a half months on three separate sampling dates. The second study (Stage II) examined only benzene concentrations immediately upstream and downstream of the same ACB odor scrubber

during a 24-hour diurnal cycle, after the bed was essentially saturated for benzene by previously collected VOC emissions. The third study (Stage III) involved a four-day, semi-continuous, diurnal sampling for benzene from the headspace above the preliminary treatment grit chambers.

The results of the UCD sorbent tube study (Stage I) supported the earlier findings of CSDLAC staff. Basically, the UCD data confirmed that the carbon beds became saturated with VOCs over relatively short periods of time and breakthrough of some compounds, such as dichloromethane, occurred quickly (within a week). The data indicated that collection efficiency appeared to change quickly with time, especially for the more volatile chlorinated compounds. Negative (more material exiting the ACB than being introduced) or low collection efficiencies were noted for both low and high volatility compounds from saturated carbon beds, DS-5 and DS-28, during the initial sampling effort.

The DS-4 unit was monitored for a one and a half month period following regeneration. As it became saturated, its collection efficiency for higher boiling point compounds decreased slowly from essentially 100%; however, the collection efficiency for some lower boiling point compounds had already become negative. The simultaneous presence of both positive and negative collection efficiencies was indicative of a saturated bed containing compounds that competed for sites on the sorbent. Because low volatility, higher molecular weight compounds usually have a greater affinity for the adsorbent, the negative collection efficiencies observed for some compounds during the extended tests are interpreted as a general trend of low molecular weight compound displacement.

Figure 1-3 is a representation of the DS-4 activated carbon bed efficiency for compounds that exhibited distinct peaks on the GC/MS chromatograms, and illustrates the displacement phenomenon;

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Figure 1-3
3-D Representation of the DS-4 ACB Efficiency
for Various PTOCs
(ACB Efficiency vs. Time in Service, vs GC retention time)
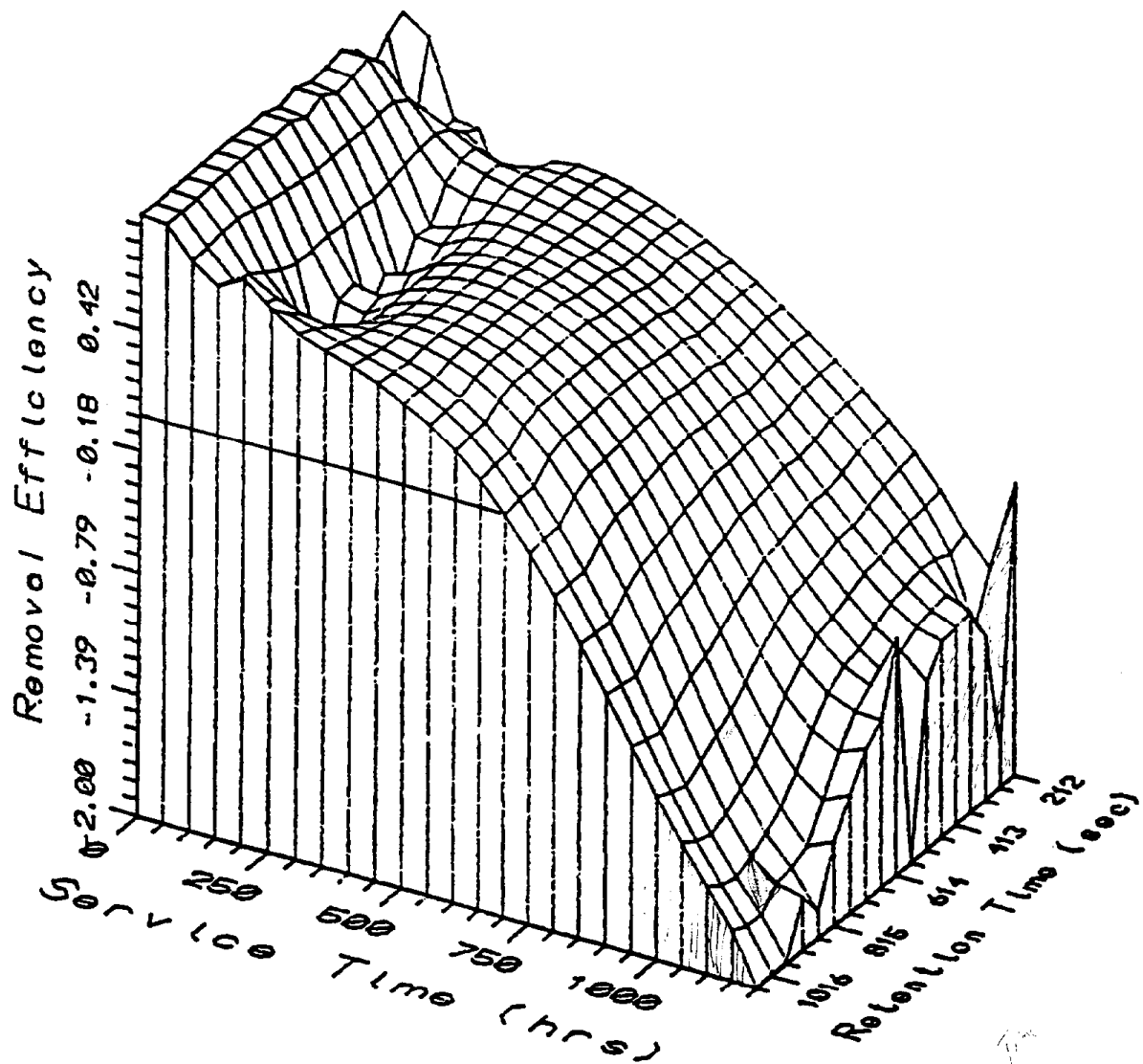
bed efficiency is plotted on the Z axis, versus length of time in service on the X axis, versus GC retention time on the Y axis. (Retention time increases moving toward the reader.) Note in particular that breakthrough (where removal efficiency drops below zero on the Z axis) for relatively volatile compounds (characterized by the short GC retention times on the Y axis) occurred within 48 hours. Readers are cautioned that the data shown in the figure have been smoothed somewhat by the plotting algorithm as a result of the fact that only four discrete sampling points are represented on the time axis; nevertheless, the plot illustrates the trends observed.

In a few cases, at a particular point in time, some of the higher volatility compounds were retained with greater efficiency than lower volatility compounds, indicating that factors other than volatility played a role in ACB collection efficiency. It appeared that the ACB regenerated modest sorptive capacity for the high volatility compounds during periods when relatively clean gas passed over the bed. Within the 1200 hour sampling period, the bed had ceased to function as an effective reactive organic gas (ROG) control device for practically all compounds even though the bed remained effective for purposes of odor control. (The reason for this is that the carbon promotes oxidation of H_2S rather than simply serving as an adsorbent.)

Semi-continuous monitoring of the inlet and outlet streams from the ACB was then conducted using a portable GC/PID during Stage II. A twenty-four hour sample, revealed that the concentration of benzene (BZ) in the headspace above the grit chambers varied with the time of day. The first sampling trip results yielded a very interesting diurnal fluctuation; the concentration ranged from less than 100 ppb at night to nearly 30 ppm during one morning peak. (See Figure 1-4.) Although breakthrough of BZ had long since occurred, the ACB did act to damp out the peak concentration. However, during periods of

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Figure 1-4
The 24 Hour Fluctuation in Benzene Concentrations
Inlet and Outlet of DS-4 (Change in Scale)
(JWPCP Stage II Study)

JWPCP – Diurnal Benzene Emissions

Concentration vs. Elapsed Time

Elapsed Time from 16:30 (minutes)
(Thousands)

□ Inlet   + Outlet

Concentration (ppb)
(Thousands)
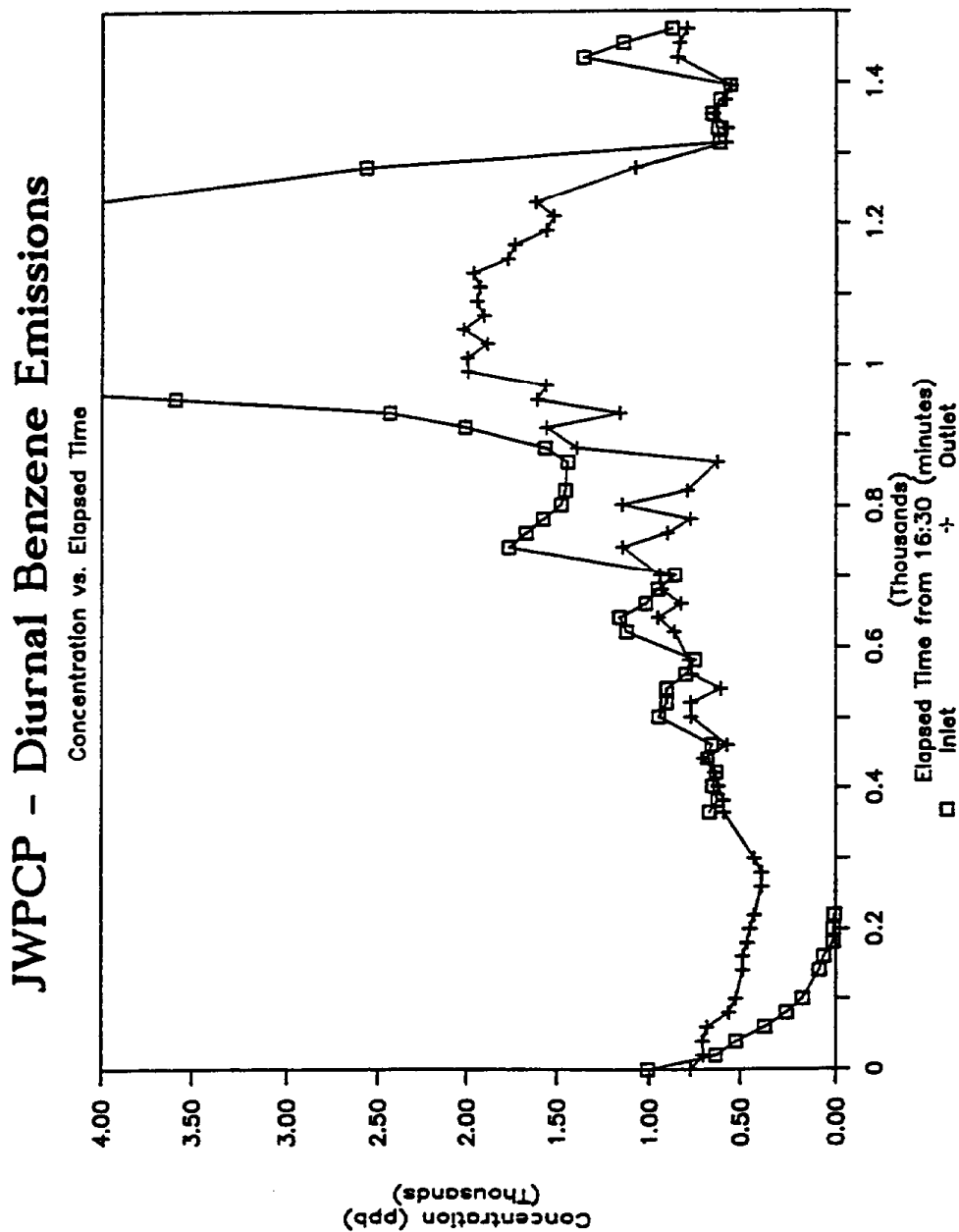
relatively clean influent gas, the concentration of BZ in the
effluent from the ACB was greater than that entering. Sampling
occurred during the interval between Christmas and New Year, thus
results may not have been representative, and additional sampling
was conducted for a longer period of time in February.

During the Stage III study, BZ concentrations were measured
in the off-gases from each of three major interceptors at the
headworks of the plant. (See Figure 1-5.) The data indicated a
degree of regularity of diurnal cycles of loading in all three of
the interceptors, but the interceptor off-gases did not exhibit
identical concentrations, the two order-of-magnitude range in
concentrations was not observed, nor were temporal patterns
identical to those noted in the December JWPCP Stage II study.
Higher concentrations still appeared in the morning hours during
February. Concentrations of BZ in the three headworks gases
varied from about 2 to 8 ppm during the four-day test period in
February, 1989, a concentration at least a factor of two greater
than the average indicated by an earlier CSDLAC sampling effort
in the same vicinity of the plant (Caballero, 1989).

The data obtained from the JWPCP showed that many of the
PTOCs of concern (such as DCM, TCM, and BZ) were being eluted
from exhausted ACBs. As a consequence of the uncertainty of
influent loading rates, ACBs would probably need to be replaced
or regenerated relatively frequently if they were to serve as a
PTOC control measure. From the observed system behavior, it can
be inferred that if ACBs are to be economical PTOC control
devices at MWTPs, they will need to be designed as regenerable
systems and possibly monitored. Upstream source control of
industrial discharges of BZ to the sanitary sewer system appeared
to be the control strategy of choice for BZ at the JWPCP. The
economics and feasibility of alternative means of control should
be examined closely, before requiring ACBs as T-BACT control
systems for MWTPs in general.

Figure 1-5
Influent Loading Concentrations Above Grit Chamber 6
(JWPCP Stage III Study, Automated Sampling GC/PID).

JWPCP Diurnal [Bz] Above Grit Chamber 6

2/13/89 - 2/17/89 UCD Results (GC/PID)

Benzene Concentration (ppb) (Thousands)

Time (Hour of Day)

□ 2/13   + 2/14   ◇ 2/15   △ 2/16   × 2/17
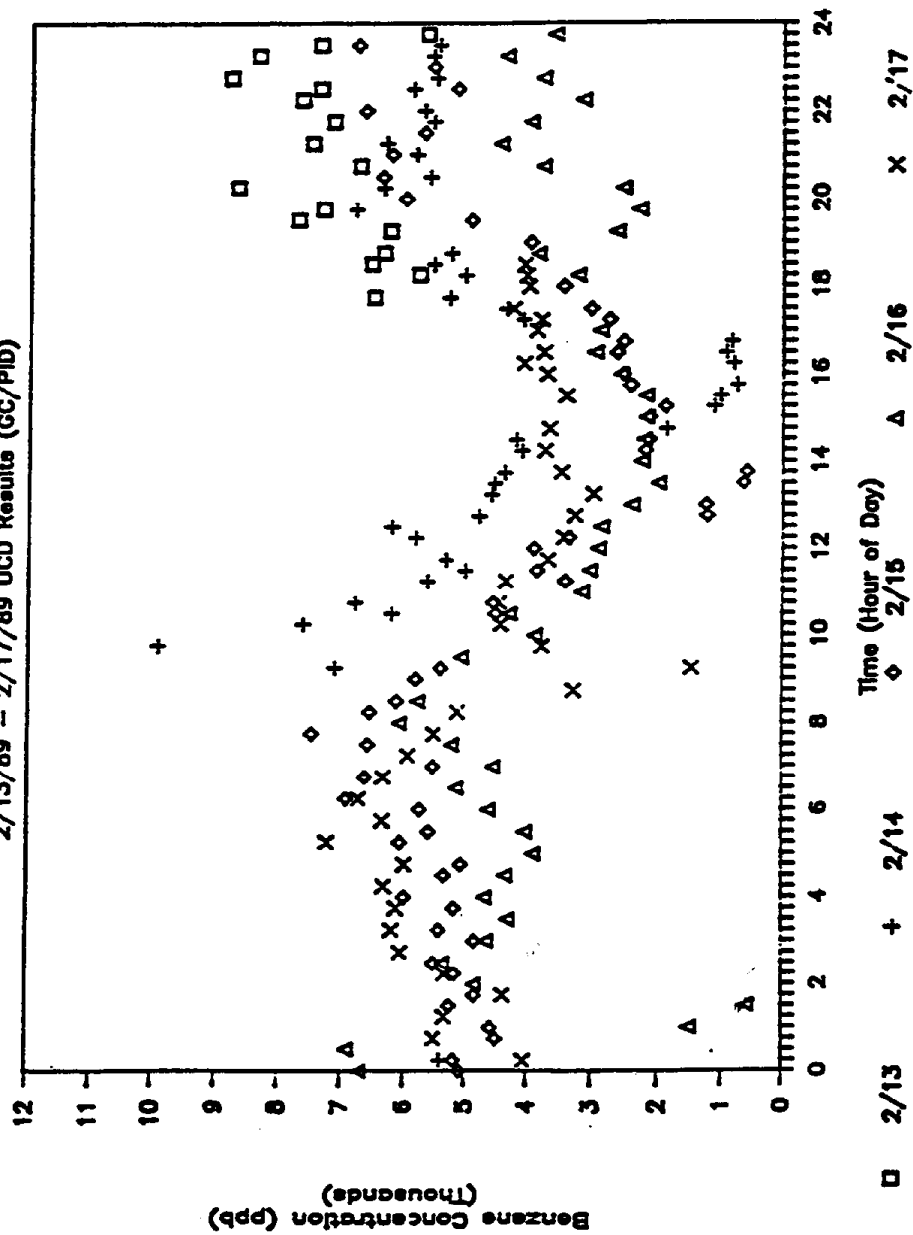
Reconciliation of Phase I and CSDLAC Measured Emissions

During the Phase II study of the JWPCP emissions, additional test data on influent liquid concentrations and measured air emissions became available for comparison with the pseudo mass balance method used to estimate emissions in Phase I. Those data are summarized in Table 1-1a,b,c,d. As can be seen from the "new" (Phase II) data in Table 1-1a, the average measured influent concentrations during the measurement period September 20 to October 25, 1989 (seven 24-hour composite samples) differ from the Phase I averages by as much as a factor of 20 for TCE, but for most compounds the differences are within a factor of 4, some compounds being higher and some being lower. Taking all of the measured compounds that were also part of the Phase I study together, the average of the ratio of Phase I to "new" Phase II data is 0.56 or within about a factor of 2. These data illustrate the nature of the uncertainties in emission estimates at MWTPs that result from variability in plant loading.

Using the more recent influent data and the CSDLAC reported emissions estimates shown in Table 1-1b- (Caballero and Griffith, 1989), the ratios of "measured" emissions to Phase I and Phase II "estimated" emissions can be formed. The Phase II estimated emissions utilized the new liquid influent data, but assumed the same fractional loss as observed from the Phase I study. As shown in Table 1-1c, these ratios differ from the Phase I and II estimates by as much as a factor of 20 for BZ to nearly unity for the more volatile, less degradable compounds such as TCA and PERC. Using modeling results (discussed in Volume 4 and in Volume 3 Appendix A) for losses at similar preliminary processes from the headworks area of the plant, i.e. bar screens and aerated grit chamber, and using Phase I and Phase II influent data, a comparison can be made with the CSDLAC total measured emissions, as shown in Table 1-1d. In this case the losses, even for the degradable compounds such as BZ, are in closer agreement with the total plant losses.

Table 1-1a
Comparison of Phase I and New (Phase II) Influent Measurements

Compound	Average Influent Concentration Phase I [μg/L]	Phase II [μg/L]	Ratio Influent Phase II/Phase I [-]
BZ	120.0	189.0	1.58
ETBZ	40.0	11.5	0.29
TOL	395.0	100.0	0.25
DCM	360.0	39.0	0.11
TCE	4.5	0.2	0.05
TCA	44.0	23.0	0.52
TCM	12.7	17.5	1.38
PERC	37.0	12.6	0.34
Average			0.56

Table 1-1b
New (Phase II) JWPCP Emission Estimates

Compound	Phase II [mtpy]
BZ	2.7
ETBZ	N.R.
TOL	3.4
DCM	4.2
TCE	2.3
TCA	N.R.
TCM	N.R.
PERC	2.6

Total plant measured values from Caballero
and Griffith (1989).

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Table 1-1c
Comparison of Measured Gas Phase Emissions With Pseudo-Mass
Balance

Compound	Pseudo Mass Balance Phase I [TPY]	Phase II* [TPY]	Measured/Phase I [-]	Measured/Phase II [-]
BZ	29.6	47.2	0.10	0.06
ETBZ	4.0	1.1	N.R.	N.R.
TOL	125.0	31.3	0.03	0.12
DCM	121.0	13.3	0.04	0.35
TCE	2.5	0.1	N.R.	N.R.
TCA	5.5	2.9	0.46	0.87
TCM	2.6	3.6	N.R.	N.R.
PERC	5.9	2.0	0.48	1.43
Total (Avg)	296.1	101.5	0.22	0.57

*Assumes same fractional loss across plant as in Phase I but
using "new" (Phase II) influent data.

Table 1-1d
Comparison of Emissions Based on Influent Loading and Preliminary
Processes Model-Estimated Losses

Compound	Modeled Losses for Phase I [TPY]	Phase II [TPY]	New JWPCP JWPCP/Phase I [-]	Measured/Model JWPCP/Phase II [-]
BZ	3.5	5.6	0.85	0.53
ETBZ	0.9	0.3	N.R.	N.R.
TOL	10.6	2.7	0.35	1.39
DCM	7.9	0.9	0.58	5.13
TCE	0.2	0.01	N.R.	N.R.
TCA	1.2	0.6	2.11	4.22
TCM	0.3	0.4	N.R.	N.R.
PERC	3.7	1.3	0.77	2.20
Total (Avg)	28.3	11.81	0.93	2.69

An explanation for the poor agreement between the measured emissions from the JWPCP and the Phase I emissions estimate can be formulated as follows. The JWPCP is somewhat unique among California treatment plants in that it has covered primary tanks whose headspace gases are essentially isolated and unvented except for negligible losses through the cover. Furthermore, the JWPCP uses pure oxygen for biological treatment, minimizing total gaseous emissions and has covers over the secondary clarifier weirs. These two factors result in most of the emissions of the degradable compounds such as BZ, TOL, ETBZ and XYL at the headworks of the plant. Relatively small amounts of BZ were captured by odor control units given the frequency of carbon replacement at that time. Thus the model-estimated headworks emissions for BZ and TOL appear to be in closer agreement with the total measured emissions from the plant. On the other hand, non-degradable compounds not lost at the headworks, for the most part pass through the biological treatment process, so that the modeled loss at the headworks, in most cases, are a smaller fraction of the losses from the entire plant. The modeled preliminary processes' losses exceed the reported measured losses by about a factor of 2. The overall agreement between the non-degradable compounds and the pseudo-mass balance approach for the entire plant overestimates the measured losses by about a factor of 2. An additional contribution to the magnitude of the uncertainty in the pseudo-mass balance approach applied to the JWPCP is the fact that only a portion of the wastewater is subjected to secondary treatment. Thus, there are substantial concentration of PTOCs remaining in the plant effluent (a blend of primary and secondary treated wastewater) which in turn results in a larger error in the mass difference caused by subtracting two numbers of the same magnitude. It is also known that the JWPCP receives a heavier load of wastewater from nearby refineries and waste activated sludge from upstream treatment plants. It is possible that the waste activated sludge and refinery wastewater represent separate phases at the headworks

and in the primary sedimentation basin. Partitioning of VOCs into these phases would also reduce emission rates predicted by stripping models that do not account for such phenomena.

The consequences of the explanation given above are the following:

1) The Phase I PTOC inventory for the State and Los Angeles County should be revised downward to reflect the lower emissions resulting from biodegradation of compounds which were assumed to be non-degradable in the pseudo mass balance approach. The simplest method for doing so would be to accept the CSDLAC values as being representative of actual emissions with an uncertainty of about a factor of 2. The change to the State inventory will be significant because TOL and DCM represented two of the largest estimated mass emissions from the JWPCP, and that facility was the estimated to be the largest single source of emissions in the State.

2) For the other MWTPs in the State, the pseudo-mass balance method is believed to be relatively accurate for non-degradable compounds (within a factor of 2), but more conservative for degradable compounds. Most facilities in the State have uncovered primaries, aeration basins, and weirs so that greater losses from volatilization are expected, than occur at the JWPCP.

In addition to the JWPCP findings, evidence for the biodegradability of arenes, e.g BZ, TOL, XYL and ETBZ, common constituents of wastewater, is mounting. Significant degradation was apparent in the data from EBMUD's pure oxygen unit and from the Ontario Ministry of the Environment study (Bell, 1988). The HTP data (discussed below) indicate that even in well aerated basins, significant degradation of benzene was likely and competed effectively with stripping as a removal mechanism. This occurred at liquid concentrations that, from the literature, would be interpreted as being too low to result in organism acclimation. This is an area requiring further study by the wastewater community.

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Emissions from the HTP Activated Sludge Aeration Basins

Two sampling efforts were undertaken at the City of Los Angeles' HTP for the purposes of determining whether ambient concentrations of PTOCs could be measured downwind of a MWTP. The HTP had been selected for study because of its favorable geometry for upwind/downwind sampling. The HTP is situated on the coast, with a minimum of upwind sources during sea-land breeze regimes. The longitudinal axes of its activated sludge aeration basins are aligned along the wind direction during certain portions of the day, and sampling was scheduled to coincide with those periods. For modeling purposes, the emissions from the aeration basins can be treated as a series of infinite cross-wind line sources approximating a rectangular area source. For the purposes of this study, emissions were treated as uniform and the terrain as flat. In reality buildings were present at the west end of the basin, and bluffs rose abruptly at the east end of the basin. The latter may have resulted in a "lifting" of the flow at the east end of the basin.

During the first trip in June of 1989, two identical 10 m sampling masts were centered and erected approximately 18 m apart along a north-south axis at the east end of the aeration basins, with gas samples drawn at the 2, 5 and 10 m levels. During the second sampling trip in October of 1989, a single sampling tower and instrumented meteorological tower were used, centered on the north-south axis, 2.5 m apart and moved westward from the east end of the basins approximately 38 m.

During the June sampling trip, difficulties were experienced with the GC/MS analysis of the samples. Thus, while meteorological conditions were favorable and good tracer data were obtained, quantitative data on airborne concentrations of only a few compounds were obtained. During the October sampling trip, meteorological conditions were unfavorable, and problems were encounter in the execution of the tracer experiment, but the GC/MS analyses were more complete. Fortunately, among the data

sets obtained, some reasonable conclusions regarding emissions from the aeration basins could be drawn.

1) For compounds commonly associated with wastewater and not expected in vehicle exhaust or ambient air coming off the ocean, e.g. DCM, TCM, PERC, LIM, DCB, UND, etc., concentrations downwind of the aeration basins were a factor of ten or higher than those measured in the upwind air.

2) The airborne flux of non-biodegradable compounds, e.g. PERC, through an imaginary plane at the downwind side of the aeration basins was in agreement (within experimental error) with the estimated flux from measured liquid phase concentrations, Henry's coefficients, aeration rate, and an assumption of bubble saturation. For partially degradable compounds the measured concentrations were significantly lower, in particular, BZ emission was about a factor of 40 less than calculated assuming complete volatilization.

3) Based upon the few PERC measurements that were made, emissions from the HTP were within a factor of two (lower) of the Phase I estimated emissions, solely from the secondary aeration basins.

4) For the "typical" afternoon seabreeze conditions encountered during the June sampling trip, the average dilution factor observed at the top of the sand dune on the east end of the aeration basin for periods of about one-half hour was about 6 to 7.

5) Some very large peaks of unidentified low boiling point compounds were observed in the upwind samples drawn on the beach. The only plausible source of these compounds were tankers moored perhaps a thousand meters offshore. An investigation of tanker off-loading and venting practices may be warranted.

Activated Carbon Beds on Operating Sewers

Besides the ACB odor control units at the JWPCP, the CSDLAC also operates ACB odor control units on sewer systems. Data were obtained from a CSDLAC in-house study of a mechanically ventilated portion of a sewer during the period April, 1988 to December 29, 1988. These data were quite extensive and obviated the need for additional measurement of ambient sewer atmospheres.

The observed behavior of ACBs on the sewer vent was similar to that of the odor control units at the JWPCP, i.e. initially high removal efficiency followed by rapid loss of capacity for lighter VOCs.

The observed gas concentrations and mass emission rates reinforced the concept that there exists potential for elevated emissions at mechanically ventilated points in the collection system, although as a fraction of PTOCs in the wastewater the emissions remain small. A rough estimate of the airborne BZ concentration in the vented sewer gases was about 100 ppb (or roughly 300 $\mu g/m^3$). It is noted that a dilution factor of over 1000 would be needed to reach an estimated lifetime cancer risk of 1 X 10^{-5} ($5.3X10^{-5}$ $\mu g^{-1}m^3$, unit risk factor).

Emissions Estimates Based Upon PEEP Factors

Additional sampling of aerated grit chambers at the JWPCP and diffused air activated sludge aeration basins (ASAB) were undertaken during the period April through July, 1990 as part of the Pooled Emission Estimation Program (PEEP, 1991). The purpose of these samples was to develop emission factors for use at similar treatment processes as allowed under Assembly Bill 2588. Although not an official requirement of the current study, ARB staff requested that comments be provided regarding the PEEP report where applicable. A summary of conclusions regarding the PEEP emission factors for grit chambers and ASABs is given here; additional discussion and comments are contained in Volume 3 and Volume 4, Appendix I. A direct comparison of emission factors for the grit chambers at the JWPCP is not possible because liquid phase concentrations were not measured during the UCD air sampling. Comparison of ASAB emission factors is based upon similar diffused air aeration basins.

Concentrations of off-gases during PEEP measurements of grit chambers at the JWPCP were lower than those encountered during the UCD sampling trips to the JWPCP. The manner in which samples

were drawn during the PEEP study (presence of an ice-bath impinger ahead of the gas sample bag) suggests that the PEEP emission factors for grit chambers underestimate actual emissions for semi-VOCs. (The term VOC is used loosely, and corresponds to compounds with boiling points below about 100 ^{o}C.) The extent to which the PEEP factors also underestimate VOC emissions is unknown. A study to determine the fractional removal efficiency of calibration gases through an ice bath impinger, in the presence of wastewater off-gases, would be needed to assess possible losses in the PEEP sampling train.

The two compounds TCM and PERC were selected from the PEEP sampling of ASABs for comparison purposes because a) they were present in all of the air samples; b) they were not considered to be biodegradable; and c) they were not strongly sorbed compounds. The PEEP liquid data clearly indicated a greater loss from the ASAB than the corresponding air samples by approximately a factor of 2, with almost total removal of PERC from the liquid. As noted previously, the PERC air sampling data are suspiciously low. The PEEP data indicated that the liquid-phase fraction of TCM removed was lower compared to PERC. These observations appear to be in rough agreement with the HTP ASAB sampling results which indicated that TCM emissions were relatively less than those of PERC. Based upon the average TCM and PERC liquid concentrations in the HTP basins on October 17th, the removal efficiencies from the ASAB were approximately 20% and 220%, respectively. (Note that a removal efficiency of greater than 100% is possible based upon the average liquid concentration, e.g. a removal efficiency of > 200% would result if exponential decay and plug flow were assumed with 99% removal by the end of the ASAB!) The PEEP TCM emission factor was comparable to, but greater than that computed for the HTP based on the UCD data. Because liquid TCM concentrations were near detection limits at the HTP, within experimental error, the average PEEP TCM emission factor of 30% does not differ from that measured at the HTP ($\approx$ 20%). However, the PERC emission factor (41%) was low compared

to both the PEEP liquid data and to the HTP measurements. Again, we are led to the conclusion that the PEEP emission factors based upon air samples underestimate the emission rates of semi-VOCs and possibly some of the higher boiling VOCs.

Chloroform Formation During Wastewater Chlorination

Chlorination of wastewater is practiced at municipal wastewater treatment plants (MWTP) for a variety of reasons, including odor control of raw wastewaters and disinfection of treated wastewater prior to discharge. On occasion, chlorine is added directly to sanitary sewers in order to control odor problems. The formation of chloroform in such systems has not been as thoroughly studied as for drinking water, the yields of chloroform formed are known only approximately, and are known to be wastewater-composition dependent.

Two preliminary studies of chloroform formation were undertaken as part of the current research contract. The purpose of these measurements was to determine the magnitude of the potential problem. The first was simply a grab sample of sewage and sewer gas, upstream and downstream of a chlorinator on a County of Sacramento sewer. Regarding the possibility of chloroform formation, it could only be said that at most there appeared to be a doubling in the concentration, which was still quite low ($\approx 3~\mu g \cdot L^{-1}$). The molar ratio would be approximately 0.0002 based upon a target 8 $mg \cdot L^{-1}$ Cl_2 target dose. Although the travel time in the sewer between the sampling points was only of the order of five minutes so that the full haloform potential may not have been realized, based on the literature, the concentration would not have increased much more than an additional factor of 2 or 3. Thus we conclude that only minor amounts of chloroform were formed (< 0.1% incorporation of the chlorine added). These observations are consistent with literature reports that chlorine (or hypochlorous acid) reacts

essentially instantaneously with inorganic compounds such as sulfides and reduced metal ions.

Additional samples of wastewaters were chlorinated and analyzed as part of a study for the Pooled Emissions Estimation Program/Bay Area Air Toxics (PEEP/BAAT) groups (Chou et al., 1990). In these studies, either screened raw wastewater or secondary effluent (nitrified and non-nitrified) buffered to pH 7.6-7.8 were dosed with 5 mg/L or 15 mg/L of chlorine. Trihalomethane formation was greatest in nitrified secondary effluent, ($\approx$ 150 μg/L or 1.3 μM after one hour). Concentrations in non-nitrified or raw wastewater were over a factor of 10 lower. These results were consistent with the literature. For the case of nitrified secondary effluent, the molar ratio was about 0.02 for the low chlorine dose and 0.01 for the higher chlorine dose.

The above results suggest that chlorination of raw sewage produces relatively lesser amounts of haloforms. The exact amount depends upon competition with inorganic species such as reduced sulfur, metals, and ammonia. On the other hand, chlorination of nitrified secondary effluent does appear to produce haloforms at levels about an order-of-magnitude greater than non-nitrified effluent. This would suggest that a study of air emissions from the chlorine contact chamber of a wastewater treatment plant that practices nitrification of secondary effluent be undertaken. Furthermore, the use of chlorine in two-stage packed tower odor control units (acidic first stage followed by basic second stage) has been reported to result in increased chloroform concentration in the effluent gas compared to the influent. Such a phenomenon, if it occurs, is consistent with ammonia removal by an acidic first stage followed by haloform formation under basic conditions in the second stage. Further research is needed to determine whether wastewater odor control units that apply chlorine actually increase chloroform emissions, and if differences exist among application methods.

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C. VOL. 4 MODELING VOLATILE ORGANIC COMPOUND EMISSIONS DURING PRELIMINARY AND PRIMARY TREATMENT

Preliminary and primary treatment steps commonly found at most wastewater treatment plants include bar screens, comminutors, and Parshall flumes in the "headworks" area, and grit removal, primary sedimentation and conveyance channels in the "primary" portion of a plant. The fate of volatile organic compounds (VOC) in preliminary and primary treatment is determined by the design and physical operation of such facilities, physico-chemical properties of the VOCs and environmental conditions. There is evidence that significant amounts of these compounds are emitted during preliminary and primary treatment (Chang et al., 1987; USEPA, 1986; Pellizzari, 1982; Petrasek et al., 1983). Selection of appropriate alternative treatment or control strategies should be based upon knowledge of the quantities of VOCs emitted and sensitivity of emission rates to operating parameters, information which is generally unavailable. The purpose of this portion of the Phase II study was to develop models that could be used to determine the importance of individual stages in the preliminary and primary operations sequence with respect to VOC emissions. Included in the study was selection of candidate operations for design or operational modification to minimize emission rates. Emission models for each unit were constructed and evaluated using time varying inputs that simulated typical diurnal loading rate variations. (In the earlier Phase I study, only steady-state inputs could be examined by the TEST model.)

Use of models requires physico-chemical data. It was determined during the course of this study that numerous values of the Henry's coefficients exist in the literature. Exactly which value to use was not at first evident. Therefore a brief study of methods for evaluating Henry's coefficients was also undertaken.

Modeling Approach

Volatilization was assumed to be the only significant removal mechanism for VOCs during preliminary and primary treatment. Previous studies indicated that volatilization dominates both adsorption and biodegradation during these portions of the treatment sequence (Pellizzari, 1982; Petrasek et al, 1983; Dobbs et al., 1989; EBMUD, 1989). Each stage or unit in the treatment train was modeled as either a single continuous-flow stirred-tank reactor (CFSTR), or as a cascade of CFSTRs. Units having short detention times and high degrees of mixing such as Parshall flumes and grit chambers were modeled as a single CFSTR while units having significant longitudinal dispersion, such as sedimentation tanks, were described as cascades.

Because only high volatility compounds were of concern in this project, liquid phase resistance was assumed to control mass transfer rates. Infinite dilution was assumed for volatilization from surfaces open to the atmosphere. However, accumulation of VOCs in rising gas bubbles was taken into account.

Three approaches were evaluated to estimate overall mass transfer coefficients, $K_La,_{VOC}$, for volatilization from surfaces open to the atmosphere: 1) modification of expressions derived for stream reaeration, 2) application of waterfall aerator expressions, and 3) application of an expression developed for aeration occurring over weirs. The results from all three models fell within the same order of magnitude and appeared to be similar to results obtained from monitoring results from full scale facilities (Pincince, 1989; Bell et al., 1988; Berglund and Whipple, 1987; Petrasek, 1983)

Coarse bubble aerators having an oxygen transfer efficiency of six percent were assumed to be used in both the grit chambers and conveyance channels. The value of $K_La,_{O2}$ was calculated using the fractional saturation expression derived for mass

transfer from or into individual rising bubbles given a mean bubble size (Meyerhofer, 1989). A natural reaeration model developed by Tsivoglou and Neal (1976) was used for conveyance channels without forced aeration. Other relationships gave similar values.

Mass transfer at weirs was modeled using an energy gradient approach, an expression for waterfall aerators, and an expression developed from aeration studies on weirs. The highest and lowest mass transfer coefficient values estimated by these methods differed by a factor of approximately five, with the weir expression giving the highest values. Emissions at weirs were found to be significant in all cases and therefore correct evaluation of losses at weirs is extremely important. Current AB 2588 emission inventory estimation efforts by various groups should yield data needed for this purpose. Because adequate data were unavailable to evaluate the models, only results from application of the energy gradient approach are presented here.

Emission Model Components

A computational model based on second order Runge-Kutta integration algorithms was used to simulate VOC emissions. The model was structured to allow non-steady state volumetric and organic loadings and had flexibility to add or delete treatment components. In order to estimate emissions from a treatment sequence, reference unit processes were sized based on an existing treatment facility in Los Angeles. Influent design flow was 6.60 $m^3 \cdot s^{-1}$ (150 MGD).

Emissions rates were determined for three VOCs at 20 $^\circ$C in order to give a range of Henry's coefficient: trichloromethane (TCM), trichloroethene (TCE), and tetrachloromethane (CT). Emission rates for each VOC were assumed to be independent of other solute concentrations, with a total VOC emission load equivalent to a summation of individual VOC emission rates. Typical daily flow and concentration curves were used in the

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models and annual emission rates were estimated with no
consideration for seasonal flow and concentration variation.

Emissions rates for VOCs were estimated for a steady
influent flow and concentration, steady flow and time variant
concentration, and time variant flow and concentration
conditions. Daily averages for influent flow and VOC
concentration were 6.6 $m^3 \cdot s^{-1}$ (150 MGD) and 100 $\mu g \cdot L^{-1}$,
respectively. Emission estimates for the three VOCs studied were
based on identical integrated products of influent flow and
concentration.

Results of Preliminary and Primary Treatment Modeling

Losses of VOCs from bar screens, comminutors, and Parshall
flumes were predicted to reach steady state in less than one
hydraulic detention time. Because of the rapid approach to
steady state, VOC losses from headworks units were estimated to
be a constant fraction of the unit influent concentration. Daily
and annual emission rates were assumed constant for the range of
flows and concentrations studied. Typical percent removal and
daily and annual VOC emission rates for bar screens, comminutors,
and Parshall flumes in the reference treatment facility are shown
in Table 1-2.

Both constant and variable loading patterns were used with
average flow rates and influent VOC concentrations of 6.6 $m^3 \cdot s^{-1}$
and 100 $\mu g \cdot L^{-1}$ respectively. Weirs at the end of the grit
chambers and sedimentation tanks were treated as separate units.
The variable influent loading rates and emissions response of the
primary units for TCM are shown in Figure 1-6. Typical percent
removal and daily and annual VOC emission rates for grit
chambers, sedimentation basin, weirs and conveyance channels in
the reference treatment facility are shown in Table 1-2.

Table 1-2
<u>Typical VOC Emission Estimates for Preliminary and Primary Treatment</u>
<u>Units</u>

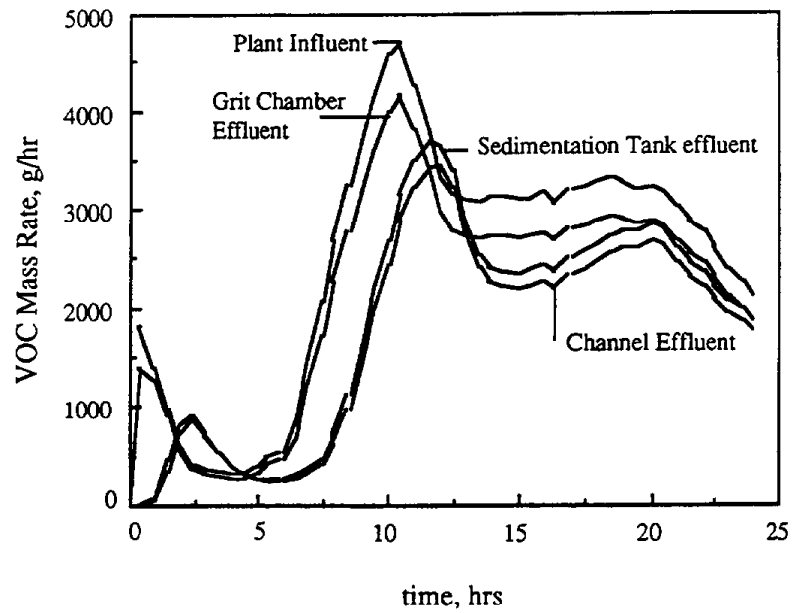| Unit,	Detention time - [s]	Headloss, [m]	$K_La,_{VOC}$ [hr^{-1}]	% Removed	Emission Rate [kg dy^{-1}]
Bar Screen	0.3	0.15	205	1.7	0.9
Comminutors	1.7	0.10	24	1.1	0.7
Parshall Flume	3.3	1.0	124	10.2	5.6
Grit Chamber	3.4-5.2	--	1.8	7.7	2.3
Sedimentation	60-100	--	$6.1-7.2 \times 10^{-4}$		<0.05
Weirs	0.007	0.3	636	3.4	1.9
Aerated Channel	4.6-6.8	1.0	0.3	1.1	0.6

Figure 1-6. Hydraulic and VOC loading rates in the liquid phase illustrating response of the primary treatment train. Note that liquid concentrations decrease from process to process, and exhibit "lagged" response. Differences in liquid phase concentrations reflect, in part, emissions to the atmosphere as well as dilution into existing capacity.

Overall emissions predicted during preliminary and primary treatment were approximately 25 percent of influent VOC load. The effect of transient loading upon the overall integrated emissions estimate was negligible. Major losses occurred in Parshall flumes, aerated grit chambers and at weirs. Not all MWTP have these units, therefore the emissions will vary from MWTP to MWTP. Losses from non-aerated tanks and conveyance channels were negligible relative to other units. Emissions predicted for headworks steps were small, but not negligible. Predicted emission losses from the headworks and the overall reduction of an influent VOC by the reference primary treatment sequence are consistent with preliminary results of a tracer study and emission measurements at municipal wastewater treatment facilities (EBMUD, 1989; Caballero, 1989).

Henry's Law Coefficients

Consistent estimates of emission rates of specific compounds from model results require that consistent compound-specific values of physico-chemical parameters be employed. An attempt was made to evaluate Henry's law coefficients. Quantitative Structure Activity Relationships (Kier and Hall, 1986) were examined for their utility in predicting and identifying outlying values. Although the effort to predict Henry's coefficients using molecular connectivity indices was of marginal value, the study demonstrated that considerable variability in Henry's coefficients exists for common PTOCs, and that the recent values of Gossett (1987) appear to be the best available for C_1-C_2 chlorinated hydrocarbons of environmental interest.

III. Considerations for Emission Control Strategies

Emission control options for POTWs include: 1) upstream source control, 2) reduction of in-plant toxics formation, 3) covering treatment units, 4) collection of off-gases followed by treatment, 5) facility modifications, e.g. submerged weirs, launder depth controls, and elimination of aeration. Application of a combination of these control techniques can be used to decrease VOC emissions from a POTW. However, it is clear that the choice of cost-effective controls is MWTP dependent. Determination of toxics best available control technology (T-BACT) will need to recognize differences in influent loadings and process stream configurations. For example for plants already having covered primary and pure-oxygen activated sludge (POAS) secondary units, T-BACT might consist of covering the headworks areas and combustion of POAS off-gases. For a plant equipped with a trickling filter, upstream source control and air-stripping at the headworks into a control system might be considered T-BACT. Flexibility in the permitting process is also needed to encourage replacement or modification of a plant to enhance both air and water pollution concerns, e.g. a POAS process appears to significantly reduce air emissions, and could be coupled to a combustion system to destroy any remaining recalcitrant compounds.

Upstream source control would appear to be a method of choice for certain compounds and situations because control of a pollutant is typically more efficient in a simpler mixture and prior to rather than after dilution. Furthermore, upstream control obviates concerns for losses from the collection system. For example, at the JWPCP, it is clear from the temporal loading patterns of benzene that upstream control of refinery wastewater discharges would lead to reduced loadings and would subsequently lower elevated air concentrations at points where the sewer vents. Furthermore, the bulk of some compounds discharged to a sewer, e.g. α-methylstyrene or tetrachloroethene (PERC), may be associated with industrial activities and amenable to source

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control, whereas other compounds may have more diffuse sources, e.g. toluene in consumer products. Upstream source control of PERC might further prove to be beneficial because it is relatively non-biodegradable, surviving aerated biological treatment; hence a significant fraction of the original waste discharged to sewers is ultimately released to the environment unless it is removed and controlled at the MWTP. However, it should be noted that PERC occurs in consumer products, so that a case-by-case evaluation of the efficacy of industrial or commercial source control is needed unless consumer product formulations change.

Prevention of in-plant formation by process modification, e.g. chloroform (TCM) by changing oxidizing agent, might prove worthwhile if coupled with source reduction. However, the effectiveness of upstream source control of TCM, e.g. by changing water disinfection practices, is still in question because the TCM formation potential of chlorine bleaches in household and commercial laundry applications remains undetermined. For other compounds such as toluene, prevention of volatilization prior to biological treatment might be effective since it appears to be readily degraded, even in a diffused air activated sludge system. Incorporation of such techniques will in some cases allow treatment plants to operate without off-gas collection and treatment.

Key regulatory issues regarding control strategies are 1) how to provide incentives to the POTWs to enhance source control and 2) how to provide a prioritization of compounds needing control, so as to channel public resources toward significant reduction of health risks. Emission reduction credits, supported by historical records of reduction of influent mass loadings would be one procedure to address the former issue.

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