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

Volume 3:

Wastewater Treatment Plant Emissions - Experimental Phase

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 3 - WASTEWATER TREATMENT PLANT EMISSIONS - EXPERIMENTAL PHASE

Final Report
Contract No. A732-085

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ABSTRACT

Volume 3 describes the measurements and experimental data obtained to assess emissions from various points within a POTW. Included are a discussion of sampling methods development, emissions studies of activated carbon bed odor control units located at various points of a large municipal wastewater treatment plant and its collection system, upwind/downwind sampling from an activated sludge aeration basins at a large municipal wastewater treatment plant, and preliminary studies of haloform formation as a result of chlorination of wastewater.

DISCLAIMER

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The California Air Resources Board and their staff have been supportive of our efforts over the past years. Mr. Bob Okamoto of the Monitoring and Laboratory Division carried out analyses of the bag samples for the EBMUD method comparison study and provided us with calibration gases. He and Kevin Mongar also participated in the sampling for chloroethene and SF_6 at the Hyperion Treatment Plant during the June effort. We will always remember the friendship and efforts of our former research project manager, Mr. Joseph R. Pantalone. Mr. Ralph Propper has capably taken over that task. We are thankful for his assistance, encouragement, patience and faith that it would be completed!

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- ACB - Activated carbon bed
- ARB - California Air Resources Board
- ASAB - Activated sludge aeration basin
- CC - Carbopak/Carbosieve™ multi-sorbent tube packing
- Chemical Acronyms
  - BFB - bromofluorobenzene (MS standard)
  - BZ - benzene
  - BZALD- benzaldehyde
  - CT - tetrachloromethane (carbon tetrachloride)
  - ClBZ - chlorobenzene
  - TCM - trichloromethane (chloroform)
  - EDC - 1,2-dichloroethane
  - DCB - dichlorobenzene isomers
  - DCE - 1,1-dichloroethene (vinylidene chloride)
  - DCM - dichloromethane
  - DEC - decane
  - ETBZ - ethylbenzene
  - IPB - isopropylbenzene
  - LIM - limonene
  - NAPH - naphthalene
  - PERC - tetrachloroethane
  - SF_6 - sulfur hexafluoride, an inert tracer gas
  - TCA - 1,1,1-trichloroethane (methyl chloroform)
  - TCE - trichloroethene (trichloroethylene)
  - TMB - trimethylbenzene
  - TOL - methylbenzene (toluene)
  - UND - undecane
  - VC - chloroethene (vinyl chloride)
  - XYL - dimethyl benzene isomers (xylene)
- CSDLAC - County Sanitation Districts of Los Angeles County
- DAF - Dissolved air floatation unit
- EBMUD - East Bay Municipal Utilities District
- ECD - Electron capture detector
- FAI - UCD Facility for Advanced Instrumentation
- GC/ECD - Gas chromatography/electron capture detector
- GC/FID - Gas chromatography/flame ionization detector
- GC/MS - Gas chromatography/mass spectrometer
- GC/PID - Gas chromatography/photo-ionization detector
- HRT - Hydraulic residence time
- HTP - Hyperion Treatment Plant
- ISCLT and ISCST - Industrial Source Complex dispersion models
- JWPCP - Joint Water Pollution Control Plant
- LAX - Los Angeles International Airport
- MGD - Million gallons per day
- MLD - Monitoring and Laboratory Division
- MSD - Mass selective detector
- mtpy - Metric tonne per year
- MVOST - Mini Volatile Organic Sampling Train
- MWTP - Municipal Wastewater Treatment Plant
- PTOC - Volatile and potentially toxic organic (inorganic)
- SASS - Source Assessment Sampling System
- SRWTP - Sacramento Regional Wastewater Treatment Plant

TA - Tenax/Ambersorb multi-sorbent tube
THM - Trihalomethanes (trichloromethane, bromodichloromethane, dibromochloromethane, tribromomethane)
TIC - Total ion count (or chromatogram)
T-BACT - Toxics Best Available Control Technology
TPY - Tons per year (English)
UCD - University of California, Davis - Civil Engineering
USEPA - United States Environmental Protection Agency
VOC - Volatile organic compound - for the purposes of this study any compound in the wastewater captured in an air sample
VOST - Volatile Organic Sampling Train

I. Introduction

Volume 3 is entitled "Wastewater Treatment Plant Emissions - Experimental Phase," and can be read as a stand-alone document. This volume combines all of the experimental efforts conducted by the Department of Civil Enginering at the University of California, Davis (UCD). It includes experimental methods development at the East Bay Municipal Utilities District (EBMUD), measurements of emissions from activated carbon beds (ACB) at the Joint Water Pollution Control Plant (JWPCP) and on a mechanically ventilated sewer, measurements of emissions from activated sludge aeration basins (ASAB) at the Hyperion Treatment Plant (HTP), and preliminary experiments dealing with haloform formation as a result of raw wastewater chlorination.

Each of these mini-studies had different objectives. Therefore they are presented in their entirety in separate sections of this report in the above stated order. An overall summary of results is presented at the end of this report along with conclusions and recommendations.

Two of the goals of the Phase II study of emissions of volatile and potentially toxic organic compounds (PTOC) included a) resolution of the discrepancy between the County Sanitation Districts of Los Angeles County's (CSDLAC) measurements of the (JWPCP) emissions and the pseudo-mass balance estimate of the JWPCP emissions performed as part of Phase I, and b) determination of whether measurable increases in ambient concentration of PTOCs could be observed across a treatment plant. Possible explanations for the difference in the emissions estimate from the JWPCP by "pseudo" mass balance and by CSDLAC measurement are presented. To address item (b) the City of Los Angeles' HTP was selected for an "upwind/downwind" study of its ASABs. Results of that sampling effort indicate that above ambient concentrations of compounds stripped from the ASABs can be observed downwind of large treatment plants.

II. EBMUD Sorbent Tube Validation Study

A. Background

Measurement of the emissions of PTOCs from municipal wastewater treatment plants (MWTP) involves a varied and complex set of physical source configurations. The applicability of common sampling and analytical methods currently in use for industrial operations have limitations when applied to POTWs because of the physical layout of emission points at a MWTP, the relatively low PTOC concentrations, the complex matrix of compounds, the presence of corrosive substances, the spatial and temporal variability of concentrations and the diffuse nature of the emissions.

This section of the report describes commonly employed sampling methods and discusses considerations that were taken into account in selecting the sampling methodologies used during this study. The three most commonly applied methods for collecting PTOC samples from MWTPs employ the use of: Tedlar® bags, sorbent tubes, or inert rigid containers, e.g. "Summa-polished" canisters. These sample collection media can be used for either grab or integrated sampling. Because PTOCs can be of concern at the low parts-per-billion by volume (ppbv) range in ambient air, concentration of an MWTP's emissions is usually necessary so that established analytical techniques will be able to detect and quantify the PTOCs. Emissions from MWTPs can also exhibit highly corrosive properties because of the presence of hydrogen sulfide, sulfur dioxide, chlorine (and chlorinated compounds), or other oxidants; thus, sampling equipment and sample preservation methods must be capable of operating in a corrosive environment. Furthermore, analytical techniques must provide for the quantification of a wide range of PTOC concentrations, and must be able to discriminate among compounds that may be present simultaneously and of similar chemical nature. Because a large number of samples must often be drawn within a short period of time, a sampling methodology that permitted sample storage for periods up to several days was desirable.

1. Tedlar® Bags

Tedlar® bags are composed of a relatively impermeable fluorocarbon polymer, and have been used to sample VOC emissions from numerous types of industrial facilities. Use of Teflon® or stainless steel valves allow for collection of PTOCs in the presence of a relatively non-reactive surfaces. Samples are usually drawn into the Tedlar® bag by placing the bag in an air-tight chamber and evacuating the chamber, creating negative pressure and causing the sample to flow into the bag. (See California Air Resources Board, 1985) Typical sample volumes collected should fill the sample bag approximately 1/2 to 2/3 full to minimize sample dilution with any gas that may have remained in the bag after cleaning, yet still allow enough excess capacity in the bag for thermal expansion.

Because the Tedlar® bag material is transparent, care must be taken to avoid exposure of the sample to sunlight during collection or storage, in order to deter potential photo-induced chemical reactions within the bag. Tedlar® bags have been demonstrated to exhibit some degree of permeability for low molecular weight compounds such as chloroethene (vinyl chloride); however, even the concentrations of benzene samples of 5-200 ppm have been noted to decrease by 7.5% over storage periods of 150 hours (California Air Resources Board, 1984). In addition, Tedlar® bags do not exhibit good storage characteristics for organic species such as alcohols (Johnson, 1986). For use at a MWTP, Tedlar® bags containing samples must be transported in an opaque container and returned to the laboratory for analysis as quickly as possible. The bags are subject to pin hole leaks that are sometimes difficult to detect. However, because bags can contain many times the volume of sample needed for one analysis, they possess the advantage that replicate sample analyses may be run to ensure analytical precision, and the bags are relatively inexpensive.

2. Sorbent Tubes

Sorbent tubes allow low concentrations of PTOCs to be collected on specialized adsorbents; the samples can then be desorbed thermally or by solvent extraction to provide a higher concentration for subsequent analysis. Typical sample volumes drawn across the sorbent tubes range from 100 mL to greater than 20 L, depending upon the concentration of the compounds being sampled. Larger sample volumes are typically used for dilute concentration gases, e.g. ambient air concentrations to concentrate the gas and improve analytical response.

Typical adsorbents are synthetic resins or carbons such as Tenax®, XAD-2, Carbotrap™ or Carbosieve™ that were developed for chromatography columns. Manufacturers provide many types of sorbent tubes that are generally tailored to collect specific PTOCs of choice most efficiently; thus, sorbent material selection should be tailored to the compounds being sampled. Activated carbon has the drawback that it also adsorbs water, and capacity can be lost in high humidity streams such as those found at MWTPs. Furthermore, the presence of too much water vapor upon desorption can lead to analytical difficulties depending upon the analytical procedure applied, e.g. direct thermal desorption into a gas chromatographic column.

The original volatile organic sampling train (VOST) system was developed by the USEPA to collect low concentration samples (ppbv), and consists of a fairly elaborate sampling train. The original VOST system consisted of heat traced sampling lines, and two sorbent canisters in series (the first containing Tenax GC and the second containing a 50:50 ratio of Tenax GC followed by activated charcoal). A modified mini-VOST method (MVOST) was also developed and results of a validation study of its use as a

VOC sampling method for hazardous waste incinerator emissions have been presented (James et al., 1986). The MVOST system is a simplified, rugged and compact sampling system that was developed to collect samples of 100 ppbv range concentrations. The sorbents studied by James et al. included: Tenax®, a polymer resin; Ambersorb® XE-340 and Ambersorb® XE-347, synthetic carbonaceous spheres; and Spherocarb, a carbon molecular sieve. James et al., indicated that Tenax® sorbents were most effective at capturing and releasing low volatility compounds, while Spherocarb® was most effective at capturing high volatility compounds. The studies indicated that sampling methods could be designed to take advantage of the properties of more than one sorbent by preparing multi-sorbent tubes.

EPA validation studies (James et al., 1986) revealed that the MVOST method using Ambersorb® XE-347 was capable of achieving 85% recovery for chloroethene, tetrahydrofuran, trichloroethene, benzene, and chlorobenzene at concentrations in the 100 ppbv range for sample volumes of up to 9.0 liters. However, 127 ppbv samples of carbon tetrachloride were noted to breakthrough at total sample volumes of greater than 4.5 liters. The validation study (James, et al., 1986) only examined one multi-sorbent tube, containing Tenax® and Spherocarb®. However, the data presented indicated that a multi-sorbent tube (composed of Tenax$^{\Psi}$ and Ambersorb$^{\Psi}$ XE-347) would probably yield comparable sample results for the compounds sampled at total sample volumes of less than 4 liters. Comparable or superior results could be expected for a Carbosieve™ III adsorbent in place of the Ambersorb XE-347 based upon a study by Betz et al. (1989).

Sorbent samples are not subject to permeation; however, diffusion of sample from the sorbent to the storage environment is possible. Fuerst, et al. (1987), noted that storage time does have a statistically significant effect upon the recovery of low boiling point compounds such as chloroethene and trichlorofluoromethane. The sorbent tube should be effectively sealed from the ambient environment to prevent loss of sample via diffusion. As with Tedlar® bags, samples must be stored away from direct sunlight. Sorbent tubes offer the advantage of portability and ease of transportation; sorbent tube samples can be transported by aircraft while Tedlar® bag samples often cannot, due to low pressure cargo storage areas and Federal Aviation Administration carry-on baggage restrictions.

Because sorbent tubes are desorbed in their entirety, typically, only one sample analysis may be run per sorbent tube. Often, the concentration of a sample is not known in advance of the analysis, therefore desorption of a heavily loaded sorbent tube can result in overloading of the analytical column of the gas chromatograph. To avert these problems, some commercial thermal desorption equipment is equipped with a "sample split" mode, in which a known portion of the sample can be saved on another sorbent tube. Alternatively, the problem of sample replication can be addressed by collecting parallel samples in multiple tubes from the same sample stream; however, parallel sampling or use of sample split doubles cleaning, collection and handling effort.

3. Summa® Polished Canisters

A Summa® polished canister is a stainless steel canister that has been electro-polished on the interior through the Molectrics SUMMA process. The extremely smooth surface is considered passivated, and is relatively free of active sites for adherence or reaction of PTOCs. Typical sample volumes are 1/2 to 3 liters, depending upon cylinder diameter.

Summa® polished canisters do not allow permeation or photochemical reactions to occur. Sample integrity tests, on compounds stored at ppbv levels for extended time periods, have shown that the Summa® polished cylinder is a viable sampling technique (Oliver et al., 1986; Holdren et al., 1986). The compounds tested by Oliver et al., collected from low humidity ambient air, and by Holdren et al., at low concentrations in ambient air, include many of those emitted by MWTPs. Numerous samples collected at a MWTP, e.g. multiple flux box measurements, would require the use of many cannisters. Because each cannister is typically approximately 8" diameter, sample handling, and transport become more difficult, and cannister costs becomes a major consideration. As with Tedlar® bags, replicate samples analysis can be run to check analytical precision. A recent study (Gholson et al., 1989) has demonstrated the stability of Summa polished canisters in samples containing HCl. Whether the canisters remain free of corrosion in humid wastewater environments (e.g. presence of H_2S or Cl_2) has yet to be determined.

B. Method Selection

After reviewing the literature, sample collection methods were chosen for the study. The use of electro-polished canisters was ruled out of the study for two reasons. First, it was unknown whether the polished interior surface of the canisters would degrade in corrosive and highly humidified environments. Stainless steel degradation in the source assessment sampling system (SASS) had been noted in studies of hazardous waste combustion emissions (Johnson, 1986). Such damage might be difficult to detect without periodic and time-consuming sample storage studies. Second, electro-polished canisters are costly (in the neighborhood of $500+ per canister) and would not be feasible for frequent sample collection at numerous sampling points or shipment to a distant laboratory.

Tedlar® bag sampling had already been validated as a sampling methodology for incinerator effluents, landfill gases, and MWTP emissions (California Air Resources Board, 1984); however, it was noted that semi-volatile compounds have a tendency to adsorb to the interior of the sampling bag and fittings, resulting in artificially low concentrations being detected, or resulting in possible background concentrations if the bags were re-used. For benzene, adsorption would not adversely affect detected concentrations, but collection and analysis of lower volatility PTOCs could be a problem. One problem noted in previous studies of benzene emissions was the possible permeability of the Tedlar® bags over time. To ensure that 98.5% of the sampled benzene is recovered from the Tedlar® bag, samples must be analyzed within 72 hours of collection (California Air Resources Board, 1984). Tedlar® bag sampling was selected as the reference method with which sorbent tube results could be compared.

Sorbent tube sampling has proven feasible as a method for collecting both volatile and semi-volatile compounds from a sample gas, provided that the sorbents used were non-reactive and suited for the collection of target compounds. Activated carbon was not chosen as the sorbent medium due to the high humidity of the sampling environment. The presence of water vapor in the sample itself should not present a problem during GC analysis because a purge and trap analytical method would be employed (Johnson, 1986); however, problems would be encountered if cryogenic trapping was employed for compounds such as chloroethene. Instead, multi-sorbents were chosen for the field studies with the initial choice of the first sorbent being Tenax® and the second sorbent being Ambersorb® (XE-340). Tenax$^{\Psi}$, a polymer of 2,6-diphenyl-p-phenylene oxide, provides for the collection of most volatile and semi-volatile compounds, and the Ambersorb®, synthetic carbonaceous spheres, ensures capture of highly volatile compounds (not normally fully adsorbed by Tenax®). Tenax® and Ambersorb® had already proven useful in other studies of MWTPs (James et al., 1986; Chasz et al., 1986; Berglund et al., 1987; Hodgson and Girman, 1990). However, thermal decomposition by-products such as benzaldehyde and 1-phenylethanone were noted in other studies with Tenax$^{\Psi}$ (Walling et al., 1986). The Walling et al. ambient concentration studies resulted in detection and quantification problems due to the interference of the Tenax$^{\Psi}$ decomposition by-products; however, at the high concentration of PTOCs found at MWTPs, Tenax® sampling problems were not expected. Because we encountered evidence of artifact formation during our initial studies, similar to those noted by Walling et al., subsequent sampling efforts were conducted using multi-sorbent tubes manufactured by Supelco which contained Carbopak™, synthetic carbonaceous spheres, and Carbosieve™ III, a carbon molecular sieve.

C. Validation Study

Both the UCD sampling team and the East Bay Municipal Utilities District (EBMUD) staff had selected multi-sorbent tube sample collection (MVOST) over Tedlar® bag sampling. A collaborative sampling effort was undertaken to gather data that could be used to provide some basis for validation of the MVOST method. 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 of chlorinated species by GC/ECD

Two sampling efforts were undertaken at the EBMUD facility. In May, 1988, UCD collected samples in Tedlar® bags to determine the mass emission rate and average concentration for eight PTOCs of concern. During the May sampling trip, EBMUD staff collected Tenax/Ambersorb samples in parallel with the UCD Tedlar® bags using the modified VOST technique. In November, 1988, an additional parallel sampling effort was undertaken by UCD and EBMUD to further evaluate the modified VOST protocol used by EBMUD staff. During the November study, additional parallel Tedlar® bag and sorbent tube samples were collected, as well as parallel samples of a gas standard.

D. Results

1. May Sampling Trip

The UCD sampling team used Tedlar® bags to collect samples from the secondary pure-oxygen treatment process, in parallel with EBMUD staff using TA sorbent tubes. The UCD team also measured the velocity head at the sampling port along the centerline of the flow using a standard pitot tube. From the data collected, UCD determined that the average flowrate of exhaust gas was 0.34 m^3/s and that the flow rate was relatively constant (within 10%) except when the oxygen plant cycled (once every ten minutes).

Four samples were drawn by UCD (Bags 1, 2, 4, and 7) for analysis. Each sample was collected over a three to five minute period and contained approximately 2 to 3 L of sample. EBMUD staff collected three sorbent tube samples in parallel with the UCD (Run 1, Run 2, and Run 3). The samples collected by UCD were returned to the ARB Monitoring and Laboratory Division (MLD) for analysis. Properties and concentrations of eight PTOCs are presented in Tables 1 and 2.

Daily mass emission rates were estimated from the gas flowrate and sample data collected by UCD and are presented in Table 3. A comparison of the three parallel runs made by UCD and EBMUD are presented in Table 4, average values and standard deviation results are presented in Table 5.

Table 1
Eight Compounds Monitored During the First EBMUD Sampling Trip

Compound	Abbr.	Molecular Weight	Boiling Point (°C)
Vinyl chloride	VC	62.5	-13.4
Fluorotrichloromethane	F11	137.4	24
Trichloromethane	TCM	119.5	61.7
1,1,1 trichloroethane	TCA	133.5	74.1
Carbon tetrachloride	CT	154.0	76.5
Benzene	BZ	78.0	80.1
Trichloroethene	TCE	131.5	87.0
Perchloroethene	PERC	166.0	121.0

Table 2
Concentrations (ppb) Determined During the First EBMUD Sampling Trip
UCD Sampling of Secondary Effluent Gas Stream

	F11	TCM	TCA	CT	TCE	PERC	VC	BZ
UCD Bag 1	16	330	600	24	100	580	28	23
UCD Bag 2	17	380	590	25	110	660	30	17
UCD Bag 4	15	390	500	20	100	620	26	16
UCD Bag 7	18	430	540	22	130	760	29	19
Average (ppb)	16.5	383	558	22.8	110	655	28.3	18.8
S.D.	1.1	35	40	1.9	12	67	1.5	2.7
C.V.	7%	9%	7%	8%	11%	10%	5%	14%
Average (μg/l)	0.10	1.87	3.05	0.14	0.59	4.45	0.07	0.05

Table 3
Estimated Daily Mass Emissions
Determined During the First EBMUD Sampling Trip
UCD Sampling of the EBMUD Secondary Effluent Gas Stream

Compound	g/day/channel*	Total g/day**
Trichlorofluoromethane (F11)	2.9	17
Trichloromethane (TCM)	54.2	325
1,1,1 trichloroethane (TCA)	88.5	531
Carbon tetrachloride (CT)	4.1	25
Trichloroethene (TCE)	17.1	103
Perchloroethylene (PERC)	129.1	775
Vinyl chloride (VC)	2.0	12
Benzene (BZ)	1.2	14

* The daily emission rate was extrapolated from grab samples. As discussed in Section 200, this is not an adequate method for determining MWTP emission rates due to diurnal emission patterns.

** A total of six aeration reactor channels were in operation during the sampling effort. Each channel does process common feed; however, calculations assume identical operations in each channel as the exhaust flows were not measured.

Table 4
Comparison of Parallel EBMUD and UCD Sample Results (μg/l)
Determined During the First EBMUD Sampling Trip
Parallel Sampling of the EBMUD Secondary Effluent Gas Stream*

	EBMUD Tenax®/Ambersorb®			UCD Tedlar® Bags		
Compound	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
F11	<0.10	<0.10	<0.10	0.09	0.08	0.10
TCM	2.50	2.80	3.03	1.83	1.88	2.07
TCA	5.10	5.00	5.44	3.18	2.70	2.91
CT	0.18	0.20	0.17	0.16	0.12	0.14
TCE	0.68	0.78	0.87	0.58	0.53	0.69
PERC	5.80	6.10	6.50	4.43	4.16	5.10
VC	<0.10	<0.10	<0.10	0.08	0.07	0.07
BZ	0.22	0.16	0.16	0.05	0.05	0.06

* Data compiled by EBMUD staff (Hellier, 1989)

Table 5
Average Values and S.D. of Parallel Sample Results (μg/l) Determined During the First EBMUD Sampling Trip
Parallel Sampling of the EBMUD Secondary Effluent Gas Stream*

	EBMUD Tenax®/Ambersorb®			UCD Tedlar® Bags		
Compound	Avg.	S.D.	C.V.	Avg.	S.D.	C.V.
F11	<0.10	N/A	N/A	0.09	0.01	7.5%
TCM	2.78	0.22	7.8%	1.93	1.10	5.4%
TCA	5.18	0.19	3.6%	2.93	2.20	6.8%
CT	0.18	0.01	6.8%	0.14	0.01	9.2%
TCE	0.78	0.08	10.0%	0.60	0.07	11.0%
PERC	6.13	0.29	4.7%	4.56	0.39	8.7%
VC	<0.10	N/A	N/A%	0.07	0.00	6.0%
BZ	0.18	0.03	15.7%	0.05	0.00	7.2%

* Data compiled by EBMUD staff (Hellier, 1989)

2. November Sampling Trip

A second parallel sampling was conducted by EBMUD staff and the UCD team at the EBMUD MWTP on November 29, 1988. Samples were drawn from the same exhaust pipe of the secondary treatment process used during the first EBMUD sampling trip. Samples were collected in Tedlar® bags by the UCD team and also in TA tubes by EBMUD staff.

Three 500 mL samples of standard gas mixture (Scott-Marin) were drawn by EBMUD (EBM 20, 5, 8). A blank bag of pure nitrogen was drawn at the pure-ox plant to ensure that contamination of samples did not occur. The UCD team also transferred about 750 mL of the five component Scott standard gas from the source Tedlar® bag into a second Tedlar® bag (9) using ARB Method 201, for EBMUD staff use, leaving enough sample in the original bag for analysis.

A total of four parallel samples were taken from the secondary treatment process within a one hour period. Samples (UCD Bags 1,2,3 and C; EBMUD Tubes 25,3,26, and 2) were all taken concurrently from the exhaust port, each sampling period was approximately five minutes. The EBMUD sampled 500 mL of exhaust gas and the UCD bags captured approximately 2 liters of exhaust gas. The fourth sample (Bag C) collected by UCD resulted in analysis anomalies and was not compared to the EBMUD sample (Tube 2).

The samples collected by UCD were returned to the ARB Monitoring and Laboratory Division (MLD) for analysis. Concentrations of seven compounds in the secondary process gas effluent (Table 6) were determined by UCD and are presented in Table 7. Table 8 compares the mass emission rates determined by the two UCD sampling efforts in May and November.

Table 6
Seven Compounds Analyzed by UCD During the Second EBMUD Sampling Trip

Compound	Abbreviation	Molecular Wt.
Trichloromethane	TCM	119.5
1,1,1 trichloroethane	TCA	133.5
Carbon tetrachloride	CT	154.0
Trichloroethene	TCE	131.5
Perchloroethene	PERC	166.0
Vinyl chloride	VC	62.5
Benzene	BZ	78.0

Table 7
Concentrations (ppb)
Determined During the Second EBMUD Sampling Trip
Parallel Sampling of the EBMUD Secondary Effluent Gas Stream

	TCM	TCA	CT	TCE	PERC	VC	BZ
UCD Bag 1	230	260	18	140	6110	34	57
UCD Bag 2	180	210	14	120	5380	22	48
UCD Bag 3	220	260	17	150	5970	33	78
UCD Bag C	130	150	10	90	4270	23	51
UCD Avg. (ppb)	210	243	16	137	5820	30	61
S.D.	22	24	1.7	13	316	5.4	13
C.V.	10%	10%	10%	9%	5%	18%	21%

Table 8
Estimated Daily EBMUD Mass Emissions from UCD Results
Determined During the First and Second Sampling Trip
Parallel Sampling of the EBMUD Secondary Effluent Gas Stream

Compound	First Trip Estimated Emissions g/day	Second Trip Estimated Emissions g/day
Trichloromethane (TCM)	325	174
1,1,1 trichloroethane (TCA)	531	226
Carbon tetrachloride (CT)	25	17
Trichloroethene (TCE)	103	122
Tetrachloroethene (PERC)	775	6873
Vinyl chloride (VC)	12	14
Benzene (BZ)	14	17

* The daily emission rate was extrapolated from grab samples. As discussed in Section 200, this is not an adequate method for determining MWTP emission rates due to diurnal emission patterns.

As can be seen in table 8, the mass emission rate estimates for the two trips differ greatly for PERC, 1,1,1-TCA, and TCM, but differ very little for CT, TCE, VC, and BZ. Because emission concentrations change from day to day, the sample results from a single sampling period cannot be extrapolated to an annual emission figure with confidence.

Samples collected by EBMUD were analyzed for 12 compounds (Table 9) at the EBMUD laboratory. Sample analysis results were tabulated and provided to UCD for comparison and are presented in Table 10 with the parallel UCD Tedlar® Bag results. Only three of the parallel analyses were reported because of a problem with one UCD sample; thus, the comparisons are listed as parallel runs 1, 2, and 3. In addition to the seven compounds monitored by both UCD and EBMUD, EBMUD also provided sample analysis results for ethylbenzene (ETBZ), toluene (TOL), o-xylenes (XYL), 1,2,4 trimethylbenzene (TMB), and isopropylbenzene (IPB). Average values and standard deviations are reported in Table 11. As can be seen in the tables, the EBMUD analysis results are all greater than those of UCD, except for CT The standard deviations were lower in most of the EBMUD sample results than in the UCD sample results for all compounds except TCE and BZ.

The analyses of the standards collected by UCD and EBMUD are summarized in Tables 12, 13, and 14. Sample results indicate that the EBMUD MVOST exhibits improved performance over the Tedlar® bag sampling methodology in terms of relative standard deviation of analyses and percent difference from nominal standard values.

Blank tubes and a blank Tedlar® bag were analyzed by EBMUD and UCD respectively (Table 15). No evidence of contamination was noted.

Table 9
Twelve Compounds Analyzed by EBMUD During the Second EBMUD Sampling Trip

Compound	Abbr.	Molecular Weight	Boiling Point (°C)
Trichloromethane	TCM	119.5	61.7
1,1,1 trichloroethane	TCA	133.5	74.1
Carbon tetrachloride	CT	154.0	76.5
Trichloroethene	TCE	131.5	87.0
Perchloroethylene	PERC	166.0	121.0
Vinyl chloride	VC	62.5	-13.4
Benzene	BZ	78.0	80.1
Ethyl benzene	ETBZ	106.2	136.0
Toluene	TOL	92.1	110.8
O-Xylenes	XYL	106.2	144
1,2,4 Trimethylbenzene	TMB	120.2	168
Isopropylbenzene	IPB	120.2	152.4

Table 10
Comparison of Parallel EBMUD and UCD Sample Results (μg/l) Determined During the Second EBMUD Sampling Trip Parallel Sampling of the EBMUD Secondary Effluent Gas Stream*

	EBMUD Tenax/Ambersorb			UCD Tedlar® Bags		
Compound	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
TCM	1.5	1.6	1.6	1.10	0.87	1.10
TCA	1.6	1.9	2.0	1.40	1.10	1.40
CT	0.1	0.1	0.1	0.11	0.09	0.10
TCE	0.7	1.0	1.1	0.70	0.64	0.80
PERC	63.1	62.0	61.0	40.0	36.0	40.0
VC	<0.10	<0.10	<0.10	0.09	0.06	0.08
BZ	0.1	0.1	0.2	0.18	0.15	0.25
ETBZ	0.7	0.6	0.7	NA	NA	NA
TOL	4.2	4.8	4.6	NA	NA	NA
XYL	2.3	2.0	2.2	NA	NA	NA
TMB	0.2	0.2	0.3	NA	NA	NA
IPB	0.2	0.2	0.2	NA	NA	NA

* Data compiled by EBMUD staff (Hellier, 1989)

Table 11
Average Values and S.D. of Parallel Sample Results (μg/l) Determined During the Second EBMUD Sampling Trip Parallel Sampling of the EBMUD Secondary Effluent Gas Stream*

	EBMUD Tenax/Ambersorb			UCD Tedlar® Bags		
Compound	Avg.	S.D.	C.V.	Avg.	S.D.	C.V.
TCM	1.6	0.05	3.0%	1.02	0.11	10.6%
TCA	1.8	0.17	9.3%	1.30	0.14	10.9%
CT	0.1	0.00	4.9%	0.10	0.01	8.2%
TCE	0.9	0.17	18.2%	0.71	0.07	9.3%
PERC	62.	0.8	1.3%	38.7	1.9	4.9%
VC	<0.1	N/A	N/A	0.08	0.01	16.3%
BZ	0.1	0.05	35.4%	0.19	0.04	21.7%
ETBZ	0.7	0.05	7.1%	NA	NA	NA
TOL	4.5	0.25	5.5%	NA	NA	NA
XYL	2.2	0.12	5.8%	NA	NA	NA
TMB	0.2	0.05	20.2%	NA	NA	NA
IPB	0.2	0.00	0.2%	NA	NA	NA

* Data compiled by EBMUD staff (Hellier, 1989)

Table 12
Concentrations (μg/l) Determined During the Second EBMUD Sampling Trip Parallel Sampling of Standards*

Standards:	TCM	TCA	CT	TCE	PERC	VC	BZ
UCD Bag	0.34	NA	0.45	NA	0.46	NA	0.21
EBM Tube 20	0.49	NA	0.62	NA	0.57	0.35	0.32
EBM Tube 5	0.51	NA	0.66	NA	0.57	0.37	0.33
EBM Tube 8	0.45	NA	0.58	NA	0.51	0.29	0.29

* Data compiled by EBMUD staff (Hellier, 1989)

Table 13
Average and Standard Deviation of Mass Concentrations (μg/l) Determined During the Second EBMUD Sampling Trip Parallel Sampling of Standards*

	EBM Mean	S.D.	C.V.
TCM	0.48	0.02	5%
TCA	NA	NA	NA
CT	0.62	0.03	5%
TCE	NA	NA	NA
PERC	0.55	0.03	5%
VC	0.34	0.04	10%
BZ	0.31	0.02	5%

* Data compiled by EBMUD staff (Hellier, 1989)

Table 14
Difference between Average Values and Expected Values of Mass Concentrations from Sampling of Standards (μg/l) Determined During the Second EBMUD Sampling Trip Parallel Sampling of Standards*

	EBMUD Tenax®/Ambersorb®			UCD Tedlar® Bag		
	Mean	Nominal	%Dif.	Mean	Nominal	%Dif.
TCM	0.48	0.48	+1%	0.34	0.48	-29%
CT	0.62	0.62	0%	0.45	0.62	-27%
PERC	0.55	0.67	-18%	0.46	0.67	-31%
VC	0.34	0.25	+35%	N/A	0.25	N/A
BZ	0.31	0.32	-2%	0.21	0.32	-34%

* Data compiled by EBMUD staff (Hellier, 1989)

Table 15
Mass Concentrations (ppb) of Blank Samples Determined During the Second EBMUD Sampling Trip

	TCM	TCA	CT	TCE	PERC	VC	BZ
Blank:							
UCD Bag	<1	<1	<1	<1	<1	<1	<1
EBMUD Tubes	ND	ND	ND	ND	ND	ND	ND

Analysis of the data collected during the second EBMUD sampling trip, revealed a number of systematic differences between the tube and bag results. The large difference in the reported chloroethene and benzene concentrations (and the difference in the precision of the values reported), can be explained by the difference in test methods used by UCD and EBMUD for analysis. The benzene concentrations reported by EBMUD have a detection limit of about 0.1 ppm, whereas the concentrations reported by UCD (ARB analysis) have a detection limit of 0.01 ppm; thus, the coefficient of variation for the EBMUD benzene analyses were higher than would have been expected had EBMUD used the same analytical instrumentation as the ARB. Based upon the results for the remaining compounds, it is evident that the EBMUD tube analyses provided better precision and accuracy for this sampling study. Although unlikely, it is possible that the bag samples collected by UCD during the second sampling trip were adversely affected by the presence of nitrogen inside the bag (nitrogen remaining from the clean and purge operation might have diluted the standard); however, this could not be confirmed after the sampling was conducted.

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 ^{o}C).

E. Additional Sorbent Tube Studies

Initially, the UCD team used Tenax-TA/Ambersorb (TA) multi-sorbent tubes for a sample collection medium. The TA tubes were manufactured by T.R. Associates, Lewisberg, PA. Each of the tubes, 20mm long by 4mm I.D., was packed with approximately a 4:3 volume ratio of Tenax and Ambersorb XE-340 (75 mg and 110 mg respectively). However, because of artifacts produced during the sampling at the JWPCP with the TA tubes (discussed in a subsequent section), additional laboratory studies were conducted at UCD to compare commercially prepared TA tubes (T.R. Associates) with Carbopak/Carbosieve™ tubes (Supelco). These studies consisted of breakthrough tests of the Supelco tubes, tests of reproducibility of both types of tubes, and tests of ozone effects on the sorbents,

Samples were collected by UCD in accordance with the EBMUD modified method 0030 in the same manner as field samples drawn during the EBMUD and JWPCP studies. The ends of all sorbent tubes were sealed with stainless steel Swagelock end cap fittings and either graphite or ceramic-filled Teflon® ferrules. The UCD team used an SKC Aircheck Sampler, Model 224 personal sampling pump which the manufacturer indicated was to provide a constant flow. However, because the pressure drop across each tube differed by as much as 30%, the flow compensation mechanism on the sample pump could not fully compensate for the difference and the sample volumes collected on each tube differed slightly. The pressure drop problem was noted after a number of studies were conducted; thus, for some analytical results, tube-to-tube concentration ratios were examined. After the pressure drop problem was noted, studies were conducted using a bubble meter to measure the actual flow across each sampling tube in the field. Also a positive displacement gas bag method was developed for the HTP testing.

Sorbent tube samples collected by UCD were analyzed within 48 hours using thermal desorption GC/MS analysis at the UCD Facility for Advanced Instrumentation (FAI), or at the Chemical and Civil Engineering Hewlett Packard GC/MS system in Bainer Hall. The samples were desorbed using helium carrier gas and an Envirochem Unacon 810 thermal desorption system, transferring the samples to a 0.32 mm x 30 m long DB-624 column (J&W Scientific, Sacramento, CA) in a Hewlett Packard model 5890A gas chromatograph. The analytical units were calibrated using a gas standard drawn in the field containing chloroethene (vinyl chloride - VC), trichloromethane (chloroform - TCM), tetrachloromethane (carbon tetrachloride - CT), benzene (BZ), and tetrachloroethene (perchloroethylene - PERC). Because sub-ambient cooling was not available, measurement of VC was not quantitative. Sample calibration was performed using a Research Triangle Institute standard (traceable to a National Institute of Standards and Testing standard) containing trichlorofluoromethane, 1,1-dichloroethene (DCE), dichloromethane (DCM), TCM, 1,1,1-trichloroethane (TCA), CT , hexadeuterobenzene (d-BZ), 1,2-dichloroethane (DCA), trichloroethene (TCE), 1,2-dichloropropane, perdeuterotoluol (d-TOL), PERC, 1,2-dibromoethane (DBA), chlorobenzene (CLBZ), ethylbenzene (ETBZ) , and o-xylene (o-XYL).

1. Breakthrough Tests of Supelco Tubes

During the sampling at the JWPCP samples were collected in TA tubes placed in series; thus, any breakthrough of compounds could be detected on the second sorbent tube. After the results of that study were reviewed, and no breakthrough was detected, even at the high concentrations encountered at the headworks, only single tubes were used throughout the remaining studies. To ensure that breakthrough would not be a problem during the field sampling efforts using the Supelco Carbopak/Carbosieve™ (CC) sorbent tubes, a laboratory experiment was conducted. Three samples of diluted standard were collected on three sets of two CC sorbent tubes connected in series. Nominal standard concentrations were approximately: TCM (31 ppb), CT (30 ppb), BZ (33 ppb), PERC (30 ppb), and VC (31 ppb). One sample each was collected for 6 minutes, 18 minutes, and 58 minutes at flow rates between 60 and 77 mL/min.

The laboratory studies conducted on the CC sorbent tubes resulted in no detectable breakthrough for 30 ppb concentrations of TCM, PERC, CT, or BZ even at sample volumes of 4 liters.

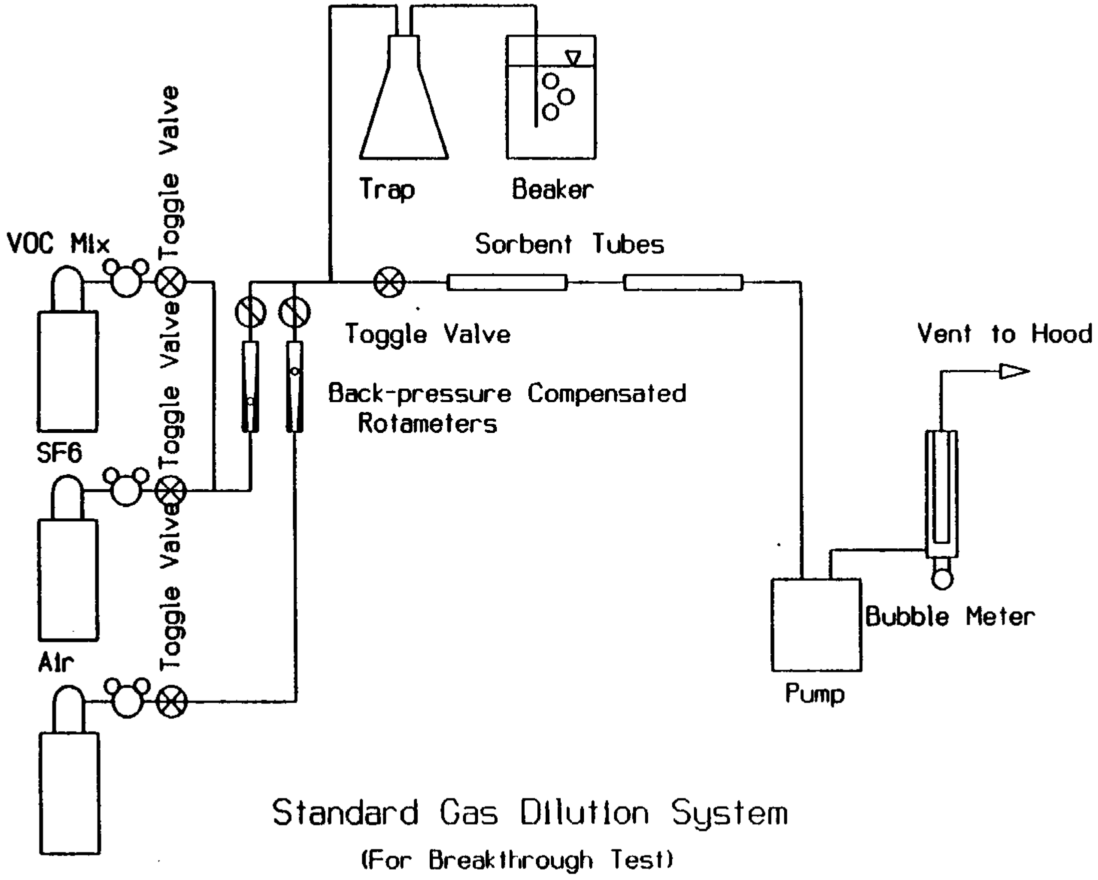


Figure 1 Standard Gas Dilution System for Breakthrough Test

2. Reproducibility

To compare the reproducibility of the TA and CC sorbent tubes, three samples were collected on TA tubes (tubes #61, #62, and #63) and three samples were collected on Supelco tubes (tubes #4, #5, and #6). Three minute samples of the standard were collected at a rate of approximately 100 mL/min on the TA tubes at a rate of approximately 110 mL/min on the CC tubes; however, the flow was interrupted during the sample collected on Supelco tube #4. To correct for any problems caused by the difference in total flow through the sample tubes, the ratios of the analytical results for each tube were examined to indicate the reproducibility of each sample.

Tables 16 and 17 contain the sample analysis results (in millions of ion counts) for the TA tubes (tubes #61, #62, and #63) and Supelco tubes (tubes #4, #5, and #6). The flow rates across the tubes during this early study were not monitored by a soap bubble meter, as the pressure drop differences discussed above had not yet been noted. As is apparent from the sample results, the total flow differed across Tenax tubes #61, #62 and #63. Because the flow rate across the TA tubes and the CC tubes differed, and because the flow was interrupted during the sample collected on CC tube #4, the analytical results for each tube cannot be directly compared. Instead, the ratio of the area counts for each compound resolved are compared with each tube as an indication of the reproducibility of each sample. Comparison of the sample analysis ratios are contained in Tables 18 and 19. Given the known problem with the CC sample tube #4, uniformity of sorbent packing appeared to be superior for the commercially available CC (Supelco) tubes.

Table 16
Reproducibility Study Results
TA Samples of Known Standards
Area in Millions of Counts

Compound	TA #61	TA #62	TA #63
Trichlorofluoromethane	138.1	215.7	103.7
1,1-dichloroethene	81.9	81.9	88.3
Dichloromethane	122.4	202.9	231.5
Chloroform	142.0	271.6	242.6
1,1,1-Trichloroethane	170.1	307.2	307.5
Tetrachloromethane	172.2	207.3	n/a
Hexadeuterobenzene	204.3	355.3	348.5
1,2 Dichloroethane	163.9	252.6	228.8
Trichloroethene	243.3	408.2	399.8
1,2 dichloropropane	168.4	303.9	292.2
Perdeuterotoluol	271.8	470.6	474.8
Tetrachloroethene	306.2	476.5	438.8
1,2 Dibromoethane	149.2	242.8	227.3
Chlorobenzene	304.8	418.4	404.7
Ethylbenzene	307.9	452.5	437.2
O-xylene	315.5	441.6	430.0

Table 17
Reproducibility Study Results
CC Samples of Known Standards
Area in Millions of Counts

Compound	CC #4	CC #5	CC #6
Trichlorofluoromethane	32.6	32.8	30.2
1,1-dichloroethene	66.0	51.9	91.8
Dichloromethane	242.8	220.3	222.5
Chloroform	354.3	317.4	309.5
1,1,1-Trichloroethane	283.4	237.4	232.4
Tetrachloromethane	291.5	242.5	245.2
Hexadeuterobenzene	418.3	316.5	315.8
1,2 Dichloroethane	220.3	206.4	196.2
Trichloroethene	459.2	376.1	371.2
1,2 dichloropropane	339.0	274.1	266.6
Perdeuterotoluol	530.7	435.0	400.7
Tetrachloroethene	531.5	444.3	433.1
1,2 Dibromoethane	293.3	233.0	227.8
Chlorobenzene	500.7	416.9	407.1
Ethylbenzene	529.0	449.4	431.6
O-xylene	519.1	435.1	429.2

Table 18
Reproducibility Study Results
TA Samples of Known Standards
Ratio of Areas for Tubes #61, #62, and #63

Compound	61/62	61/63	62/63
Trichlorofluoromethane	.640	1.331	2.080
1,1-dichloroethene	1.000	.928	.928
Dichloromethane	.603	.529	.876
Chloroform	.523	.585	1.120
1,1,1-Trichloroethane	.554	.554	.999
Tetrachloromethane	.831	n/a	n/a
Hexadeuterobenzene	.575	.586	1.020
1,2 Dichloroethane	.649	.716	1.104
Trichloroethene	.596	.609	1.021
1,2 dichloropropane	.554	.576	1.040
Perdeuterotoluol	.578	.572	.991
Tetrachloroethene	.642	.698	1.086
1,2 Dibromoethane	.614	.656	1.068
Chlorobenzene	.728	.753	1.034
Ethylbenzene	.680	.704	1.035
O-xylene	.714	.734	1.027
Average	.655	.702	1.099
S.D.	.117	.195	.279
C.V.	18%	28%	25%

Table 19
Reproducibility Study Results
CC Samples of Known Standards
Ratio of Areas for Tubes #4, #5, and #6

Compound	4/5	4/6	5/6
Trichlorofluoromethane	0.993	1.079	1.086
1,1-dichloroethene	1.272	0.719	0.565
Dichloromethane	1.102	1.091	0.990
Chloroform	1.116	1.144	1.026
1,1,1-Trichloroethane	1.194	1.219	1.022
Tetrachloromethane	1.202	1.189	0.999
Hexadeuterobenzene	1.322	1.325	1.002
1,2 Dichloroethane	1.067	1.123	1.054
Trichloroethene	1.221	1.237	1.013
1,2 dichloropropane	1.237	1.272	1.028
Perdeuterotoluol	1.220	1.324	1.086
Tetrachloroethene	1.196	1.227	1.026
1,2 Dibromoethane	1.259	1.288	1.023
Chlorobenzene	1.201	1.230	1.024
Ethylbenzene	1.177	1.226	1.041
O-xylene	1.193	1.209	1.014
Average	1.186	1.200	1.000
S.D.	.079	.152	.115
C.V.	7%	13%	12%

3. Ozone Effects

The presence of ozone in air sampled onto Tenax has been theorized to interfere with GC/MS results for trace VOC samples (Walling, 1987). Benzaldehyde had previously been noted as the most common Tenax degradation by-product, with an accompanying increase in benzene, and toluene levels. To determine if ozone might have had an appreciable effect upon the samples collected on Tenax sorbent tubes during the field investigations in the Los Angeles area, the UCD team examined the effect of relatively high concentrations of ozone on the TA and CC sorbent tubes.

Samples of air were collected on TA and CC tubes at the UCD Primate Center from an ozone exposure chamber so that analytical results between the two types of sorbents could be compared. The chambers at UCD are normally used to produce known concentrations of ozone for the purposes of determining biological effects. The ozone was generated from oxygen with a silent-arc discharge ozonizer (Edwin Sander Elektro Apparatebau G.m.b.H. & Co. KG., Am Osterberg 22, D-3151, Eltze, West Germany) and the concentration in the chamber was monitored with a calibrated UV ozone analyzer (Dasibi Corporation Model 1000A).

One blank TA and one blank CC tube (exposed to ambient air in the ozone generation chamber in the absence of ozone) were analyzed to establish a contaminant baseline. Two tubes of each type were drawn (TA #61 and #62, CC #1 and #2) from the ozone generation chamber at an ozone concentration of 500 ppb. One tube of each type was drawn (TA #63, CC #3) from the ozone generation chamber at an ozone concentration of 5 ppb.

Each of the blank tubes were analyzed for the presence of BZ, TCE, TOL, 1-bromo-3-fluorobenzene (BFB), and benzaldehyde (BZALD). The BFB served as an internal standard to compare desorption efficiency between the tube types. Each of the ozone exposed samples were similarly analyzed for the presence of BZ, TCE, TOL, and BZALD. Tables 20, 21, and 22 contain the sample analysis results for the blank tubes and the tubes that were used to sample ozone laden ambient air.

Table 20
Sample Results from the Ozone Exposure Study
Blank Tube Samples (0 ppb Ozone Exposure)
(Millions of Counts)

Compound	CC Tube	TA Tube
Benzene	18.10	63.02
Trichloroethene	16.82	13.52
Toluene	23.68	38.81
1-bromo-3-fluorobenzene	184.70	182.65
Benzaldehyde	<5.00	51.77

Table 21
Sample Results from the Ozone Exposure Study
Tenax Tubes Exposed to Ozone
(Millions of Counts)

	500 ppb Ozone		5 ppb Ozone
Compound	TA #61	TA #62	TA #63
Benzene	77.09	64.23	77.84
Trichloroethene	13.62	<5.00	<5.00
Toluene	47.36	34.47	61.10
Benzaldehyde	67.05	67.43	86.28

Table 22
Sample Results from the Ozone Exposure Study™
Carbopak/Carbosieve™ Tubes Exposed to Ozone
(Millions of Counts)

	500 ppb Ozone		5 ppb Ozone
Compound	CC #1	CC #2	CC #3
Benzene	16.42	11.14	28.95
Trichloroethene	10.40	<5.00	<5.00
Toluene	16.49	20.72	28.49
Benzaldehyde	20.92	7.83	16.68

The blank TA tube analysis exhibited the presence of BZALD, indicating that the decomposition by-product was already present on the TA tubes prior to ozone sampling (or on the TA traps used in the thermal desorption unit). The TA tubes exposed to 500 ppb ozone yielded a slight increase in benzaldehyde concentrations above the blank sample; however, the TA tube exposed to only 5 ppb ozone also appeared to yield a slight increase in BZALD concentration. The data collected are insufficient to draw any conclusions except that there appeared to be no statistically significant change in BZALD concentrations for the TA. It is clear that the baseline values of both blank and ozone exposed CC tubes were lower than that of TA tubes for all compounds examined. In subsequent use of CC tubes after changing the concentrator traps, the BZ and BZALD peaks did not appear, again suggesting that the TA traps on thermal desorption unit were the source of the artifact.

The experimental results indicate that the presence of ozone at ambient concentrations will not appreciably affect the presence of BZALD in the sample analysis, if the TA tubes are properly conditioned for sampling. However, the CC tubes appeared to be superior to the TA tubes for collecting samples from MWTP processes.

III. Emissions Study of Carbon Bed Adsorbers at the JWPCP

A study of activated carbon bed (ACB) breakthrough and emissions was carried out for comparison with the earlier findings of the CSDLAC. The UCD sampling team conducted emission studies at the JWPCP treatment facility in three stages. The first study (Stage I) involved sampling of a large number of compounds, including benzene, immediately upstream and downstream from a freshly recharged ACB used for odor control (dry scrubber unit #4, JWPCP designation DS-4) and additional units which had been in service for periods of at least several months, DS-5 and DS-28. The temporal variation of ACB collection efficiency was followed over a period of about six weeks 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. In addition, results from CSDLAC sampling of vent-gases from an ACB located on a sewer lift station are reported.

A. Background

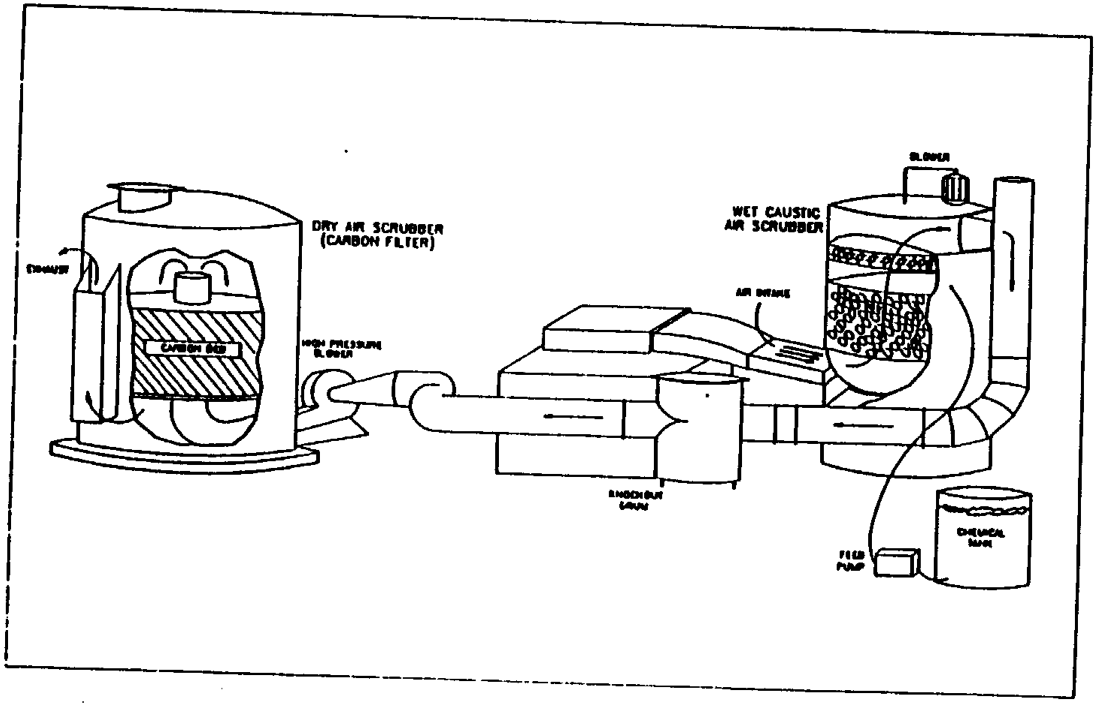
The CSDLAC staff at the JWPCP had previously determined that the ACBs used in the odor control systems operated at the facility quickly became saturated with hydrocarbon emissions (Caballero, 1989). Thus it was believed that the ACBs could not account for the difference between pseudo mass balance emissions and those actually measured. The primary purpose of the study at the JWPCP was to determine whether the earlier findings of the CSDLAC were correct or if there was a problem with the sampling methodology employed. This objective was accomplished by examining breakthrough of PTOCs from a freshly recharged ACB over a period of time.

A description of the facilities follows. It was provided to UCD by staff of the JWPCP (Chang et al., 1989), and has been paraphrased for this report. The odor control facilities currently in use at the JWPCP were designed in the mid-1970s for the sole purpose of reducing the release of H_2S to levels that would not be detectable outside of the plant boundary. A total of 28 odor control units were installed. The majority were two-stage odor control units, consisting of a caustic packed-tower scrubber and a dry ACB scrubber. Seven odor control units employed only caustic scrubbing. The remaining units utilized only dry carbon scrubbing. Figure 2 illustrates a typical two-stage odor control unit. Two-stage units were used at locations where untreated off-gas air had H_2S concentrations of 10 ppm v/v or greater. A total of 15 of these units were employed, mainly at various locations within the headworks and primary treatment areas of the plant. Three of these units, WS/DS-1, WS/DS-4, and WS/DS-5, were included in this study. (See Figure 3b for locations of the ACBs.) Sources of untreated offgas air having H_2S levels less than 10 ppm v/v were treated by only an ACB unit. These units are generally located at solids handling facilities. The DS-28 odor scrubber was such a unit, and was included in this study.

The inlet blower at each odor control unit drew H_2S contaminated air from covered tanks, wet wells, bar rakes, conveyance channels, etc. In doing so, ambient air was pulled in through numerous small openings in the covers, diluting the off-gases. The blowers were sized to insure that air in each of the enclosed spaces was replaced an average of 10 times per hour. Maintaining these high flow rates ensured that any open spaces or cracks in the covers were under a slight vacuum, thereby preventing release of untreated, noxious fumes into the immediate area. Furthermore, a flow rate of this magnitude ensured constant air movement underneath the covers and minimized H_2S concentrations, thereby reducing the tendency to form sulfur oxidizing bacteria on the concrete. Experience had shown that

Figure 2 **Typical Configuration of Scrubber and ACB Units at JWPCP**

(Caballero, 1989)



under low or stagnant air flow conditions, concrete was rapidly corroded by these bacteria to the point where the structural integrity of the tanks and conveyance channels was compromised.

Highly contaminated air streams (> 10 ppm v/v H_2S) were sent initially to a wet chemical scrubber. These employed, a caustic solution (pH > 12) which trickled down through an 18 inch deep bed of dumped packing consisting of Pall ballast rings (90 mm dia, 93% void space, 24 ft^2/ft^3, packing factor 16 ft^{-1}). This descending flow countercurrently contacted the air stream which was passed up through the wetted bed. H_2S was transferred from the gas phase to the liquid phase where, because of the high pH, the H_2S dissociates into the HS^- and $S^=$ anions, and hence was trapped in solution. The caustic solution was continuously recycled until the pH fell below 12, at which point a portion of the solution was wasted and replaced with fresh solution. The cleansed gas passed through a demister and then exited the scrubber. The existing wet scrubbers, as presently designed, remove approximately 50% of the H_2S from the inlet air streams. The contact time of the gas with the wetted bed ranges from 0.1 second to 1.6 seconds, with approach velocities ranging from 70 fpm to 500 fpm.

Air containing <10 ppm v/v H_2S was conveyed through metal ductwork to a moisture knockout drum and into the ACB. Both the demister in the packed tower and the knockout drum were only marginally effective in removing water vapor from the air stream, and humidity of air streams ranged from 75% to 100% of saturation upon exit. The air then entered a compressor used to overcome the pressure drop associated with the carbon bed (8-inch H_2O) and was channeled up through the middle of the grating as shown in Figure 2. The air filled the upper portion of the structure and was subsequently pushed down through the carbon bed, through the grating, and out the discharged vent located on the side of the unit.

All carbon beds were 3 ft. deep. Carbon used was typically Calgon BPL, a non-impregnated, coal-based carbon. The physical and adsorptive properties of this carbon are listed in Table 1. Approximately 1400 lb of carbon were in odor scrubber DS-5, 3,700 lb were in DS-4 and DS-28, and 8,300 lb were in each of the two DS-1 scrubbers. Detention time of the air in the ACBs ranged from 4.2 sec. to 1.1 sec, with the superficial velocities ranging from 35 fpm to 130 fpm.

The activated carbon provided numerous catalytic sites that allowed for oxidation of H_2S to elemental sulfur and water. Both the adsorption and the oxidation steps were exothermic, and thus, the exhaust temperature is 5 to 10 ^{o}C degrees warmer than the inlet temperature. Fresh carbon lowered the H_2S concentration of the treated air to 1 ppm v/v or less. The carbon was monitored weekly, and was scheduled for regeneration when the H_2S concentration in the exhaust rose above 10 ppm v/v (as determined by colorimetric indicator tubes). The effective life of the carbon typically ranged from 6 months to several years. Exhausted carbon was removed from the ACB and sent out for steam regeneration. Removal efficiencies of volatile or semi-volatile organics was not a consideration used to determine when to regenerate the carbon.

The general plant schematic and the location of the odor control units studied are displayed in Figures 3a and 3b. Odor control units WS/DS-1 employed both caustic scrubbing and activated carbon adsorption to treat malodorous air from the headspaces of the inlet works bar screen units and from two of the plant's main tributary sewers. An inlet headworks pump lift station immediately downstream of the inlet bar screens acted as an air block, preventing any movement of air from downstream treatment processes from entering the WS/DS-1 odor control units. Thus, this odor control unit effectively drew air from approximately the first 8 km (5 miles) of its tributary sewers.

Figure 3 **Process Schematic for the JWPCP Treatment Facility**

(Caballero, 1989)

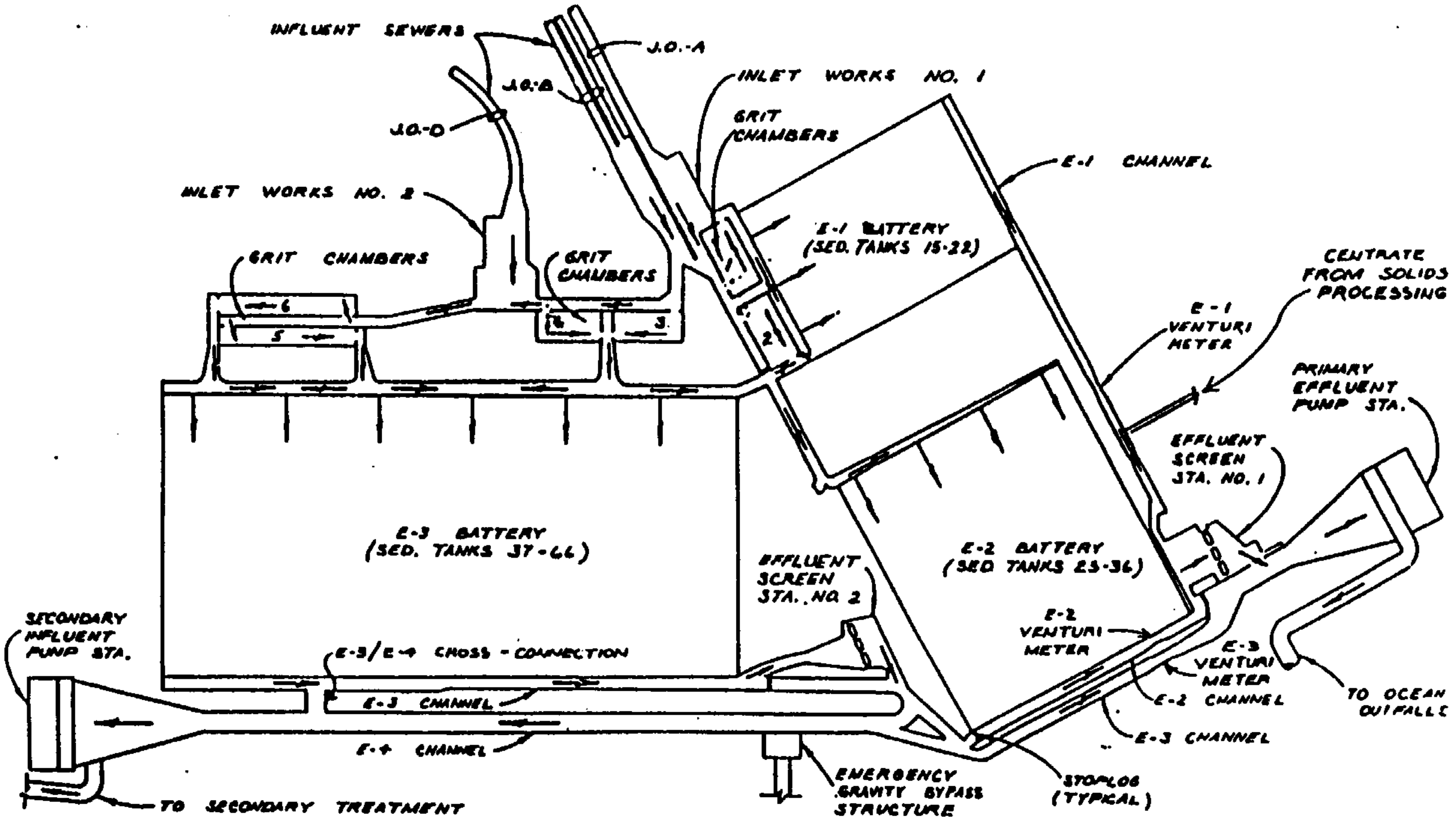
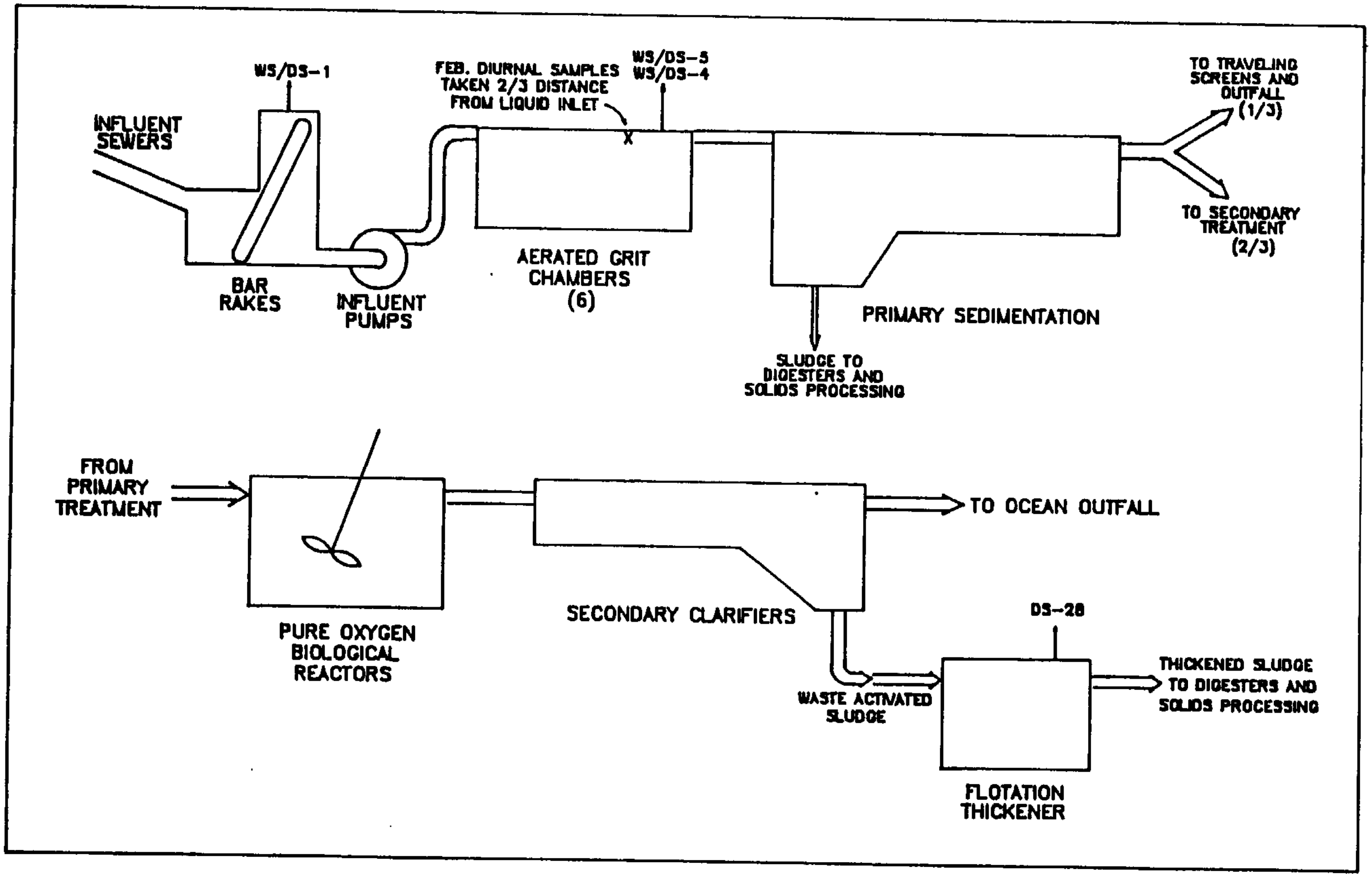


Figure 3B Location of Odor Control Units at JWPCP

Sampling Locations at the JWPCP



Following influent pumping, the wastewater was treated by six aerated grit chambers. Odor control units WS/DS-4 and WS/DS-5 each scrubbed the off-gases from two separate grit chambers, respectively. The liquid exiting these grit chambers was sent to the primary influent conveyance channels that were aerated to prevent the settling of solids in the channel. The off-gases from two of these channels were also scrubbed by odor scrubbers WS/DS-4 and WS/DS-5.

All of the sewage received advanced primary treatment, consisting of polymer-aided primary sedimentation and fine mesh screening. Sixty percent of the plant flow was further treated by pure oxygen activated sludge secondary treatment. Excess biomass produced in that process was wasted. The wasted portion was sent to a dissolved air flotation (DAF) unit for thickening prior to anaerobic digestion. The off-gases from this thickening process and from the thickened waste activated sludge wet-well were scrubbed by odor control unit DS-28. The unit contained only a demister, a compressor, and an ACB. There was no caustic scrubber at that site.

In August of 1986, CSDLAC staff conducted a study of PTOC emissions before and after recharging of an ACB. Commercially available 10 L Tedlar® bags were used by CSDLAC staff to collect samples. The procedure used to clean the bags was to fill and purge them three times with organic-free nitrogen, and to leak check the bags before each sample was collected. Separate CSDLAC staff studies indicated that the three bag purges were sufficient to eliminate any significant error introduced by using non-virgin Tedlar® for sampling; however, these quality control studies were not examined as a component of this study.

The August 1986 results indicated that breakthrough occurred within 30 days for each class of VOC studied. A second experiment was then performed to compare the performance of virgin activated carbon to regenerated activated carbon in two similar units scrubbing the same gas. The experiment found that both carbons were equally ineffective at removing VOCs over sustained periods. Figure 4 illustrates the removal efficiency of these units for benzene (BZ), trichloromethane (TCM), and dichloromethane (DCM). Before the carbon was changed, bed capacity of both units was exhausted. Within three weeks of carbon change, breakthrough of the chlorinated organics was noted. Even the less volatile chlorinated compounds such as tetrachloroethene (PERC) achieved breakthrough within four weeks. Benzene was the first aromatic to breakthrough and was typical of the aromatics studied, in that breakthrough was not noted for about 7 weeks. By the end of eight and one half weeks, only ethylbenzene (ETBZ) and xylenes (XYL) were experiencing any degree of removal by the bed.

The overall performance of the activated carbon beds can be seen in Figure 5, which shows the removal efficiency, based upon the sum of the mass concentration of 23 different PTOCs. The total removal of VOCs can drop to below 0% within 60 days at these units, such that more mass was being desorbed from the bed than was being adsorbed by the bed.

Based upon the results of the previous UCD sampling at the EBMUD, and previously noted temporal behavior of the JWPCP ACBs, an additional purpose of the present study was to examine diurnal emission patterns from preliminary sewage treatment processes. If a regular diurnal pattern was observed, it might be possible to identify sources of PTOC emissions, provide information that could be used for development of source control strategies, and serve as input for further development of emission models for MWTPs.

Figure 4 Removal Efficiency for Benzene, Chloroform, and Dichloromethane (JWPCP Activated Carbon Bed Study)

(Caballero, 1989)

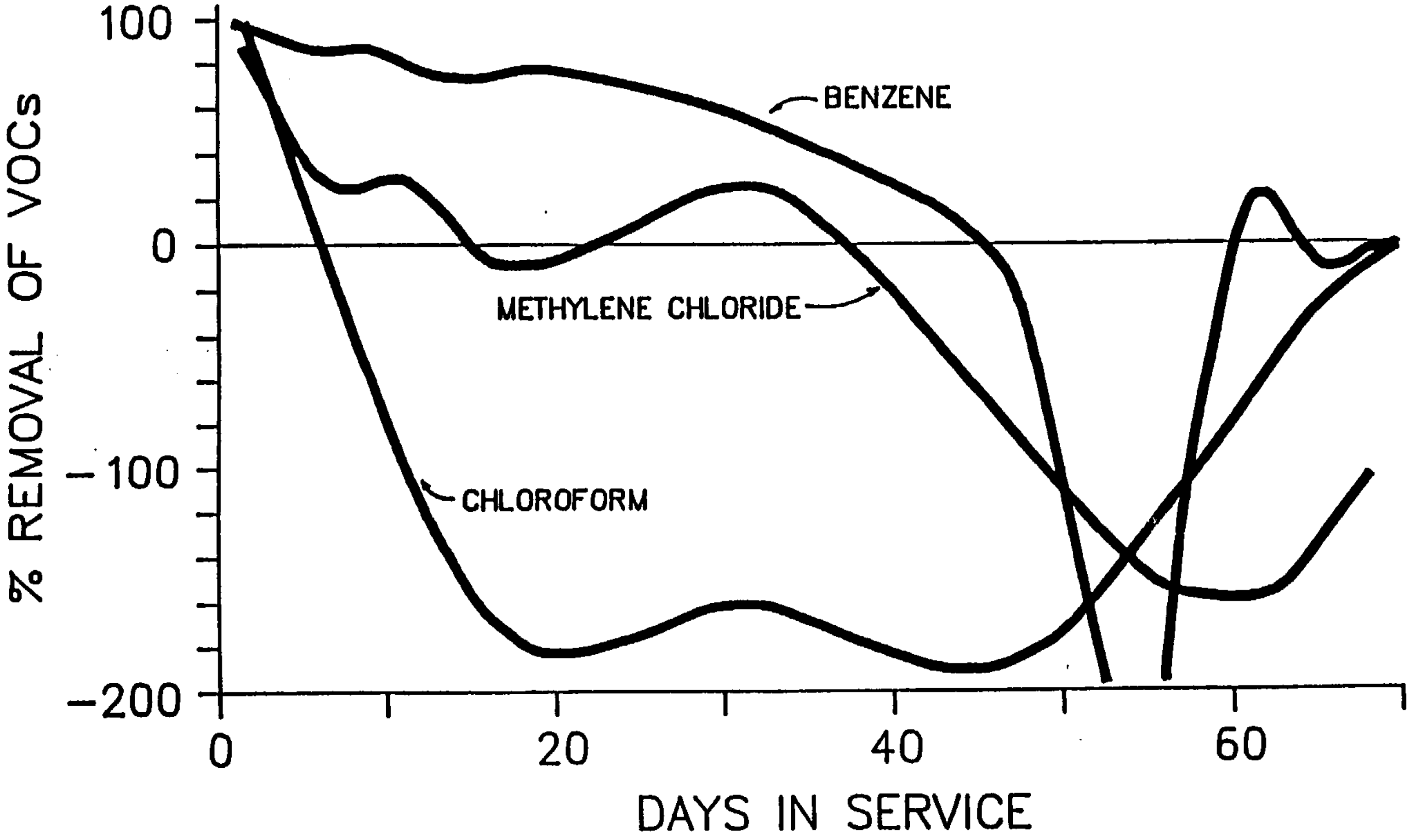
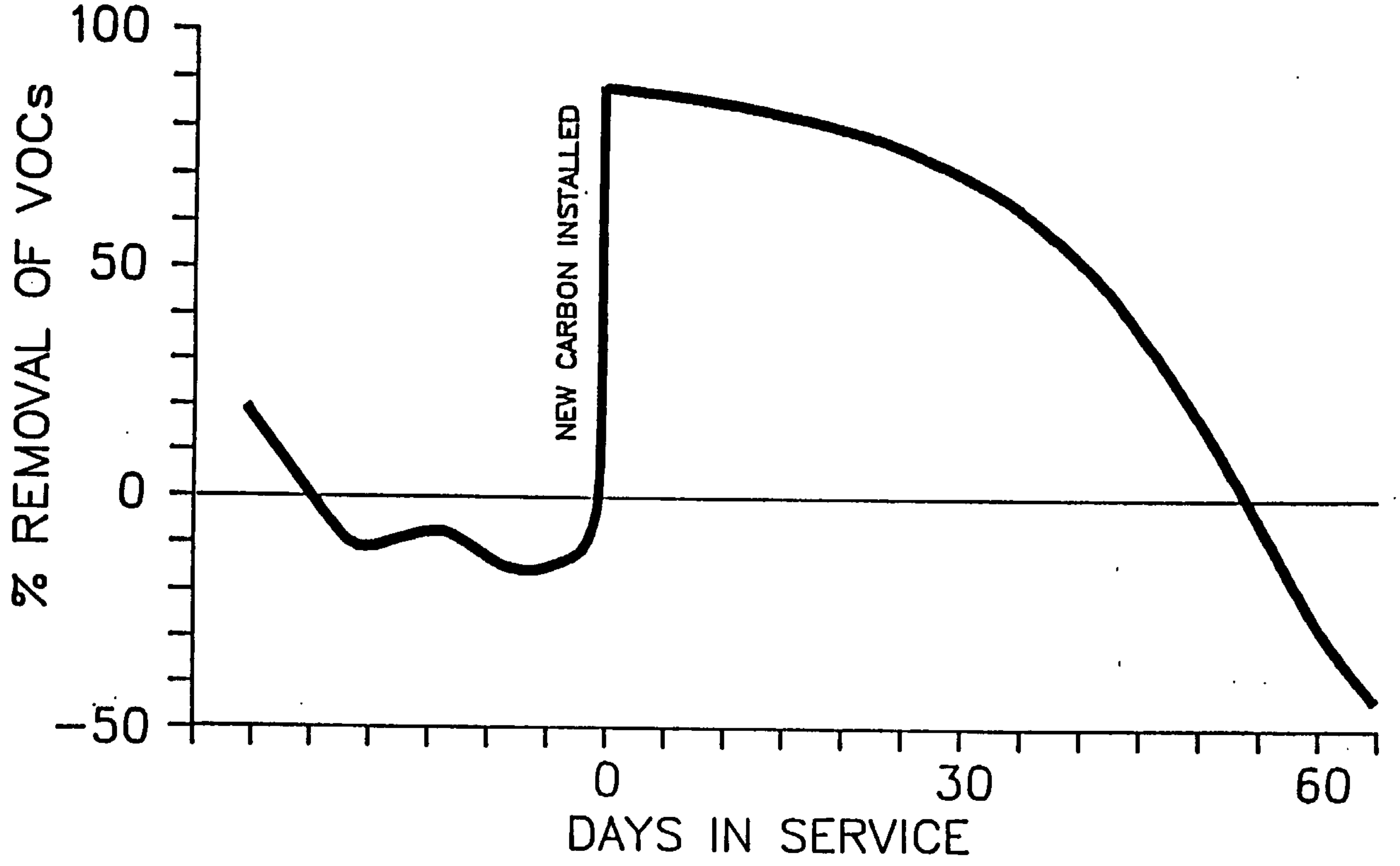


Figure 5 **Overall Performance of the ACBs in Removing VOCs (JWPCP Activated Carbon Bed Study)**

(Caballero, 1989)



1. JWPCP Sampling and Analytical Methods and Equipment

The UCD sampling team used TA multi-sorbent tubes previously described in the EBMUD validation study. Sorbent tubes were shipped by air package express and analyzed within 48 hours at the FAI using the methods described earlier. Analysis for chloroethene (VC) was not performed by the UCD group. Thus only four compounds were quantified by the UCD team.

Samples and standards collected during the first study at JWPCP were stored in glass test tubes with a single silicon septa end cap. The gas standards were transferred onto sorbent tubes in the field. There was no evidence of sample storage loss using the glass tubes and silicon septa end caps during this test because sample tubes were analyzed within 36 hours of the time they were drawn. In subsequent studies the ends of all sorbent tubes containing samples were sealed with stainless steel Swagelock fittings and Vespel, ceramic-filled Teflon® or graphite ferrules by the UCD team. Ceramic-filled Teflon® ferrules were ultimately selected for use in sealing the end caps because they were less costly, chemically inert, and they could be hand-tightened without risk of breaking the sample tubes.

Access to the sampling points at the ACBs was provided by connecting 1/4" stainless steel tubing to a Swagelock bulkhead fitting in the wall. The tubing was bent at a 90° angle and centered in the duct such that the opening faced in the direction of the flow. Teflon® tubing, 1/8 inch o.d., was inserted through the 1/4 inch stainless tubing and bulkhead fitting, and connected to the sorbent tubes.

During the parallel sampling conducted by UCD and CSDLAC staff, Tedlar® bag samples were collected in accordance with Air Resources Board Method 201 (vacuum chamber). Tedlar® bag samples were analyzed by CSDLAC staff at the JWPCP facility. Samples, ranging in size from less than 2 mL for highly concentrated samples to 500 mL for ambient air, were injected manually into a cryogenic trap and then into a Varian 6000 gas chromatograph equipped with a J&W Scientific DB-624 Megabore capillary column for separation. After the initial freeze-out, the trap was swept with helium to remove oxygen and nitrogen, and the sample then passed into a second cryo-focussing trap to obtain narrower peaks and improved resolution. The separated sample was analyzed by an electron capture detector (ECD), a photo-ionization detector (PID), and a Hall electrolytic conductivity detector (HECD) connected in series.

The UCD team also used a Photovac Model 10S70 GC/PID, manufactured by Photovac Incorporated, New York, NY, for Stage II and Stage III of the JWPCP study. The Photovac 10S70 GC/PID was equipped with a 10.6 eV lamp and PID; thus, the PTOC of interest to this study, BZ, could be detected. In the automated sampling mode, an internal pump located at the end of the sampling system drew the sample gas into the unit for analysis. The sample line and sample loop were purged for 10 seconds, valves were automatically closed and a 1 mL sample trapped in the sample loop. The sample was then flushed from the sample loop into a 6 inch SE-30 pre-column followed by a four foot SE-30 analytical column for separation. The SE-30 column, provided a high affinity for BZ separation, producing a relatively broad, but nicely separated peak on the PID even though numerous other compounds were detected. Seventy seconds after each sample was injected, the compounds of interest had entered the analytical column. The pre-column was then back-flushed with organic-free nitrogen carrier gas to reduce the potential for column contamination by high molecular weight compounds, thereby reducing the length of the cycle time. Cycle time, between consecutive sample analysis, was between 12 and 20 minutes, depending upon the length of time allowed before back-flushing the pre-column.

In the manual injection mode, the sample was injected directly through a septum into the sample loop with the aid of a gas-tight syringe. The back-flushing and cycle time parameters were not always the same when operated in manual or automated sampling modes. Cycle time adjustments were required to compensate for temperature differences in the automated unit. The Photovac GC/PIDs were not equipped with internal ovens to maintain a constant column temperature; therefore, periodic recalibration with a known standard was required to identify and quantify peaks. When the Photovacs were deployed for semi-continous monitoring, all sample transfer lines were 1/8 inch O.D. Teflon® tubing (less than 25 feet in length) and connected with stainless steel Swagelock fittings. All components that contacted the sample gas were constructed of either 316 stainless steel, glass, Viton®, or Teflon®.

A number of trip blanks (unexposed tubes) and field blanks (exposed only to the ambient air at the treatment facility) were analyzed to determine potential contamination problems and the effects of ambient air exposure during tube handling on the sample results. During the initial sampling effort, samples were collected through two multi-sorbent tubes in series to determine if breakthrough occurred. After the initial sampling effort, and one additional laboratory study, only single tubes were used to collect samples because breakthrough of the compounds of interest was not observed at the flow rate and volumes employed for the sample concentrations.

For quality assurance during follow-up sampling efforts at JWPCP, sorbent tubes collected by the UCD team were spiked with a known amount of 4-bromofluoro-benzene (BFB) as an internal standard to account for possible VOC diffusion loss. Trip blanks, containing nitrogen, were also carried into the field by CSDLAC staff and never exposed to the MWTP atmosphere. Blank bags were returned to the laboratory for analysis with the samples. In addition, a field blank of organic-free nitrogen was collected in the same manner as a MWTP gas sample to ensure that samples were not contaminated by equipment used in sampling.

Due to the qualitative nature of the headworks sampling (Stage II and III), quality assurance and quality control procedures for the PID sampling were minimal. The Photovac GC/PID was calibrated with a benzene standard of either 250 ppb, ARB supplied, or 112 ppb (Scott-Marin, Riverside CA). However, measured sample gas concentrations ranged from 150 ppb to about 30 ppm. The use of a single point calibrant likely resulted in errors in concentrations reported, most likely underestimating high concentrations.

The nature of the single point calibration may raise questions about the accuracy of the data presented in the studies involving the Photovac GC/PID; however, the study does present very useful semi-quantitative, if not quantitative, data. A potential confounding factor that may have existed was the fact that the standard used for calibration was not humidified.

2. JWPCP Sampling Descriptions

The UCD sampling team conducted three benzene emission studies at the JWPCP treatment facility. 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). The temporal variation of ACB collection efficiency was followed over a period of about one and a half months. 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 diurnal sampling for benzene of the headspace above the primary treatment grit chambers.

B. JWPCP Sampling Results

1. JWPCP Stage I

Beginning in August, 1988, the UCD and CSDLAC teams conducted a collaborative sampling effort at a freshly charged (five days earlier) ACB odor control unit (DS-4) and two additional ACBs, DS-5 and DS-28, which had been in service for many months. The DS-4 and DS-5 units were located near the grit chambers and primary sedimentation basins, while DS-28 collected off-gases from a dissolved air flotation unit (DAF) near the end of the JWPCP's treatment train.

Three 500 mL samples of a known standard gas mixture (Scott-Marin) were collected on sorbent tubes (31, 32, and 33) for calibration during analysis. Standard samples were drawn at a rate of 100 mL/min. The analytical results for two of the three 500 mL samples of standard are presented in Table 23. As discussed previously, there was uncertainty in the sampled volume because of the variable tube-to-tube pressure drops. The third sample of standard was invalid due to a pump malfunction and is not reported. The compound, scan (retention time), total ion count (TIC), and known concentration are reported in the table. Normalized instrument response is presented in Table 24 (TIC Area/mL/ppb).

A total of five sample pairs were collected upstream and downstream from the DS-4 unit, which processed exhaust gas from grit chamber 4 and the conveyance channels leading from the grit chamber to the primary sedimentation tanks. Two sample pairs (upstream/downstream) were collected on 8/16/88 (#4/#7, #8/#10). A second two sample pairs were collected on 8/18/88 (#26/#27, #38/#39), and the last sample pair was collected on 8/25/88 (#49/#50). The sample pairs collected on 8/16/88 were collected at a flow rate of 25 mL/min upstream and 100 mL/min downstream over a ten minute period (approximately 250 mL upstream and 1000 mL downstream). The samples collected on 8/18/88 and 8/25/88

Table 23
Sample Results from Sampling of Standard Collected During the JWPCP Stage I Study by UCD

Compound	Scan #	Tube 31 TIC	Tube 32 TIC	Average TIC
Trichloromethane	381	2827	3617	3222
Tetrachloromethane	409	2213	3232	2723
Benzene	425	7680	9071	8376
Tetrachloroethene	635	4660	5591	5126

Table 24
Normalized Instrument Response from Sampling of Standard Collected During the JWPCP Stage I Study by UCD
(TIC/mL/ppb from 500 mL samples)

Compound	Standard (ppb)	Average TIC	TIC per mL	TIC/mL per ppb
Trichloromethane	103	6444	12.89	.063
Tetrachloromethane	102	2723	5.45	.053
Benzene	112	8736	17.47	.156
Tetrachloroethene	99	5126	10.25	.104

were collected at a flow rate of 25 mL/min upstream and 100 mL/min downstream over a five minute period (approximately 125 mL upstream and 500 mL downstream), after it was established that concentrations were sufficiently high to be quantifiable with the lower sample volume collected. Back-up sample tubes were also drawn to determine if breakthrough of any sample components of interest had occurred. A final sampling of DS-4 with sorbent tubes occurred in October, 1988 after about 40 days in service.

Two sample pairs were collected upstream and downstream from the DS-28 ACB serving the dissolved air flotation (DAF) unit. Both sample pairs were collected on 8/16/88 (#19/#42, #19/#46). The sample pairs were collected at a flow rate of 25 mL/min upstream and 100 mL/min downstream for a period of ten minutes (approximately 250 mL upstream and 1000 mL downstream).

Two samples were collected upstream and downstream from the DS-5 ACB which served grit chamber #5. Both sample pairs were collected on 8/18/88 (#41/#42, #48/#46). The samples were collected at a flow rate of 25 mL/min upstream and 100 mL/min downstream for a period of five minutes (approximately 125 mL upstream and 500 mL downstream).

Analytical results for the samples collected upstream and downstream from three of the ACBs, DS-4, DS-5 and DAF, are presented in Tables 25, 26, and 27 respectively. Average concentration of the samples were calculated by dividing the average TIC per mL of sample by the normalized instrument response in Table 26, because the exact standard and sample volumes collected had a somewhat greater uncertainty than expected due to the variable pressure drop across each tube, the concentration results should be treated as estimates within about 30%.

Removal efficiencies were calculated as the difference in influent and effluent concentrations divided by the influent concentration. For those compounds where standards were not available to determine concentration, linear instrument response was assumed and removal efficiency was calculated as:

[(TIC area/mL inlet) - (TIC area/mL outlet)]/(TIC area/mL inlet).

Again, because of sample volume uncertainty, removal efficiencies are estimates. Negative collection efficiencies for PTOCs were noted across the bed, during periods of relatively clean influent air, even when the bed had been in operation for less than one week. The reader is advised that large negative %-removals do not necessarily translate into large emissions because the influent concentrations could be relatively small during those samples (clean sweep air passing across the bed).

The data collected for the freshly recharged bed indicated that although the bed was performing well at removing most PTOCs, breakthrough of DCM began after less than five days in service, and along with TCA was yielding a negative collection efficiency after less than one week. The data indicate that collection efficiency appears to change quickly with time, especially for the more volatile chlorinated compounds. Negative or low collection efficiencies were noted for both low volatility and high volatility compounds from saturated carbon beds, DS-5 and DS-28 (DAF), during the initial sampling effort.

The carbon bed at DS-4 was monitored for a seven week period following carbon bed regeneration, as it became saturated, the collection efficiency for the higher boiling point compounds decreased slowly from 100%; however, the collection efficiency for the lower boiling point compounds was already negative. The presence of positive and negative values for collection efficiency indicated that the saturated bed contained compounds that were competing for sites on the sorbent. Because low volatility, higher molecular weight compounds usually have a greater affinity for the adsorbent, the extended tests appear to show a general trend of lighter-end compound displacement.

Table 25a
Sample Results from Activated Carbon Unit DS-4 Collected by UCD on 8/16/88 During the JWPCP Stage I Study

Compound	Scan #	250 mL Upstream Tube 4 TIC	250 mL Upstream Tube 8 TIC	Average ppb
Dichloromethane	247	29886	55201	NA
Trichloromethane	381	1236	2785	128
1,1,1-trichloroethane	394	1188	4237	NA
Tetrachloromethane	409	0	0	0
Benzene	425	38714	35793	955
Trichloroethene	477	0	0	0
Toluene	586	45930	75094	NA
Tetrachloroethene	635	16423	16379	631

Compound	Scan #	1000 mL Downstream Tube 7 TIC	1000 mL Downstream Tube 10 TIC	Average ppb
Dichloromethane	247	37373	32143	NA
Trichloromethane	381	0	0	0
1,1,1-trichloroethane	394	0	0	0
Tetrachloromethane	409	0	0	0
Benzene	425	2312	1127	11
Trichloroethene	477	0	0	0
Toluene	586	638	503	NA
Tetrachloroethene	635	0	0	0

Compound	Scan #	Average Removal Efficiency DS-4
Dichloromethane	247	80%
Trichloromethane	381	99+%
1,1,1-trichloroethane	394	99+%
Tetrachloromethane	409	NA
Benzene	425	99+%
Trichloroethene	477	NA
Toluene	586	99+%
Tetrachloroethene	635	99+%

Table 25b
Sample Results from Activated Carbon Unit DS-4 Collected on 8/18/88 During the JWPCP Stage I Study by UCD

Compound	Scan #	125 mL Upstream Tube 26 TIC	125 mL Upstream Tube 38 TIC	Average ppb
Dichloromethane	247	4795	12099	NA
Trichloromethane	381	526	382	58
1,1,1-trichloroethane	394	2056	3765	NA
Tetrachloromethane	409	0	0	0
Benzene	425	35428	27873	1623
Trichloroethene	477	0	0	0
Toluene	586	40662	32820	NA
Tetrachloroethene	635	5223	6374	446

Compound	Scan #	500 mL Downstream Tube 27 TIC	500 mL Downstream Tube 39 TIC	Average ppb
Dichloromethane	247	45549	24856	NA
Trichloromethane	381	0	0	0
1,1,1-trichloroethane	394	215	0	NA
Tetrachloromethane	409	0	0	0
Benzene	425	1928	982	19
Trichloroethene	477	0	0	0
Toluene	586	751	529	NA
Tetrachloroethene	635	0	0	0

Compound	Scan #	Average Removal Efficiency DS-4
Dichloromethane	247	-4%
Trichloromethane	381	100%
1,1,1-trichloroethane	394	99%
Tetrachloromethane	409	NA
Benzene	425	99%
Trichloroethene	477	99+%
Toluene	586	99+%
Tetrachloroethene	635	99+%

Table 25c
Sample Results from Activated Carbon Unit DS-4 Collected on 8/25/88 During the JWPCP Stage I Study by UCD

Compound	Scan #	125 mL Upstream Tube 49 TIC	ppb
Dichloromethane	247	5665	NA
Trichloromethane	381	1645	209
1,1,1-trichloroethane	394	4542	NA
Tetrachloromethane	409	0	0
Benzene	425	51592	2646
Trichloroethene	477	0	0
Toluene	586	58151	NA
Tetrachloroethene	635	7184	553

Compound	Scan #	500 mL Downstream Tube 50 TIC	ppb
Dichloromethane	247	11668	NA
Trichloromethane	381	3369	107
1,1,1-trichloroethane	394	22547	NA
Tetrachloromethane	409	0	0
Benzene	425	77218	990
Trichloroethene	477	0	0
Toluene	586	74736	NA
Tetrachloroethene	635	15834	305

Compound	Scan #	Approximate Removal Efficiency DS-4
Dichloromethane	247	48%
Trichloromethane	381	49%
1,1,1-trichloroethane	394	-24%
Tetrachloromethane	409	NA
Benzene	425	63%
Trichloroethene	477	NA
Toluene	586	68%
Tetrachloroethene	635	45%

Table 26
Sample Results from Activated Carbon Unit DS-5 Collected on 8/18/88 During the JWPCP Stage I Study by UCD

Compound	Scan #	125 mL Upstream Tube 41 TIC	125 mL Upstream Tube 48 TIC	Average ppb
Dichloromethane	247	13655	16018	NA
Trichloromethane	381	505	625	72
1,1,1-trichloroethane	394	0	0	0
Tetrachloromethane	409	0	0	0
Benzene	425	32757	31465	1647
Trichloroethene	477	0	0	0
Toluene	586	31780	31128	NA
Tetrachloroethene	635	1673	2588	164

Compound	Scan #	500 mL Downstream Tube 42* TIC	500 mL Downstream Tube 46 TIC	Average ppb
Dichloromethane	247	5929	7760	NA
Trichloromethane	381	0	383	6
1,1,1-trichloroethane	394	0	719	NA
Tetrachloromethane	409	0	0	0
Benzene	425	60364	37070	625
Trichloroethene	477	0	0	0
Toluene	586	119579	52453	NA
Tetrachloroethene	635	6424	6721	126

Compound	Scan #	Average Removal Efficiency DS-5
Dichloromethane	247	88%
Trichloromethane	381	92%
1,1,1-trichloroethane	394	ND
Tetrachloromethane	409	NA
Benzene	425	62%
Trichloroethene	477	NA
Toluene	586	32%
Tetrachloroethene	635	59%

* Tube #42 was analyzed in conjunction with the sample saver feature at a ratio of 13:44 (13 parts were analyzed, 44 parts diverted to sorbent tube for later analysis. All data for Tube 42 have been multiplied by 57/13 to correct for the decreased sample volume; this procedure may have resulted in some additional uncertainty.

Table 27
Sample Results from Activated Carbon Unit DS-28 (DAF) Collected on 8/16/88 During the JWPCP Stage I Study by UCD

Compound	Scan #	250 mL Upstream Tube 14 TIC	250 mL Upstream Tube 19 TIC	Average ppb
Dichloromethane	247	1028	2750	NA
Trichloromethane	381	588	1149	55
1,1,1-trichloroethane	394	747	1193	NA
Tetrachloromethane	409	0	0	0
Benzene	425	2599	3785	82
Trichloroethene	477	0	0	0
Toluene	586	2744	3815	NA
Tetrachloroethene	635	4994	10009	289

Compound	Scan #	1000 mL Downstream Tube 16 TIC	1000 mL Downstream Tube 21 TIC	Average ppb
Dichloromethane	247	22412	25918	NA
Trichloromethane	381	907	1220	17
1,1,1-trichloroethane	394	3537	4987	NA
Tetrachloromethane	409	0	0	0
Benzene	425	3279	3353	21
Trichloroethene	477	0	0	0
Toluene	586	1345	1388	NA
Tetrachloroethene	635	19075	27096	222

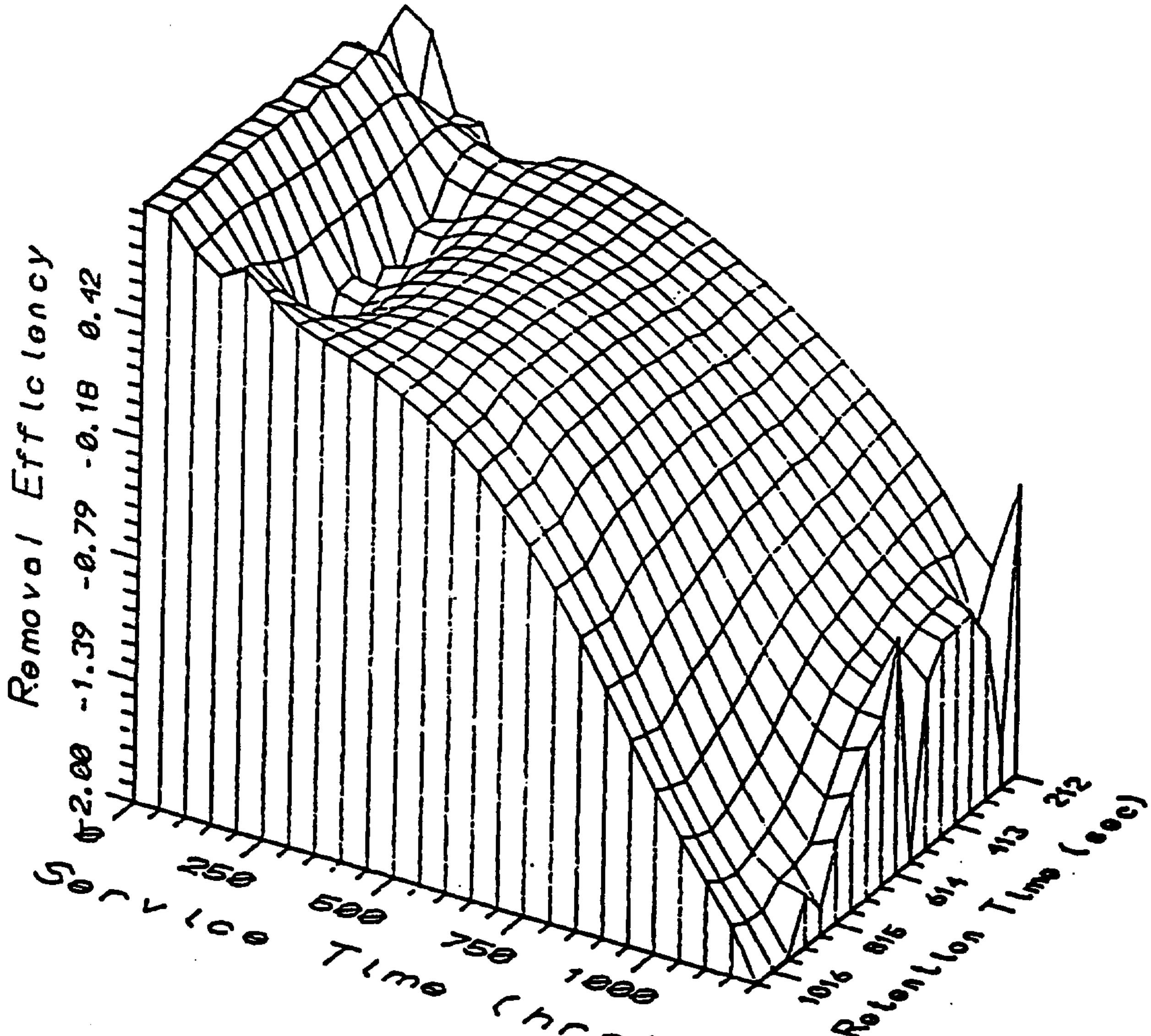
Compound	Scan #	Average Removal Efficiency DS-28
Dichloromethane	247	-220%
Trichloromethane	381	69%
1,1,1-trichloroethane	394	-10%
Tetrachloromethane	409	NA
Benzene	425	74%
Trichloroethene	477	NA
Toluene	586	90%
Tetrachloroethene	635	23%

Figure 6 represents the DS-4 activated carbon bed efficiency for various PTOCs and illustrates the displacement phenomenon; 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. 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. The data have been smoothed somewhat by the plotting routine because only four discrete sampling periods were available; nevertheless, the plot does demonstrate the trends observed.

The general trend illustrated in Figure 6 was that the retention efficiency decreased most rapidly for high volatility compounds, less rapidly for medium volatility substances, and least rapidly for the least volatile substances. As points of reference, the previous tables list the approximate GC retention times for several species of interest. In a few cases, some of the higher volatility compounds were retained with greater efficiency than the lower volatility compounds, indicating that factors other than volatility played a role in bed efficiency. It appeared that the bed was able to regenerate some limited sorptive capacity for the high volatility compounds. As discussed later during the continuous monitoring phase, periods of relatively clean gas passing over the bed could result in some regeneration of sorptive capacity. Within 1200 hours the bed had ceased to function as an effective VOC control method even though the bed remained effective as an odor control measure.

Because these data indicate that many of the PTOCs of concern (such as TCM, DCM, and to some extent BZ) were being stripped from the exhausted ACB, ACBs would probably need to be replaced or regenerated frequently if they were to serve as a PTOC control measure. Because of the uncertainty of loading rates, some type of monitor would probably be needed in order to know when breakthrough of a particular compound had occurred.

Figure 6 3-D Representation of the DS-4 ACB Efficiency for Various PTOCs
(ACB Efficiency vs. Time in Service, vs GC retention time)



a. JWPCP Stage I Findings on TA Sorbent

When the field data were first analyzed, there was concern that breakthrough of the TA tubes had occurred for certain compounds. The values on one back-up tube (TA 15) exceeded the highest value observed on field blanks. However, after additional data were analyzed, it was determined that no breakthrough had occurred. The scan numbers were not identified with PTOCs of concern and appeared to have resulted from degradation of the Tenax sorbent.

During the August sampling effort, inlet samples were analyzed immediately, as well as one back-up tube from an inlet sample (TA 15, the back-up tube for TA 14). The remaining back-up tubes (17, 20 and 22) were analyzed five days after their corresponding inlet sample tubes 16, 19, and 21. The delayed analysis results for some compounds in back-up tubes (TA 17, 20, and 21) yielded significantly higher values than those of their respective sample tubes and the field blanks; whereas, the same compounds on the immediately analyzed back-up tube (TA 15) were less than those of its respective sample tube and the field blanks. The high values for some compounds on the back-up tubes with delayed analysis indicated that either: 1) the three back-up tubes were contaminated during the five day storage period, 2) that compounds on the three back-up tubes reacted during storage to form new compounds, 3) the delayed analysis of the three back-up tubes resulted in further release of degradation products from within the Tenax to form the new compounds.

Certain characteristic peaks appeared that corresponded to Tenax$^{\Psi}$ degradation products previously reported in the literature; hence, it was unlikely that the higher values resulted from contamination or reactions of the sample during storage. It was remotely possible that the oxygen or ozone in the ambient air sorbed deep into the Tenax during storage and then reacted with the Tenax when samples were desorbed. However, a more likely explanation is that when UCD staff originally thermally cleaned the tubes, insufficient time was allowed to purge oxygen out of the Tenax before it became hot. As a result, when the tubes were "cleaned," the resin may have thermally degraded. Over time, thermal degradation products deep within the polymer diffused to the surface; thus, the longer the tubes were stored after being cleaned, the more degradation product appeared. We believe this to be the case. For the PTOCs of concern, these artifacts did not prevent identification, however, for compounds such as phenylethanone, phenol, benzaldehyde, etc. it could not be determined whether the compounds were present in the wastewater off-gases. If Tenax is to be used as a adsorbent medium, care must be given to thoroughly purge oxygen that may reside within the resin prior to thermal cleaning.

b. Additional Compounds Identified

Since GC/MS analyses were performed in "scanning" mode on all sorbent tube samples, identification of additional species was attempted by using the spectral library capabilities of the VG data system. Such an approach proved to be relatively fruitless since complete separation of all compounds was not achieved, and ions from the unresolved background of compounds would appear in the spectra of resolved species, leading to poor library "matches." However, an attempt was made to identify some of the resolved peaks by searching for the ion spectra of compounds thought to be present in the wastewater. In such a procedure, individual ions known to be produced by a specific compound are identified from the total ion scans of the sample and replotted. If peaks are observed for <u>each</u> of the ions known to be produced by a specific compound, and if its retention time corresponds to the approximate boiling point of the unknown peak, one can be fairly certain of the identity of the compound that produced the unknown peak. Using such a procedure almost all of the 16 PTOCs of concern were found in the grit chamber gases with the exception of chloroethene (VC) and 2-propenenitrile (AN).

However, with the exceptions of DCM, BZ, TOL, ETBZ, and PERC, their concentrations were relatively small (estimated at less than about 100 ppb).

Two examples of the specific ion search technique are given in figures 6A, 6Ba and 6Bb and figures 6Ca and 6Cb. The total ion chromatogram (TIC) corresponding to a sample from the inlet of the WS/DS-4 odor control unit is shown in figure 6A. Four ions characteristic of dichlorobenzene (DCB), b.p. 172 - 180 ^{o}C, or naphthalene (NAPH), b.p. 218 ^{o}C, were identified by the VG Trio software and corresponded to ion scans 918 and 1122, respectively, of figure 6A. The selected ion spectra are shown in figures 6Ba, 6Bb, 6Ca and 6Cb. Note that only for scan 918 are all the DCB ions present, and likewise only for scan 1122 are all the ions characteristic of NAPH present. The DCB co-eluted with another compound at 918 (a branched unsaturated alkene) and would not have been recognized as being present without this procedure. The total ion count for the 918 peak was about 2.1% of the TIC. A rough visual estimate of the DCB ion contribution to the mass spectrum would be about 1/5, hence about 0.4% of the TIC; NAPH was well-resolved and was 0.2% of the TIC. These represent, very roughly, concentrations about 1/6 to 1/12 as much as BZ (peak 424, 2.4%) respectively, and hence would have been present at about the 100's to 10's of ppbv range. The single largest peak in the chromatogram (12%) was identified as 1-methylethenylbenzene (α-methylstyrene). The dimethylbenzenes (XYL) were also present at substantial concentrations, but as was the case for α-methylstyrene, was not on the target list of 16 PTOCs. As indicated by the key for the largest peaks shown in figure 6A, the majority of the mass appears to be associated with hydrocarbon components with boiling points greater than 100 ^{o}C. The general shape of the chromatogram is similar to that reported by the EBMUD (1989). Thus we conclude that the volatilization of semi-VOCs from wastewater can be appreciable.

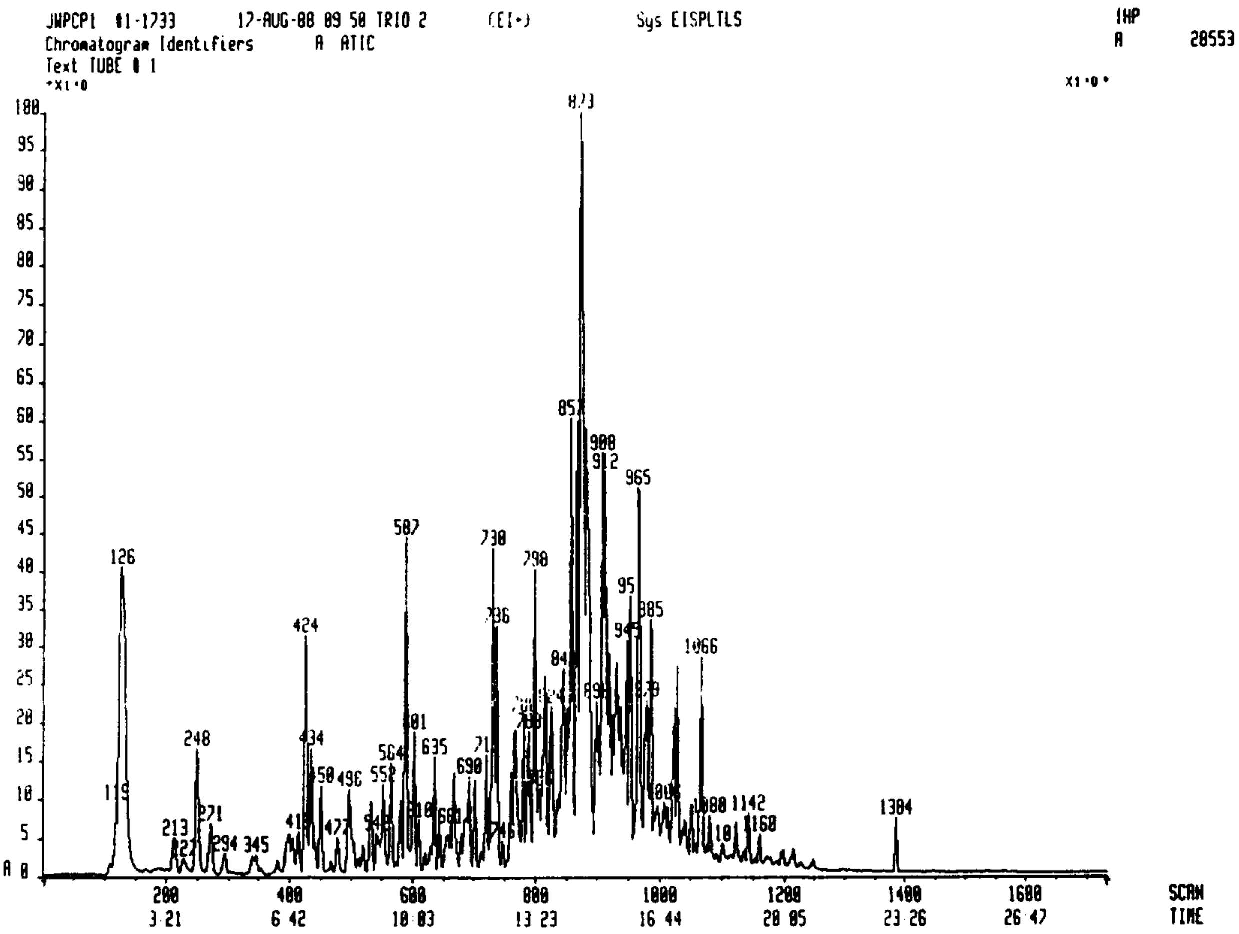


Figure 6A Total Ion Chromatogram of Sample from Inlet to WS/DS-4

JWPCP Tube #1 - WS-4 Inlet

Comp'd	Scan	Comp'd	Scan
COS + SO2	119	XYL	765
SO2	126	isopropylbenzene	798
2-propanone	213	trimethyloctane?	857
DCM	248	unst'd HC	866
BZ	424	a-methyl styrene	873
2,2,3,3-tetramethylbutane	434	isobutylbenzene	882
3-methylhexane	450	TMB	886
methylcyclohexane	496	2-propyl-1-heptanol?	908
dimethyldisulfide	564	LIM	912
TOL	587	DCB + trimethylhexene?	918
octane	601	isopropylmethylbenzene?	951
PERC	635	UND?	965
ETBZ	719	dimethylethylbenzene	1027
XYL	730		
nonane	736		

Figure 6Ba Selected Ion Chromatograms of Ions Specific to Dichlorobenzene

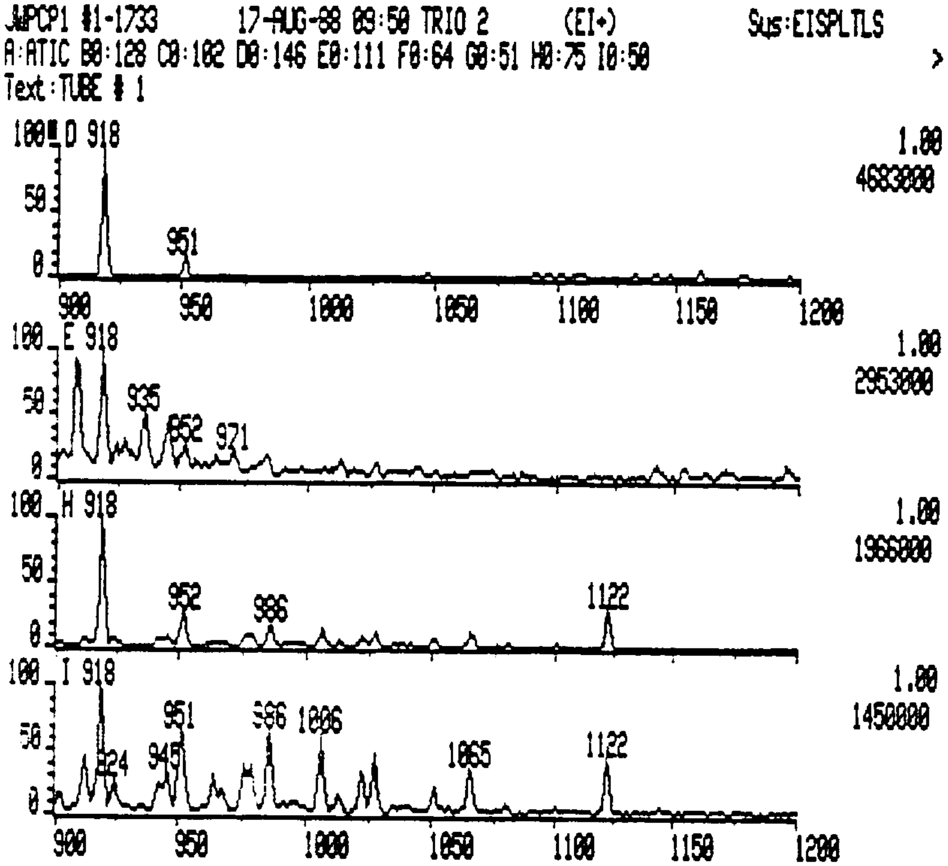


Figure 6Bb Ion Spectrum of Dichlorobenzene

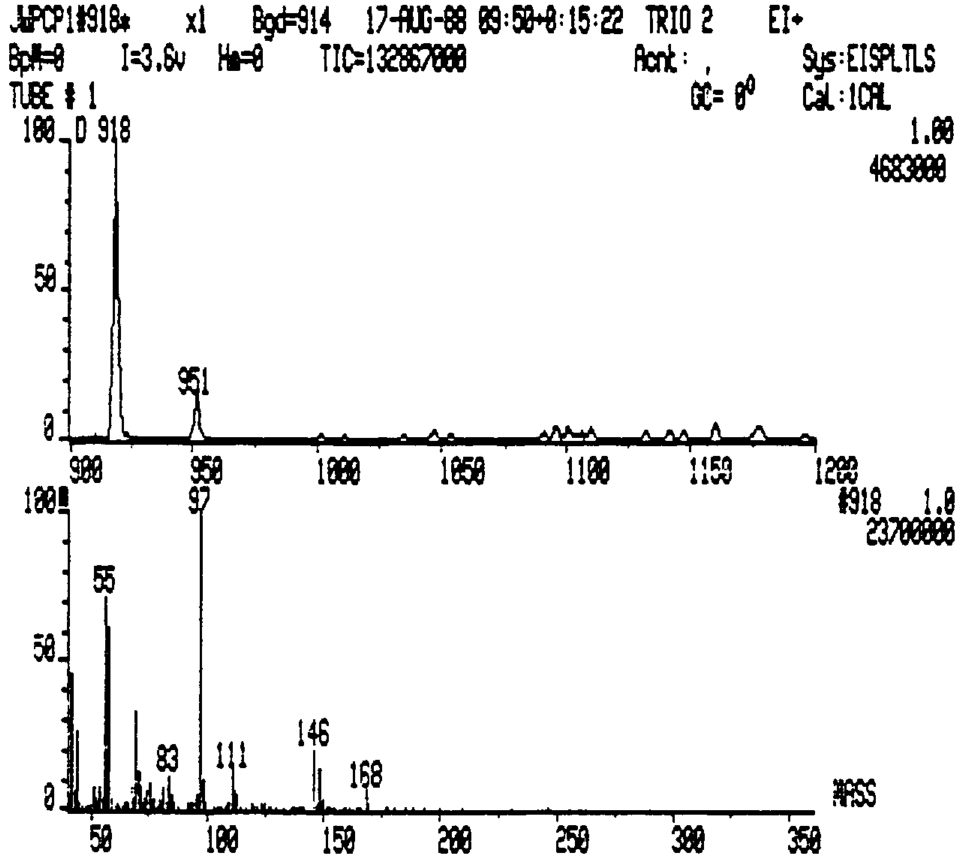


Figure 6Ca Selected Ion Chromatograms of Ions Specific to Naphtalene

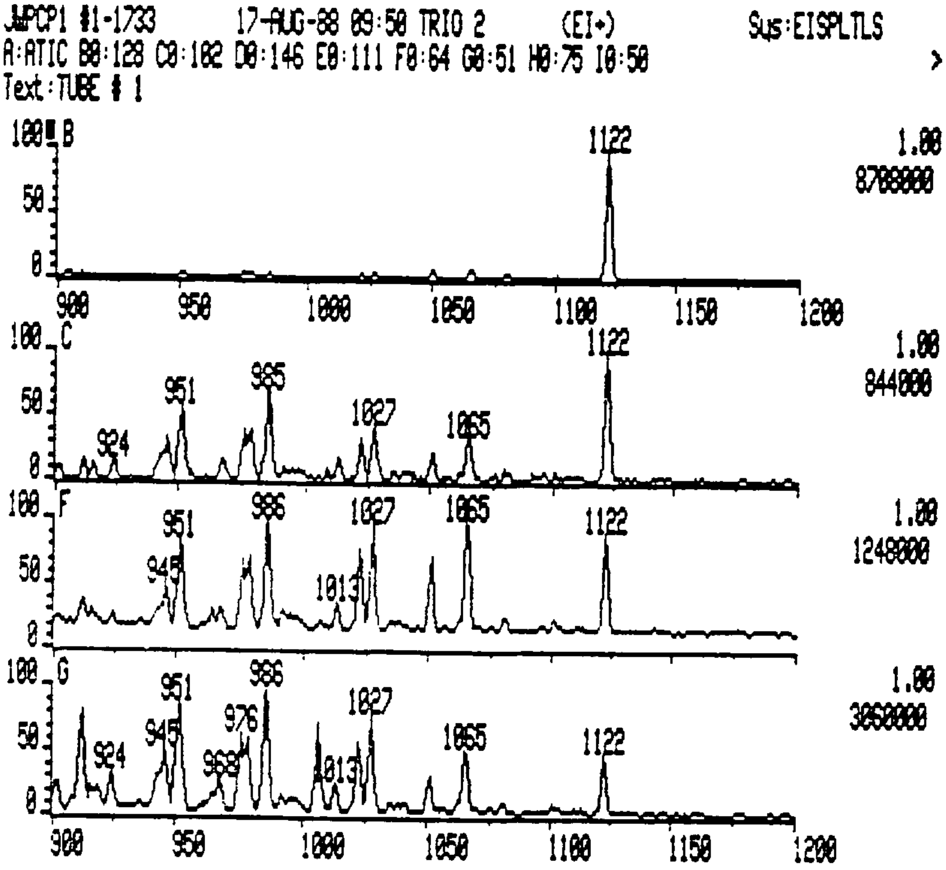


Figure 6Cb Ion Spectrum of Naphthalene