2. JWPCP Stage II

The non-sequential breakthrough of organics noted in the JWPCP Stage I study, and the apparent re-development of limited sorptive capacity on the ACBs indicated that an understanding of diurnal loading patterns was important. A Stage II study was conducted on December 27, 1988, in an effort to gather data on diurnal influent and effluent patterns.

A van outfitted with two Photovac® Model 10S70 portable GC/PIDs was sited approximately ten feet from the ACB at the grit chambers. The DS-4 ACB was known to have been fully saturated by hydrocarbon emissions as the bed had last been replaced in August of 1988. Both portable GC/PIDs were equipped to perform automated analysis of samples drawn directly from the gas stream. One instrument was used to collect samples immediately upstream of the carbon bed and the second instrument collected samples immediately downstream from the ACB.

The GC/PIDs were calibrated with a 250 ppb BZ standard provided in two electro-polished stainless steel cylinders by the ARB's Monitoring and Laboratory Division. Each GC/PID was calibrated with the same calibration gas through a T-fitting; connections to the calibration gas cylinder were made with virgin 1/8 inch Teflon® tubing. Because the van did not provide a controlled temperature environment, the cycle times on the Photovacs were set to provide one single point calibration every two hours.

The twenty-four hour semi-continuous sampling, revealed that the concentration of BZ in the headspace above the grit chambers varied with the time of day. The first sampling trip results yielded an interesting diurnal fluctuation; the concentration ranged from less than 100 ppb at night to nearly 30 ppm during one morning peak (Figure 7). Several smaller peaks in benzene influent concentration were also noted and can be examined in the smaller scale graph (Figure 8).

Figure 7 The 24 Hour Fluctuation in Benzene Concentrations
Inlet and Outlet of DS-4
(JWPCP Stage II Study)

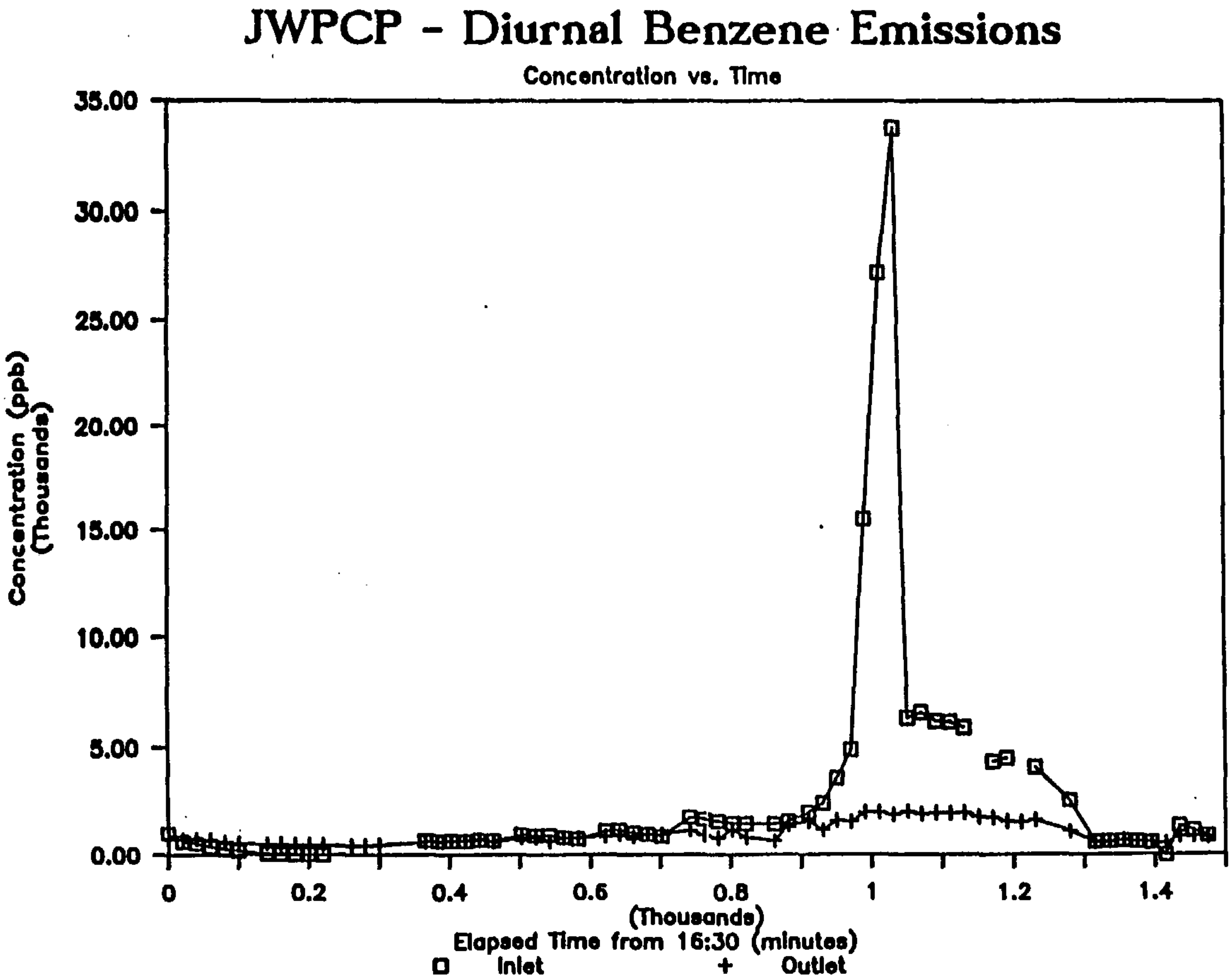
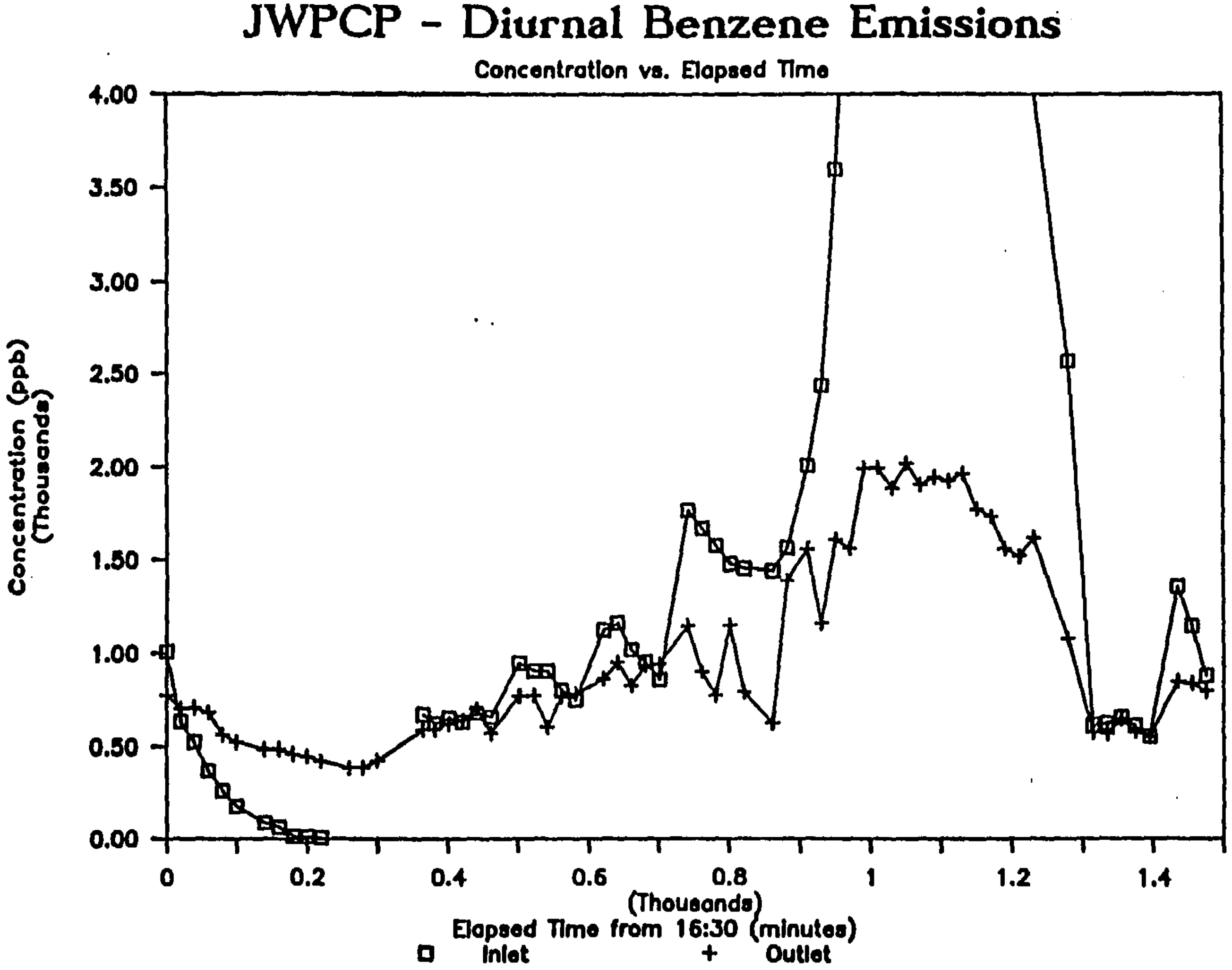


Figure 8 The 24 Hour Fluctuation in Benzene Concentrations
Inlet and Outlet of DS-4 (Change in Scale)
(JWPCP Stage II Study)



Interestingly, the ACB served to damp out the peaks, but the exhaust concentrations still generally followed the fluctuations in inlet concentration. Furthermore, there were periods when negative collection efficiencies were noted and the exhaust benzene concentration exceeded the inlet concentration. Thus, during periods of relatively clean air, the ACB apparently regenerated some capacity to adsorb even the lower molecular weight substances.

The data should be interpreted with some caution as a single point calibration may not yield highly accurate results, especially when a 250 ppb standard is used as the reference concentration to measure concentrations in the greater than 10 ppm range. Previous ARB experience indicated that when a 250 ppb standard is employed, sample values in the ppm range may be underestimated, depending upon instrument configuration (Okamoto, 1989). However, even with the single point calibration nature of our the data and the minor problems encountered during analysis, sufficient information was gathered to warrant a more detailed analysis of the diurnal emission pattern.

3. JWPCP Stage III

The Stage III study was conducted to determine if the Stage II study results were an anomaly. A second sampling trip employing the use of portable Photovac Model 10S70 GC/PIDs was conducted in February 1989, providing a four-day round-the-clock sampling of gas above the grit chambers at the facility. The two Photovac GC/PID units used in Stage II were used again in the Stage III sampling trip. One GC/PID was deployed in a van adjacent to the sampling area, and one GC/PID was located in an office trailer where Tedlar® bag samples collected by CSDLAC staff were analyzed. The Photovac unit in the van was configured for automatic sampling and the Photovac in the trailer was configured for manual sample injection.

The GC/PID located in the van cycled automatically and was run continuously for periods in excess of 24 hours, recording sample analysis in 15-30 minute increments. The field GC/PID configuration was essentially the same as used during the Stage II sampling study. Samples were collected from the headspace above the grit chamber serving influent line JOD (CSDLAC designation).

The office trailer GC/PID cycled manually at least two times every hour for sample analysis plus occasional calibration. The office trailer GC/PID configuration employed manual injection of samples into the sample loop using a gas tight syringe. For the office trailer GC/PID analysis, samples were collected in Tedlar® bags from above the grit chambers 3 and 6 serving influent lines JOA and JOB by CSDLAC student employees once every hour. A 100 μL aliquot of sample was injected via a gas-tight syringe directly into the sample loop of the GC/PID, entering the SE-30 column. The Tedlar® bags used by CSDLAC staff were purged three times with organic free nitrogen and reused for each hourly sampling effort.

During Stage III, each GC/PID was calibrated with a NBS traceable gas standard (Scott-Marin, Riverside, CA) that contained a nominal 112 ppb benzene, which was a lower concentration than the 250 ppb benzene standard used in Stage II. The Photovac unit in the van was calibrated once every two or three sample analyses depending upon environmental temperature fluctuation (the temperature fluctuation was much greater in February than was experienced in December, due to weather conditions). To ensure that sufficient calibrant gas would be available for the extended study, it was contained in an onboard gas cylinder (Scott-Marin, Riverside, CA). The Photovac located in the trailer was calibrated every two to three hours with a 500 μL aliquot of the same 112 ppb benzene standard (Scott-Marin, Riverside, CA) taken earlier in the day in a Tedlar® bag from the cylinder onboard the sampling van. Because the temperature in the office trailer remained fairly constant, and because operator practice appeared to occasionally influence the adequacy of injection of the 500 μL calibration gas sample, the average calibration value determined by all calibration runs was used to calculate the concentration (ppbv) of the headspace gas samples.

The results from the JWPCP Stage II study cannot be compared directly to the results of the JWPCP Stage III study because samples were collected from different locations of the headworks. However, there were some similarities in the diurnal behavior of the headworks gas emissions as well as obvious differences. The Stage III study indicated that regular diurnal cycles of loading were present in all three of the interceptors leading to the plant, but they did not exhibit exactly the same temporal pattern as was noted in the December JWPCP Stage II study, nor was a two order-of-magnitude range in concentrations noted. Higher concentrations still appeared in the morning hours during February; however, the concentration range was different than that identified in December.

The influent loading concentrations sampled by CSDLAC student staff for grit chambers 1 and 3 are presented in Figures 9 and 10; two and one half days of data were collected and analyzed by manual injection GC/PID. The influent loading concentrations monitored by the automated sampling GC/PID at grit chamber 6 are presented in Figure 11; four and one half days of data were collected. In addition, three of the sample analyses collected on February 17 were examined to determine if the instrument response for each unknown compound was proportional from sample to sample. Table 28 contains the results of the analysis and indicates that the relative concentrations of unknowns vary with time, as noted by the high standard deviations. Thus, a 20% decrease in BZ concentration is not necessarily associated with a 20% decrease in the concentration of other unknown PTOCs sampled.

Figure 9 Influent Loading Concentrations Above Grit Chamber 1 (JWPCP Stage III Study, Manual Injection GC/PID).

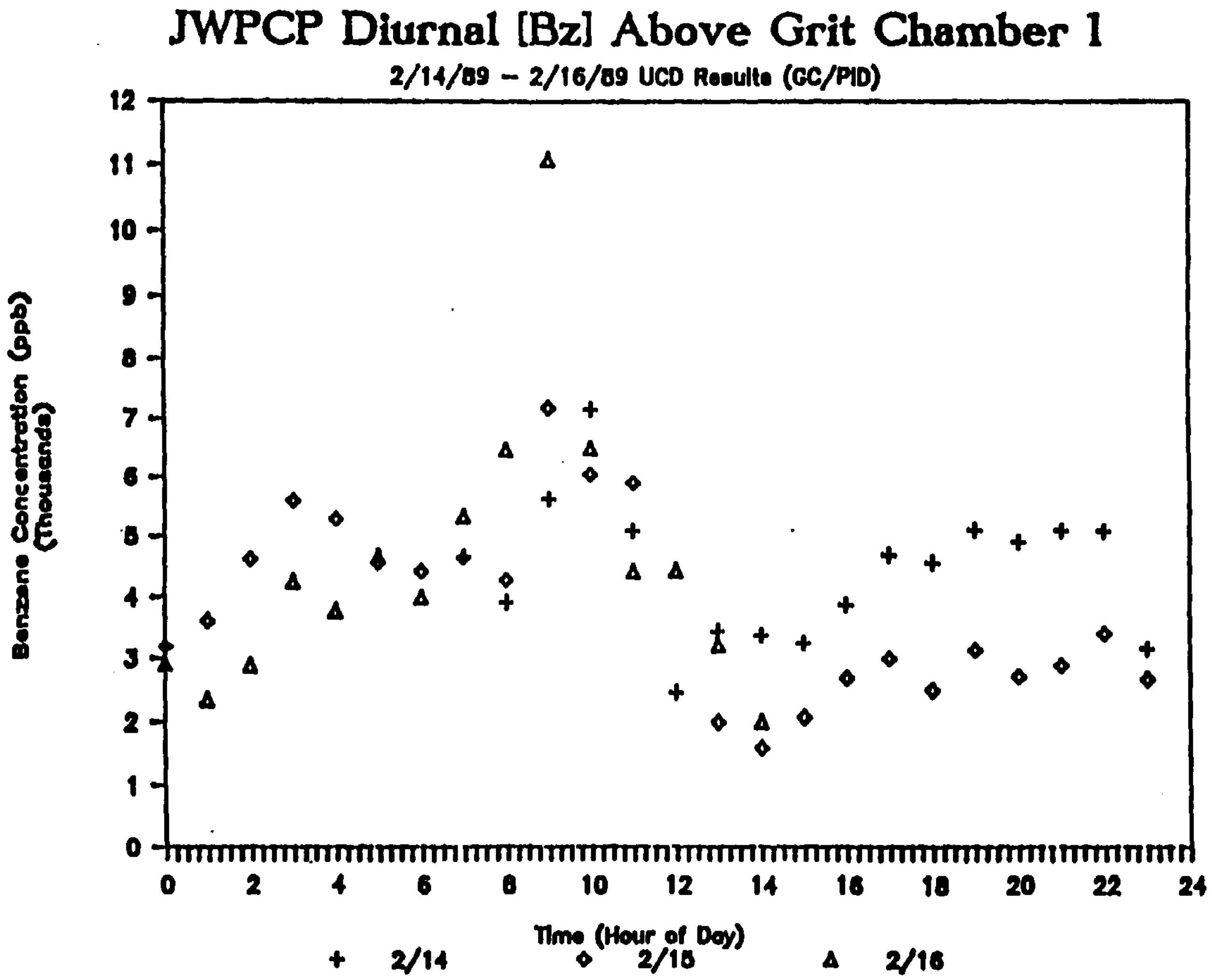


Figure 10 Influent Loading Concentrations Above Grit Chamber 3 (JWPCP Stage III Study, Manual Injection GC/PID).

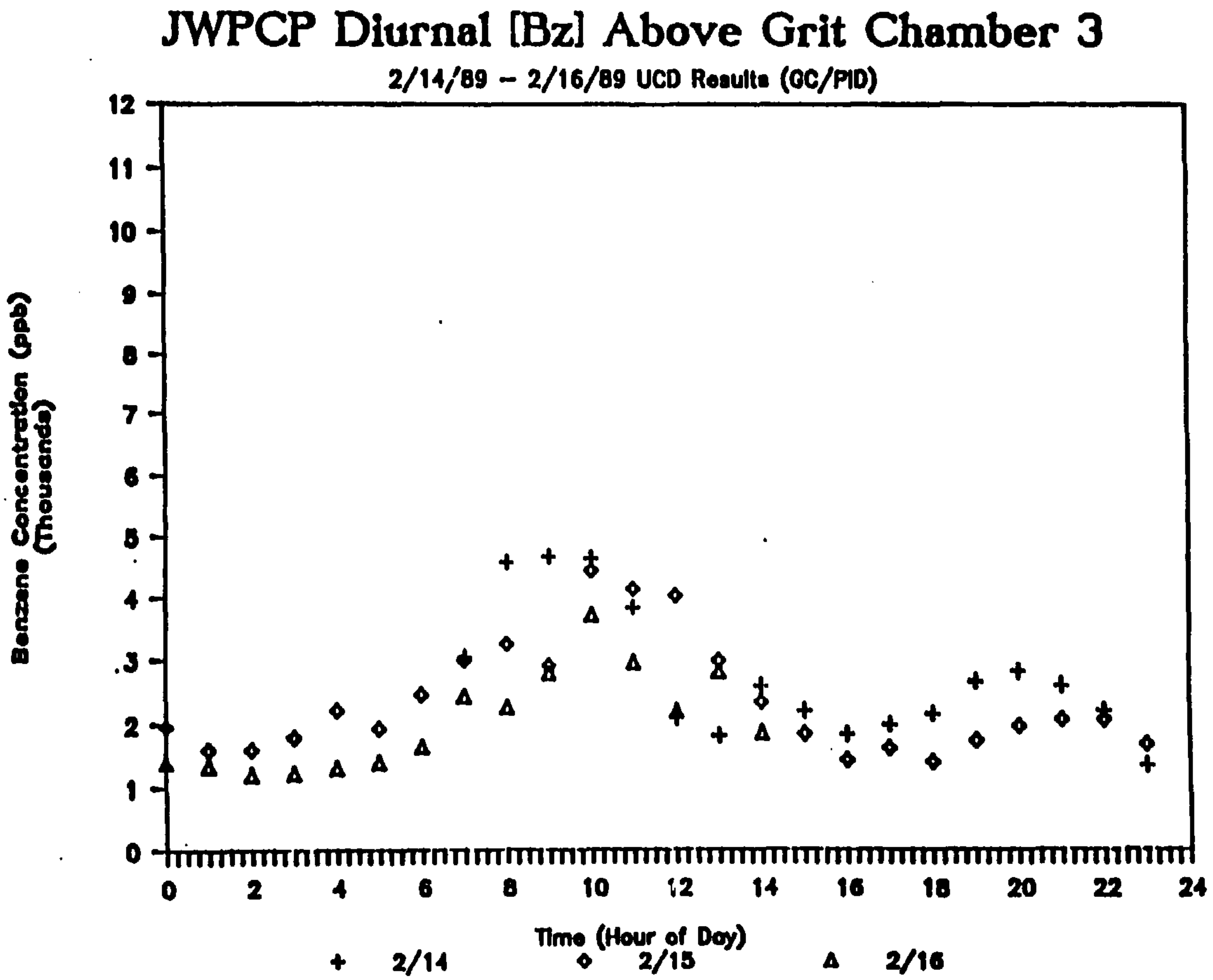


Figure 11 Influent Loading Concentrations Above Grit Chamber 6 (JWPCP Stage III Study, Automated Sampling GC/PID).

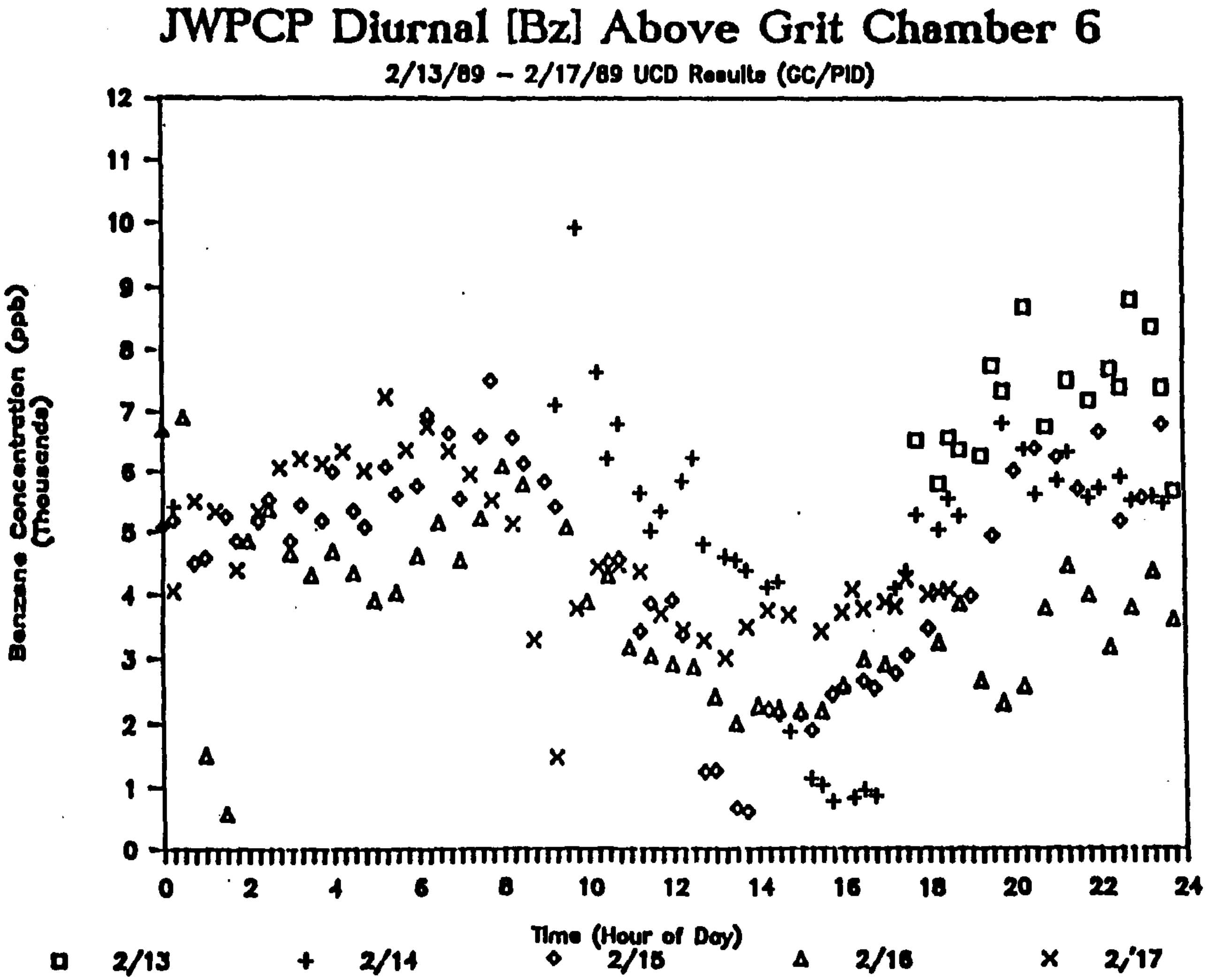


Table 28
Relative Concentrations of Unknown Compounds as Indicated by PID Instrument Response Determined During the Stage III Sampling Effort on 2/17/89

Retention Time	Instrument Response (mV-sec) for the Analysis Time 05:46	06:46	07:16
46.7	23.1	25.7	21.7
60.7	14.9	13.1	15.0
71.1	10.9	11.9	12.5
99.7	0.78	1.1	1.6
115.9	1.2	1.9	2.9
137.6	2.5	0.8	2.3
173.2	0.65	1.6	0.92
198.2	0.93	1.0	2.4
223.8	0.55	0.74	1.6
260.5	0.52	0.42	1.3
277.3	0.47	1.7	0.69
323.2	1.1	ND	2.2
352.9*	ND	49.04	ND
354.7*	ND	ND	21.04
Benzene (ppb)	6.36	6.34	5.95

Retention Time	Ratio of Instrument Response for the Analysis Time 05:46/07:16	05:46/07:16	07:01/07:16
46.7	0.90	1.06	1.18
60.7	1.14	0.99	0.87
71.1	0.92	0.87	0.95
99.7	0.71	0.49	0.69
115.9	0.63	0.41	0.66
137.6	3.09	1.09	0.35
173.2	0.41	0.71	1.74
198.2	0.93	0.39	0.42
223.8	0.74	0.34	0.46
260.5	1.24	0.40	0.32
277.3	0.28	0.68	2.46
323.2	N/A	0.50	N/A
352.9	N/A	1.00	N/A
354.7	1.00	N/A	N/A
Benzene	1.00	1.07	1.07
Average	1.00	0.71	0.93
S.D.	0.65	0.28	0.61

* Because these two compounds fell inside the benzene window, the instrument response was in ppb rather than mV-seconds

The results from the Stage III study indicate that the typical BZ concentrations above the grit chambers range from about 2 ppm to 8 ppm. The two order-of-magnitude variation in concentrations noted in the December JWPCP Stage II study may have been the result of a single discharge of waste into the sewage effluent after an extended Christmas holiday weekend.

C. Discussion of JWPCP Sampling Results

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

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

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

Semi-continuous monitoring of the inlet and outlet streams from the ACB was then conducted using a portable GC/PID during Stage II. A twenty-four hour sample, revealed that the concentration of BZ in the headspace above the grit chambers varied with the time of day. The first sampling trip results yielded a very interesting diurnal fluctuation; the concentration ranged from less than 100 ppb at night to nearly 30 ppm during one morning peak. Although breakthrough of BZ had long since occurred, the ACB did act to damp out the peak concentration. However, during periods of relatively clean influent gas, the concentration of BZ in the effluent from the ACB was greater. Because sampling occurred during the interval between Christmas and New Year, it was felt that the results might not be representative, and additional sampling was conducted for a longer period of time in February.

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

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

D. Reconciliation of Phase I and CSDLAC Measured Emissions

During the Phase II study of the JWPCP emissions, additional test data on influent liquid concentrations and measured air emissions became available for comparison with the pseudo-mass balance method used to estimate emissions in Phase I. Those data are summarized in Table 29a,b,c,d. As can be seen from the "new" (Phase II) data in Table 29a, the average measured influent concentrations during the period from September 20 to October 25, 1989 (seven 24-hour composite samples) differ from the Phase I averages by as much as a factor of 20 for TCE, but for most compounds the differences are within a factor of 4, some compounds being higher and some being lower. Taking all of the measured compounds that were also part of the Phase I study together, the average of the ratio of Phase I to "new" Phase II data is 0.56 or within about a factor of 2. These data

Table 29a
Comparison of Phase I and New (Phase II) Influent Measurements

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

Table 29b
New (Phase II) JWPCP Emission Estimates

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

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

Table 29c
Comparison of Measured Gas Phase Emissions With Pseudo-Mass Balance

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

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

Table 29d
Comparison of Emissions Based on Influent Loading and Preliminary Processes Model-Estimated Losses

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

illustrate the nature of the uncertainties in emission estimates at MWTPs as a result of variability in plant loading.

Using the more recent influent data and the CSDLAC reported emissions estimates shown in Table 29b (Caballero and Griffith, 1989), the ratios of "measured" emissions to Phase I and Phase II "estimated" emissions can be formed. The Phase II estimated emissions utilize the new liquid influent data, but assumes the same fractional loss as observed from the Phase I study. As shown in Table 29c, the ratios differ from the Phase I and II estimates by as much as a factor of 20 for BZ to nearly unity for the less degradable compounds such as TCA and PERC. Using modeling results (discussed in Volume 4 and in Appendix A) for losses at similar preliminary processes from the headworks area of the plant, i.e. bar screens and aerated grit chamber, and using Phase I and Phase II influent data, a comparison can be made with the CSDLAC total measured emissions, as shown in Table 29d. In this case the losses, even for the degradable compounds such as BZ, are in closer agreement with the total plant losses.

An explanation for the poor agreement between the measured emissions from the JWPCP and the Phase I emissions estimate can be formulated as follows. The JWPCP is somewhat unique among California treatment plants in that it has covered primary tanks whose headspace gases are essentially isolated and unvented except for negligible losses through the cover. Furthermore, the JWPCP uses pure oxygen for biological treatment, minimizing total gaseous emissions and has covers over the secondary clarifier weirs. These factors result in most of the emissions of the degradable compounds, such as BZ, TOL, ETBZ and XYL, at the headworks of the plant. Relatively small amounts of BZ were captured by odor control units given the current frequency of carbon replacement. Thus the model-estimated headworks emissions for BZ and TOL appear to be in closer agreement with the total measured emissions from the plant. On the other hand, non-degradable compounds not lost at the headworks for the most part pass through the biological treatment process, so that the modeled losses at the headworks, in most cases, are a smaller fraction of the losses from the entire plant. The modeled preliminary processes' losses exceed the reported measured losses by about a factor of 2. The overall agreement between the <u>non-degradable compounds</u> and the pseudo-mass balance approach for the entire plant overestimates the measured losses by about a factor of 2. An additional contribution to the magnitude of the uncertainty in the pseudo-mass balance approach applied to the JWPCP is the fact that only a portion of the wastewater (60 %) is subjected to secondary treatment. Thus, there are substantial concentrations of PTOCs remaining in the plant effluent (a blend of primary and secondary treated wastewater) which in turn results in a larger error in the mass difference caused by subtracting two numbers of the same magnitude. It is also known that the JWPCP receives a heavier load of wastewater from nearby refineries and waste activated sludge from upstream treatment plants. It is possibly that the waste activated sludge and refinery wastewater represent separate phases at the headworks and in the primary sedimentation basin. Partitioning of VOCs into these phases would also reduce emission rates predicted by stripping models that do not account for such phenomena.

The consequences of the explanations given above are the following:

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

2) For the other MWTPs in the State, the pseudo-mass balance method is believed to be relatively accurate for non-degradable compounds (within a factor of 2), but

> more conservative for degradable compounds. Most facilities in the State have uncovered primaries, aeration basins, and weirs so that increased volatilization losses are expected to occur than do at the JWPCP.

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

E. Emissions Estimates Based Upon PEEP Factors

Additional sampling of the aerated grit chambers at the JWPCP was undertaken during the period April through July, 1990 as part of the Pooled Emission Estimation Program (PEEP, 1991). The purpose of these samples was to develop emission factors for use at similar treatment processes as allowed under Assembly Bill 2588. Although not an official requirement of the current study, ARB staff requested that comments be provided regarding the PEEP report where applicable. Therefore, we have examined the relevant PEEP data for the aerated grit chambers and for activated sludge aeration basins. The aeration basin factors are discussed in a later section of this volume dealing with sampling at the HTP. We discuss PEEP emission factors for grit chambers here; additional comments can be found in Volume 4, Appendix I.

The PEEP sampling train protocol included an initially "dry" impinger, immersed in an ice bath, ahead of a gas sample bag. This train was used for all process stream samples. The ostensible purpose of the impinger was to prevent moisture from condensing in the sample bags and possibly causing either reactions within the bag or interferences in subsequent analysis. However, it appears that the protocol did not call for the analysis of the impinger contents unless a minimum quantity of condensate was collected; exceedance of the minimum amount never occurred. Instructions to purge the contents of a "dry" impinger into the bags at the end of a test, in order to flush out any components that might have sorbed to the impinger walls, were not included in the protocol.

The presence of the ice bath impinger was noticed because the reported emission of dichlorobenzene (DCB) was 0.0% from the grit chamber (and from many other processes tested). Furthermore, a compound with a high Henry's coefficient, PERC appeared to be measured at lower than expected concentrations in some PEEP analyses of the data, e.g. losses over weirs. As reported above (see figure 6Ba, b), clear identification of DCB (at substantial concentration) was possible from the GC/MS analyses of the sorbent samples drawn from air near the grit chambers (WS/DS-4). A reason for the apparent discrepant observations was sought, and the presence of an ice bath impinger in the sampling train was noticed.

It has been our experience that even at room temperature, compounds with boiling points comparable to or higher than PERC (b.p. 121 °C) tend to adsorb to surfaces such as stainless steel or Tedlar®. The EBMUD bag/tube comparisons exhibited consistently lower recovery of PERC from bags than the sorbent tubes. The DCB has a b.p. of 174 °C and much of it could have been lost in the ice bath impinger. Compounding the wall adsorption problem is the presence of semi-VOCs in the wastewater off-gases. (They appear to make up the bulk of the total ion chromatograms as can be seen in Figure 6A). These compounds could have easily condensed into a film on the walls of the ice bath impinger, after which compounds of higher volatility could have sorbed into and onto the film.

Further circumstantial evidence for possible sorption losses in the PEEP sampling train is available. The highest 8-hour average BZ concentration reported by the PEEP of an air sample from the grit chambers was about 0.8 ppm. During the UCD Stage III continuous Photovac®sampling above the grit chambers, measurements of BZ indicated average 24-hr concentrations ranging from about 2 to 5 ppm. Although we cautioned the reader that the portable GC/PID data were based upon a single point calibration at a much lower concentration (0.1 ppm), we do not believe the results to be that much in error since the typical shape of an PID instrument response curve would underestimate rather than overestimate high concentrations. Thus unless discharges of BZ had been reduced between the sampling in February of 1989 and April of 1990, it appears that PEEP data for BZ may be low. (We note that the influent liquid concentration of BZ reported by the PEEP appear to be in the same historical range for the JWPCP, about 60 μg/L, and that when influent minus effluent is averaged over the three rounds of sampling, a higher BZ emission rate is indicated than measured in the air.)

The evidence presented above leads us to conclude that the PEEP emission factors for grit chambers underestimate actual emissions for semi-VOCs. (We use the term VOC here loosely, corresponding to compounds with boiling points below about 100 ^{o}C) The extent to which the PEEP factors also underestimate VOC emissions is unknown. A study to determine the fractional removal efficiency of calibration gases through an ice bath impinger, <u>in the presence of wastewater off-gases</u>, would be needed to assess possible losses in the PEEP sampling train.

F. Activated Carbon Beds on Operating Sewers

Besides the ACB odor control units at the JWPCP, the CSDLAC also operates ACB odor control units on sewer systems. Data were obtained from a CSDLAC in-house study of a mechanically ventilated portion of a sewer during the period April, 1988 to

December 29, 1988. These data were quite extensive and obviated the need for additional measurement of ambient sewer atmospheres. One of two essentially identical ACBs had been operation for about 123 and 151 days, respectively, since the last carbon recharge at the first sampling period on April 11 (East) and May 9 (East). It and a second bed (West) were recharged with fresh carbon, successively, on October 5, 1988 and December 1, 1988, and were operated sequentially with essentially all flow through the East ACB from October through December 1st and through the West ACB from December 1st through 29th. The data are summarized in Tables 30a through 30d. Average volumetric flows through the two units during the October through December period of service were approximately 4700 cfm (2.2 m^3/s)and 4800 cfm (2.3 m^3/s) respectively. An estimate of the average estimated emission rate of several PTOCs of interest (influent to and effluent from the ACB) is also given in Tables 30a through 30d on an assumed annual basis.

The observed behavior of the ACBs is similar to that of the odor control units at the JWPCP, i.e. initially high removal efficiency for all but the most volatile compounds, e.g., DCM. The period of efficient collection is followed by rapid breakthrough of the most volatile compounds, with negative collection efficiencies for some compounds, i.e. immediately following breakthrough negative efficiencies are observed for a period of time, then some minor adsorptive capacity appears to be restored so that the bed acts to dampen fluctuations. Net collection efficiency after the initial period remains zero overall. For example, note that DCM inlet and outlet concentrations are about equal for the April/May samples after the ACBs has been in service for over four months. However, during the December sampling, after about two weeks to one month of service, the outlet concentrations of DCM are much greater than the inlet concentrations, because competitive sorption had driven the previously collected DCM off the bed.

The observed concentrations and mass emission rates also reinforce the comments made in Volume 2 of this report regarding the potential for elevated emissions at mechanically ventilated points in the collection system, even though the total fraction of PTOCs in the liquid that are emitted remain small. A rough estimate of the airborne BZ concentration in the vent sewer gases is about 100 ppb (or roughly 300 $\mu g/m^3$). It is noted that a dilution factor of over 1000 would be needed to reach an estimated lifetime cancer risk of 1 X 10^{-5} (5.3X10-^{5} $\mu g^{-1} m^3$, unit risk factor).

Table 30a
Estimate of Emissions from a Mechanically Ventilated Interceptor with ACB Odor Scrubber

Dates	4/11/88	5/09/88	
Location	East	East	
Days since loaded	123	151	
Days w/blower	56	84	Assumed T
Flow - [cfm]	6899	6707	298 K

Concentration Compound	MW	In [ppb]	Out [ppb]	In [ppb]	Out [ppb]	Avg In [ppb]	Mass [kg/yr]
DCM	85	68	33	22	25	45.0	9.3E-01
TCM	119.5	170	160	110	120	140.0	2.1E+00
TCA	133.5	1100	190	39	80	569.5	7.5E+00
TCE	131.5	21	60	7.7	12	14.4	1.9E-01
PERC	166	290	86	38	>220	164.0	1.7E+00
1,1-DCA	99	11	2.8	2	1.7	6.5	1.2E-01
BZ	78	43	420	33	500	38.0	8.6E-01
TOL	92	500	190	40	210	270.0	5.2E+00
XYL	94	460	78	58	90	259.0	4.8E+00
Total							2.3E+01

Table 30b

Dates	10/27/88	11/03/88	
Location	East	East	
Days since loaded	22	29	
Days w/blower	7	14	Assumed T
Flow - [cfm]	4672	4800	298 K

Concentration Compound	MW	In [ppb]	Out [ppb]	In [ppb]	Out [ppb]	Avg In [ppb]	Mass [kg/yr]
DCM	85	130	400	150	300	140.0	2.9E+00
TCM	119.5	150	62	320	200	235.0	3.5E+00
TCA	133.5	420	400	1200	950	810.0	1.1E+01
TCE	131.5	38	2.6	50	6.1	44.0	5.9E-01
PERC	166	120	93	130	60	125.0	1.3E+00
1,1-DCA	99	-	-	-	-	0.0	0.0E+00
BZ	78	86	65	170	160	128.0	2.9E+00
TOL	92	790	110	1100	120	945.0	1.8E+01
XYL	94	186	300	2400	340	1293.0	2.4E+01
Total							6.4E+01

Table 30c

Dates	12/06/88	12/13/88	
Location	West	West	
Days since loaded	6	13	
Days w/blower	6	13	Assumed T
Flow - [cfm]	4723	4966	298 K

Concentration Compound	MW	In [ppb]	Out [ppb]	In [ppb]	Out [ppb]	Avg In [ppb]	Mass [kg/yr]
DCM	85	80	34	50	200	65	1.3E+00
TCM	119.5	190	48	160	47	175	2.6E+00
TCA	133.5	420	160	730	240	575	7.6E+00
TCE	131.5	20	13	43	15	31.5	4.2E-01
PERC	166	140	3.4	180	7.2	160	1.7E+00
1,1-DCA	99	<10	2.1		14	0	0.0E+00
BZ	78	60	320	130	340	95	2.1E+00
TOL	92	180	27	200	16	190	3.6E+00
XYL	94	360	45	280	37	320	6.0E+00
Total							2.5E+01

Table 30d

Dates	12/22/88	12/29/88	
Location	West	West	
Days since loaded	22	29	
Days w/blower	22	29	Assumed T
Flow - [cfm]	4864	4876	298 K

Concentration Compound	MW	In [ppb]	Out [ppb]	In [ppb]	Out [ppb]	Avg In [ppb]	Mass [kg/yr]
DCM	85	<20	460	40	280	<30	6.2E-01
TCM	119.5	180	200	120	NA*	150	2.2E+00
TCA	133.5	320	>1000	810	1000	565	7.4E+00
TCE	131.5	<10	15	<10	13	<10	1.3E-01
PERC	166	100	10	63	8.8	81.5	8.6E-01
1,1-DCA	99	<10	15	<10	20	<10	1.8E-01
BZ	78	60	440	90	460	75	1.7E+00
TOL	92	210	26	490	12	350	6.7E+00
XYL	94	210	67	460	26	335	6.3E+00
Total							2.6E+01

* Interference with analysis

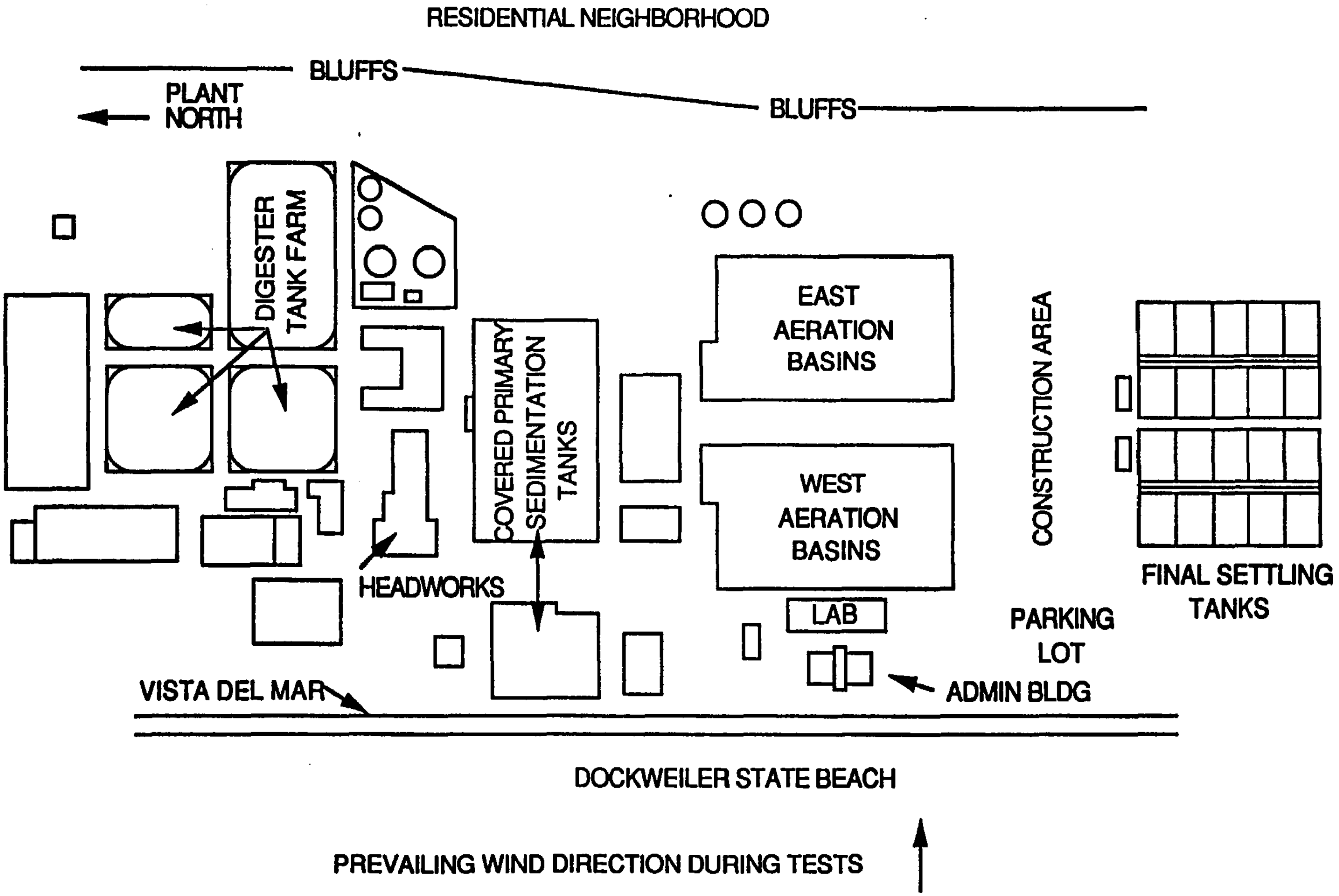
IV. Sampling of Hyperion Treatment Plant Activated Sludge Aeration Basins

A potentially major source of emissions from an MWTP that practices secondary biological treatment using air-activated sludge are its aeration basins (ASAB). Hydraulic residence times (HRT) in such basins are typically of the order of several hours. Based upon the relatively large liquid-to-gas ratios applied to maintain aerobic conditions and laboratory studies of the reversible stripping of VOCs sorbed to activated sludge (Dobbs et al., 1989), a large fraction of VOCs in solution are anticipated to be stripped unless rapid uptake and biodegradation occur. For these reasons, a measurement of the emissions from such a basin was undertaken in an attempt to determine whether a) measurable increases in downwind concentrations could be attributed to the aeration basins, and b) the magnitude of their source strength. The aeration basins at the City of Los Angeles' Hyperion Treatment Plant (HTP) were selected for study. They provided a favorable geometry relative to commonly prevailing winds, and there were a minimal number of upwind sources, thereby providing moderately clean background air for a site in the South Coast Air Basin.

A. Background

The HTP is located about one-half mile south of Los Angeles International Airport (LAX). To the south of the HTP is a power plant and to the immediate west of the HTP are a two-lane highway and Dockweiler State beach which includes a small parking lot. Due east of the plant, a bluff rises (approximately 100 ft) rather abruptly into a residential neighborhood. A schematic diagram of the HPT's configuration is shown in Figure 12. During the late morning through the afternoon of summer and early fall days, a prevailing southwesterly to northwesterly turning of an onshore flow of air can be expected in the absence of Santa Ana-like conditions. For a brief period of time each day, winds would originate from due west, minimizing source contribution

Figure 12 Diagram of Hyperion Treatment Plant



from LAX, the power plant, and other sources at the HTP. It was during those periods that sampling was attempted.

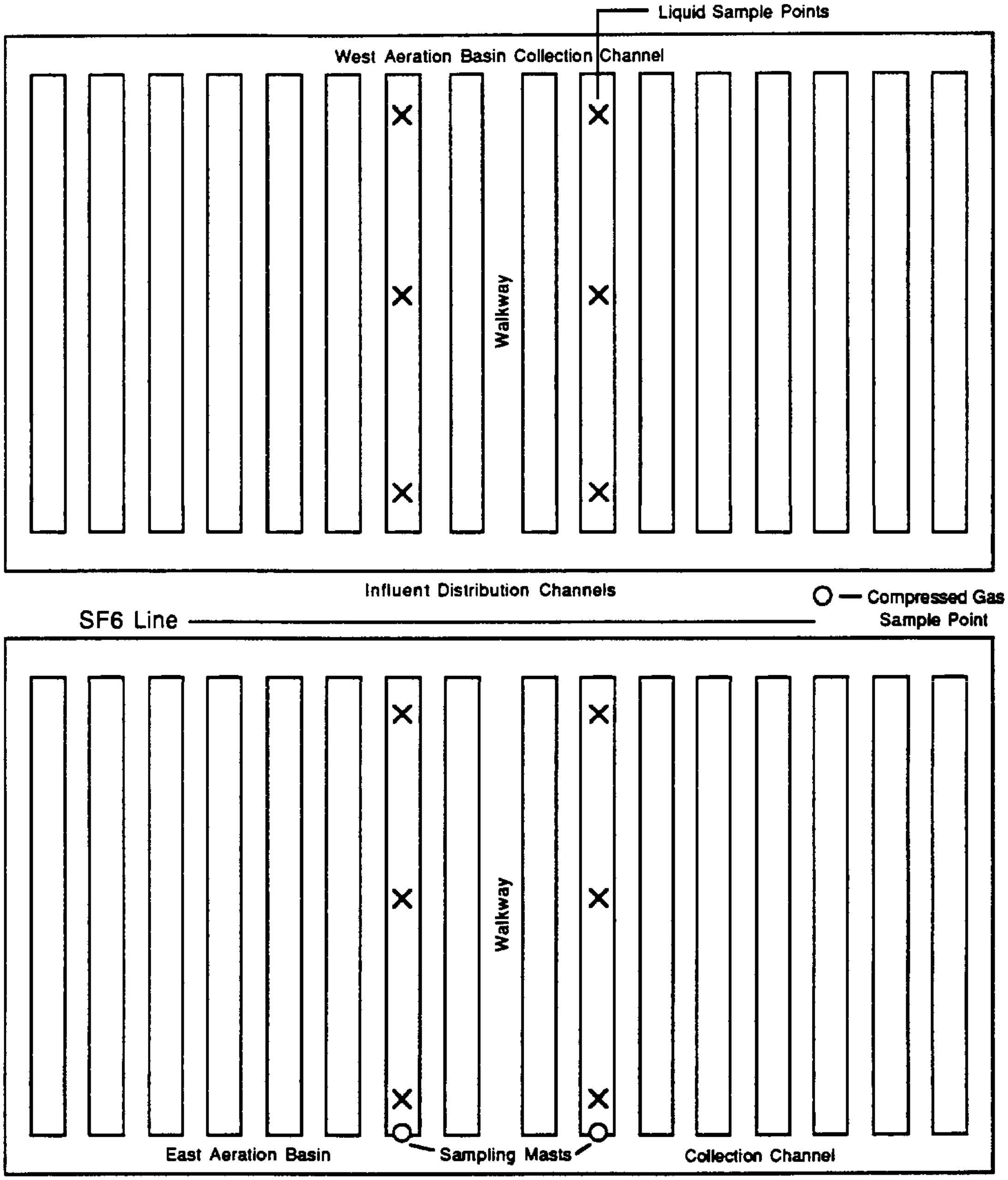
The configuration of the basins approximated that of a rectangular area source consisting of two batteries of ASABs. At the time of the sampling, the HTP treated a flow of wastewater of approximately 320 MGD from the City of Los Angeles. The treated primary effluent flowed from north to south and return activated sludge from the aeration basins flowed from south to north in uncovered parallel central distribution channels, joining the primary influent at the north end of the ASAB batteries. The central distribution channels were located midway between the East and West batteries of the ASAB as shown in Figure 13. The flow was then divided among the sixteen rectangular ASABs in each of the two batteries, flowing from west to east in the East battery and from east to west in the West battery. At the end of each basin, the flow was collected into an open channel and conveyed south to the final settling tanks. For the purposes of this study, emissions from the ASAB were treated as uniform and the terrain as flat. In reality, at the west end of the ASAB there were some buildings which could result in a disturbance to the flow field, and at the east end of the ASAB, bluffs rose abruptly, as previously described.

B. Sampling Methodology

The basic sampling strategy was to draw a sample of the air supplying the aeration basin and liquid samples from the basin, while two upwind (2 m) and two downwind (2, 5, and 10 m) air samples were drawn. The upwind samples were drawn on the beach side of the road as well as directly in front of the administration building on the downwind side of the road. In an attempt to account for the upwind buildings' possible disturbance to the wind profile across the basin, sulfur hexafluoride (SF_6) was released from a pseudo-line source, transverse to the wind, along the flow distribution channel at the center of the aeration

Figure 13 Schematic of Sampling Layout

(June)



basin. In addition, the 2 and 10 m windspeeds and the 10 m wind direction were measured.

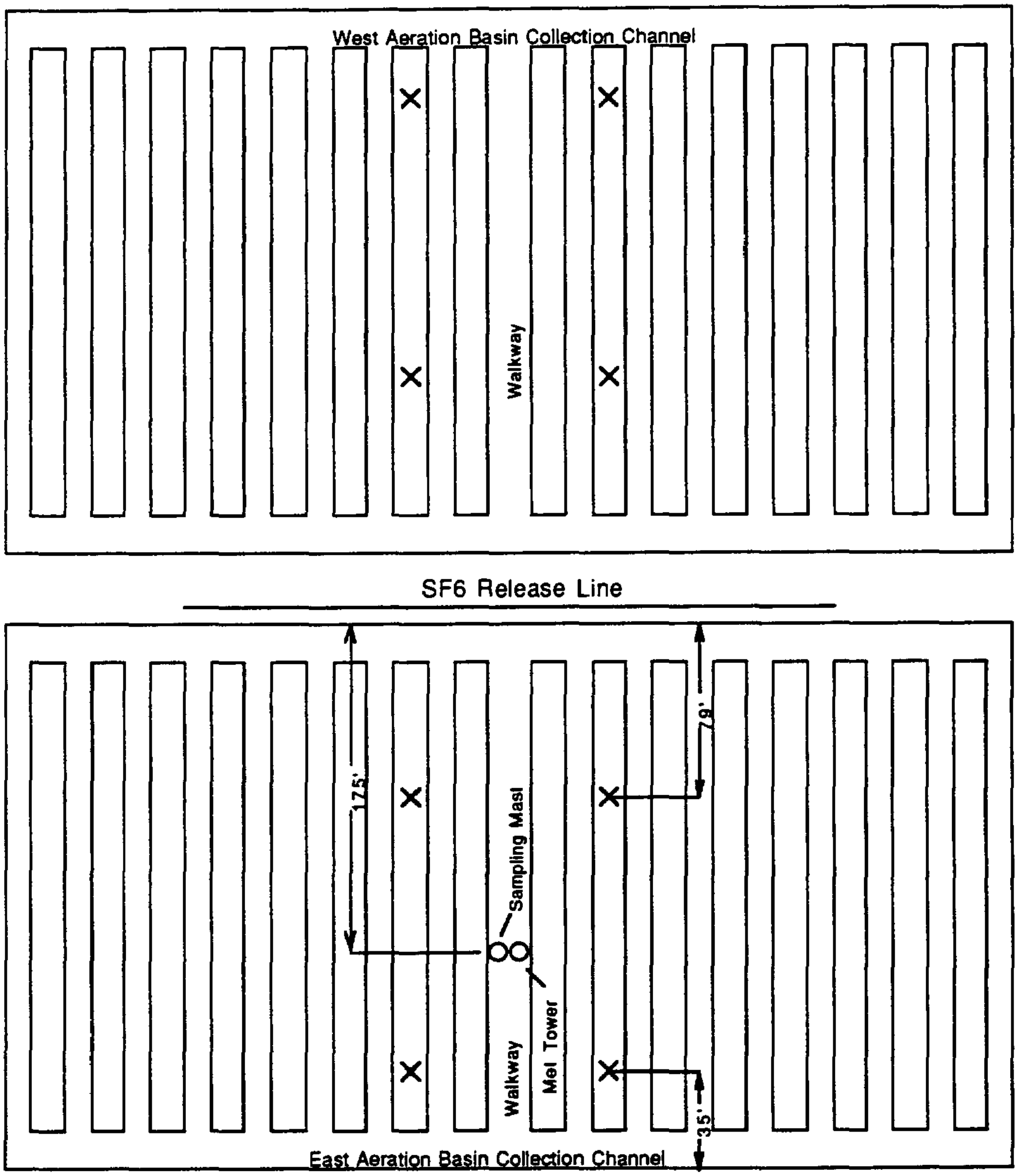
During the first sampling trip in June of 1989, two identical 10 m sampling masts were centered along a north-south axis at the east end of the aeration basins and erected approximately 18 m apart with gas samples drawn at the 2, 5 and 10 m levels. Figure 13 provides a plan view sketch of the relative locations of the gas and liquid sampling points, as well as the location of the ARB's mobile laboratory. During the second sampling trip in October of 1989, a single sampling tower with sampling locations 15 cm apart and an instrumented meteorological tower were used, centered on the north-south axis, of the SF_6 release line, 2.5 m apart and moved westward from the east end of the basins approximately 38 m. A plan view of the sampling configuration for that effort is shown in Figure 14.

Liquid samples were drawn from the basins at the approximate locations shown in Figures 13 and 14. A submersible pole, which held the 40 ml sample vials and admitted liquid into the vials after submergence, was used. Gas samples were drawn on Supelco carbopak/carbotrap (CC) multi-sorbent tubes described in the earlier EBMUD validation studies. It was determined that the SF_6 was not adsorbed by the sorbent tubes during laboratory studies. As a result, a novel method of sampling was used in which the SF_6 was passed through the sorbent tube and sampling pump into Tedlar® bags as illustrated in Figures 15a,b. The volume of gas sampled through the tubes and trapped in the Tedlar® bags could later be determined using a water displacement measurement technique. The SF_6 was analyzed by expressing the bag contents into a gas sampling loop attached to a GC/ECD.

Supplementary measurements were made by the ARB's Monitoring and Laboratory Division's (MLD) Mobile Laboratory during the June sampling trip and by ARB staff. The mobile laboratory was used to determine if chloroethene (VC) was present in the air since the analytical method applied by the UCD sampling team did not

Figure 14 Schematic of Sampling Layout

(October)



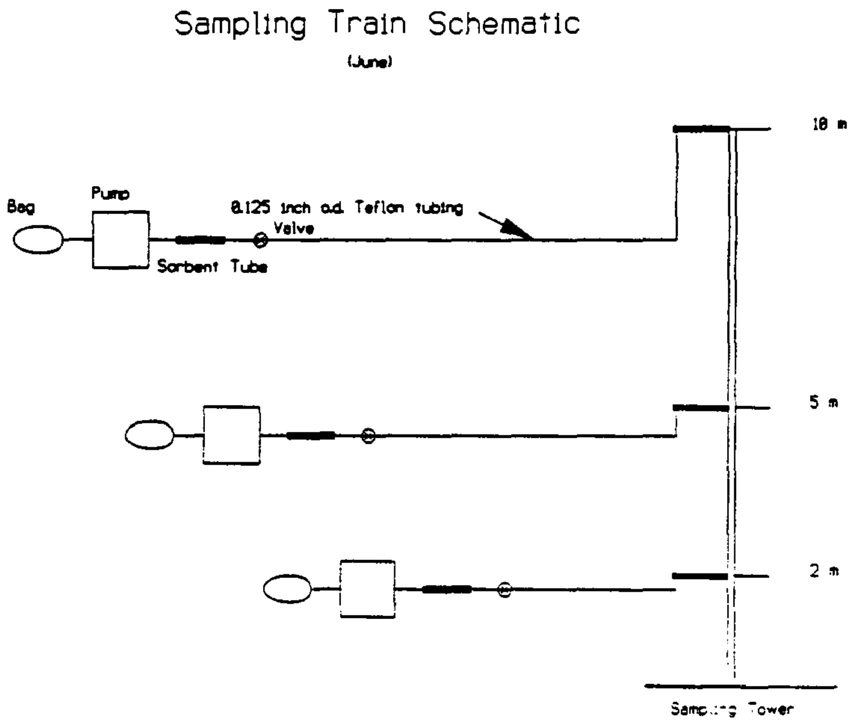


Figure 15a **Sampling Train Schematic June**

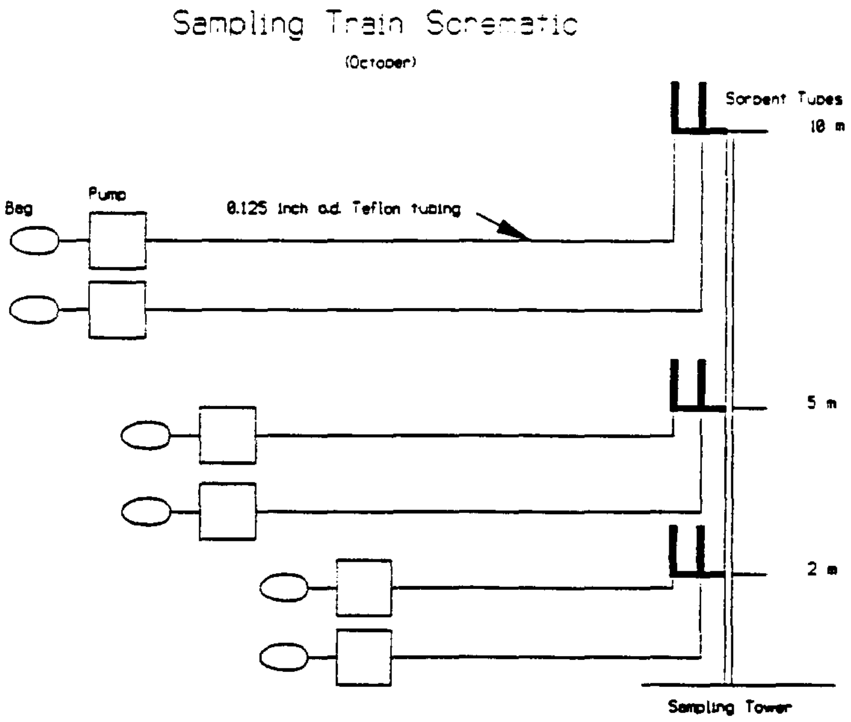


Figure 15b **Sampling Train Schematic October**

determine VC. A portable GC/PID (Photovac 10S70) was used to sample for VC at the downwind side of the ASAB as well. Syringe samples of SF_6 were drawn from the top of the bluff, centered upon the aeration basins to determine the approximate dilution that had occurred at the property line.

C. Sampling Results

Results of meteorological measurements, gas and liquid sampling are summarized in this section. Only those compounds for which "positive" GC/MS identifications were obtained are presented. The data for the measurement days in June, 1989 and October, 1989 are presented in two sets.

1. June 1989 Sampling Measurements

Meteorological data obtained from 2 and 10 m anemometers and wind direction from the 10 m height are shown in Figures 16, 17, 18, and 19. The meteorological tower was located at the eastern edge of the aeration basin. Sampling and tracer release occurred for one-half hour from about 14:25 - 14:55 on the 21st and from about 11:00 - 11:30 on the 22nd. On the 21st, during the actual release period, the wind shifted a bit, but was more-or-less slightly out of the West-Southwest. The atmosphere was neutral to very slightly unstable based upon Pasquill-Gifford categories. On the 22nd, the wind speed was slightly lower and the sky was overcast corresponding to neutral atmospheric stability.

Sorbent tubes collected at the site were shipped air package express to the UCD campus for analysis. A few of the liquid samples were transferred to sorbent tubes by purge-and-trap in the field. Additional liquid samples were refrigerated and subsequently analyzed upon return of the sampling team to UCD. Two of the air sampling tubes broke during shipment, and several of the liquid sample vials froze and cracked, however, most of the samples were intact. The volume of the sample bags were measured in the field at the end of the sampling day,

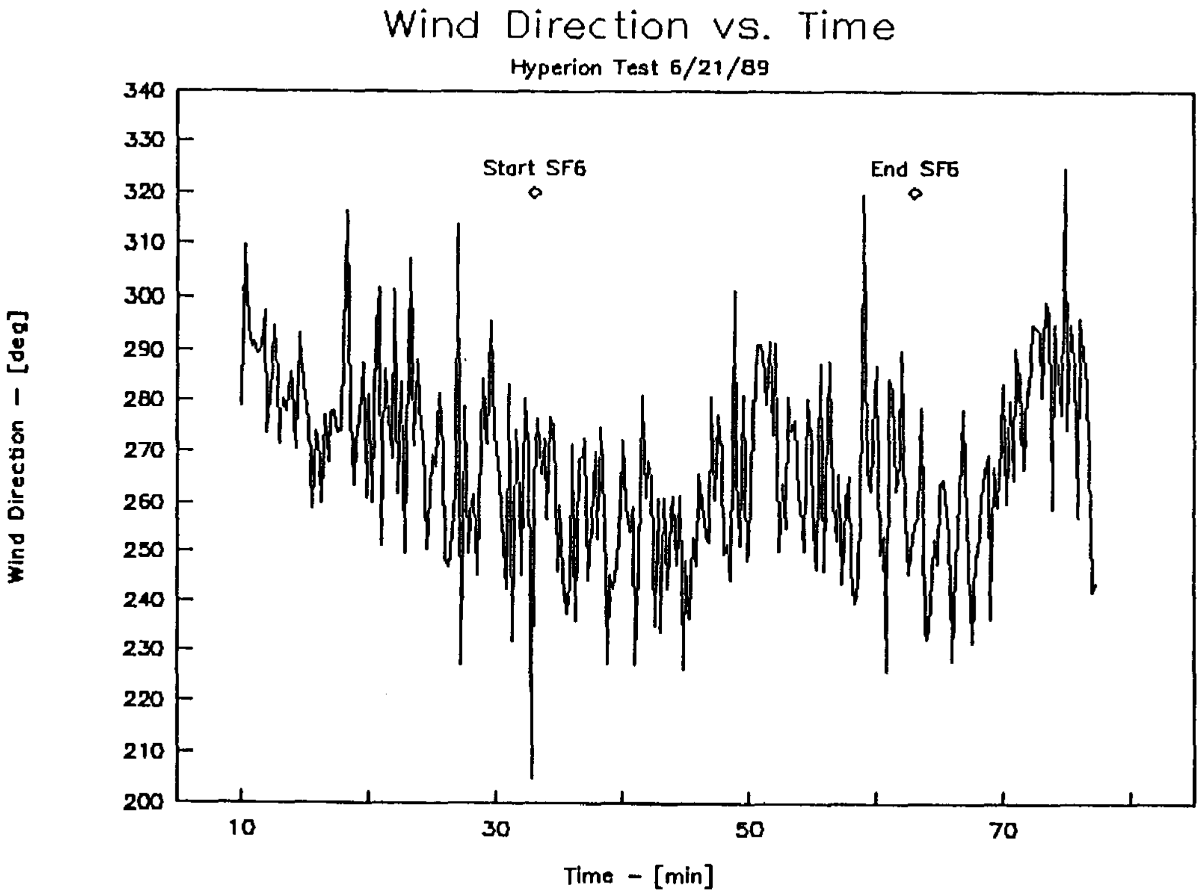


Figure 16 **Wind Direction vs. Time for Hyperion Test 6/21/89**

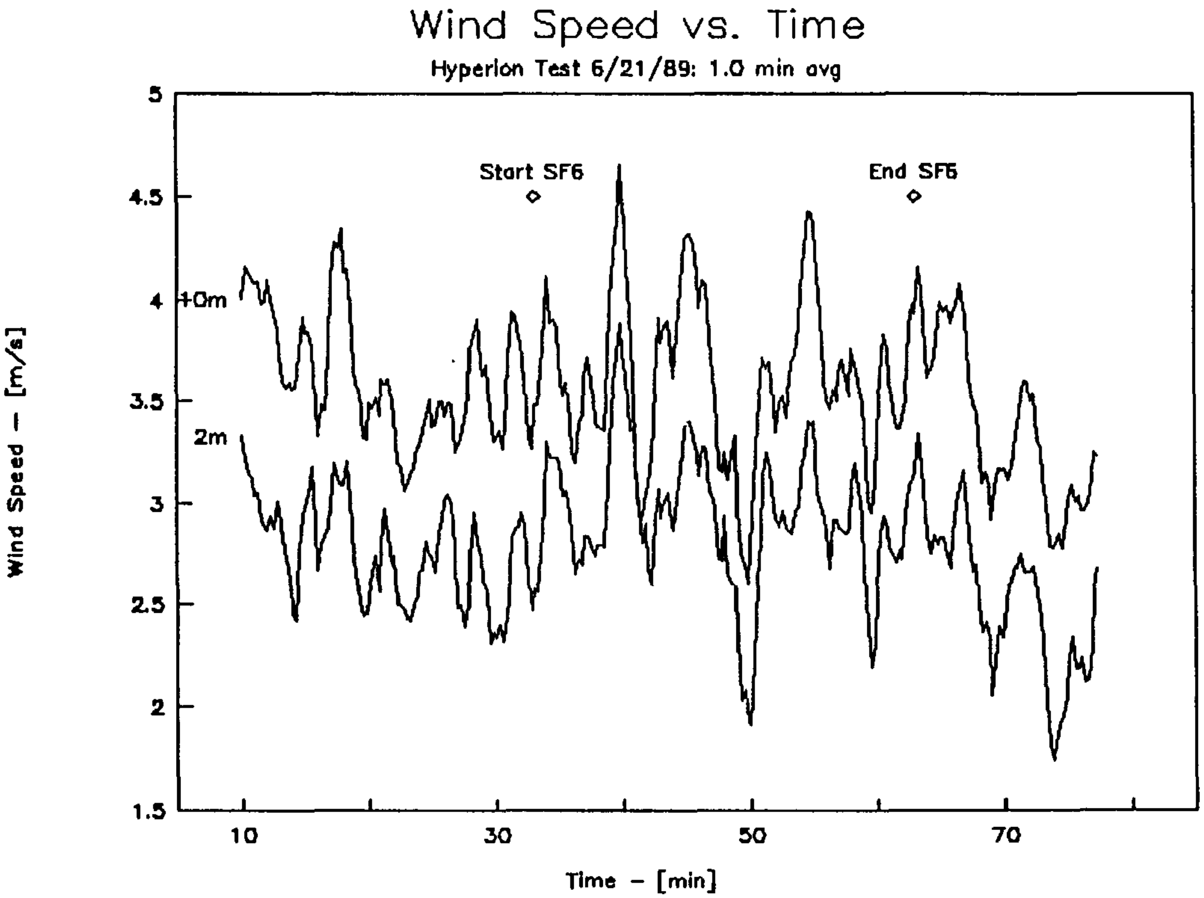


Figure 17 Wind Speed vs. Time for Hyperion Test 6/21/89

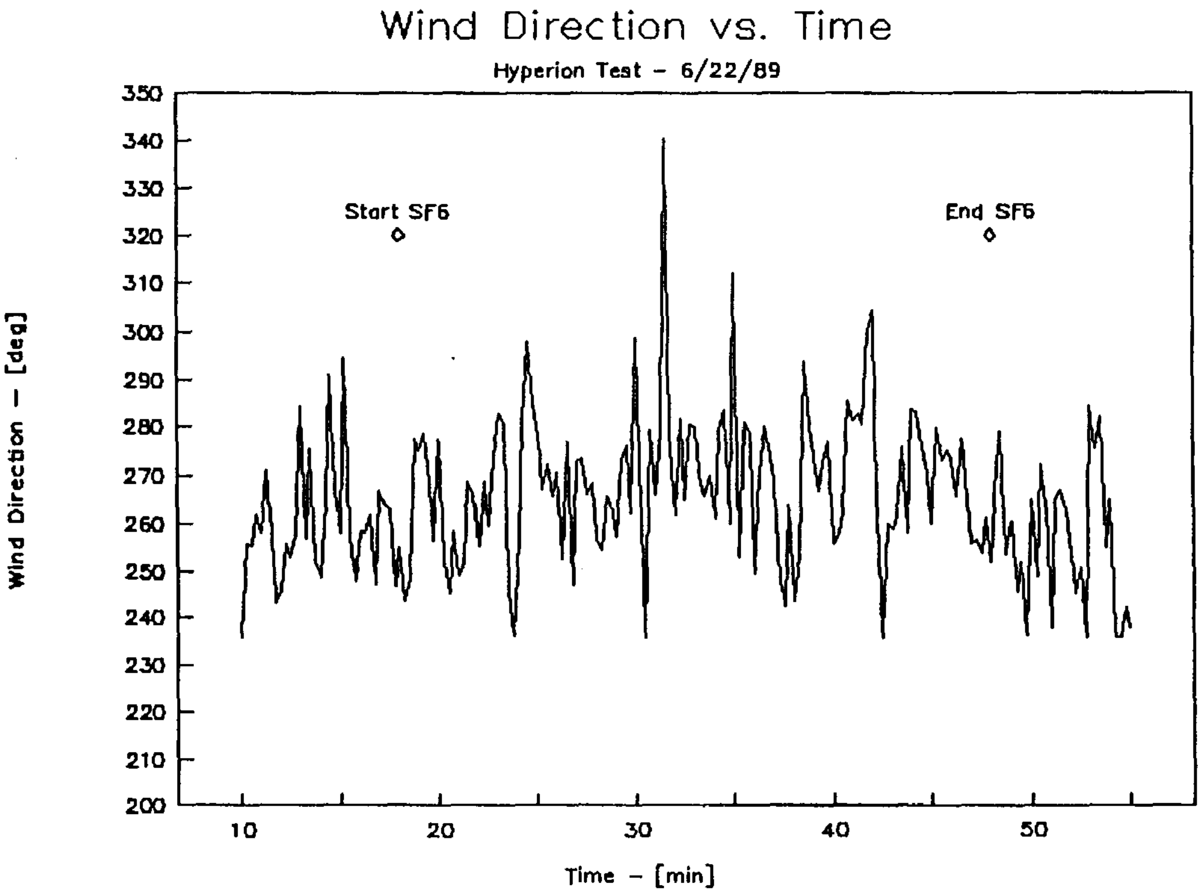


Figure 18 Wind Direction vs. Time for Hyperion Test 6/22/89

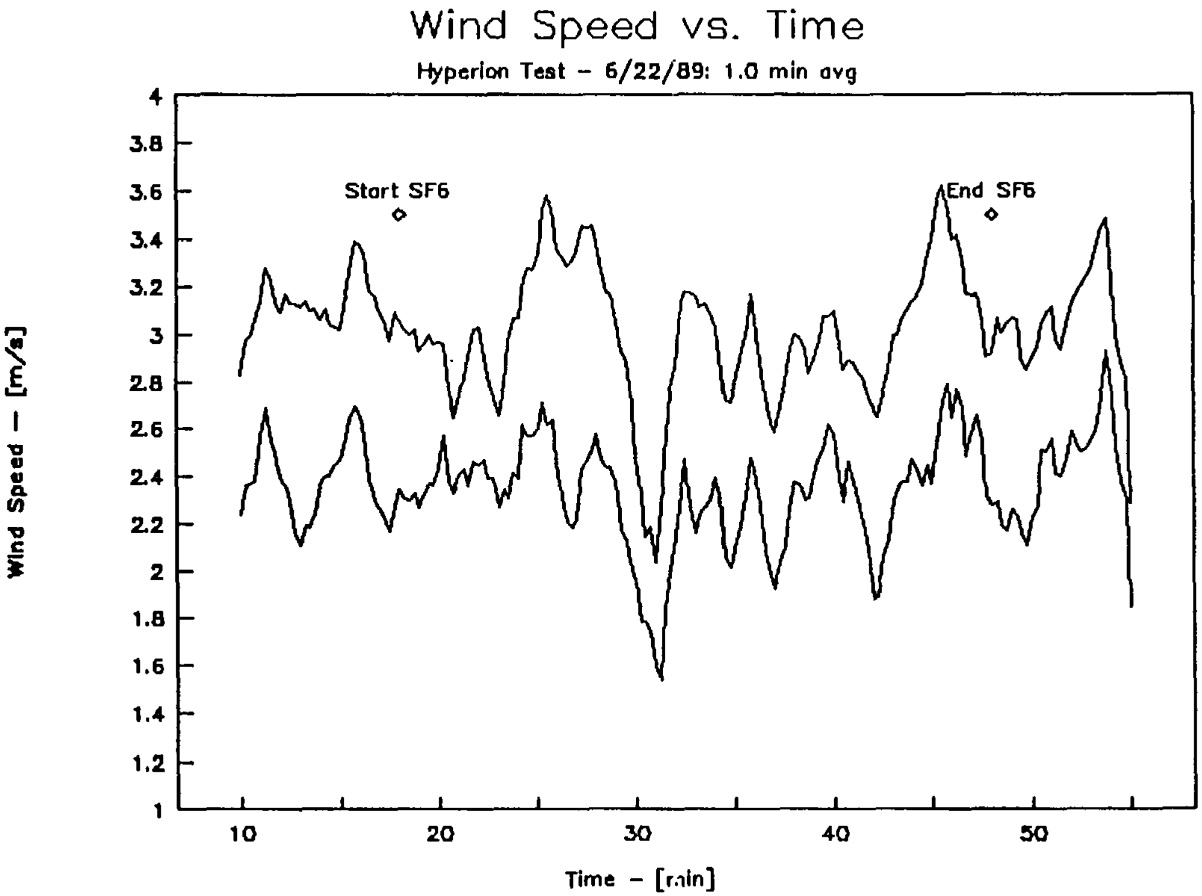


Figure 19 Wind Speed vs. Time for Hyperion Test 6/22/89

Table 31 SF_6 Analysis and Gas Volume Analysis from Hyperion Sampling Trip

Position [m]	Volume [ml]	Concentration [ppb]	Hillside Time	Samples Concentration [ppb]
6/21/89				
North 2m		26.3	2:30	4.4
North 5m		22.0	2:35	1.9
North 10m		18.6	2.41	1.3
South 2m		21.2	2:46	5.3
South 5m		4.9	2:50	7.9
South 10m		8.0	2:55	1
			3:02	0
6/22/89				
North 2m	5010	45.7	11:01	0
North 5m	1450	67.3	11:06	10.8
North 10m	1270	45.7	11:12	4.7
South 2m	2040	52.7	11:16	>12
South 5m	1350	47.0	11:21	9.4
South 10m	1250	45.3	11:26	10.4
			11:31	1.1
			11:36	0

and the bags returned to UCD with the sampling team for GC/ECD analysis for SF_6.

Analyses of the SF_6 collected at the sampling towers and at the top of the bluff overlooking the basins are shown in Table 31. The 5 and 10 m south tower samples were slightly lower in concentration than the north tower. It is believed that the pseudo-line source of release of SF_6 was slightly too short for the west-southwest wind, and that the difference between the south and north tower concentrations represent an "edge effect" of the "finite" line source. On the 22nd, the agreement between the north and south tower concentrations was much better, so the VOC analyses from the 22nd are summarized and reported in Appendix A. Additional care was given to ensure that the sampling bags were fully evacuated before the run, and the wind was more consistently from the West. Both of these factors led to less dilution compared to the 21st and hence a higher observed concentration. The data from the 22nd indicate that even though the overall atmospheric stability was neutral, if the concentrations were averaged, the centerline of the SF_6 appeared to be slightly higher than the approximately 1 m release height. This point will be discussed later.

The sorbent tube analyses were complicated by several factors on the first sampling trip: there was a water vapor interference that obscured the total ion chromatograms (TIC) from about 5 minutes retention time to about 12 minutes retention time; although the sample tubes were conditioned prior to use, they had been received only a few days before the trip and a large siloxane interference was present on the tubes (siloxanes were used by the manufacturer to remove active sites from glass beads and glass wool packed in the tubes); the GC/MS ion source was dirty, which was further confounded by the large siloxane interference, leading to noisier than normal background. Compounds of interest whose retention times fell in the obscured time period included trichloromethane (TCM), 1,1,1-

trichloroethane (TCA), trichloroethene (TCE), benzene (BZ), dichloroethane (DCA), methylbenzene (TOL), ethylbenzene (ETBZ) and tetrachloroethene (PERC). During the analysis the TIC chromatograms appeared normal, so that the analyst did not realize there was a problem. Subsequently, using selected ion integrations and the known retention times of the compounds, it was possible to determine TOL and ETBZ, whose peaks were sufficiently large so as not to be obscured. Selected ion integration data for higher boiling compounds were also determined and the data for identified, consistently observed compounds are presented.

Figures 20 - 28 illustrate the measured areas relative to the internal bromofluorobenzene (BFB) standard obtained from the two sampling masts. The data are plotted as stacked bar graphs with each bar representing the sampling height, and the area of each segment of the bar representing the amount of each compound observed at the two sampling stations. Greater amounts of almost all compounds were observed at the 5 and 10 m levels at the north tower, whereas greater amounts of almost all compounds were observed at the 2 m level from the south sampling station. In addition, two other features are noted: a) the TOL and XYL areas increased with height and were much greater for the north tower than for the south tower, whereas for all other compounds the values are more nearly the same being within approximately a factor of 2; b) the concentrations appear to peak at the 5 m level. These observations are more evident in Figure 28 which displays the averages of the two samples for each sampling height.

The concentration, SF_6 and wind observations are interpreted to mean that there was a strong localized source of TOL and XYL to the southwest of the ASAB. It is believed that the sources corresponded to heavy construction activity just to the southwest of the ASAB (part of the HTP plant expansion) and lesser traffic contributions from the highway and parking lot. These sources,

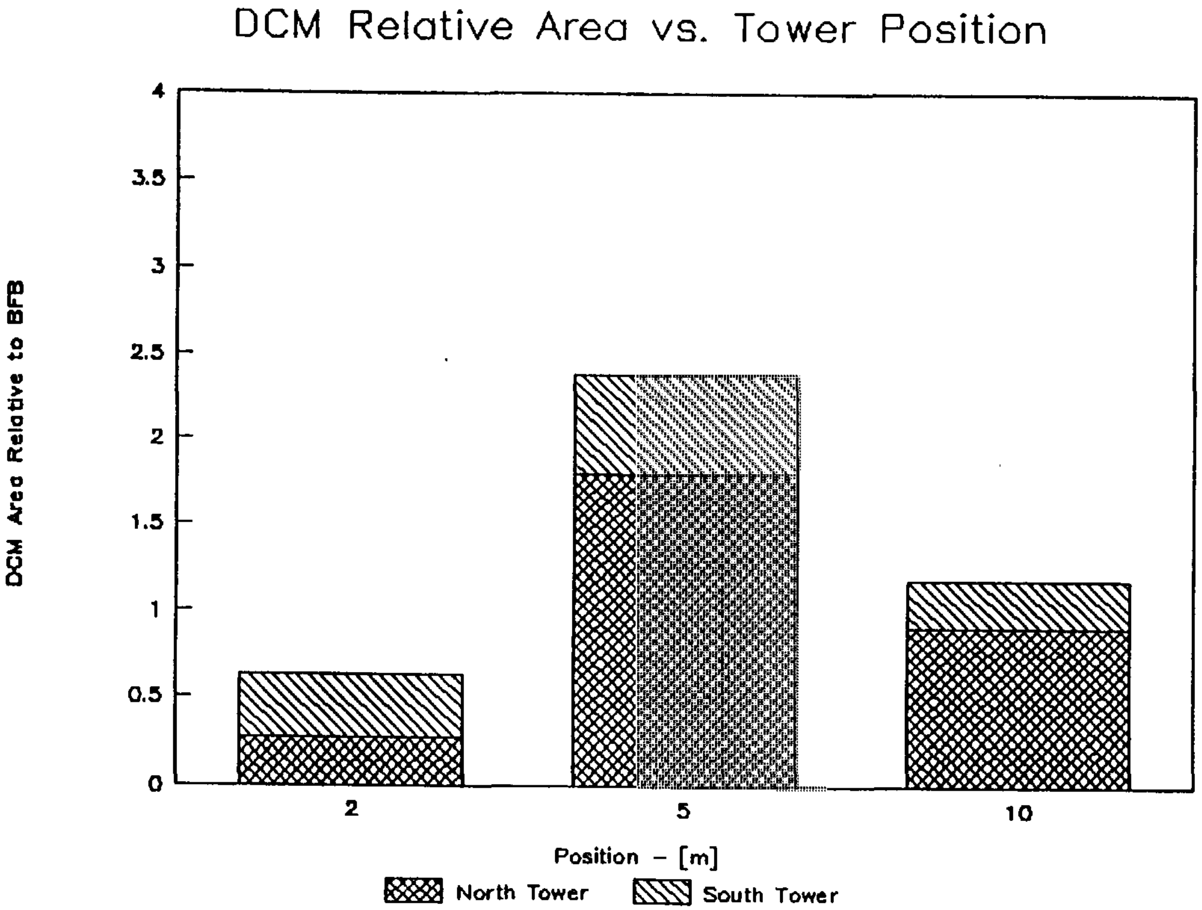


Figure 20 DCM Relative Area vs. Tower Position

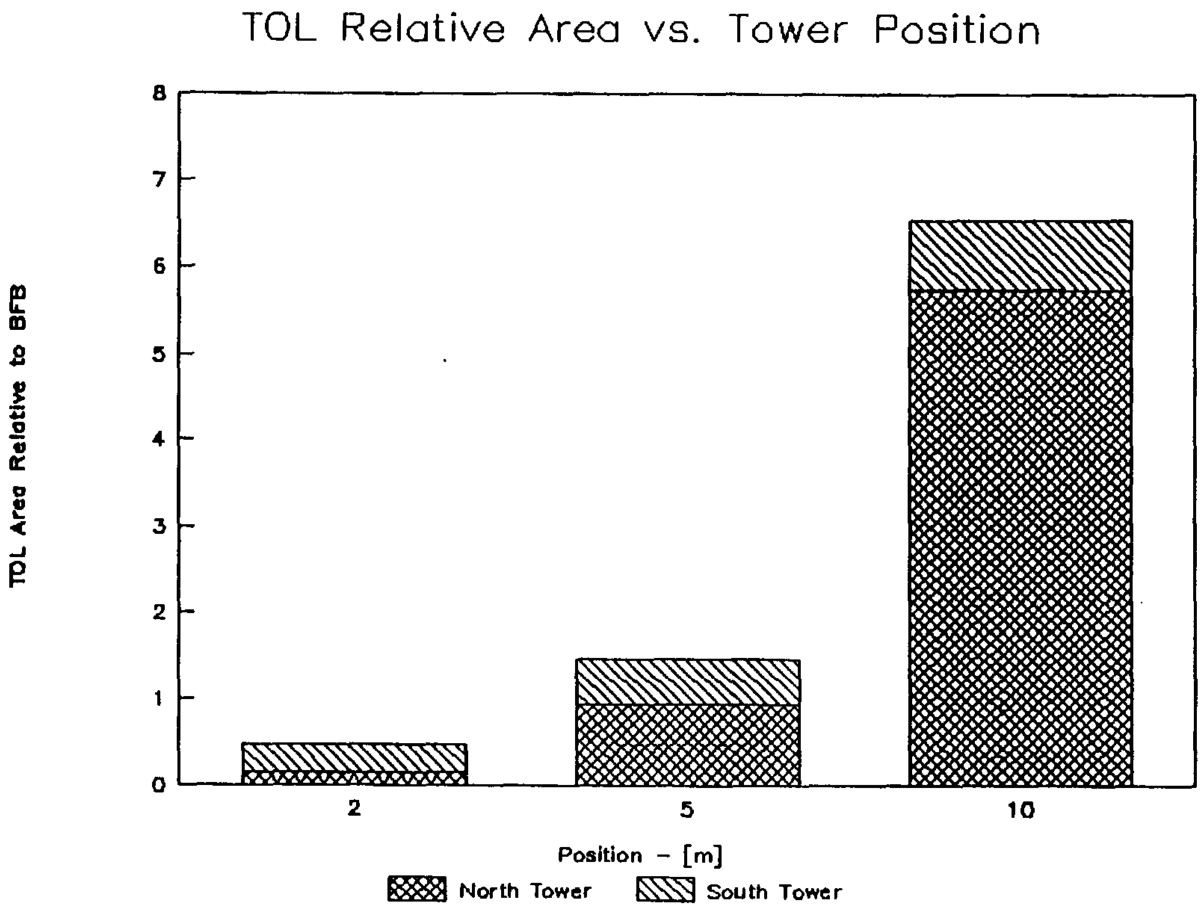


Figure 21 TOL Relative Area vs. Tower Position

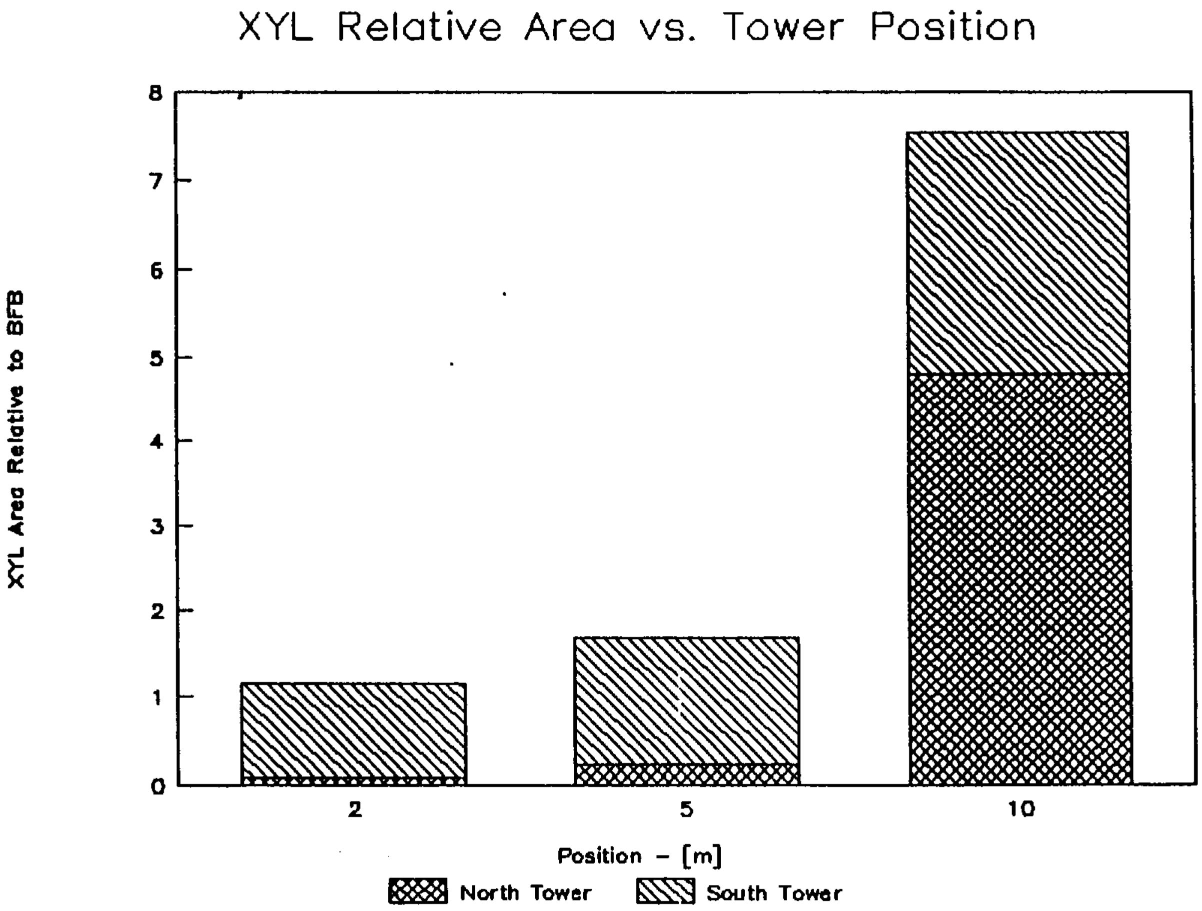


Figure 22 XYL Relative Area vs. Tower Position

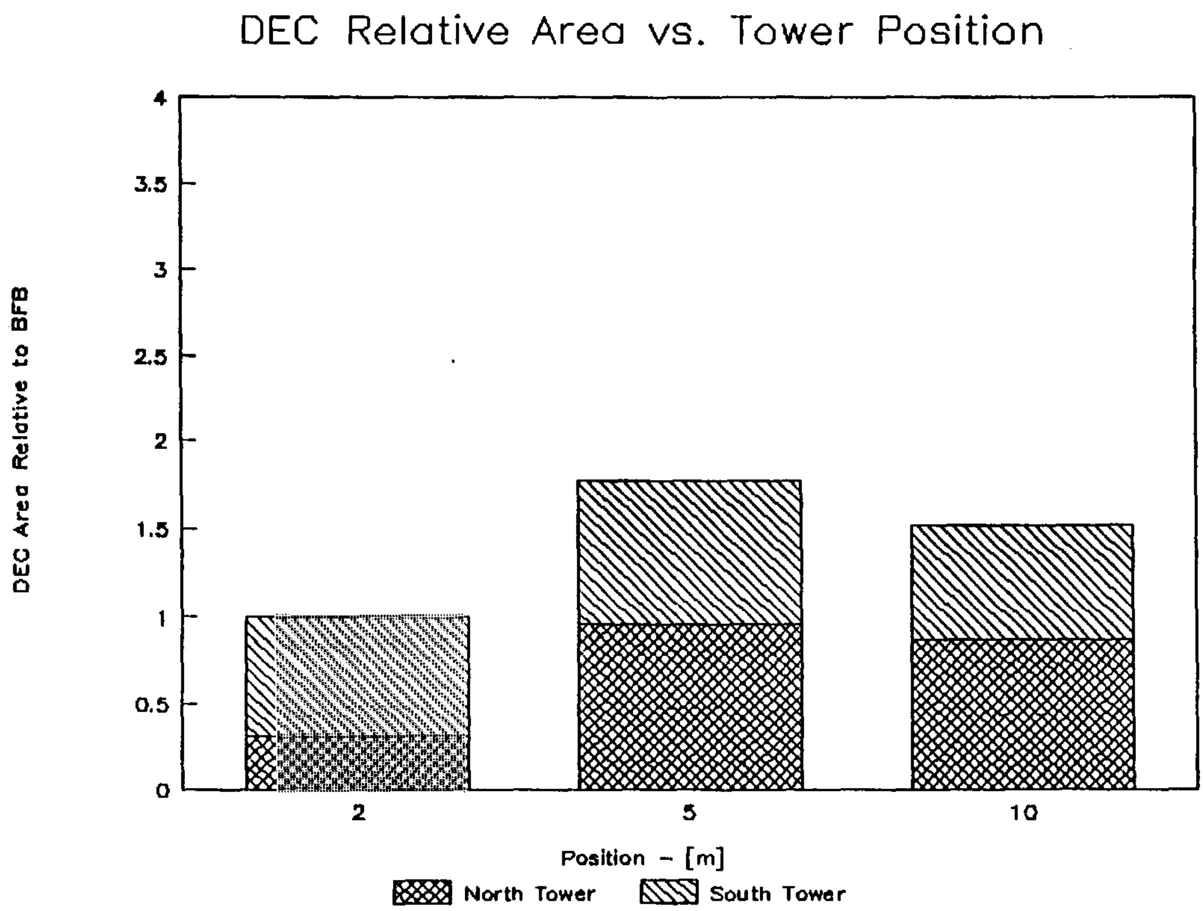


Figure 23 **DEC Relative Area vs. Tower Position**

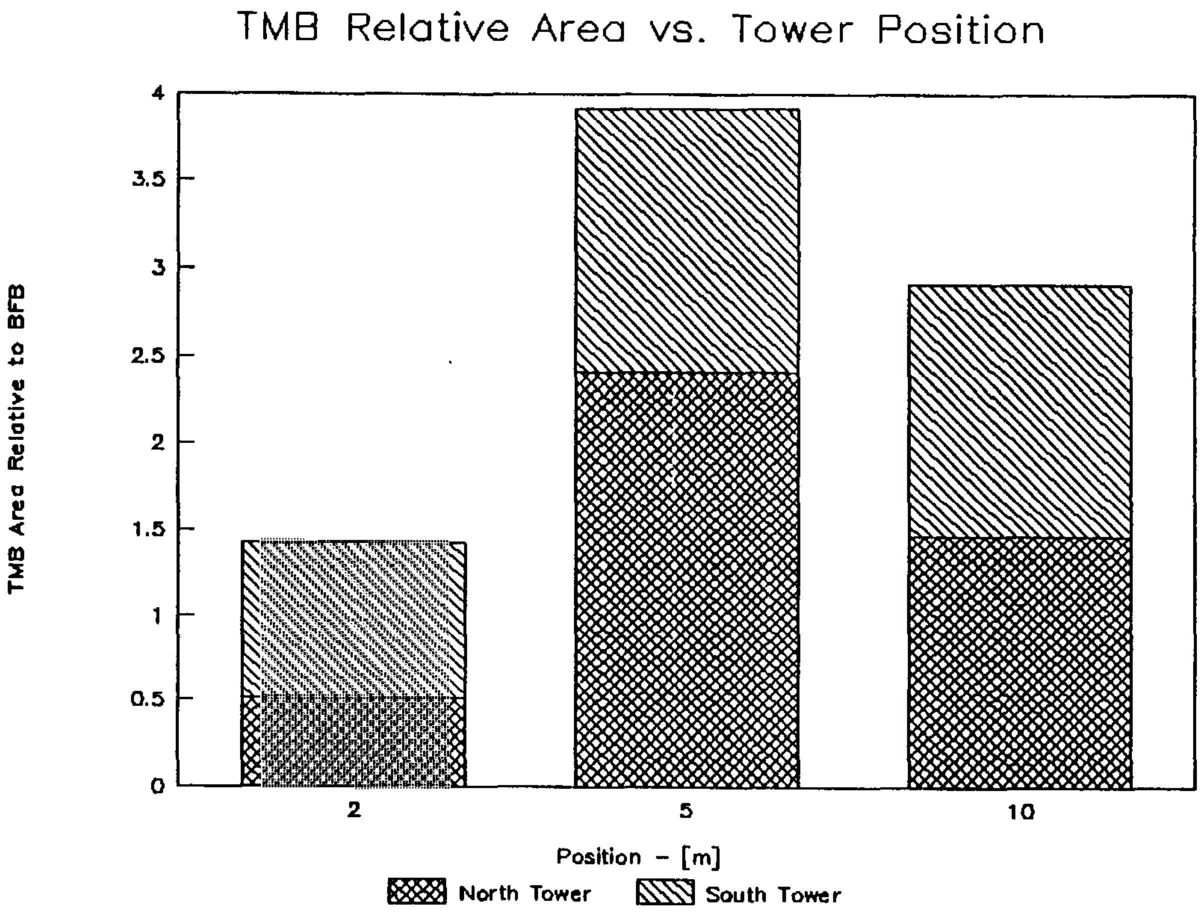


Figure 24 **TMB Relative Area vs. Tower Position**

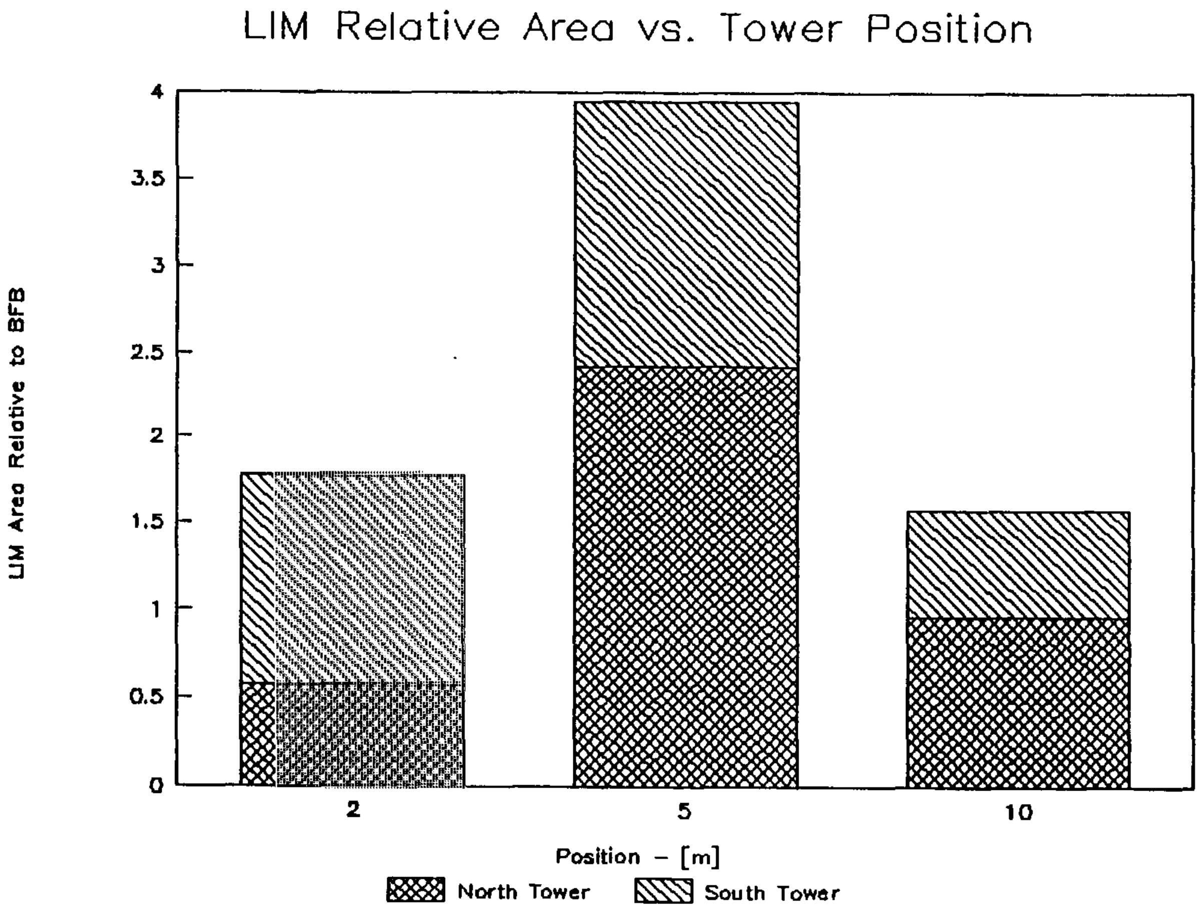


Figure 25 LIM Relative Area vs. Tower Position

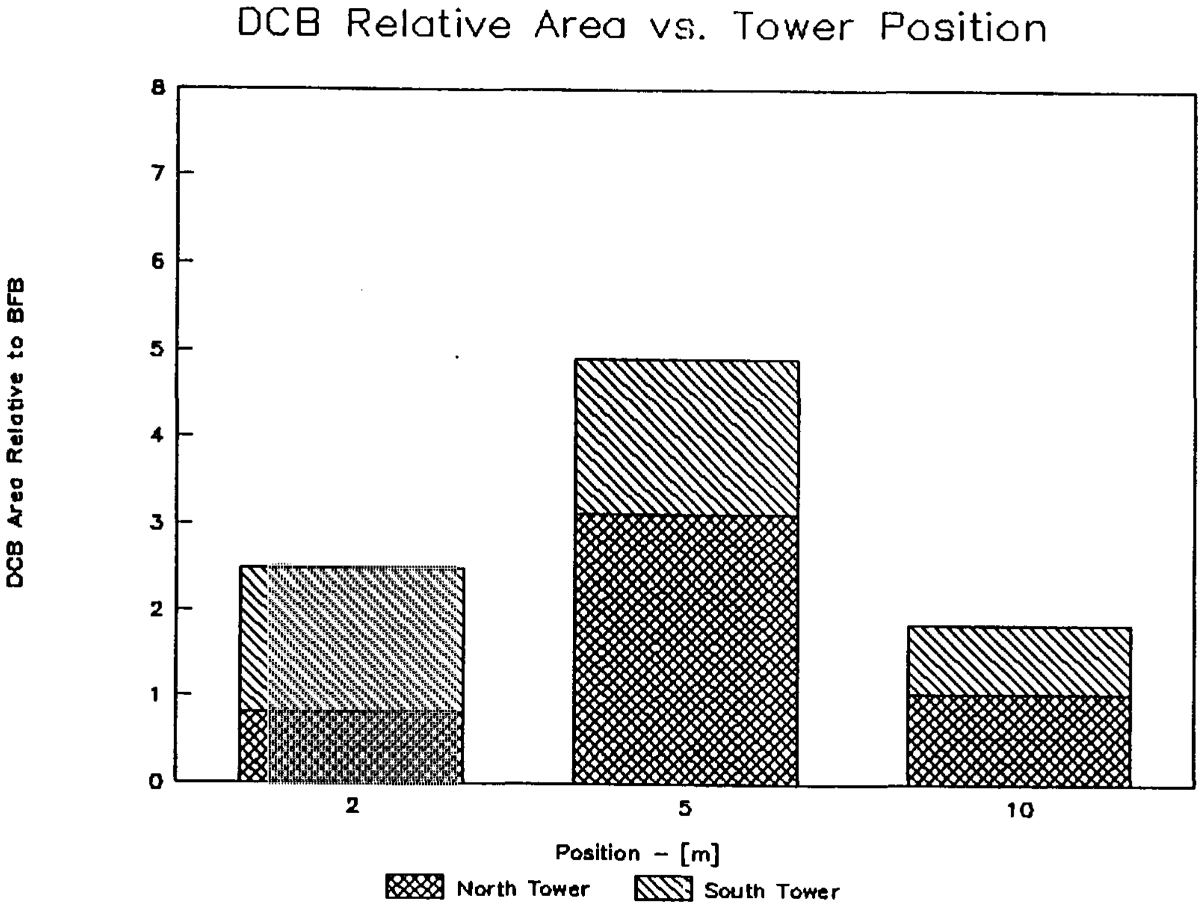


Figure 26 DCB Relative Area vs. Tower Position

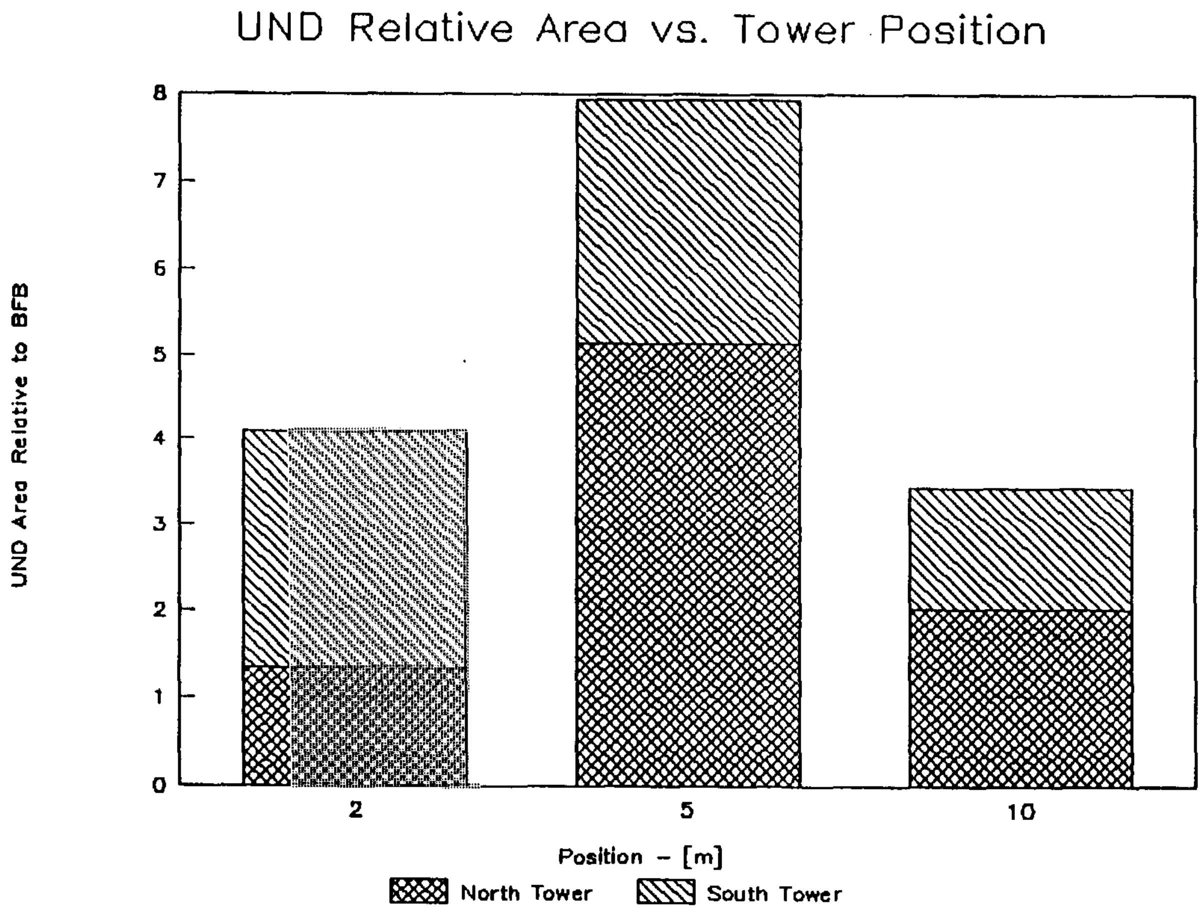


Figure 27 UND Relative Area vs. Tower Position

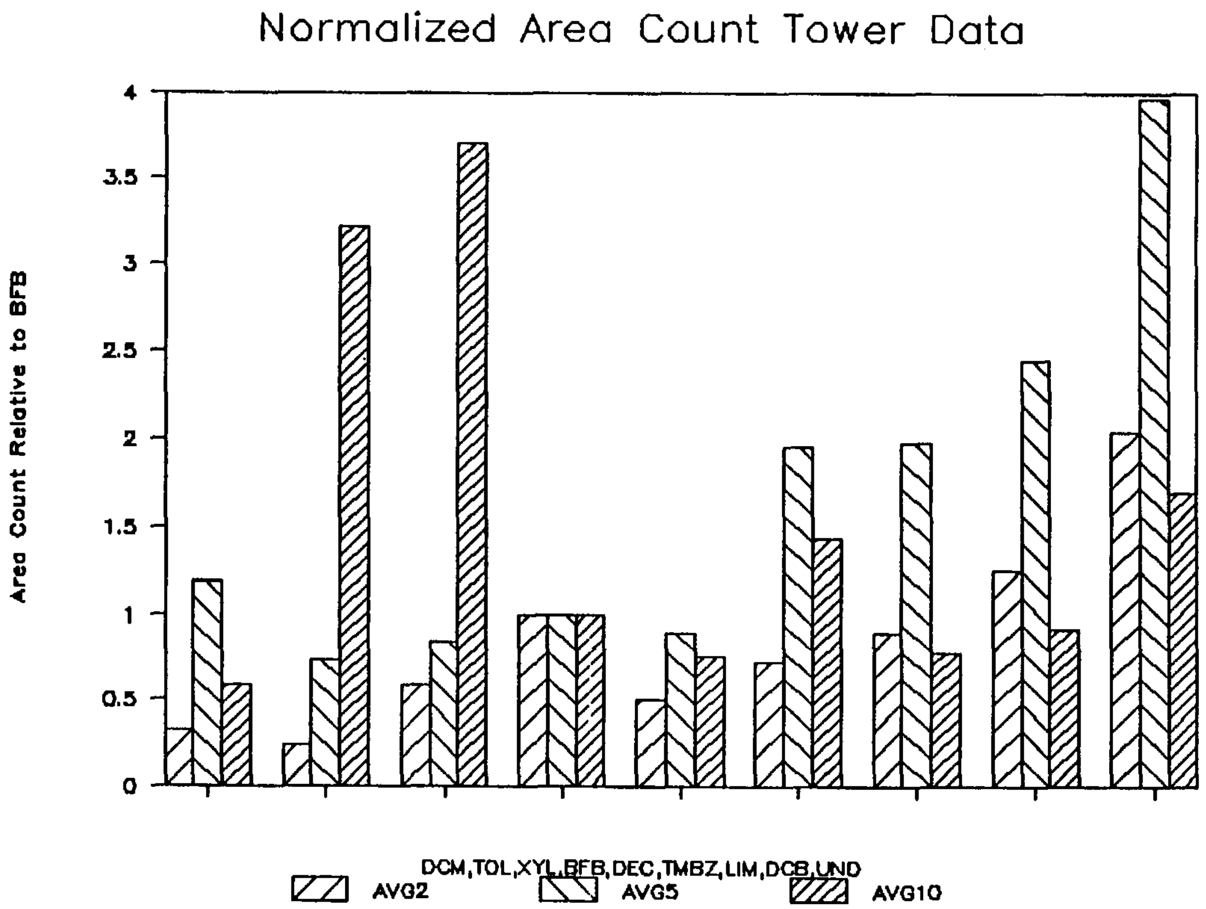


Figure 28 Normalized Area Count Tower Data

possibly vehicle exhaust, dominated the emissions of TOL and XYL from the ASAB. Other compounds present in the aeration basins, were detected in the upwind air samples at concentrations from about 5 to 10 times lower, if detected at all. These compounds were also present in the compressed air supply to the ASAB, but at concentrations lower than in the ambient air. Of particular interest is the compound limonene (LIM), which was present in all of the domestic wastewater sampled throughout this study. Limonene could prove to be useful as a tracer characteristic of POTW wastewater emissions. It should be noted however that LIM is present in many consumer products and would probably be a poor tracer for transport studies, but might useful in source testing. All of the compounds observed in the gas phase were also present in the wastewater. A tabular summary of the liquid and gas samples' TIC data from June 22nd is presented in Appendix A.

2. October 1989 Sampling Measurements

The meteorological data for the October sampling period are shown in figures 29 to 32. Windspeeds were comparable to the June tests on the 16th, but were much lighter on the morning of the 17th, and wind direction was more variable. Furthermore, because of a mild Santa Ana condition on both days, the wind had been blowing offshore only shortly before the tests, especially on the morning of the 17th, so that analysis of the upwind samples showed that they contain many of the compounds seen at the ASABs. Although "sloshing" of the air mass occurred, the upwind concentrations were still much lower than at the ASABs.

Additional temperature difference measurements were performed during the second sampling trip to check the atmospheric stability above the aeration basin. These data are shown in Table 32. It was discovered that there was almost a 1 ^{o}C temperature difference from the surface to the 10 m height. This meant that the air immediately above the basins was unstable, and that enhanced buoyancy resulted in a lifting of the "plume" and a greater amount of initial dilution of the

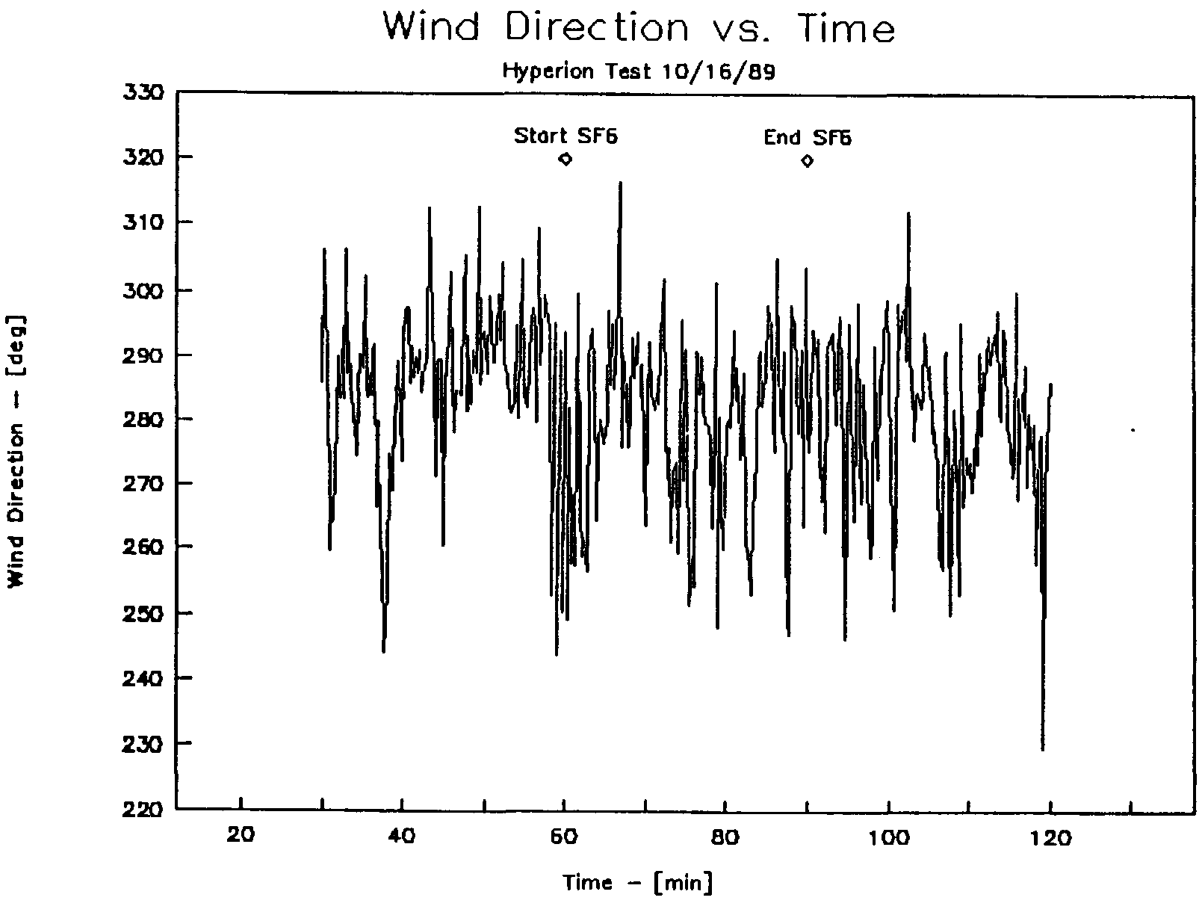


Figure 29 Wind Direction vs. Time for Hyperion Test 10/16/89

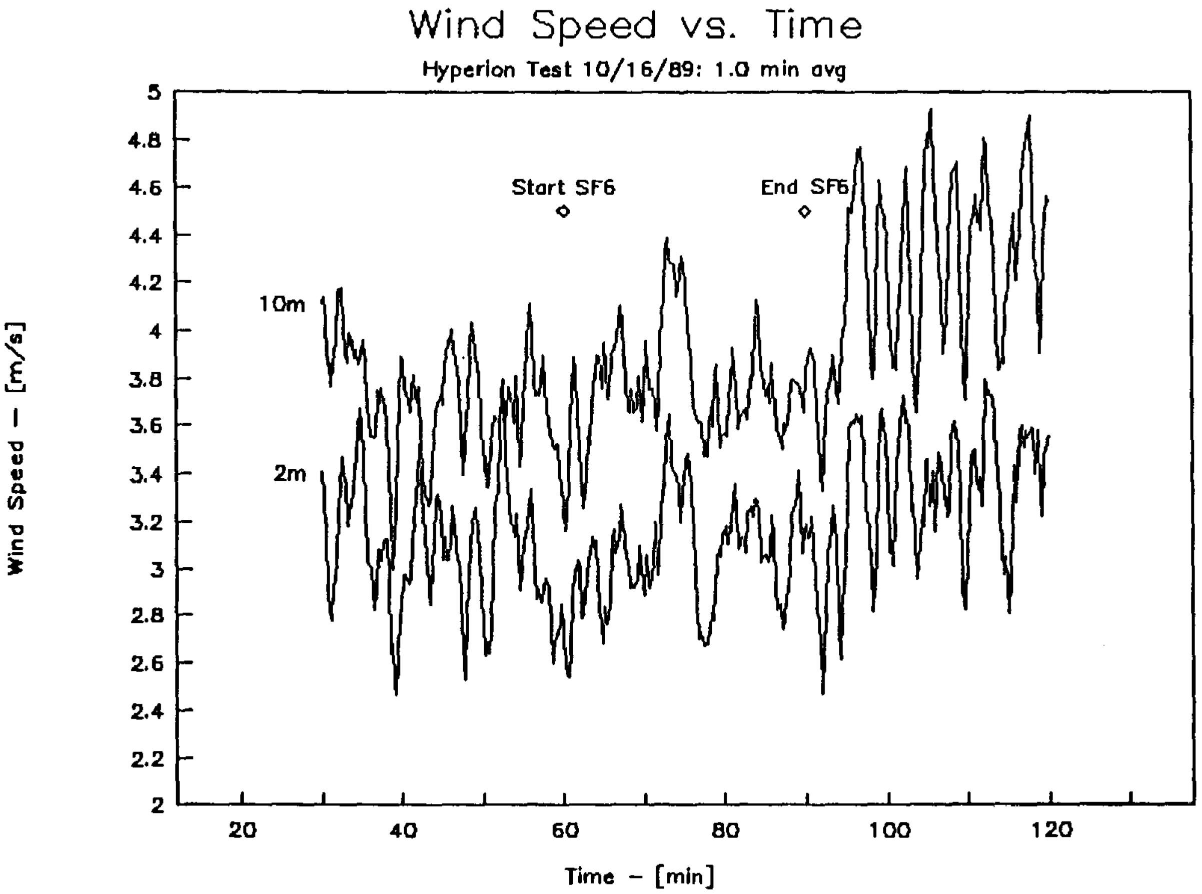


Figure 30 **Wind Speed vs. Time for Hyperion Test 10/16/89**

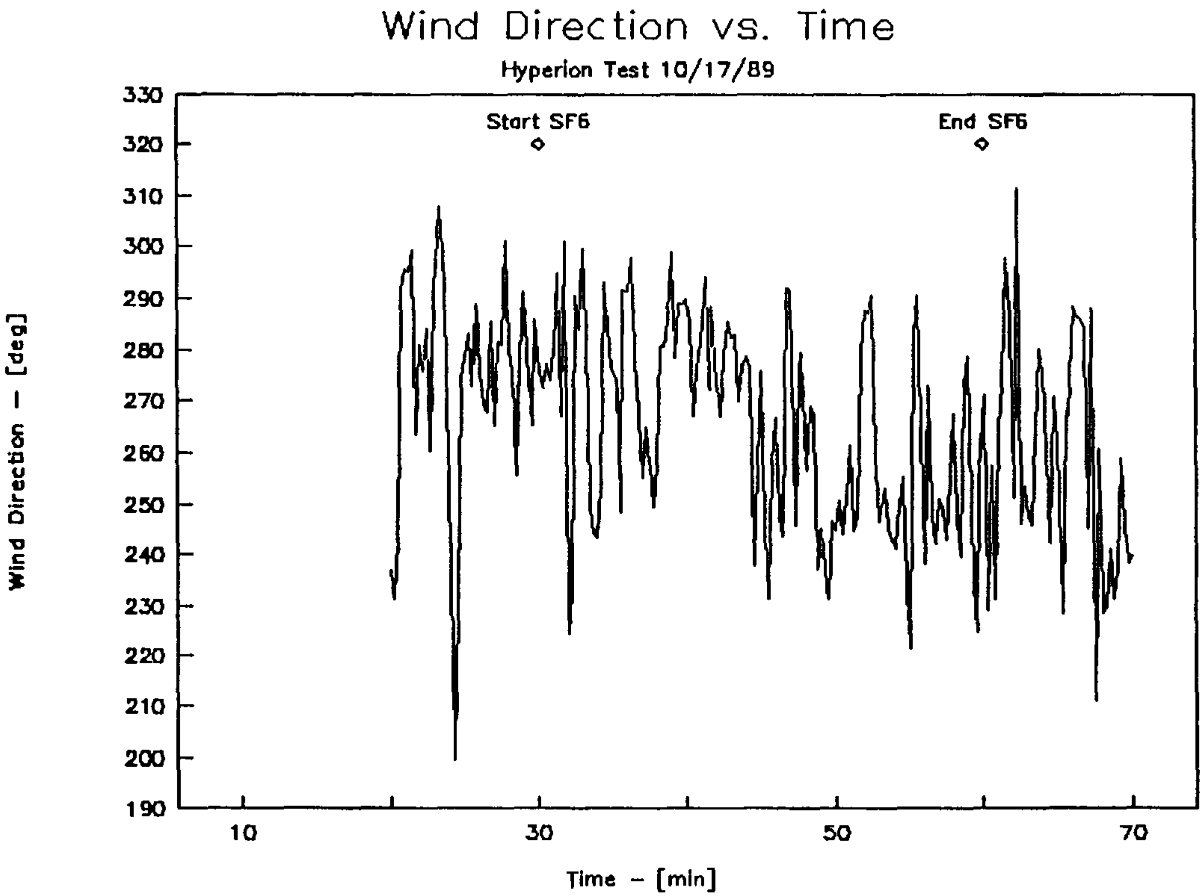


Figure 31   Wind Direction vs. Time for Hyperion Test 10/17/89

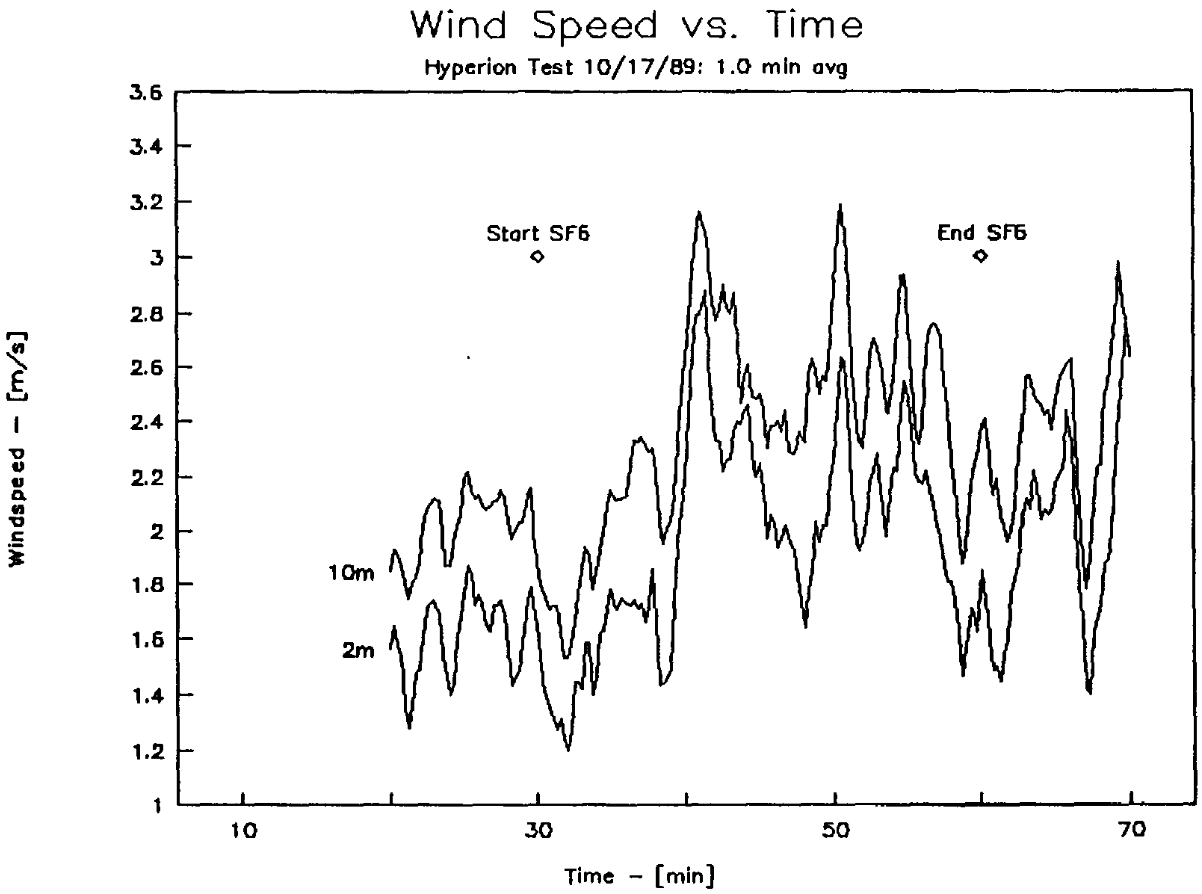


Figure 32 Wind Speed vs. Time for Hyperion Test 10/17/89

emissions. On the morning of the 17th, the slight lifting was confirmed visually when water vapor condensation from the aeration basins was observed. The top of the steam plume appeared to rise to about the 5m level. The initial buoyancy of the air is the probable explanation for the maximum in concentration observed above the surface.

The SF_6 data for the 16th and 17th are contained at the bottom of Table 33. The "a" and "b" sample locations were only six inches apart on the mast and their large differences are indicative of problems with the sampling on the 16th. It was discovered that the gas sampling manifold was not connected properly during the first few minutes of the run, and in retrospect leaks may have been present in the new tube holders. Note the relatively larger gas volumes collected from the towers on the 16th in comparison to the 17th. Therefore, we believe that the "b" samples on the 16th are in error, and that the data should be discarded. The SF_6 data from the 17th are about an order-of-magnitude higher than on the 16th. This was a sampling artifact and was caused by a last minute attempt to position the release line so as to be centered on the constantly shifting wind. The release line was inadvertently disconnected from the SF_6 tank during the first two minutes of the experiment, after which the problem was discovered and corrected. As a result, the bag concentrations are dominated by an effective "point source release" for the first two minutes followed by the pseudo-line source release for the duration of the sampling period. These data are not useful except as an indication of the highly variable light winds and possible indication of plume buoyancy (particularly on the 16th).

A summary of the gas and liquid sample results is contained in Appendix A. Although the mass spectrometer source had been cleaned and tested, and the sorbent tubes were conditioned to ensure that the siloxane "bleed" was acceptably small, a "water" interference continued to be present. We do not know with

Table 32
Hyperion Test 2 Delta T Measurements in ^{o}C

10/16/89		10/17/89	
Time [min]	Delta T [deg]	Time [min]	Delta T [deg]
0	0.90	0	0.68
10	0.76	11	0.89
22	0.94	20	1.00
		27	0.71

Measured by differential thermocouple and microvolt meter.
TC Calibration 42.3 microvolts = 1 degree C

Table 33
SF6 Analysis and Gas Volume Analysis from Hyperion Sampling Trip

Position	Volume	Concentration
10/16/89		
2a	1915	1020
5a	975	383
10a	3045	4540
2b	5040	93
5b	1575	92
10b	2090	394
10/17/89		
2b	1615	57300
5b	1060	29300
10b	1130	11300

Note: The SF6 was emanating from a "point" source for the first 2 minutes. Samples 5b and 10b were reversed, but are corrected on this summary.

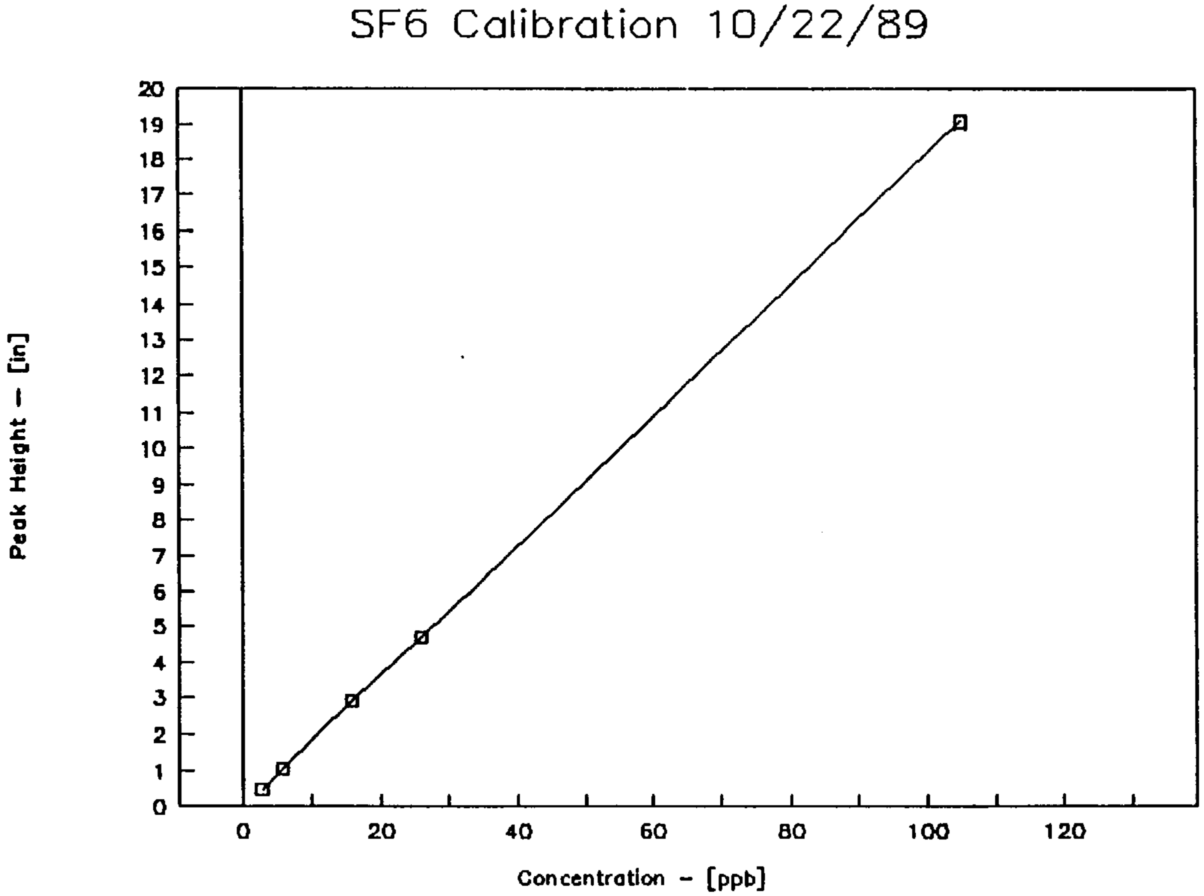


Figure 32A SF6 Calibration 10/22/89

certainty why only the sample tubes above the basin experienced this problem, whereas the upwind samples from the beach or in front of the Administration building did not have the same interference. One initial thought was that "sea salt" had been sampled into the tubes, however, the problems were not severe in the upwind samples. The only other logical explanation seems to be that an aerosol was generated above the ASAB that contained a hygroscopic material that deposited on the tubes. Thus during the desorption process sufficient water was carried onto the internal traps of the UNACON concentrator that the water was transferred to the column during analysis.

A solution for the interference problem was found and applied after one half of the samples from the October 16th sampling trip had been analyzed. The UNACON concentrator had a "tube saver" option in which part of the contents from one tube could be desorbed and directed onto another identical sorbent tube while the remainder passed through the concentration steps to the gas chromatograph. The second tube had reduced water retention, since it was not exposed to the postulated aerosol, and could then be analyzed normally. In the summary table of the gas samples, those samples marked "B" correspond to application of this procedure, and a correction for the volume change was applied during later data analyses. Selected ion integration was performed for all compounds that could be identified with reasonable certainty from the mass spectral library, known boiling point versus retention time, and which appeared consistently in both liquid and gas samples. These compounds included 1,1-DCE, DCM, TCM, 1,1,1-TCA, BZ, 1,2-DCA, TCE, TOL, PERC, ETBZ, XYL, TMB, LIM, DCB, and UND. Absence of a particular compound does not mean that it was not present, but that it was below detection limits (BDL) of the analysis, or it was not present consistently at detectable levels, e.g. bromodichloromethane (BDM).

As explained earlier with the SF_6 analyses, there were apparent leakage problems with the new sorbent tube fixtures on the sampling mast. This was apparent from the large volumes collected in some sample bags. For these reasons, the data obtained on October 16th should be considered qualitative at best. The data from the October 17th sampling effort are considered to be reliable since the leakage problem was noted on the previous day and tube fittings tightened. Because of the mild Santa Ana conditions that occurred on both days, wind direction reversal occurred shortly before sampling, particularly on the 17th. Thus material emitted by the HTP and other sources, were present in the return flow upwind sample, but at levels an order-of-magnitude lower than above the ASAB, except for those compounds characteristic of vehicle exhaust. In particular, limonene (LIM), a compound which our experience indicates is highly characteristic of domestic wastewater, was below detection limits.

D. Discussion of Results

During the June sampling trip, difficulties were experienced with the GC/MS analyses of the samples. Thus, while meteorological conditions were favorable and good tracer data were obtained, quantitative data on airborne concentrations of only a few target compounds were obtained. As a result, a second sampling effort was scheduled. During the October sampling trip, meteorological conditions were unfavorable, and problems were encounter in the execution of the tracer experiment, but the GC/MS analyses were more complete. Fortunately, among the data sets obtained, some reasonable conclusions regarding emissions from the aeration basins could be drawn.

One immediate observation was that while the liquid samples were generally consistent for most compounds, i.e. the ASAB could be treated as a homogeneous source, some of the more volatile chlorinated solvents, e.g. DCM, DCA, and TCA, showed greater spatial variability. A second, initially puzzling, observation

Table 34
Comparison of Liquid Emission Rate with
Airborne Flux[a] - Data from June 22, 1989 Experiment

Compound	Liquid Conc.	Hc	Calc. Bubble Conc.	Calc. Flux	Measured Gas Conc.	Measured Flux	Ratio (M/C)
	[μg/L]	[-]	[μg/L]	[μg/min]	[μg/m3]	[μg/min]	[-]
DCM	2.86E+00	9.0E-02	2.57E-01	1.07E+06	7.4	1.79E+06	1.7E+00
TOL	7.64E+00	2.7E-01	2.06E+00	8.68E+06	115.2	2.78E+07	3.2E+00
XYL	NA	2.9E-01	NA	NA	4.9	1.19E+06	NA
	[Area/L]	[-]	[Area/L]	[Area/min]	[Area/L]	[Area/min]	[-]
DEC	1.98E+08	2.8E+02	5.53E+10	2.30E+17	2.18E+06	5.25E+14	2.3E-03
TMB	5.83E+08	2.4E-01	1.40E+08	5.82E+14	4.05E+06	9.76E+14	1.7E+00
LIM	1.40E+07	1.9E+03	2.69E+10	1.12E+17	3.43E+06	8.26E+14	7.4E-03
DCB	2.11E+09	1.0E-01	1.26E+08	8.75E+14	4.29E+06	1.03E+15	1.2E+00
UND	5.44E+08	7.5E+02	4.07E+11	1.70E+18	7.27E+06	1.75E+15	1.0E-03

[a] Assumes bubble saturation for emission rate and constant concentration to 10m height for airborne flux calculation.

Notes: Hc is the dimensionless Henry's constant.
Hc values from Mackay and Shiu for DEC, UND, TMB, XYL, and DCB.
Hc value from Gossett for DCM.
Hc value extrapolated from Nirmalankhandan and Speece for LIM.
Volumetric gas flow - 4420 scmm.
Volume flux to 10 m - 2.41E+05 scmm.
Average wind speed - 2.6 m/s.

Table 35
Comparison of Liquid Emission Rate with Airborne Flux[a] - Data from October 17, 1989

Compound	Liq Conc [µg/L]	Hc 25C [-]	Bub Conc [µg/L]	Meas Conc [ppb]	Meas Conc [µg/m3]
TCM[c]	1.3	0.15	0.20	0.39	1.33
BZ[b]	61	0.22	13.53	2.26	7.18
PERC[c]	1.1	0.72	0.80	2.53	17.14
	[Area/L]		[Area/L]		[Area/m3]
DCE[c]	2.1E+08	1.07	2.2E+08		8.7E+09
DCM[c]	1.8E+09	0.09	1.6E+08		5.3E+09
TCA[c]	4.8E+08	0.70	3.4E+08		1.3E+10
DCA[c]	5.2E+09	0.23	1.2E+09		2.1E+10
DCB[b]	6.5E+08	0.10	6.5E+07		8.9E+09

Volumetric Gas Flow - [scmm] 4418
Volume Flux to 10 m - [scmm] 2.04E+05

	Calculated Mass Flux		Measured Flux		Ratio
	[µg/min]	[mtpy]	[µg/min]	[mtpy]	
TCM	8.62E+05	0.45	2.71E+05	0.14	0.31
BZ	5.98E+07	31.41	1.46E+06	0.77	0.02
PERC	3.51E+06	1.85	3.49E+06	1.83	0.99
	[Area/min		[Area/min		
DCE	1.8E+15		1.8E+15		1.00
DCM	1.3E+15		1.1E+15		0.85
TCA	2.7E+15		2.6E+15		0.97
DCA	9.4E+15		4.2E+15		0.45
DCB	5.1E+14		1.8E+15		3.54

[a] Assumes bubble saturation for emission rate and constant concentration to 10m height for airborne flux calculation.
[b] Hc for BZ, DCB from Mackay and Shiu
[c] Hc for TCM, DCE, DCM, TCA, DCA and PERC from Gosset

was that although biodegradation was known to be occurring, very weak gradients of the biodegradable compounds were observed, whereas, the degree of mixing from the fine bubble diffusers in the ASAB should have served to make the long rectangular channels appear to be "plug-flow" reactors. Thus an exponential decay of concentration from the central distribution channel toward the collection channel would be a reasonable expectation. Two apparently conflicting observations were present, i.e. essentially uniform concentrations for most compounds that should not have been uniform because of biodegradation, from which one would infer "well-mixed" conditions in the ASAB, but spatially variable concentrations for other relatively non-degradable compounds, indicative of temporally variable inputs and "plug-flow" in the ASAB.

Assuming that the analytical data for liquid samples are representative, which we believe to be the case, the following hypothesis is offered. Caballero and Griffith (1989) suggested that sorption of a significant fraction of some compounds to solids occurred and could possibly explain their experimental observations. They had observed an inverse dependence of the ratio of fine-to-coarse bubble concentrations with Henry's law coefficient. This explanation was initially dismissed by us based upon literature reports of completely reversible sorption of even semi-volatile compounds by purge-and-trap methods (Dobbs et al., 1989), and the relatively low partition coefficients for the compounds in question, TCM, TCE, TCA, PERC and CT. However, for compounds with large octanol-water partition coefficients (Kow), e.g. compounds which are hydrophobic such as larger hydrocarbon molecules, reversible sorption <u>is</u> significant. In fact, although vapor pressure typically decreases with increasing molecular weight, the Henry's coefficient, Hc, increases with increasing molecular weight for non-polar compounds, indicative of a compound's tendency to escape from the aqueous phase. Thus, the lack of spatial variability of some compounds may be the result of the biomass serving as a significant reservoir of the compounds. Those compounds that are not readily adsorbed, such as the lower molecular weight chlorinated species, correspondingly exhibit greater spatial variability reflecting "plug-flow" conditions and temporal variability of inputs, i.e. they are solvents that often appear in concentrated discharges. On the other hand, species sorbed to the biomass would appear to be more uniformly distributed because the biomass would damp out fluctuations in concentration. Furthermore, once sorbed to the biomass, the rate of desorption to the liquid could be limiting and thus the efficiency of stripping greatly diminished. However, in purge-and-trap studies where rate limitations are not at issue, the compounds would be reversibly desorbed. Further studies of the possible importance of desorption rate limitations are needed to clarify this matter.

An effort was made to relate the measured airborne concentrations to the liquid concentrations and expected air-stripping based upon values of Hc. To perform this comparison, it was somewhat arbitrarily assumed that, to a first approximation, the "plume" from the ASAB was confined vertically to the first 10 meters at the east end of the ASAB. (Estimates of Gaussian plume dispersion parameters indicate that this should be the case for neutral stability conditions.) The concentrations at the 2, 5, and 10m levels were simply averaged and assumed constant, the average wind speed was computed and assumed to be constant with height, and a flux of a species through a vertical plane 10 m high was computed. This value was compared to the amount that would be expected to be air-stripped by the known volume of aeration air, literature values of Henry's coefficient, and average liquid concentration in the basin. The results of the airborne measured prediction of the flux and the calculated flux of material air-stripped from the ASAB is given in Tables 34 and 35, for the June 22nd and October 17th tests.

Perhaps serendipitously, for the relatively non-biodegradable compounds, DCE, DCM, TCA, DCA, TCM, PERC, and DCB, the ratios are within a factor of about 3 (shown in the last column of each Table). In fact for several of the compounds, e.g. PERC, DCE, and TCA, the ratio is practically unity and the arithmetic average of the nine values for both days is 1.2! On the other hand, for compounds known to be biodegradable or to have very high Kow's or Hc's (BZ, DEC, LIM, UND), the ratio of the measured to calculated fluxes is about 0.02 to 0.03 or smaller. As discussed above, for some compounds both sorption and biodegradation appear to be more significant than anticipated on the basis of our Phase I literature review and emission estimate. It should also be noted that the both the June and October samples were drawn upwind of the East collection channel. The collection channels were areas of high turbulence and energy dissipation, so that at least a portion of the emissions from the ASABs was not measured. A more refined dispersion model computation would simulate the plume concentration distribution more faithfully, but would not be expected to alter the calculated airborne flux estimates substantially.

E. Discussion of PEEP Emission Factors for ASABs

Three rounds of tests of three different diffused air activated sludge aeration basins (ASAB) were performed during the PEEP sampling program. Two of the basins (A and B) were covered and vented, while one was covered but did not have a convenient vent (C). Emissions were measured with a "flux chamber" methodology, but all sample trains employed the ice-bath impingers ahead of the bags as discussed earlier. Two of the ASABs employed "fine bubble" diffusers (A and C) while one used a medium bubble membrane diffuser. Liquid sample analyses were performed on a single 24-hour composite of influent or effluent for each test. Two inlet and outlet air samples were collected over 24-hr periods with an additional duplicate of the outlet samples drawn in some cases. Results of those tests for two compounds TCM and PERC are summarized in Table 36.

Table 36

PEEP Data on Diffused Air Activated Sludge Emissions

Liquid Samples

	TCM			PERC		
WWTP	Ci [ppb]	Co [ppb]	(Ci-Co)/Ci [%]	Ci [ppb]	Co [ppb]	(Ci-Co)/Ci [%]
A	5	3	40%	4	<1	88%
	7	4	43%	n.d.	n.d.	NA
	8	4	50%	n.d.	n.d.	NA
B	10	6	40%	n.d.	n.d.	NA
	11	4	64%	n.d.	n.d.	NA
	7	1	86%	7	<1	93%
C	3	<1	83%	26	<1	98%
	3	1	67%	21	2	90%
	4	1	75%	19	1	95%
Average Loss			61%			93%

Note: Co assumed to be 1/2 detection limit if b.d.l. for purposes of removal efficiency calculation.

PEEP Reported Emission Factors Based on Air Samples

WWTP	TCM [%]	PERC [%]
A	14%	28%
	15%	n.d.
	60%	n.d.
B	26%	n.d.
	19%	n.d.
	28%	34%
C	45%	76%
	36%	33%
	27%	33%
Average Loss	30%	41%

Note: "n.d." = not detected in the liquid. PERC was detected in all air samples.

The two compounds TCM and PERC were selected from the PEEP data for discussion purposes because a) they were present in all of the air samples; b) they are not considered to be biodegradable; and c) they are not strongly sorbed compounds. The liquid data clearly indicate a greater loss from the ASAB than the air samples by approximately a factor of 2, with almost total removal of PERC from the liquid. As noted previously, the PERC air samples are suspiciously low because of the presence of the ice bath impinger. Furthermore the fraction of TCM removed in comparison to PERC is lower. This appears to be in rough agreement with the HTP sampling results which indicated that TCM emissions were relatively less than that of PERC. Based upon the average TCM and PERC liquid concentrations in the HTP basins on October 17th, the removal efficiency from the ASAB was approximately 20% and 220%, respectively. Clearly the PERC removal efficiency could not have been greater than 100%. However, since the influent PERC concentration to the basin was not measured, it is not unreasonable for the PERC emissions to exceed 100% based upon the average liquid concentration. (A removal efficiency of > 200% would result if exponential decay and plug flow was assumed with 99% removal by the end of the ASAB!) The PEEP TCM emission factor is comparable to, but greater than that computed for the HTP. Because liquid TCM concentrations were near detection limits at the HTP, within experimental error, the average PEEP emission factor of 30% does not differ with that observed at the HTP (20%). However, the PERC emission factor of 41% appears to be low compared to both the PEEP liquid data and to the HTP measurements. Again, we are led to the conclusion that the PEEP emission factors based upon air samples underestimate the emission rates of semi-VOCs and possibly some of the higher boiling VOCs.

To summarize, on the basis of the HPT sampling trips the following conclusions and recommendations have been drawn.

1) For compounds commonly associated with wastewater and not expected in vehicle exhaust or ambient air

coming off the ocean, e.g. DCM, TCM, PERC, LIM, DCB, UND, etc., concentrations immediately downwind of the aeration basins were a factor of ten or higher than those measured in the upwind air.

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

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

4) For the "typical" afternoon sea breeze conditions encountered during the June sampling trip, the average dilution factor observed on top of the bluff at the eastern end of the aeration basin was about 6 to 7 for periods of about one-half hour. This amount of dilution will reduce measured concentrations from the plant to near "background" ambient levels at the property line if the "background" is determined during periods when polluted air transported off-shore (e.g. nighttime land-sea breeze) returns onshore.

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

6) Initial plume buoyancy can be a factor in dispersion modeling for health risk estimation purposes, particularly in near field calculations from large warm area sources. The ability to account for this phenomenon for large area sources in commonly used gaussian models such as ISCST or ISCLT does not have a firm basis and further model development may be warranted.

7) Studies of the rate of desorption of semi-volatile compounds from biomass and oils should be undertaken to determine their possible influence on total emissions and air-stripping models.

8) The PEEP emission factors appear to underestimate the emissions of semi-VOCs. A study of losses through the ice bath impinger needs to be undertaken if the PEEP air-based emission factors are to be used for semi-VOCs.

9) Use of bag sampling for semi-VOCs that make up a substantial portion of the air emissions of reactive organic compounds from WWTPs needs to be re-examined. Sorbents may be a better choice of sampling media for such cases.

V. Chloroform Formation During Wastewater Chlorination

Chlorination of wastewater is practiced at municipal wastewater treatment plants (MWTP) for a variety of reasons, including odor control of raw wastewaters and disinfection of treated wastewater prior to discharge. On occasion, chlorine is added directly to sanitary sewers in order to control odor problems. The formation of chloroform in such systems has not been as thoroughly studied as for drinking water, the yields of chloroform formed are known only approximately, and are known to be wastewater-composition dependent. The literature on chloroform formation is extensive and the reader is referred to Chou (1990) for a recent summary of haloform formation literature.

A. Selected Literature Citations

Jolley (1975) examined the incorporation of gaseous ^{36}Cl into organic compounds upon chlorination of settled primary effluent and biologically treated secondary effluent. The study found that similar compounds were formed, though more from the primary than the secondary effluent. The author concluded that the additional formation from the primary chlorinated effluent was the result of a higher initial chlorine dose rather than greater amounts of organic material. Over 60 peaks were detected by HPLC with dual UV detector. Organic compounds identified with standards eluting at the same time included 5-chlorouracil, 5-chlorouridine, 8-chlorocaffeine, 6-chloroguanine, 8-chloroxanthine, 2-, 3-, and 4-chlorobenzoic acids, 5-chlorosalicylic acid, 4-chloromandelic acid, 2-, 3-, and 4-chlorophenols, 4-chlorophenylacetic acid, 4-chlororesorcinol, 3-chloro-4-hydroxybenzoic acid, and 4-chloro-3-methylphenol. The author estimated about 0.5 to 1.0 % incorporation of chlorine occurred on the basis of the quantity of ^{36}Cl incorporated into organics. The quantity of haloforms formed was not reported. The author reported on slight differences in the compounds formed when chlorine or hypochlorous acid was used as the form of the chlorine, but concluded that essentially equivalent results were obtained regardless of the form of chlorine added.

Chow and Roberts (1981) found that filtered, nitrified wastewater had greater potential for forming chloroform than non-nitrified wastewater. Development of total THM appeared to continue for periods approaching 24 hours of contact time and about 4 to 5 μM solutions of organic halogen atoms were formed in the nitrified wastewater at a dose of from 20 to 40 mg/L as Cl_2, i.e. about 1 mM of Cl. Total incorporation of chlorine into organic compounds was estimated at about 1% of the amount applied. This figure is in approximate agreement with the earlier study by Jolley. Lower amounts of haloforms were formed in the nitrified wastewater or when chlorine dioxide was applied.

Cooper et al. (1983) studied the effect of the chlorine dosage on the formation of THM, examining different positions along the breakpoint chlorination curve. They concluded that even with substantial amounts of ammonia initially present in the water (5 - 12 mg/L), organochlorine and THMs were formed, up to about 1 μM as chloroform equivalent, at dosages of 20 mg/L as Cl_2. The maximum molar yield of THMs was approximately 0.004 (ratio of THM equivalent to Cl_2) and was larger when "free" chlorine residual was largest. Organohalogen compounds were found to be formed up to 24 hours after chlorine addition, with about one-third to one-half of the full amount formed within the first 15 minutes. In the presence of bromide ion from salt-water intrusion, bromoforms were also formed.

B. Preliminary Chloroform Formation Experiments

Two preliminary studies of chloroform formation were undertaken as part of the current research contract. The purpose of these measurements was to determine the magnitude of the potential problem. The first was simply a grab sample of sewage and sewer gas, upstream and downstream of a chlorinator on a

County of Sacramento sewer. Because the samples were drawn immediately upstream of the junction of an interceptor and lateral, and the liquid concentrations in the lateral were not sampled, one cannot conclude with certainty that increases in downstream concentrations of some chlorinated compounds were a direct result of chlorination. Some of the non-chlorinated compounds actually increased downstream as well, indicating that either the measurement precision was not better than a factor of two, or that there were higher concentrations in wastewater from the lateral. Also, since standards were not available for several of the compounds identified by the GC/MS library, concentrations could not be determined. However, some representative results of relative area counts for compounds identified with reasonable certainty are presented in Table 37. For compounds such as TCE, TOL, HEPT, PERC, DCB and UND there was no significant change in concentration from the upstream to downstream liquid sample. However, for DCM, TCM, TCA, ETBZ and XYL there appear to be increases by as much as a factor of two or higher, particularly for DCM. In the gas phase, upstream concentrations of DCM appear to be higher than downstream, whereas for most compounds there were no significant differences. A plausible explanation for the observed results is that there was a significantly higher concentration of DCM in the lateral, and that the increased turbulence at the junction caused some of the DCM to be released to the gas phase.

Regarding the possibility of chloroform formation, it can only be said that at most there appeared to be a doubling in the concentration, which was still quite low ($\approx 3\ \mu g \cdot L^{-1}$). The molar ratio would be approximately 0.0002 based upon a target 8 $mg \cdot L^{-1}$ Cl_2 target dose. However, since the travel time in the sewer between the two access points was only on the order of five minutes, the full haloform potential may not have been realized. Based on the literature, the haloform concentration would not have been likely to increase much more than an additional factor

Table 37

Sacramento County Sewer Sampling Study Results
(TENAX/Ambersorb Tubes)

Most Abundant Ion Area Count Arbitrary Units

Compound Name	Gas Std.	Gas Up	Gas Down	Liquid Up	Liquid Down
DCM	5.0E+05	4.8E+04	1.4E+04	2.6E+04	1.5E+05
TCM	2.5E+06	2.9E+06	3.1E+06	2.7E+05	6.1E+05
TCA	2.1E+06	3.6E+06	3.3E+06	5.2E+04	1.7E+05
BZ	5.2E+06	1.5E+06	2.6E+06	1.5E+06	8.5E+05
HEPT	NA	1.3E+06	2.4E+06	1.2E+05	1.6E+05
TCE	2.5E+06	4.8E+05	1.4E+05	2.9E+04	3.1E+04
TOL	5.2E+06	3.9E+06	5.5E+06	1.2E+06	1.1E+06
PER	3.0E+06	4.0E+06	4.1E+06	3.8E+05	4.0E+05
ETB	6.4E+06	2.1E+06	2.4E+06	1.6E+05	3.0E+05
XYL	NA	4.6E+06	4.6E+06	4.6E+05	8.5E+05
XYL	6.0E+06	4.4E+06	4.2E+06	3.6E+05	6.2E+05
TMB	NA	6.0E+06	6.0E+06	7.5E+05	1.3E+06
DCB	NA	3.0E+06	2.5E+05	8.5E+05	8.0E+05
UND	NA	NA	1.4E+06	9.5E+05	1.4E+06

Approximate Concentration

	[ppbv]	[ppbv]	[µg/L]	[µg/L]
DCM	6	2	1.1E+00	6.4E+00
TCM	70	74	3.2E+00	7.3E+00
TCA	103	94	8.2E-01	2.7E+00
BZ	17	30	5.6E+00	3.2E+00
HEPT	NA	NA	NA	NA
TCE	12	3	3.8E-01	4.1E-01
TOL	45	63	5.3E+00	4.9E+00
PER	80	82	5.2E+00	5.5E+00
ETB	20	23	6.6E-01	1.2E+00
XYL	NA	NA	NA	NA
XYL	44	42	1.6E+00	2.7E+00
TMB	NA	NA	NA	NA
DCB	NA	NA	NA	NA
UND	NA	NA	NA	NA

of 2 or 3. Thus we conclude that only minor amounts of chloroform were formed (< 0.1% incorporation of the chlorine added). These observations are consistent with literature reports that chlorine (or hypochlorous acid) reacts essentially instantaneously with inorganic compounds such as sulfides and reduced metal ions. It was unlikely that there was any free chlorine residual remaining in the wastewater.

There appeared to be a trace of gas phase chlorobenzene in the downstream gas sample, a compound which was not evident in either the upstream gas or liquid. Substitution reactions of the methyl group on toluene have been reported with %-range efficiencies but only at much higher organic and chlorine levels. Thus, it appears that the chlorine added to the sewer was primarily consumed in oxidation reactions of inorganics, e.g. reduced metal ions, sulfides and ammonia, and secondarily by direct oxidation reactions of some organics. That oxidation reactions had occurred was evidenced by the disappearance of a rather large dimethyldisulfide peak in the downstream liquid sample.

A second experiment was conducted with secondary effluent from the UCD treatment plant. Hypochlorite was introduced into a Tedlar® bag containing 4 L of effluent to provide a chlorine dose of 80 $mg \cdot L^{-1}$. Samples were drawn from the bag and analyzed by GC/MS with the result that about 0.8 $\mu g \cdot L^{-1}$ of chloroform was present after 30 minutes and 1.2 $\mu g \cdot L^{-1}$ after 60 minutes. The molar ratio in this case would be approximately 0.00001. The campus effluent may not be representative of MWTPs in that the plant influent does not have a representative mix of sources, and the water supply is from a deep groundwater aquifer, probably with lesser concentrations of haloform precursors than a surface water supply.

Additional samples of effluent were analyzed as part of a study for the Pooled Emissions Estimation Program/Bay Area Air Toxics (PEEP/BAAT) groups (Chou et al., 1990). In these studies, 3.0 L of either screened raw wastewater or secondary effluent (nitrified and non-nitrified) buffered to pH 7.6-7.8 were dosed with 5 mg/L or 15 mg/L of chlorine (in the form of hypochlorous acid). Samples were drawn from a magnetically stirred, "headspace-free" Tedlar® bag at 7.5, 15, 30 and 60 minutes after injection of the chlorine solution. The samples were analyzed by purge-and-trap using the Envirochem concentrator and HP GC/MS system previously described. Selected ion monitoring for chloroform, bromodichloromethane, dibromochloromethane and bromoform was conducted. Results of those analyses (see Figures 33a-35b) indicated that total trihalomethane formation was greatest in nitrified secondary effluent, (1.3 μM after one hour). Concentrations in non-nitrified and raw wastewater were over a factor of 10 lower. These results are similar and consistent with those reported by other investigators. For the case of nitrified secondary effluent, the molar ratio was about 0.02 for the low chlorine dose and 0.01 for the higher chlorine dose.

The above results in conjunction with the evidence from the literature suggests that chlorination of raw sewage produces relatively lesser amounts of haloforms, but that about 1% or less of the total chlorine added is incorporated into organic compounds. The exact amount depends upon competition with inorganic species such as reduced sulfur and metals. On the other hand, chlorination of nitrified secondary effluent does appear to produce haloforms at levels about an order-of-magnitude greater than non-nitrified effluent. This would suggest that a study of air emissions from the chlorine contact chamber of a wastewater treatment plant that practices nitrification of secondary effluent be undertaken.

A further report in the literature (Card, 1989) indicates that chlorination reactions might be occuring in two-stage packed bed scrubbers used for odor control. These scrubbers employ an acidic first stage followed by a basic second stage and chlorine oxidation. The ostensible purpose of the first stage is to remove ammonia that can form odorous chloramines. In the second stage hydrogen sulfide is absorbed at high pH, and chlorinated scrubber solution is used to oxidize the sulfide. On the basis of the literature on haloform formation, these would be almost ideal conditions for producing haloforms from 2-propanone (acetone) and 2-butanone (methylethylketone), both of which were present in combined domestic/industrial wastewaters at the JWPCP. We strongly recommend that a follow-on study of emissions from two-stage packed bed odor scrubbers be undertaken.

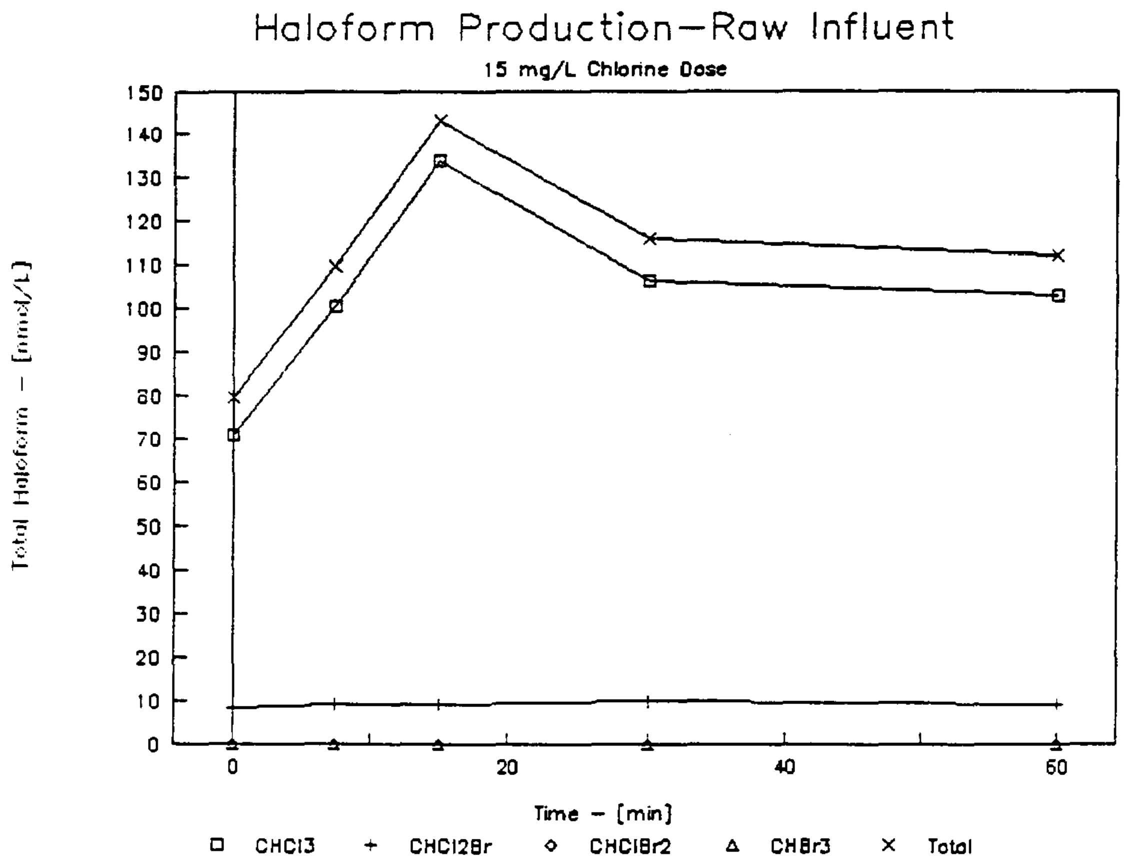


Figure 33a Haloform Production—Raw Influent, 15 mg/L Chlorine Dose

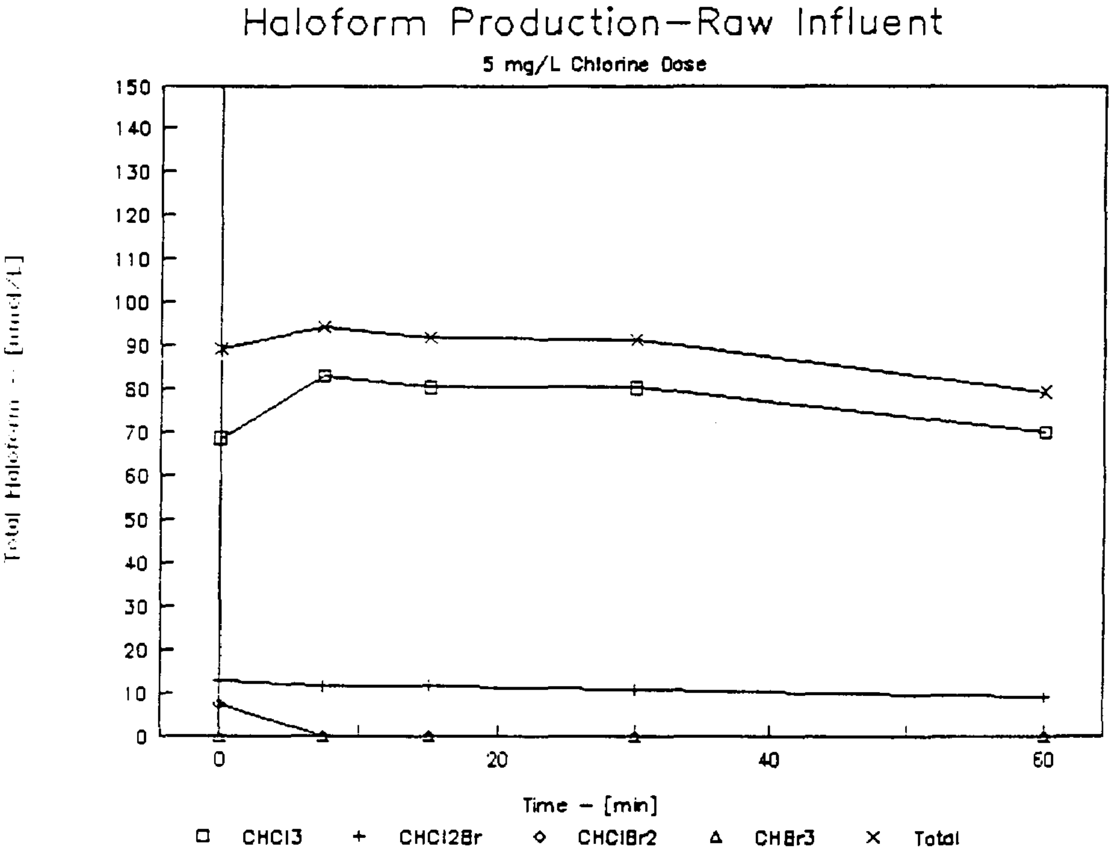


Figure 33b Haloform Productions—Raw Influent, 5 mg/L Chlorine Dose

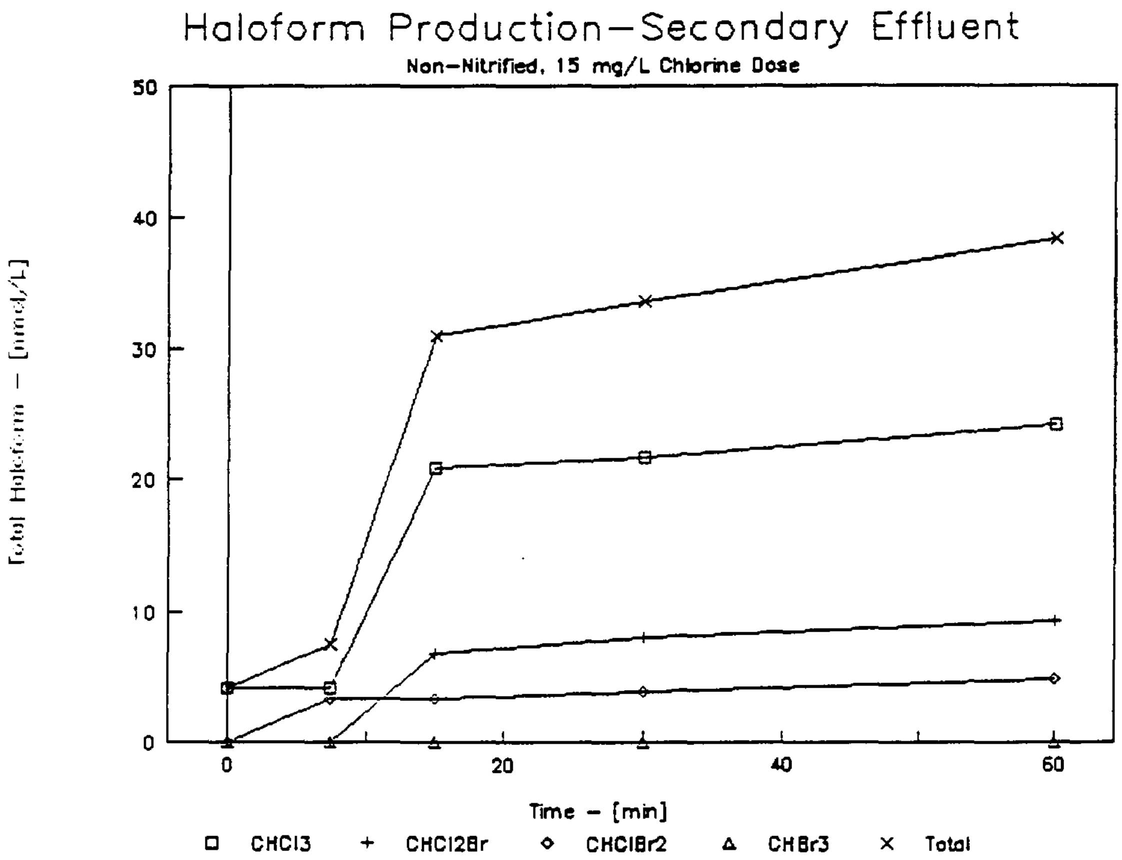


Figure 34a **Haloform Production—Secondary Influent, Non-Nitrified, 15 mg/L Chlorine Dose**

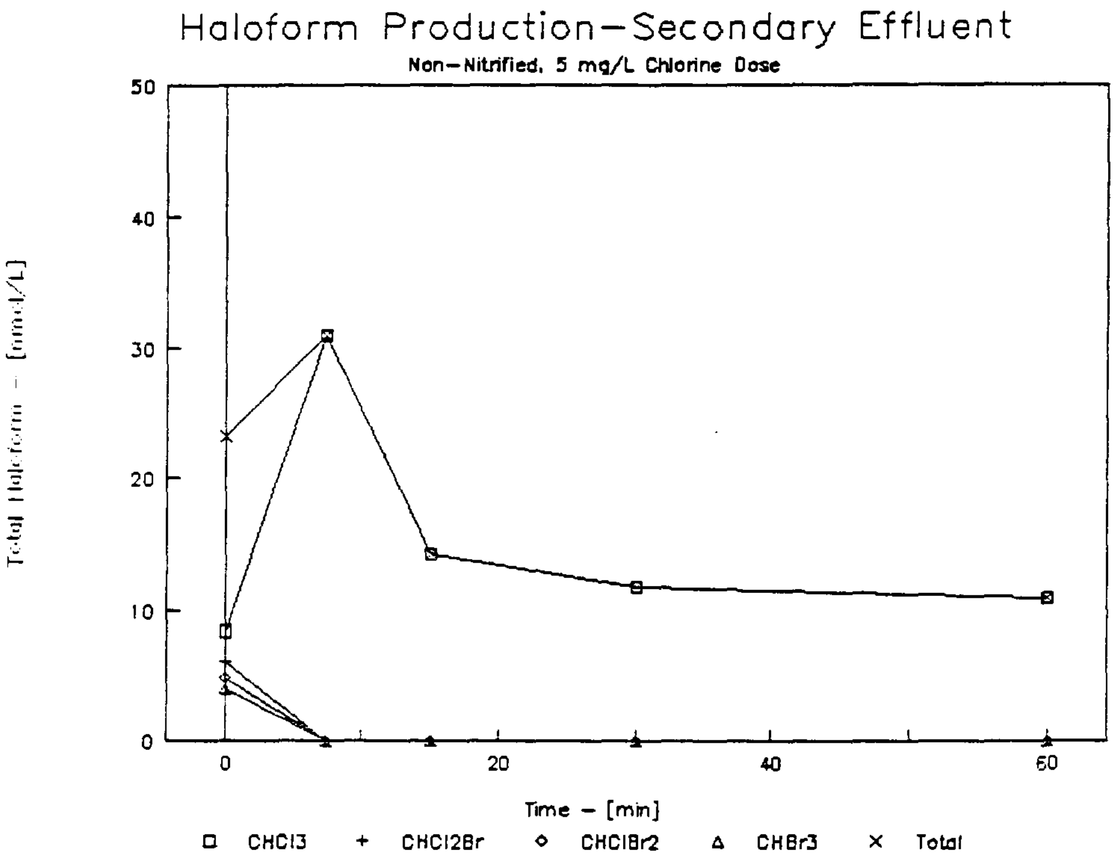


Figure 34b Haloform Production—Secondary Influent, Non-Nitrified, 5mg/L Chlorine Dose

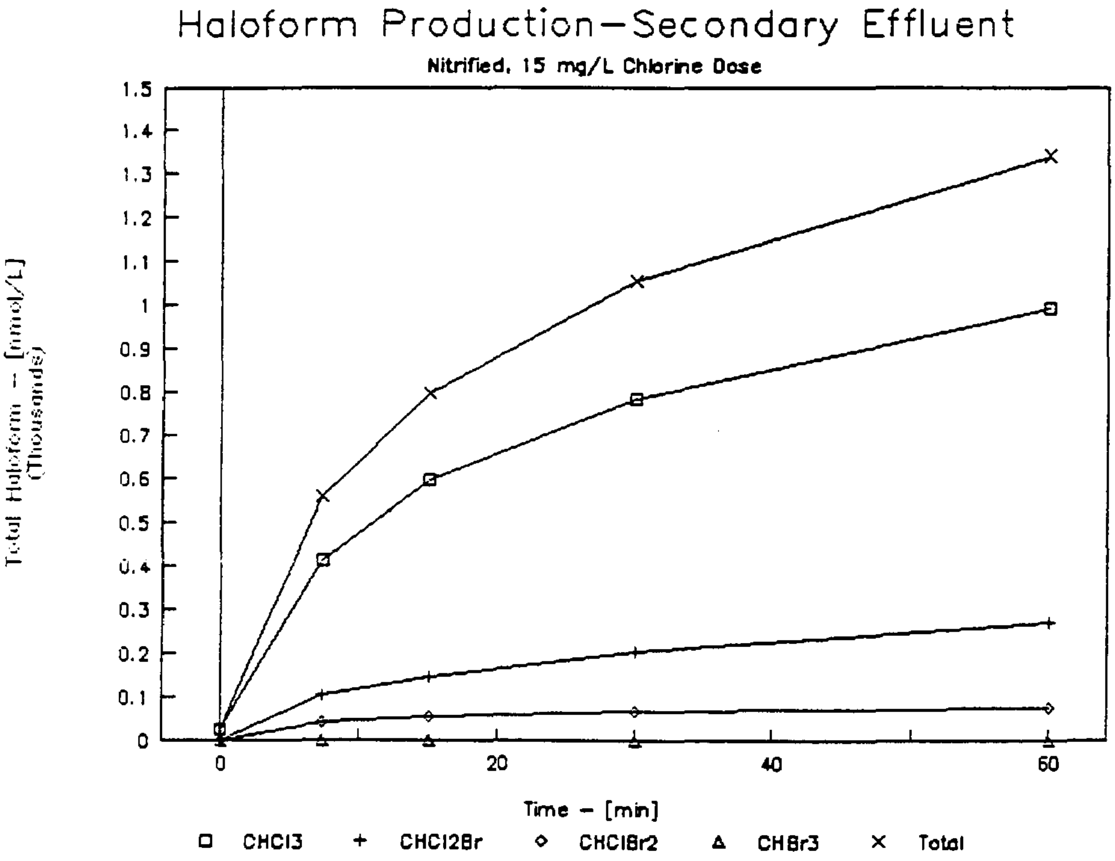


Figure 35a **Haloform Production—Secondary Effluent, Nitrified, 15 mg/L Chlorine Dose**

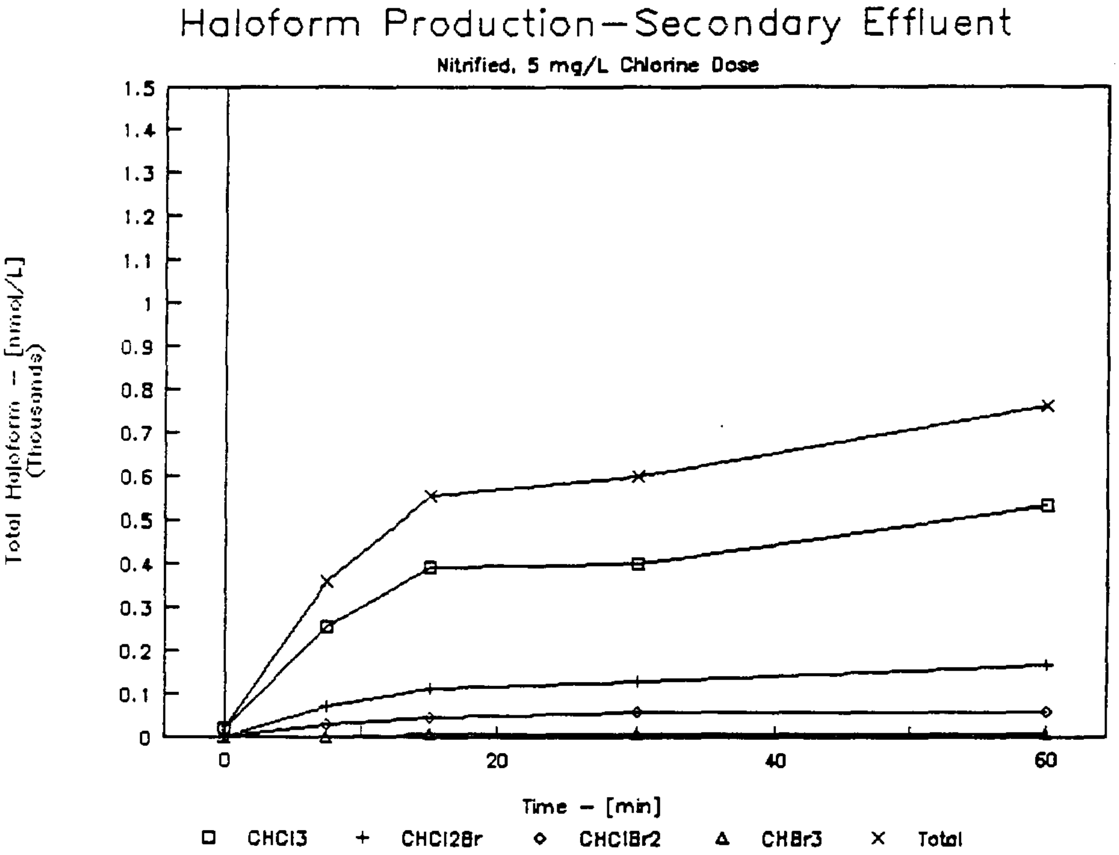


Figure 35b Haloform Production—Secondary Effluent, Nitrified, 5 mg/L Chlorine Dose

VI. Overall Conclusions and Recommendations

During the course of this study, experimental data from sampling of preliminary treatment processes at the JWPCP were obtained as well as upwind/downwind sampling from a secondary treatment process (activated sludge aeration basins - ASAB) at the HTP. In addition, some data were obtained on sewer vent gases from the CSDLAC, a pure-oxygen activated sludge process at the EBMUD, and wastewater chlorination of raw wastewater, nitrified and non-nitrified secondary effluent. Some development of VOC sampling methods from wastewater off-gases also took place. Observations, conclusions and recommendations that have resulted from these efforts are summarized below.

A multi-sorbent tube sampling methodology was evaluated and compared with bag sampling in conjunction with the EBMUD. Based upon limited testing, the multi-sorbent tube sampling method provided higher recoveries and comparable or lower variability than Tedlar® bag samples. Two commercially available sorbent combinations were used, a Tenax/Ambersorb (TA) and a Carbotrap/Carbosieve™ (CC). The TA combination was observed to produce low levels of sampling artifacts such as benzene, toluene, benzaldehyde, phenylethanone, etc., previously reported in the literature. As a result of incomplete purging of air from the sorbent tube during thermal conditioning, large quantities of Tenax decomposition products were observed with increasing storage duration. The CC tubes were observed to produce lesser amounts of these sampling artifacts, and in fact, those that were observed might have originated from the concentrator unit employed, which contained Tenax. However, one batch of CC sampling tubes was received from the manufacturer with unacceptably high residual levels of siloxane contaminants (from treatment of active sites on the glass components). This problem can be remedied by proper conditioning of the sorbent tubes, and is not an inherent problem with the sorbents used.

The multi-sorbent tube methodology permits collection and analysis of some semi-volatile compounds that are known to exhibit low recovery from Tedlar® bags. Significant quantities of volatilized organics having boiling ranges greater than 100 °C are observed during analyses of municipal wastewater off-gas samples when the sorbent tubes are used. In addition to evaluation of the multi-sorbent tubes, a sampling train for simultaneous collection of VOCs and SF_6 was developed. It was determined that SF_6 had essentially no retention in the CC sorbent tubes and could be collected downstream of the tubes with Tedlar® bags. The bags also provided a convenient method for determining total gas volume sampled.

From the sampling of activated carbon beds (ACB) used for odor control at the preliminary treatment processes at the JWPCP, it is believed that competitive adsorption of VOCs and successive compound displacement from the ACB occurred. This led to periods when larger concentrations of a given compound were being emitted from the ACB than were in the influent gases to the ACB. Unsteady loading of the ACB was also observed and believed to result in regeneration of some capacity to adsorb high volatility organics even after breakthrough of lower volatility compounds had occurred. Thus the ACBs were observed to dampen input concentrations, but to have no substantial reduction of emissions of VOCs over extended periods of time (weeks) when operated in their normal odor control mode. Similar behavior of ACBs on a mechanically ventilated sewer system was also observed. It is concluded that if ACBs are to be used as PTOC control devices at MWTPs or collection systems, they will probably need to designed as regenerable systems for economic reasons, and closely monitored, if used at all. Upstream source control of industrial discharges of benzene to the sanitary sewer system appears to be the control strategy of choice for benzene at the JWPCP. The economics and feasibility of alternative means of control should be examined closely, before ACBs are required as T-BACT for MWTPs in general.

Based upon the additional measurements obtained from the JWPCP and the HTP, it appears that biodegradation of several aromatic compounds can compete efficiently with air-stripping from the wastewater, even at levels considered to be too low for organism acclimation. These findings indicate that the Phase I emission estimates for biodegradable compounds such as benzene and toluene have been overstated for plants practicing secondary biological treatment. Further research into <u>desorption kinetics</u> from biomass and emulsions is needed for emissions model development and to refine the inventory estimate. Reliance upon equilibrium partition coefficients does not appear to provide an adequate description of the actual sorption processes for many high volatility or degradable compounds.

A reconciliation of Phase I emissions estimate and pseudo-mass balance methodology with the CSDLAC emissions measurements for the JWPCP was attempted. It was determined that the JWPCP has several unique features that increase the uncertainty of the pseudo-mass balance approach when applied at the JWPCP. The results of the analysis indicate the following:

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

2) For the other MWTPs in the State, the pseudo-mass balance method is believed to be relatively accurate for non-degradable compounds, but <u>conservative</u> for degradable compounds. The reason for this is that most facilities in the State have uncovered primaries or uncovered aeration basins so that increased volatilization losses are expected to occur.

Emission measurements from a mechanically ventilated sewer reach indicate that elevated emissions from collection systems can occur as discussed in Volume 2. Thus even though the total fraction of PTOCs in the liquid that are emitted is small by comparison, the vent gas concentrations can be significant. A rough estimate of the airborne BZ concentration in the vent sewer gases was about 100 ppb (or roughly 300 $\mu g/m^3$). To reach a level of 1 in 100,000 for the estimated lifetime cancer risk ($5.3X10^{-5}$ $\mu g^{-1} m^3$, unit risk factor) a dilution factor of over 1000 would be needed.

A measurement of the emissions from activated sludge aeration basins was undertaken in an attempt to a) determine whether measurable increases in downwind concentrations could be attributed to the aeration basins, and b) determine the magnitude of their source strength. The aeration basins at the City of Los Angeles' Hyperion Treatment Plant (HTP) were selected for study. On the basis of the HPT sampling trips the following conclusions and recommendations have been drawn.

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

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

3) Based upon the few PERC measurements that were made, emissions from the HTP were within a factor of two

(lower) of the Phase I estimated emissions, solely from the secondary aeration basins.

4) For the "typical" afternoon sea breeze conditions encountered during the June sampling trip, the average dilution factor observed on top of the bluff at the eastern end of the aeration basin was about 6 to 7 for periods of about one-half hour. This amount of dilution will reduce measured concentrations from the plant to near background ambient levels during periods when polluted air transported off-shore (e.g. nighttime land-sea breeze) returns onshore.

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

6) Initial plume buoyancy can be a factor in dispersion modeling for health risk estimation purposes, particularly in near field calculations. The ability to account for this phenomenon for large area sources in commonly used Gaussian models such as ISCST or ISCLT does not have a firm basis and further model development may be warranted.

7) Studies of the rate of desorption of semi-volatile compounds from biomass and oils should be undertaken to determine their possible influence on total emissions and air-stripping models.

An effort was made to evaluate the "PEEP" emission factors for grit chambers and diffused air ASABs: processes similar to those tested during this study. That evaluation revealed the presence of an ice bath impinger in the sampling train that possibly reduced the measured gas phase concentrations of compounds sampled. Generally speaking for BZ, PERC, and DCB, the PEEP emission factors appear to produce significantly lower poredicted airborne concentrations than observed at the JWPCP or HTP.

1) The PEEP emission factors appear to underestimate the emissions of semi-VOCs. A study of losses through the ice bath impinger needs to be undertaken if the PEEP air-based emission factors are to be used for semi-VOCs.

2) Use of bag sampling for semi-VOCs that make up a substantial portion of the air emissions of reactive organic compounds from WWTPs needs to be re-examined. Sorbents may be a better choice of sampling media for such cases.

Two preliminary studies of chloroform formation were undertaken as part of the current research contract. The purpose of these measurements was to determine the magnitude of the potential problem. The first was simply a grab sample of sewage and sewer gas, upstream and downstream of a chlorinator on a County of Sacramento Sewer. In the second set of measurements either screened raw wastewater or secondary effluent (nitrified and non-nitrified) buffered to pH 7.6-7.8 were dosed with 5 mg/L or 15 mg/L of chlorine (in the form of hypochlorous acid).

In conjunction with the evidence from the literature the results of these experiments suggest that chlorination of raw sewage produces relatively lesser amounts of haloforms, but that about 1% or less of the total chlorine added is incorporated into organic compounds. The exact amount depends upon competition with inorganic species present, such as reduced sulfur and metals. On the other hand, chlorination of nitrified secondary effluent appeared to produce haloforms at levels about an order-of-magnitude greater than for non-nitrified effluent when chlorine dose does not exceed the "breakpoint. Thus the presence of ammonia in the effluent competes effectively for the "free" chlorine.

A study of air emissions from a chlorine contact chamber at a WWTP that practices nitrification of secondary effluent is suggested by the above findings. Formation of haloforms in two-stage packed bed odor control towers that use chlorine as an oxidant should also be studied. This recommendation is based upon a plausible hypothetical mechanism for enhanced chloroform formation and a literature report regarding increased emissions of chlorinated organics from such odor control units.

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APPENDIX A

This Appendix briefly describes computations used to estimate the modeled emissions reported in Table 29d. The calculations were based upon recent influent data (24 hr composites on 6 days) obtained from the CSDLAC for the period 9/20/89 to 10/25/89. One day's data (9/26/89) were discarded because of obvious problems in the sampling or with the analysis (essentially all compounds were below detection limits).

Estimated emissions were calculated as:

$$E = (L_1 + L_2)*(1-a)*C_{in}*Q_t$$

where

L_1 = fractional loss from bar screens = 0.01 (based on Volume 4 results)

L_2 = fractional losses from aerated grit chambers assuming bubble saturated was achieved and using values of the dimensionless Henry's coefficient reported by Bell et al. (1988).

a = fraction of compound adsorbed on solids at equilibrium assuming Dobbs et al. (1989) correlation for octanol/water partition coefficient (K_{ow}) and solids organic carbon partition (K_p'); also assuming JWPCP solids concentration of 0.44 g/L and a fractional volatile suspended solids of 0.7.

C_{in} = measured influent concentration

Q_t = total plant influent

The actual values of "a" used were as follows: Bz (0.17); ETBZ (0.43); TOL (0.3); DCM (0.03); TCE (0.20); TCA (0.17); TCM (0.04); PERC (0.24). Use of the equilibrium adsorbed fraction "a" assumes that the liquid phase is in equilibrium with the solids upon entering the bar screens and grit chamber, but that transfer to the gas phase of the adsorbed fraction does not occur because of desorption kinetic limitations, effectively reducing the emissions by the adsorbed fraction.

APPENDIX B

This Appendix contains raw data from measurements obtained at the Hyperion Treatment Plant. Tables 38 through 40 provide the raw selected ion integration area counts from liquid, and air samples and the standards that were used to reduce the liquid and air data from the June 22, 1989 sampling of the ASABs. Tables 41 through 44 contain the raw data from the October, 1989 sampling trip. Table 45 reports the ARB measurements of the HTP from June 22, 1989.

Table 38

Analysis of Hyperion Test #1 GC/MS Data for Limited Compounds

Liquid Samples from 6/22/89

Compound	Time [min]	Peak Ion	East Basin Ion Abundance 2	3	4	5	6	Avg.	Avg. (Area/L)	Conc. (μg/L)
DCM	4.3	49	2.55E+06	3.86E+06	5.05E+06	1.27E+06	6.53E+06	3.85E+06	7.71E+08	3.53E+01
TOL	9.5	91	8.40E+06	1.45E+06	8.04E+05	8.30E+05	9.52E+05	2.49E+06	4.98E+08	2.86E+00
DMB	12.1	91	1.46E+07	NA	NA	NA	NA	NA	NA	
BFB	13.0	174	NA	NA	NA	NA	NA	NA	NA	
DEC	13.8	43	1.16E+06	1.35E+06	3.38E+05	6.64E+05	1.56E+06	1.01E+06	2.03E+08	
TMB	14.3	105	3.88E+06	3.17E+06	2.90E+06	2.12E+06	3.02E+06	3.02E+06	6.04E+08	
LIM	14.8	68	8.85E+05	7.85E+05	6.35E+05	5.84E+05	6.79E+05	7.14E+05	1.43E+08	
DCB	14.9	146	6.91E+06	3.23E+06	1.38E+07	1.39E+07	1.01E+07	9.59E+06	1.92E+09	
UND	15.8	43	3.94E+06	5.81E+06	1.61E+06	2.50E+06	2.09E+06	3.19E+06	6.38E+08	
Lq. Purged	[ml]		5	5	5	5	5			

Compound	Time [min]	Peak Ion	West Basin Ion Abundance 2	3	4	5	Avg.	Avg. (Area/L)	Conc. (μg/L)
DCM	4.3	49	4.86E+06	8.29E+06	4.49E+06	7.59E+06	6.31E+06	1.26E+09	5.78E+01
TOL	9.5	91	7.72E+05	8.01E+05	1.12E+06	7.75E+05	8.67E+05	1.73E+08	9.95E-01
DMB	12.1	91	NA	NA	NA	NA	NA	NA	
BFB	13.0	174	NA	NA	NA	NA	NA	NA	
DEC	13.8	43	8.42E+05	1.03E+06	8.62E+05	1.10E+06	9.60E+05	1.92E+08	
TMB	14.3	105	2.83E+06	2.78E+06	3.08E+06	2.53E+06	2.81E+06	5.61E+08	
LIM	14.8	68	6.31E+05	7.94E+05	5.56E+05	7.90E+05	6.93E+05	1.39E+08	
DCB	14.9	146	1.57E+07	1.38E+07	2.83E+06	1.33E+07	1.14E+07	2.29E+09	
UND	15.8	43	2.34E+06	2.18E+06	2.42E+06	2.06E+06	2.25E+06	4.50E+08	
Lq. Purged	[ml]		5	5	5	5	5.00E+00	1.00E+03	

Table 39

Summary of Hyperion Test #1 GC/MS Data for Limited Compounds

Gas Samples from 6/22/89

Compound	Time [min]	Peak Ion [-]	NT 2m [Area/L]	NT 5m [Area/L]	NT 10m [Area/L]	ST 2m [Area/L]	ST 5m [Area/L]	ST 10m [Area/L]	Plant Upwind [Area/L]	Beach Upwind [Area/L]	Comprss'd Air Avg [Area/L]
DCM	4.3	49	6.8E+02	3.5E+03	3.6E+03	1.2E+03	1.7E+03	9.6E+02	1.7E+02	1.1E+02	4.72E+02
TOL	9.5	91	3.8E+02	1.8E+03	2.3E+04	1.0E+03	1.6E+03	2.7E+03	1.0E+03	4.3E+02	2.71E+03
XYL	12.1	91	1.9E+02	4.5E+02	1.9E+04	3.5E+03	4.3E+03	9.5E+03	2.2E+02	7.3E+01	4.10E+03
BFB	13	174	5.1E+02	1.3E+03	3.1E+03	1.6E+03	2.2E+03	2.8E+03	9.0E+02	6.2E+02	2.46E+03
DEC	13.8	43	7.8E+02	1.8E+03	3.5E+03	2.3E+03	2.4E+03	2.3E+03	3.6E+02	3.2E+02	9.84E+02
TMB	14.3	105	1.3E+03	4.6E+03	5.9E+03	3.0E+03	4.5E+03	5.0E+03	2.9E+03	1.0E+03	1.64E+03
LIM	14.8	68	1.5E+03	4.6E+03	3.8E+03	3.9E+03	4.6E+03	2.2E+03	BDL	BDL	1.42E+02
DCB	14.9	146	2.1E+03	6.0E+03	4.2E+03	5.5E+03	5.3E+03	2.8E+03	1.3E+02	8.2E+01	9.20E+01
UND	15.8	43	3.4E+03	9.9E+03	8.1E+03	8.9E+03	8.3E+03	5.0E+03	1.2E+03	1.1E+03	3.18E+03

Table 40

100 ppb Gas Standard

Used for Analysis of 6/22/90 Air Samples

Compound	Std 1 [Area]	Std 2 [Area]	Normalized Avg [Area/ppb/L/BFB]
DCM	3.54E+07	1.50E+07	3.31E-01
d-TOL	3.60E+06	3.11E+06	4.71E-02
XYL	1.36E+08	8.97E+07	1.54E+00
BFB	4.34E+06	2.95E+06	NA

Note: The deuterated toluene response was assumed to be the same as that for toluene.

100 ppb Gas Standard

Used for Analysis of 6/22/90 Liquid Samples

Compound	Std 1 [Area]	Std 2 [Area]	Std 1 [Area/µg]	Std 2 [Area/µg]	Average [Area/µg]
DCM	6.35E+05	4.38E+05	2.37E+07	2.00E+07	2.18E+07
TOL	3.80E+06	4.53E+06	1.41E+08	2.07E+08	1.74E+08
XYL	3.69E+06	3.17E+06	1.38E+08	1.45E+08	1.41E+08
Vol. [ml]	76	62			

Table 41

Selected Ion Counts of Peak Ions for Standard Gas

Normalized ion count = raw ion count/volume gas standard delivered/concentration

(Hyperion II Sampling Trip: 10/16/89-10/17/89)

Compound	Concentration		Rich1	Rich2	Rich3	Field1	Field2	Field3	Field4	For Lq1	For Lq2	For Lq3	For Lq4
	Lab	Field	(Air13B)	(Air14B)	(Air15B)	(Air13)	(Air14)	(Air17)	(Air18)	(Std.31)	(Std.28)	(Std.13)	(Std.21)
	[ppb	[ppb]			**	(10/16/89)		(10/17/89)		(10/19/89)		(10/20/89)	
TCM	5	103	6.25E+06	6.60E+06	6.68E+06	3.38E+06	5.08E+06	4.97E+06	5.00E+06	2.57E+06	2.99E+06	4.38E+06	3.78E+06
CT	1	102	2.44E+06	2.85E+06	2.93E+06	1.25E+06	2.12E+06	2.18E+06	2.18E+06	1.30E+06	8.59E+05	1.80E+06	8.45E+05
BZ	25	112	6.84E+06	7.60E+06	3.59E+06	4.34E+06	6.30E+06	6.62E+06	6.68E+06	4.39E+06	4.72E+06	6.82E+06	5.53E+06
PERC	1	99	6.20E+06	5.90E+06	6.07E+06	3.07E+06	4.17E+06	2.85E+06	2.93E+06	1.33E+06	1.35E+06	2.95E+06	2.26E+06

** Detector saturated for benzene

	AVG	STDEV	CV	AVG	STDEV	CV	AVG	STDEV	CV
TCM	6.51E+06	1.84E+05	2.8%	4.61E+06	7.08E+05	15.4%	3.43E+06	7.00E+05	20.4%
CT	2.74E+06	2.16E+05	7.9%	1.93E+06	3.94E+05	20.4%	1.20E+06	3.92E+05	32.7%
BZ	6.01E+06	1.74E+06	28.9%	5.98E+06	9.62E+05	16.1%	5.36E+06	9.36E+05	17.4%
PERC	6.06E+06	1.23E+05	2.0%	3.26E+06	5.34E+05	16.4%	1.97E+06	6.78E+05	34.4%

Table 42a
Selected Ion Integration of Peak Ion for Liquid Samples
(Hyperion II Sampling Trip: 10/16/89)

Compound	Peak Ion	Retention Time	East Basin			West Basin				Avg
			2	3	4	1	2	3	4	
			(Water8B)	(Water9)	(Water17)	(Water12)	(Water14)	(Water15)	(Water5)	
1,1-DCE	61	3.6	1.44E+06	1.31E+06	BDL	1.60E+06	BDL	BDL	BDL	1.45E+06
DCM	49	4.4	6.21E+06	1.66E+07	1.32E+06	1.53E+06	1.33E+06	8.50E+07	1.68E+06	1.62E+07
1,1,1-TCA	97	6.7	2.10E+06	1.40E+06	BDL	BDL	BDL	BDL	2.21E+06	1.90E+06
BZ	78	7.2	2.70E+06	3.72E+06	4.21E+06	7.86E+06	6.64E+06	6.86E+06	1.04E+07	6.05E+06
1,2-DCA	62	7.2	8.41E+06	3.24E+07	1.05E+07	2.14E+07	1.24E+07	1.38E+08	5.00E+07	3.90E+07
TCE	130	8.1	1.60E+06	3.69E+06	8.93E+05	5.03E+05	2.08E+06	1.91E+07	6.59E+06	4.92E+06
TOL	91	9.9	6.15E+06	9.74E+06	3.24E+06	1.64E+07	6.80E+06	4.55E+07	3.55E+07	1.76E+07
PERC	166	10.7	1.26E+06	1.02E+06	BDL	1.73E+06	1.63E+06	9.40E+05	2.56E+06	1.52E+06
ETBZ	91	12.0	6.03E+06	4.67E+06	BDL	2.25E+06	2.88E+06	9.47E+05	2.52E+06	3.22E+06
XYL	91	12.2	1.84E+07	1.39E+07	9.68E+06	8.37E+06	9.84E+06	2.40E+07	8.91E+06	1.33E+07
XYL	91	12.8	6.29E+06	4.23E+06	3.61E+06	2.58E+06	2.15E+06	3.72E+06	2.11E+06	3.53E+06
TMB	105	14.7	7.06E+06	6.36E+06	6.24E+06	2.00E+06	3.41E+06	5.91E+06	3.30E+06	4.90E+06
LIM	68	15.2	7.45E+05	9.35E+05	2.77E+06	6.60E+05	5.97E+05	7.28E+05	8.30E+05	1.04E+06
DCB	146	15.3	1.53E+07	6.15E+06	3.25E+06	1.81E+06	3.02E+06	2.36E+06	2.28E+06	4.88E+06
UND	43	16.1	1.82E+06	1.79E+06	2.20E+06	1.32E+06	1.88E+06	2.16E+06	1.59E+06	1.82E+06
Sample - [ml]			5.0	4.8	5.0	5.0	5.0	5.0	5.0	5.0

Table 42b
(Hyperion II Sampling Trip: 10/17/89)

Compound Name	Peak Ion	Retention Time	East Basin		West Basin			Avg
			1	2	1	2		
			(Water4)	(Water32)	(Water7)	(Water20)		
1,1-DCE	61	3.6	BDL	3.55E+05	BDL	4.79E+05		4.17E+05
DCM	49	4.4	5.95E+06	3.88E+06	2.14E+06	2.23E+06		3.55E+06
TCM	83	6.5	9.46E+05	1.09E+06	1.02E+06	BDL		1.02E+06
1,1,1-TCA	97	6.7	6.25E+05	1.62E+06	8.64E+05	7.58E+05		9.67E+05
BZ	78	7.2	1.62E+07	4.72E+07	6.52E+06	1.63E+07		2.16E+07
1,2-DCA	62	7.2	1.75E+07	5.78E+06	9.37E+06	8.59E+06		1.03E+07
TCE	130	8.1	2.83E+06	7.90E+05	1.52E+06	1.73E+06		1.72E+06
TOL	91	9.9	1.80E+07	8.98E+06	1.34E+07	1.57E+07		1.40E+07
PERC	166	10.7	3.54E+05	3.80E+05	2.89E+05	5.27E+05		3.88E+05
ETBZ	91	12.0	1.69E+06	1.07E+06	1.14E+06	1.60E+06		1.37E+06
XYL	91	12.2	8.02E+06	4.18E+06	5.68E+06	5.84E+06		5.93E+06
XYL	91	12.8	2.40E+06	1.47E+06	1.72E+06	1.54E+06		1.78E+06
TMB	105	14.7	1.89E+06	2.02E+06	2.01E+06	3.08E+06		2.25E+06
LIM	68	15.2	3.70E+05	4.43E+05	5.28E+05	5.53E+05		4.74E+05
DCB	146	15.3	8.70E+05	1.33E+06	1.15E+06	1.80E+06		1.29E+06
UND	43	16.1	9.21E+05	7.38E+05	7.63E+05	8.74E+05		8.24E+05
Sample - [ml]			2.0	2.0	2.0	2.0		2.0

Table 43a
Selected Ion Integration of Peak Ion for Gas Samples
(Hyperion II Sampling Trip: 10/16/89)

Compound Name	Peak	Retention	Beach	Plant	Inside	Sampling	Mast	Outside	Sampling	Mast	Compressed
	Ion	Time	Upwind	Upwind	2m	5m	10m	2m	5m	10m	Air
			(Air3)	(Air12B)	(Air9)	(Air7)	(Air5)	(Air11B)	(Air8B)	(Air6B)	(Air2)
1,1-DCE	61	3.6	7.97E+05	Detected	5.65E+06	1.99E+06	1.03E+06	6.00E+06	3.83E+06	3.27E+06	4.89E+06
DCM*	49	4.4	4.50E+07	1.31E+06	1.76E+06	7.89E+05	3.46E+05	1.86E+08	2.14E+06	5.86E+06	2.84E+07
1,1,1-TCA	97	6.7	7.75E+05	2.01E+06	6.28E+06	3.12E+06	9.25E+05	3.90E+07	3.95E+06	2.08E+06	1.29E+06
BZ	78	7.2	2.95E+06	3.33E+07	3.13E+06	2.19E+06	2.40E+06	2.84E+07	2.71E+07	7.55E+06	1.63E+07
1,2-DCA*	62	7.2	1.48E+07	3.07E+07	2.24E+06	1.42E+06	4.23E+05	1.37E+08	9.33E+06	3.09E+07	5.83E+07
TCE	130	8.1	2.01E+06	6.99E+07	5.34E+05	6.24E+05	3.44E+05	6.39E+07	1.22E+07	2.32E+07	1.23E+07
TOL	91	9.9	6.48E+06	9.28E+07	3.84E+06	3.51E+06	1.90E+06	2.02E+08	1.77E+08	2.68E+07	4.26E+07
PERC	166	10.7	N/A	1.21E+06	2.37E+06	1.30E+06	6.77E+05	9.20E+07	3.98E+07	2.68E+07	1.31E+06
ETBZ	91	12.0	4.56E+05	5.98E+06	1.05E+06	5.34E+05	N/A	1.95E+07	1.48E+07	1.24E+07	2.68E+06
m,p-XYL	91	12.2	2.46E+05	2.19E+07	4.28E+05	3.23E+05	6.53E+06	4.93E+07	3.61E+07	2.90E+07	1.43E+07
o-XYL	91	12.8	N/A	8.28E+06	1.52E+06	2.59E+05	3.15E+06	1.59E+07	1.04E+07	1.04E+07	6.56E+06
TMB	105	14.7	3.41E+06	1.54E+07	2.77E+06	5.21E+06	4.74E+06	1.96E+07	1.34E+07	2.23E+07	8.98E+06
LIM	68	15.2	N/A	4.26E+05	1.11E+07	4.03E+06	1.94E+06	1.58E+07	1.10E+07	4.35E+06	9.29E+05
DCB	146	15.3	5.97E+05	6.11E+05	7.16E+06	3.62E+06	2.18E+06	1.22E+07	5.79E+06	4.96E+06	1.18E+06
UND	43	16.1	N/A	N/A	3.26E+06	1.73E+06	2.15E+06	9.16E+06	4.16E+06	4.41E+06	1.94E+07
Gas vol - [ml]			3600	3600	1915	975	3045	5040	1575	2090	

Table 43b
(Hyperion II Sampling Trip: 10/17/89)

Compound Name	Peak	Retention	Plant	Inside	Sampling	Mast	Outside	Sampling	Mast	Compressed	Air
	Ion	Time	Upwind	2m	5m	10m	2m	5m	10m		
			(Air19B)	(Air28B)	(Air25B)	(Air22B)	(Air29B)	(Air23B)	(Air27B)	(Air20)	(Air21)
1,1-DCE	61	3.6	5.33E+06	2.08E+07	4.33E+06	8.30E+06	1.68E+07	3.94E+06	1.02E+07	7.40E+06	6.07E+06
DCM	49	4.4	1.51E+06	8.89E+06	7.27E+06	6.70E+06	6.22E+06	4.02E+06	6.17E+06	2.05E+06	1.05E+06
TCM	83	6.5	BDL	4.52E+06	3.39E+06	1.88E+06	2.22E+06	1.79E+06	1.72E+06	N/A	2.24E+06
1,1,1-TCA	97	6.7	3.79E+06	1.98E+07	2.73E+07	1.11E+07	9.51E+06	2.14E+07	6.40E+06	6.18E+06	5.60E+06
BZ	78	7.2	1.17E+07	1.12E+07	3.11E+07	1.02E+07	1.04E+07	3.88E+07	1.01E+07	1.31E+07	9.10E+06
1,2-DCA	62	7.2	9.29E+06	7.81E+06	3.61E+07	1.63E+07	4.07E+07	2.17E+07	3.20E+07	5.10E+06	7.38E+07
TCE	130	8.1	1.52E+06	1.84E+06	1.49E+07	3.14E+06	5.32E+07	9.35E+06	6.87E+06	1.23E+06	1.56E+07
TOL	91	9.9	1.43E+07	1.58E+07	1.01E+08	1.52E+07	2.24E+08	8.05E+07	1.66E+08	1.02E+07	2.05E+07
PERC	166	10.7	1.25E+06	1.88E+06	7.52E+06	1.09E+06	2.04E+07	6.18E+06	1.49E+07	1.02E+06	8.10E+05
ETBZ	91	12.0	2.42E+07	1.95E+07	1.05E+07	2.26E+06	1.81E+07	9.36E+06	1.68E+07	7.34E+05	8.69E+05
m,p-XYL	91	12.2	6.88E+07	5.49E+07	2.90E+07	1.12E+07	4.59E+07	2.67E+07	4.62E+07	3.67E+06	3.36E+06
o-XYL	91	12.8	2.62E+07	2.42E+07	9.85E+06	4.45E+06	1.48E+07	9.67E+06	1.58E+07	1.10E+06	1.32E+06
TMB	105	14.7	2.50E+07	2.58E+07	9.68E+06	2.53E+07	1.33E+07	8.84E+06	1.44E+07	3.41E+06	2.36E+06
LIM	68	15.2	N/A	1.46E+07	3.54E+06	4.22E+06	8.65E+06	2.80E+06	6.96E+06	2.06E+05	N/A
DCB	146	15.3	3.04E+06	2.56E+07	4.95E+06	1.03E+07	1.28E+07	3.55E+06	8.81E+06	3.29E+05	3.00E+05
UND	43	16.1	2.67E+06	1.26E+07	4.09E+06	1.41E+07	7.77E+06	2.70E+06	6.76E+06	3.53E+06	2.88E+06
Gas vol - [L]			3.6				1.61	1.06	1.13	1.00	1.00

Note: Retention time is from outside 2m.
B in filenames means sample saver.
Tubes 23B and 27B were reversed in the field but have been corrected based on SF6.
*Suspected laboratory contamination

**** Sample Split Ratio ****
Trap 1 : 15/65 (0.23)
Sample Saver: 50/65 (0.77)

Table 43c

(Hyperion II Sampling Trip: 10/17/89)

Corrected area count per liter assuming "B" and split volumes

Compound	Plant	Cmprs'd	Inside	Sampling	Mast	Outside	Sampling	Mast
	Upwind	air	2m	5m	10m	2m	5m	10m
	(Air19B)	(Avg)	(Air28B)	(Air25B)	(Air22B)	(Air29B)	(Air23B)	(Air27B)
1,1-DCE	1.92E+06	6.74E+06	1.68E+07	3.49E+06	6.69E+06	1.36E+07	3.18E+06	8.23E+06
DCM	5.44E+05	1.55E+06	7.17E+06	5.86E+06	5.40E+06	5.02E+06	3.24E+06	4.98E+06
TCM	BDL	1.12E+06	3.64E+06	2.74E+06	1.51E+06	1.79E+06	1.44E+06	1.39E+06
1,1,1-TCA	1.37E+06	5.89E+06	1.59E+07	2.20E+07	8.98E+06	7.67E+06	1.73E+07	5.16E+06
BZ	4.23E+06	1.11E+07	9.01E+06	2.51E+07	8.25E+06	8.41E+06	3.13E+07	8.14E+06
1,2-DCA	3.35E+06	3.94E+07	6.30E+06	2.91E+07	1.32E+07	3.28E+07	1.75E+07	2.58E+07
TCE	5.47E+05	8.41E+06	1.48E+06	1.20E+07	2.53E+06	4.29E+07	7.54E+06	5.54E+06
TOL	5.17E+06	1.53E+07	1.27E+07	8.14E+07	1.23E+07	1.81E+08	6.49E+07	1.34E+08
PERC	4.51E+05	9.16E+05	1.52E+06	6.06E+06	8.80E+05	1.65E+07	4.99E+06	1.20E+07
ETBZ	8.74E+06	8.02E+05	1.58E+07	8.50E+06	1.82E+06	1.46E+07	7.55E+06	1.36E+07
m,p-XYL	2.48E+07	3.52E+06	4.43E+07	2.34E+07	9.03E+06	3.70E+07	2.15E+07	3.72E+07
o-XYL	9.45E+06	1.21E+06	1.96E+07	7.94E+06	3.59E+06	1.19E+07	7.80E+06	1.27E+07
TMB	9.03E+06	2.88E+06	2.08E+07	7.81E+06	2.04E+07	1.07E+07	7.13E+06	1.16E+07
LIM	BDL	1.03E+05	1.18E+07	2.85E+06	3.41E+06	6.98E+06	2.26E+06	5.61E+06
DCB	1.10E+06	3.15E+05	2.06E+07	3.99E+06	8.29E+06	1.03E+07	2.87E+06	7.10E+06
UND	9.63E+05	3.21E+06	1.02E+07	3.30E+06	1.13E+07	6.26E+06	2.18E+06	5.45E+06

Compound	Standard Gas 17th		Plant	Cmprs'd	2m	5m	10m
	Field3	Field4	Upwind	air	(Avg)	(Avg)	(Avg)
			(Air19B)	(Avg)			
	[#/L/ppb]	[#/L/ppb]	[ppb]	[ppb]	[ppb]	[ppb]	[ppb]
TCM	4.97E+06	5.00E+06	BDL	2.25E-01	4.85E-01	3.75E-01	3.08E-01
BZ	6.62E+06	6.68E+06	6.37E-01	1.67E+00	1.91E+00	2.75E+00	2.11E+00
PERC	2.85E+06	2.93E+06	1.56E-01	3.17E-01	2.16E+00	2.46E+00	2.97E+00

Table 44
Hyperion II Sampling Trip: Standard Gas Analysis Use for Liquid Samples

Compound Name	Standard Gas Area/[μg]	Avg Conc 10/17/90 [μg/L]
TCM	3.86E+08	1.3E+00
BZ	3.51E+08	6.1E+01
PERC	3.57E+08	1.1E+00

Summary of ARB Measurements at the HTP (6/22/89)

The Monitoring and Laboratory Division's (MLD) Mobile Laboratory was supporting monitoring for chloroethene (VC) because the UCD analytical procedures did not determine that PTOC. A Photovac 10S70 portable GC/PID was deployed at various locations throughout the aeration basins area. All measurements were reported to be below the limits of quantitation which was 5 ppb.

A portable Hewlett Packard GC/MSD was also being field tested and was sampling from the north edge of the aeration basins, approximately centered on the distribution channels. The following observed values were reported by the MLD.

Table 45
ARB Reported Concentrations by GC/MS (6/22/89)
[ppb]

Compound	Am17	Am18	Am19	Am22	Am23
DCM	n.d.	n.d.	n.d.	.93	1.6
TCM	n.d.	n.d.	0.4	0.47	0.59
TCA	0.80	0.62	2.0	4.3	4.3
PERC	0.39	0.69	0.74	0.61	1.9
BZ	n.d.	n.d.	det.	0.27	0.48
TOL	1.2	1.4	2.3	3.1	1.6
ETBZ	0.52	0.23	0.72	0.46	n.d.
XYL	0.58	1.8	2.1	0.27	0.48

There was considerable variability of concentrations with sample location and time, but the general range observed was similar to that of the UCD sorbent tube analyses.