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VOLATILE ORGANIC COMPOUNDS IN THE AMBIENT AIR NEAR A LARGE, REGIONAL SEWAGE PLANT IN NEW JERSEY

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Abstract - Industrial and commercial discharges to sewage treatment plants (STP) in many areas of the country are substantial. A significant quantity of the wastes disposed of at STP contain volatile organic compounds (VOC) and because of the nature of STP, significant losses of VOC to the air environment are expected. The present study provides information related to the air quality impacts from a large, regional STP in New Jersey. Of the twenty three target compounds measured, only eleven were recorded on a regular basis. The levels of selected VOC found at the STP were greatly elevated compared to similar measures at urban/industrial and hazardous waste sites in NJ. For some substances such as toluene, methylene chloride, chloroform and 1,1,1-trichloroethane the levels found at the STP were two orders of magnitude higher than typical ambient air levels at urban/industrial sites in the state.

Introduction - Many volatile organic compounds (VOC) are associated with industrial and commercial processes (Wise and Fahrenthold 1981) and through the use of VOC in these various applications, releases occur to the air environment. As a result of such losses to the atmosphere, measurable quantities of certain VOC have been found in the air in many urban locations (Harkov et al 1984, Nelson and Quigley 1982, Singh et al 1982, Lillian et al 1975, Grosjean and Fung 1984). These workers have generally found that most individual VOC at background urban sites occur at levels less than about 10 ppb_v on a 24 hr basis. Additional studies have been concerned with certain sources of VOC to the air environment, such as abandoned hazardous waste sites and industrial locales (Harkov et al 1985, Pellizzarri 1982, Sexton and Westburg 1980). The levels of VOC found at these sites were generally greater than or equal to those found at background urban locales.

For many areas of the country, direct discharge of industrial effluents into nearby waterbodies has been discouraged as a result of the Federal Water Pollution Control Act of 1972 (USEPA 1979). The response by many industrial/commercial concerns to these regulations has been the direction of these waste streams to sewage treatment plants (STP) as a common means of treatment. In New Jersey, it has been estimated that 75% of the industrial effluent produced in the state is directed towards STP (P.C. - Ken Goldstein, NJDEP-NJPDES Program). Since many industrial processes involve the use of VOC, it would not be surprising to find that large quantities of these pollutants are disposed of through effluent discharges to STP. Most STP have processes which increase the turbulence and temperature of the effluent and expose the waste stream to the open atmosphere. Thus the losses of VOC to the atmosphere at STP may be quite large. The present study is an attempt to characterize the impact of STP VOC emissions on the air quality in the vicinity of such a facility. Recently, US-EPA (Haemisegger et al 1985) has indicated that STP may be a significant source of VOC exposures in certain urban areas, however they found that adequate air quality data related to this source category is lacking. Data from the present study can be used to indicate the level of VOC in the atmosphere associated with STP, with comparable impacts occuring for individuals exposed in the vicinity of these facilities.

Methods

Site Description - The current study was conducted at the Middlesex County Utilities Authority (MCUA) located in Sayreville, NJ. This facility is designed to handle 120 mgd of influent, of which 27% is estimated to be industrial (P.C. Ken Goldstein, NJDEP-NJPDES Program). The MCUA plant design includes secondary wastewater treatment with aerobic sludge digestors and secondary settling followed by chlorination (Figure-1). During the present study influent flow to the facility was in the range of 90-124 mgd. Because the MCUA is not located directly adjacent to an industrial facility but in an area with a large number of such sites, background locations were important to delimit off-site influences on VOC levels in the vicinity of the plant.

Sampling - During the course of the present study samples were collected using four Nutech-221-1MC air pumps equipped with 1.1gm Tenax-GC (35/60 mesh) loaded glass cartridges. The pumps were run at a flow rate of approximately 60 ml/min and samples were generally collected over a 6 hr interval. Total sample volumes were designed to minimize compound break-through for lightweight halogenated species such as methylene chloride. (Brown and Purnell 1979). Because only four samplers were available during the course of this study, the sampling scheme was as follows; a sampler was kept near the grit/screen chamber (GSC, influent-site#1) for each sampling period, with the other three samplers being moved to eleven other sampling locations (sites #2-#11) plus background locales (#15). Previous work by Haggert and Harkov (1984) at a limited number of STP in NJ indicated that the GSC area often had the highest levels of VOC at a facility. Thus it was felt that maintaining a sampler near this site throughout the study would be useful to indicate any changes in VOC input into the STP. During the course of this project a meteorological station (Climatronics EWS) was established to measure wind speed, wind direction and temperature. The collection of samples occured during the latter part of January through February 1985.

Analysis - All analyzes occured in a mobile laboratory (MMU) equipped with a Hewlett Packard 5995 GC/MS. The MMU has been previously described by Haggert and Harkov (1984). Prior to thermal desorption three internal standards were added to the cartridges (bromodichloromethane, 2-chloro,2-bromopropane and 1,4-dichlobutane). The Tenax-GC cartridges were then thermally desorbed at 225°C with a 25 ml/min He flow into a cryofocusing trap maintained at -148°C. The sample was heated, then injected onto a 60/80 mesh carbopack-B, 1% SP-1000 glass column (2.4 M x 1/8" ID). Oven temperatures began at 40°C and were raised to 224°C at 14°C/min. The mass spectrometer scanned 35-320 amu. All cartridges were analyzed within 48 hours of sampling.

Quality Assurance/Quality Control (qa/qc) - During the course of this study a number of qa/qc steps were carried out. These procedures included the use of internal standards, calibration curves, field blanks, laboratory blanks, and tandem and duplicate cartridges. Prior to sampling thermal flexing of the Tenax-GC resin was accomplished for all cartridges utilizing a triplicate 2 hour heating/cooling cycle followed by thermal desorption

(Nutech 340-14). Precision estimates based on analysis of 14 compounds on 5 duplicate cartridges were approximately ±23% at the 95% confidence interval. The minimum detection limits (MDL) were set at approximately three times the signal to noise ratio, while the minimum quantitation limit (MQL) were set at 2.5 times the MDL. The MDL's varied from 0.02 ppbv (25°C, 760mm) for toluene and ethylbenzene to 0.15 ppbv for methylene chloride.

Results - The monitoring data is summarized in Table-1, while site specific information is provided for eleven selected compounds in Table-2. Of the twenty three substances studied, quantitative results were only consistently found for eleven compounds, with four substances occassionally being found. The remaining compounds were not detected in any of the samples. While the absolute concentrations of the selected VOC varied from site-to-site (Table-2), and day-to-day (Figure-2), the levels were significantly above the background locations. In addition, the values recorded were significantly higher than those recorded for urban/industrial and hazardous waste sites in NJ (Harkov et al 1984, Harkov et al 1985).

Patterns of pollutant dynamics at MCUA are best illustrated by Figure-2. Variations in pollutant levels were poorly correlated ($p>0.05$) with ambient conditions (temperature, wind speed, direction, precipitation) or influent parameters (flow rate, BOD, suspended solids). Shifts in the concentration of various pollutants often showed a predictable pattern. For example, tetrachloroethylene, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane were highly correlated ($r=0.99$, $p<0.01$) during the study when data from all the sites other than the GSC were combined. However, benzene was highly correlated with many substances (methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, toluene) at the GSC but not at the remaining sites at the facility (Table-3). The correlation between pollutants at the facility is a function of coincidental source contributions to the STP and the fate of the pollutants within the system.

Discussion - Adequate studies of air quality impacts from a complex source such as a STP are very difficult to obtain. For example, in the present STP effort some twelve locations were monitored throughout a one month period. Although, it would have been preferable to have placed samplers at all twelve locations throughout the monitoring period, equipment and financial resources precluded such a level of effort. Thus we have obtained a somewhat abbreviated picture of the air quality impacts from MCUA. In spite of the short comings of this study, to the best of our knowledge, it represents the only data set of STP contributions to VOC levels in ambient air.

As an alternative to an air quality study of MCUA, an emissions study was considered. However, it was our opinion that the technical limitations of characterizing emissions rates at such a diverse source would be so enormous as to make any emissions estimates of questionable quality. To adequately determine emission rates at a STP a combination of vent sampling and surficial techniques such as the use of flux boxes (Aneja et al 1981) or micrometeorological towers (Thibodeaux et al. 1981, Balfour and Schmidt 1984, Seely et al 1983) would be needed. Because of the general, non-steady state conditions at MCUA vents and open surfaces, emission estimates would be very difficult to quantify. Finally, an emission study would require a large increase in the number of samples collected and analyzed compared to an air quality study thus making the cost for such a effort extremely prohibitive.

The VOC detected in the present study are high use industrial and commercial solvents (Wise and Fahrenthold 1981, SAI 1981). Generally the flux of many pollutants through MCUA occurs as pulses, perhaps due to the use of batch processes by the majority of the industrial contributors to the influent. For example, daily fluxes of Cd in the effluent passing through MCUA during the present study varied by more than eight-fold (MCUA-NJPDES Data, 2/85). Ambient air levels of methylene chloride, chloroform, benzene and toluene near the GSC varied by nearly 181,22,250 and 6 fold respectively, thus illustrating the extreme variability in the fluxes of solvents into the STP (Figure 2). Toluene appears to be the most important solvent entering the facility in terms of the persistently high concentrations found near the GSC. As an example, on 2/7/85 when most of the VOC at the GSC were at levels similar to the background site, the toluene values were sixty times the background levels. Of all the chlorinated VOC, methylene chloride was consistently found at the highest levels at MCUA, probably a reflection of the large number of industrial/commercial applications for this solvent (Verschueren 1983).

An additional observation was that for certain chlorinated VOC such as methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene persistently high ambient levels were found at sites away from the influent. Conversely, generally the highest ambient levels of aromatic VOC such as benzene, toluene and ethylbenzene were found near the GSC. This information suggests that the solubility of VOC in the STP influent is an important factor determining the persistence of compounds in the MCUA waste stream. The more soluble chlorinated VOC would be present at higher levels at various points in the STP than at the GSC if significant quantities of these materials were not released as the influent enters the turbulent and open GSC. Carefull review of the correlation matrix reveals a dramatic shift in the relationship of those substances found at the GSC compared with the remainder of the monitoring sites (Table 3). Such information provides additional support for the importance of aqueous solubility in determining the release of VOC from the MCUA facility into the ambient air.

From this preliminary study it appears that STP can be a very significant source of VOC to the air environment. The results from the present study indicate that the contribution of STP VOC emissions to the air environment is significant even though the ambient temperature throughout the bulk of the current project varied from -7°C to +10°C. It may be expected that higher VOC levels would be associated with the warmer portions of the year. Concentrations of substances such as methylene chloride, toluene, and 1,1,1-trichoroethane were often found between one or two orders of magnitude higher than levels reported for urban/industrial and hazardous waste sites in NJ (Harkov et al 1984, Harkov et al 1985). Although the present study includes primarily 6 hr samples as compared to the 24 hr samples collected in previous VOC studies in NJ, these shorter sampling intervals results appear reflective of 24hr values found at MCUA. Two pairs of sequential 12-hr samples collected at the GSC on a 2/4/85 and 2/7/85 (Table-4) indicated that elevated VOC levels occured at this site on a 24 hr basis.

The sources of VOC to air associated with a STP are quite diverse. Thus besides open surfaces and vents other portions of the facility can be a significant source of VOC. For example, a short (2 min) grab sample at a small crack on the side of the aerobic digestor revealed levels of chloroform and carbon tetrachloride of 1.3 ppm_v and 2.4 ppm_v respectively (Table-2). At one of the pumping stations along the influent pipes to the facility the indoor concentrations of methylene chloride, chloroform, carbon tetrachloride and toluene were each greater than 300 ppb_v (Table 2).

Considering the elevated VOC levels measured in the vicinity of MCUA and that approximately 75% of the industrial effluents in the state is directed to STP, it appears that serious attention needs to be directed to reduce the losses of these pollutants to the air environment from these facilities. The VOC emission rates for STP are probably significantly greater than other uncontrolled VOC sources in NJ such as municipal solid waste landfills. The reduction of VOC emissions at STP would reduce the emission of some photochemically active hydrocarbons such a ethylbenzene, thus contributing to ozone control, and also lessen the ambient levels of toxic air pollutants in those communities associated with these facilities. Although an industrial pretreatment program is currently underway in NJ, it appears that air pollution controls at STP may be necessary to adequately reduce the emission rates of VOC from these plants.

Conclusions - The impact of VOC emissions from STP on local air quality appears to significant. Levels of selected VOC recorded at the MCUA facility in NJ were elevated when compared to urban/industrial and hazardous waste sites in the state. The current study indicates that carefull consideration should be given to the implementation of an air pollution control program at STP in NJ.

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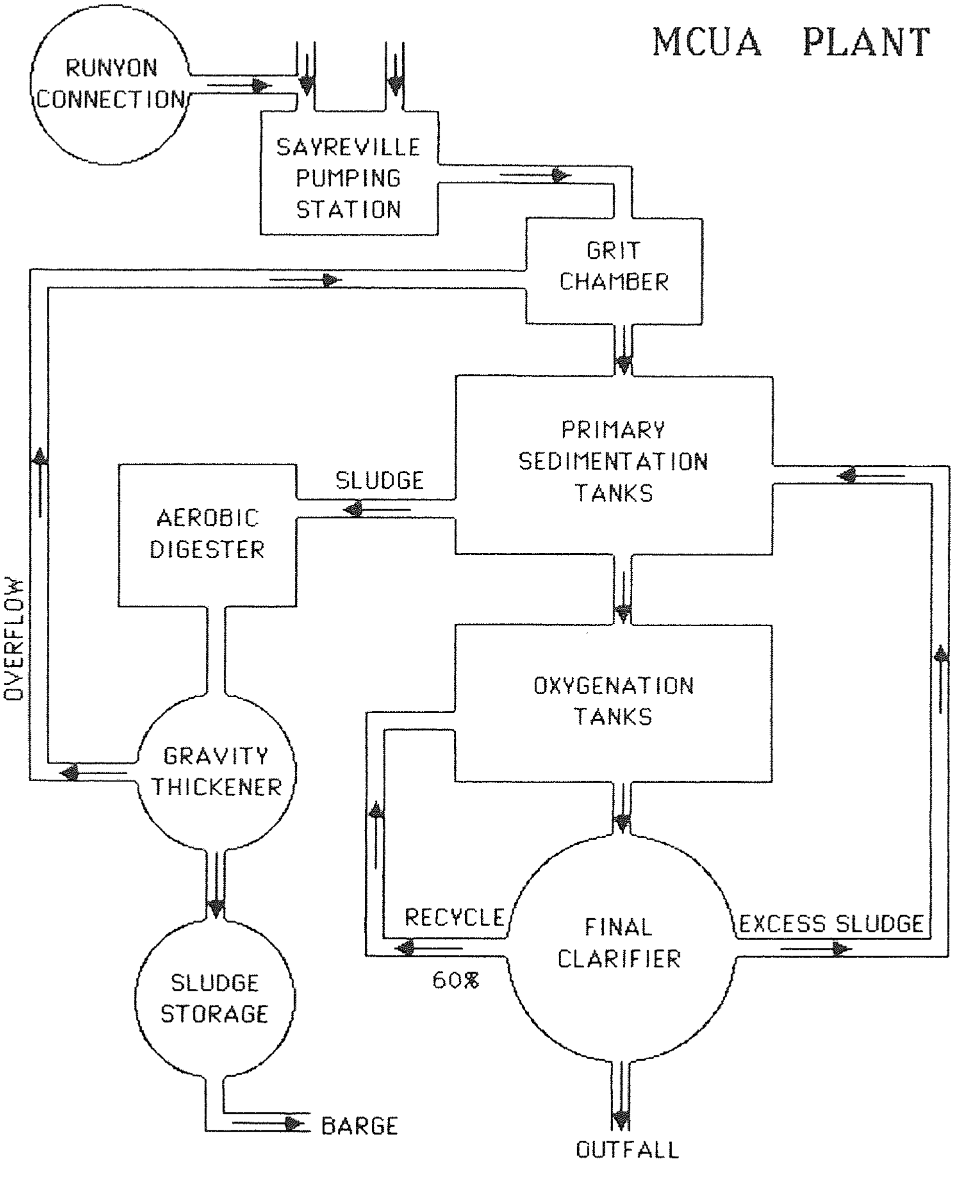


Figure 1 Schematic of the Middlesex County Utilities Authority and on site sample locations.

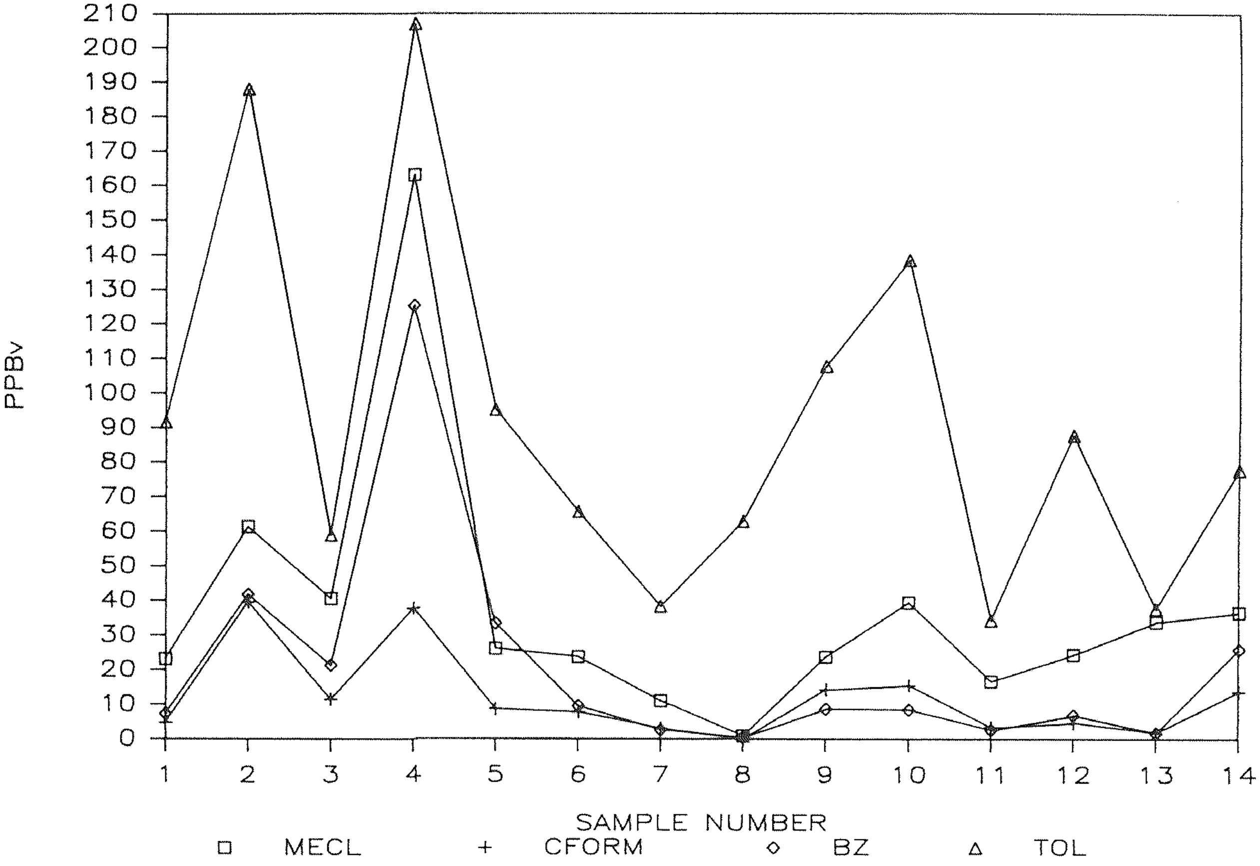
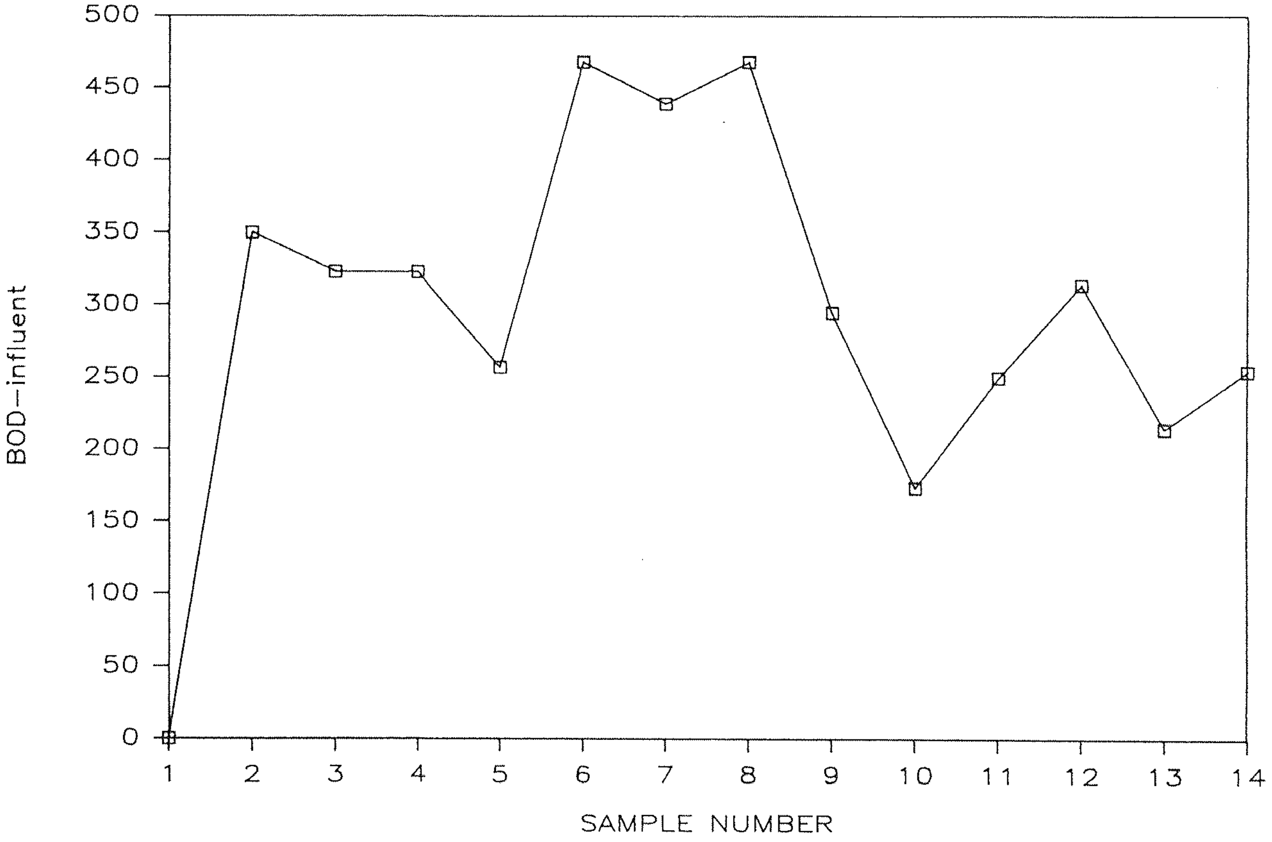
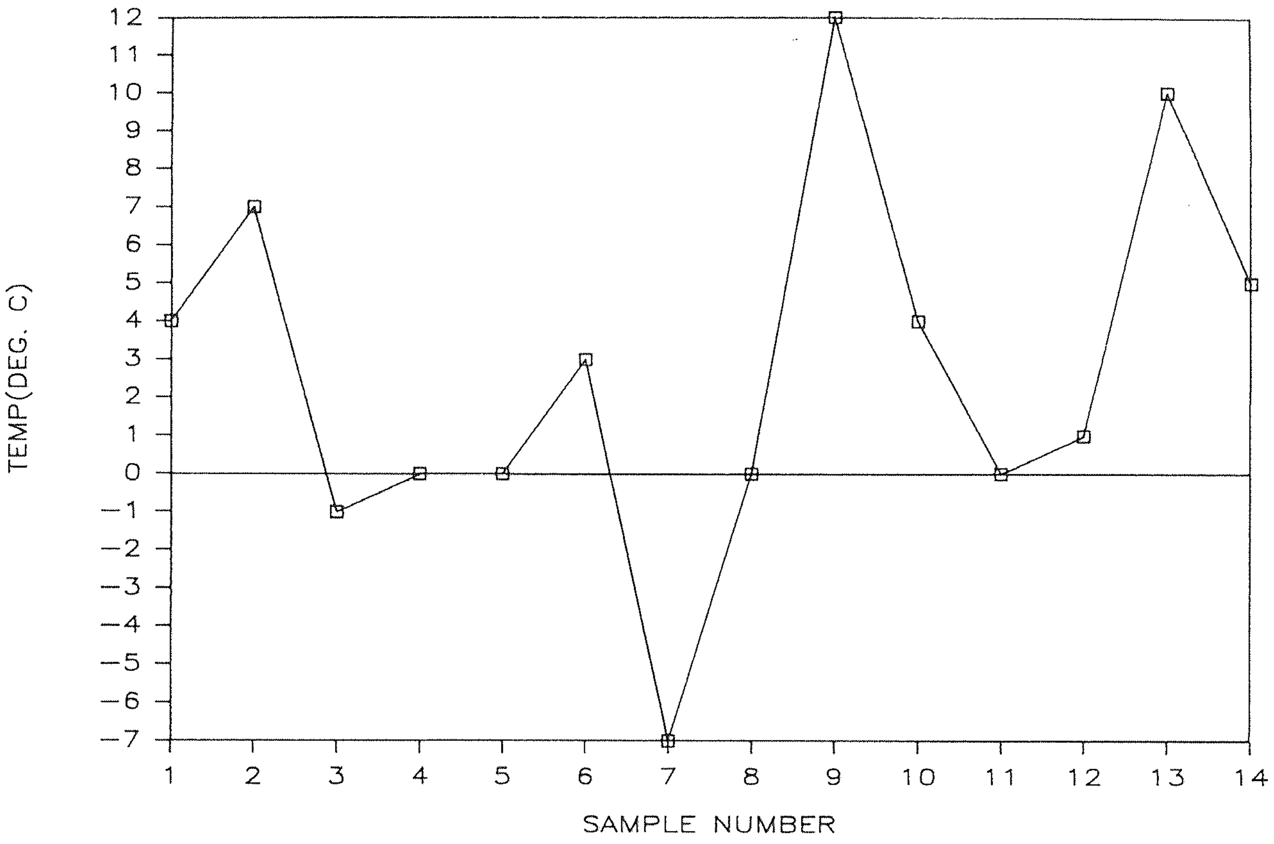


Figure 2 a - Day-to-day concentration changes at the grit/screen chamber for methylene chloride (MECL), chloroform (CFORM), benzene (BZ)



b - BOD of influent during sampling at grit/screen chamber.



c - Ambient temperature during sampling at grit/screen chamber.

Table-1 Monitoring Results for selected VOC measured at MCUA.

Found in at least 75% of samples

Methylene chloride (MECL)
Chloroform (CFORM)
1,2-dichloroethane (EDC)
1,1,1-trichloroethane (1,1,1-T)
Carbon tetrachloride (CTET)
Trichloroethylene (TCE)
Benzene (BZ)
Tetrachloroethylene (Perc)
1,1,2,2-tetrachloroethane (1,1,2,2-T)
Toluene (Tol)
Ethylbenzene (ETBZ)

Not Found in any samples

Dichloropropane
Cis-dichloropropene
1,1,2-trichloroethane
chlorodibromomethane
Bromoform

Found in less than 25% of samples

1,1-dichloroethene
1,1-dichloroethane
t-dichloroethene
bromo-dichloroethane
Chlorobenzene

Table-2 Mean and Maximum levels (ppb_v) of selected VOC at MCUA[a]

Site[b]		N	MECL	CFORM	EDC	1,1,1-T	CTET	TCE	Perc	1,1,2,2-T	BZ	TOL	ETBZ
1-GSC	X	15	35.8	11.3	0.7	25.2	8.4	2.4	3.9	0.3	9.9	88.7	4.4
	max		163.3	39.8	2.3	127.7	59.2	23.4	25.1	1.5	125.6	188.0	14.1
2-PST	X	2	21.5	6.9	0.8	7.7	12.2	0.4	2.0	ND	6.7	49.6	1.3
	max		28.9	11.1	0.9	8.8	22.5	0.8	2.6	ND	10.2	50.0	2.2
3-PEO	X	2	21.3	9.2	0.7	23.9	2.5	1.8	3.7	0.4	5.1	92.2	2.4
	max		23.9	10.5	0.8	26.0	3.7	2.7	4.7	0.8	7.2	115.7	3.6
4-O_2V	X	4	100.8	28.8	1.5	72.0	6.7	3.2	12.9	4.7	1.3	6.2	0.5
	max		151.4	37.1	2.6	96.6	16.1	6.6	24.1	8.2	3.4	20.6	1.1
5-GT	X	3	121.9	43.5	6.9	73.5	5.3	10.3	10.0	0.2	5.7	62.0	5.6
	max		176.1	55.9	11.2	100.0	13.4	22.9	12.1	0.7	10.4	108.0	12.8
6-Clar	X	2	86.2	22.3	4.8	22.0	1.8	1.5	5.2	0.6	1.1	3.4	0.8
	max		127.9	23.0	5.3	26.5	2.7	1.7	5.8	0.7	1.2	4.0	0.9
7-AO_2V	X	2	40.0	60.4	17.0	76.3	9.7	20.0	26.4	4.0	1.0	8.1	1.8
	max		64.0	71.1	32.9	84.7	10.5	30.2	30.3	5.0	1.6	12.3	3.5
8-SE	X	3	115.9	15.3	1.0	28.8	1.4	11.3	5.3	0.6	0.9	4.2	0.6
	max		219.7	21.4	1.6	29.4	3.2	28.8	6.3	0.7	1.0	5.6	0.8
9-ME	X	2	33.1	6.4	0.7	11.6	3.5	0.3	2.2	0.3	1.3	4.9	1.1
	max		44.3	6.9	0.7	12.2	6.5	0.4	3.5	0.5	1.4	10.0	1.4
10-SST	X	2	129.1	12.9	1.4	11.0	ND	8.1	2.9	0.8	0.11	111.9	1.6
	max		140.2	13.5	1.8	12.5	ND	8.7	3.1	1.6	0.2	140.8	2.1
11-Char	X	1	70.9	21.3	0.6	28.9	ND	28.8	5.0	0.4	1.0	3.0	0.4
12-AC[c]	X	2	309.6	650.4	38.6	1234.6	115.4	22.9	307.7	3.45	7.3	13.1	15.5
	max		617.5	1290.7	76.6	2448.9	228.1	45.5	612.4	69.9	14.5	24.4	31.0
13-SPS[d]	X	2	472.9	358.4	22.3	90.4	285.1	21.4	12.5	1.4	194.1	338.9	77.8
	max		485.2	392.4	37.9	105.3	301.8	23.5	21.5	2.2	328.2	657.9	154.1
14-RC[d]	X	1	14.3	0.4	0.6	0.8	1.0	1.3	2.5	ND	6.0	28.6	1.7
15-BG[e]	X	7	1.0	<0.1	ND[f]	0.5	<0.1	<0.1	0.1	<0.1	1.1	2.9	0.2
	max		2.8	0.3	ND	1.2	0.2	0.3	0.5	0.5	2.0	5.5	0.4

Table-2 (Continued)

a- See Table-1 for compound abbreviations

b- GSC - Grit/Screen Chamber
PST - Primary sedimentation tank
PEO - Primary effluent overflow
O_2V - Oxygen vent
GT - Gravity thickners
Clar - Chlorine clarifers
AO_2V - Aerobic O_2 vent
SE - Secondary effluent
ME - Main effluent
SST - Sludge storage tank
Char - Charcoal filter
AC - Aerobic crack
SPS - Sayreville Pumping Station
RC - Runyon connection
BG - Background

c- Short Grab (2min) samples
d- Indoor samples
e- Four different sites were used for the background locales
f- Below MDL

Table-3 Correlation matrix of selected VOC measured at the Grit/Screen Chamber and all other sites[a]

								Grit/Screen Chamber		
	MECL	CFORM	1,1,1-T	CTET	TCE	Perc	1,1,2,2-T	BZ	Tol	ETBZ
MECL		0.79	0.94		0.96	0.95		0.96	0.77	
CForm	0.84		0.72		0.65[b]	0.78		0.79	0.92	
1,1,1-T	0.66	0.95			0.95	0.94		0.95	0.79	
CTET	0.92	0.74	0.48[c]							0.70
TCE	0.77	0.74	0.66	0.67		0.97		0.93	0.69	
Perc	0.66	0.95	0.99	0.48[b]	0.65			0.96	0.76	
1,1,2,2-T	0.65	0.93	0.99		0.67	0.99				
BZ	0.56			0.74					0.76	
TOL	0.63			0.83				0.71		
ETBZ	0.68			0.85	0.44			0.60	0.96	

Other Sites

a - For compound abbreviations see Table-1
b - All values significant (p<0.01), except p=0.025
c - p = 0.015

Table-4 Sequential Twelve hour samples collected at the Grit/Screen Chamber (ppbv)[a]

Date		MECL	CFORM	EDC	1,1,1-T	CTET	TCE	Perc	1,1,2,2-T	BZ	Tol	ETBZ
2/4	A[b]	40.6	11.5	0.9	26.3	1.9	1.1	3.8	1.5	21.3	59.1	2.1
	B	163.3	38.1	1.4	127.7	12.8	23.4	25.1	1.1	125.6	206.9	6.7
2/7	A	23.4	7.7	0.5	9.9	4.1	0.3	0.0[c]	ND[d]	9.5	65.8	3.4
	B	0.9	0.0	0.2	0.0	0.0	0.0	3.8	ND	0.5	63.1	1.1

a - see Table-1 for compound abbreviations
b - A-first twelve hours, B-next twelve hours
c - Below MQL.
d - Below MDL.