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Project Summary

Volatile Organics in Aeration Gases at Municipal Treatment Plants

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When the volatility of certain priority pollutants is considered, it could be assumed that these compounds would be transferred from the aqueous solution to the atmosphere during treatment at a municipal treatment plant. When this study began, there were virtually no data that either qualitatively or quantitatively addressed this process. The purpose of this study was to develop sampling techniques to monitor emissions of organics from biological aeration basins. Additionally, an attempt was made to correlate emissions with aqueous concentrations and to investigate the influence on volatility of the sorption of the compounds on sludge solids.

^{14}C-Radiolabeled compounds were used to determine sorption by solids in raw wastewater and mixed liquor suspended solids (MLSS). The Freundlich adsorption isotherm relationship was used to describe the sorption capacity and intensity. The results indicated large variations in K (capacity) and n (intensity) among differing solids and different compounds. It was concluded that the sorption of volatile compounds to the solid phase in activated sludge cannot be ignored when attempting to predict the concentration in the off-gas by using liquid phase concentrations. In contrast, sorption on solids in raw wastewater was considered to have a negligible effect.

A pilot study and two experiments were conducted to determine the levels of volatile priority pollutants in the off-gas from aeration basins in activated sludge and raw wastewater at the Northside Treatment Plant in Durham, North Carolina. Some 13 volatile compounds were detected in the off-gas. In general, the concentrations of the compounds in the off-gas were higher (by a factor of 2 to 3) at the front end of the aeration basin than at either the middle or end of the basin. In contrast, the concentrations of the same priority pollutants in the mixed liquor of the activated sludge showed no change at the same sampling points.

The emission of compounds from the entire composite aeration tank area of the plant was computed for a number of priority pollutants. Four compounds exhibited emission rates of > 1 kg/hr, with the highest observed for chloroform and tetrachloroethylene with emission rates attaining 5.7 and 7.0 kg/hr, respectively.

The effect of superchlorination of sludge was also investigated. Sampling and analysis for chlorinated compounds in superchlorinated sludge revealed the presence of several hundred constituents. Analysis of the solid phase after superchlorination indicated the presence of 2% to 5% organic chlorine.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

It would be simpler if the concentrations of volatile organics in the off-gas from aeration basins could be predicted from their concentrations measured in the liquid phase; acquiring liquid samples from the treatment facility presents fewer problems. To predict the concentrations of volatiles in the off-gas, it is necessary to recognize the potential equilibria of compounds between the solid, liquid, and gas phases that exist in the aeration basins of the activated sludge process. A material balance equation of the interactions leads to a first-order rate expression that allows the calculation of the concentration at a point in time (t). The integrated form of the equation is given by:

$$C_{w(t)} = C_{w(o)}e^{-K_{iL}(C_w - P_i/H_i)}$$

C_w = concentration of the chemical in water

K_{iL} = mass transfer coefficient

P_i = partial pressure of the chemical

H_i = Henry's Law Constant

It follows that the concentration of the chemical in the liquid phase should decrease with the time of forced air aeration in a body of liquid such as an activated sludge aeration basin.

Sorption on Sludge Solids

A study was conducted to determine the sorption of selected ^{14}C-labeled priority pollutants onto the solids in activated sludge. The purpose was to determine whether sorption could be ignored and the simple Henry's Law relationship could be used to approximate the rate of volatilization. At the same time the sludge was sampled, the concentrations of the liquid flow were also determined at the entrance and exit of the aeration basin to determine whether the above equation indeed applies.

Sorption Tests

Sorption tests were conducted on solids obtained from raw wastewater and from activated sludge; the solids were placed in contact with solutions of ^{14}C-labeled volatile organic compounds in capped centrifuge tubes that were maintained at 4 °C to minimize biodegradation. Analysis for residual compound was determined with a liquid scintillation spectrometer. Results were expressed by using the Freundlich equation as follows:

$$C_s = KC_w^n \text{ or } \log C_s = \log K + n \log C_w$$

where:

C_s = concentration of the organic on the solid phase in μg/g

C_w = concentration in the liquid phase at equilibrium expressed at μg/L

K and n = parameters of the equation

Table 1 shows results of the sorption tests on a single compound, chloroform, for sludge sampled during two different time periods and from three locations in the aeration basin. These data and results obtained with other compounds show that there is a variation in sorption capacity of activated sludge taken at two different times (Periods 1 and 2) and indicate a decline in capacity with location in the aeration basin starting at the front end (1), middle (2), and exit (3).

Sorption data were obtained for the following compounds: chloroform, carbon tetrachloride, chlorobenzene, toluene, benzene, and trichloroethylene.

Table 1. *Freundlich Adsorption Parameters for Chloroform on Activated Sludge**

Period	Location	Initial Conc. (μg/L)	Log C_w	Log C_s	Slope (n)	Intercept Log K (K)**	Corr. Coef. (r)
1	1	5.0	0.432	0.894			
		49.8	1.253	2.026	1.002	0.55 (3.54)	0.961
		99.5	1.746	2.164			
1	2	5.0	0.512	0.766			
		49.8	1.536	1.711	1.057	0.20 (1.58)	0.988
		99.5	1.754	2.154			
1	3	4.6	0.441	0.788			
		46.1	1.521	1.634	0.828	0.41 (2.57)	0.998
		92.2	1.797	1.935			
2	1	5.0	0.455	0.855			
		49.8	1.438	1.873	0.890	0.48 (3.02)	0.987
		99.5	1.783	1.983			
2	2	5.0	0.498	0.894			
		49.8	1.438	1.873	0.921	0.46 (2.88)	0.992
		99.5	1.811	2.065			
2	3	4.6	0.538	0.583			
		46.1	1.470	1.743	1.435	-0.21 (0.62)	0.985
		92.2	1.608	2.236			

*Sludge concentration 0.3 g/L.
**K expressed as μg/g of dry sludge solids.

Emission of Volatiles

Studies were conducted to determine the levels of purgeable priority pollutants in raw wastewater, activated sludge, and the off-gas from aeration basins stripped by the aeration process. The objective was to determine the relationship of off-gas concentrations at the front end and exit of an aeration basin to the concentration in the activated sludge collected at the same locations in the basin.

The sampler and analytical techniques were the same as those previously developed and described for off-gas determination.* A pilot test and two studies conducted on different days were obtained at the Northside Treatment Plant, Durham, North Carolina. In tests No. 1 and 2, the air streams were sampled in triplicate at three locations (beginning, middle, and end). The two sampling periods covered a total of 4.5 hr. Concurrently, at the beginning, middle, and end of the air sampling period, activated sludge samples were taken from the same locations in the tank.

Selected results of two time periods of the sampling and analysis are shown in Table 2. Samples were taken at the entrance (L1) end of the aeration tank. Complete sampling data show a decreasing concentration of compounds in the off-gas between flow entrance (L1) and exit of the tank. Further, concentrations in the sludge were relatively constant or slightly increased at each of the locations.

From these data, the mass emission rate of the priority pollutants in the off-gas from the entire plant aeration tank surface area could be calculated. The results for selected compounds are shown in Table 3. The highest rates were observed for chloroform and 1,1,2,2-tetrachloroethylene with emissions reaching 5.7 and 7.0 kg/hr, respectively.

Superchlorination of Sludge

Superchlorination of sludge for stabilization is being practiced in some plants. Because the sludge cake generated from this process can eventually be deposited in a landfill or used as a fertilizer, it is important to know whether potentially toxic compounds are generated by this process. Sampling and analysis were conducted at two plants on sludges before and after superchlorination and on sludge cake from drying beds. Total organic chlorine

*"Collection and Analysis of Purgeable Organics .mitted from Wastewater Treatment Plants," EPA-600/2-80-017.

Table 2. *Priority Pollutant Levels in Airstreams and Activated Sludge Northside Treatment Plant, Durham, NC*

| Priority Pollutant | Location L1 | | | |
| | 1200-1415 hr | | 1415-1630 hr | |
	Air	Sludge[a]	Air	Sudge
Chloromethane	ND[b]	ND	ND	ND
Dichlorofluoromethane	ND	ND	ND	ND
Bromomethane	ND	ND	ND	ND
Vinyl chloride	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND
Methylene chloride	27.7±6.3[c]	18.5±7.8	23.7±2.0	34.2±21.6
Trichlorofluoromethane	ND	ND	ND	ND
1,1-Dichloroethylene	8.0±0.2	4.0±0.4	6.8±0.2	3.9±0.8
1,1-Dichloroethane	2.8±0.5	ND	3.8±0.5	ND
trans-1,2-Dichloroethylene	ND	ND	ND	ND
Chloroform	125±47.7	27.8±13.2	108±13.8	16.7±5.8
1,2-Dichloroethane	1.1±0.1	ND	T[d]	0.2±0
1,1,1-Trichloroethane	27.6±7.4	1.4±0.3	34.0±4.4	1.2±0.1
Carbon tetrachloride	ND	0.2±0	T	0.3±0.1
Bromodichloromethane	4.7±0.8	ND	3.4±0.1	ND
Bis(2-chloroethyl)ether	ND	ND	ND	ND
1,2-Dichloropropane	ND	ND	ND	ND
trans-1,2-Dichloropropene	ND	ND	ND	ND
Trichloroethylene	10.7±0.4	0.4±0	9.4±2.8	0.6±0.1
Dibromochloromethane	ND	ND	T	ND
cis-1,3-Dichloropropane	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	T	ND
Benzene	21.2±4.2	1.0±0.2	18.8±1.5	1.1±0.1
2-Chloroethyl vinyl ether	ND	ND	ND	ND
1,1,2,2-Tetrachloroethylene	119±26.3	4.3±0.7	281±20.4	12.2±2.1
Bromoform	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND
Toluene	136±52.4	3.1±1.1	130±15	3.5±1.0
Chlorobenzene	T	ND	T	ND
Ethylbenzene	26.4±8.4	0.7±0.2	23.4±6.6	0.4±0.4
Acrolein	ND	ND	ND	ND
Acrylonitrile	ND	ND	T	ND
m-Dichlorobenzene	38.1±13.2	3.6±0.4	36.3±6.9	3.9±1.2
o-Dichlorobenzene	11.3±2.4	2.5±0.6	10.5±2.6	2.5±0.8

[a]*Priority pollutants were measured in sludge at the beginning and end of time period with mean value of quadruplicate analyses reported.*
[b]*ND = not detected.*
[c]*mean values are in ppb with standard deviation.*
[d]*T = trace.*

was determined by a combustion technique, volatile organics by purge and trap, and chlorinated organics by electron impact and negative ion chemical ionization capillary GC/MS.

The organic chlorine content of the sludge solids before chlorination was

<0.6 ± 0.3%, which was at the limit of detection by the Schöniger method; after chlorination, the concentration ranged from 2.15% to 5.28%.

The results of analysis for purgeable organics (Table 4) are for two sets of samples from one plant and for sludge

Table 3. Estimated Emission Rates Calculated for Selected Priority Pollutants from Aeration Basins at Northside Treatment Plant, Durham, NC

	Emission Rates (g/hr)		
Priority Pollutant	August 19, 1979	January 29, 1980	May 14, 1980
Methylene chloride	572	280±86	205±3
1,1-Dichloroethane	--	14±4	19±2
Chloroform	5,756	703±11	944±103
1,2-Dichloroethane	--	10±7	±2
1,1,1-Trichloroethane	301	191±27	252±23
Bromodichloromethane	288	130±42	43±1
Trichloroethylene	704	103±11	111±8
Benzene	668	62±9	122±8
1,1,2,2-Tetrachloroethylene	7,007	940±15	1,969±710
Toluene	4,819	264±216	741±86
Ethylbenzene	• 871	16±8	171±21
o-Dichlorobenzene		148±3	478±71
	4,689		
m-Dichlorobenzene		609±44	155±13

cake from the drying beds. Comparison of the concentrations of the purgeable organics between the unchlorinated influent and the chlorinated effluent sludge indicates that several compounds increased appreciably: notably, chloroform, carbon tetrachloride, and p-chlorotoluene. The remaining compounds remained relatively constant.

Extensive analyses were also conducted for the nonvolatile compounds using GC/MS techniques. In addition, sample fractions that are normally excluded by EPA's analytical protocol were also analyzed. Certain compounds were identified but not quantified, but most of the results are presented as GS/MS profiles. These profiles reveal the presence of "hundreds" of unidentified compounds resulting from chlorination.

Conclusions

Certain ^{14}C-radiolabeled priority pollutant compounds were used to deter-

Table 4. Levels[a] of Selected "Purgeable" Organics in Liquid Sludge Before and After Superchlorination (ppb)[b]

Compound	INF/1S[c]	EFF/1S[c]	INF/2S	EFF/2S	Bed Samples
Chloromethane	20±15	32±9	54±32	15±1	27±5
Dichlorodifluoromethane	8±8	27±8	4±4	20±4	14±1
Bromoethane	3±2	T[d]	T	T	T
Methylene chloride	260±110	376±12	203±40	264±27	338±28
Trichlorofluoromethane	390±229	118±26	74±26	276±86	135±50
1,1-Dichloroethylene	10±3	16±2	9±1	15±3	15±5
1,1-Dichloroethane	24±22	39±10	41±41	32±6	15±4
Freon 113	15±2	14±1	11±0	15±5	12±1
Chloroform	9±7	1,037±140	6±5	1,104±125	490±110
1,1,1-Trichloroethane	175±51	211±23	69±34	179±17	86±28
Carbon tetrachloride	ND[d]	847±47	ND	989±135	395±140
Bromodichloromethane	ND	ND	ND	6±4	ND
trans-1,3-Dichloropropene	ND	9±7	ND	10±8	T
Trichloroethylene	86±5	81±1	66±1	85±10	75±18
Benzene	50±23	48±20	354±279	39±11	39±11
1,1,2,2-Tetrachloroethene	139±32	182±18	102±24	149±10	106±34
1,1,2,2-Tetrachloroethane	ND	ND	ND	T	ND
Toluene	778±64	1,213±66	1,432±127	739±14	2,165±644
Chlorobenzene	ND	15±1	11±11	16±1	12±2
Ethylbenzene	9±8	13±1	6±6	12±0	14±0
p-Chlorotoluene	ND	951±90	T	1,586±269	762±273
Dichlorobenzene isomer	11±10	25±1	9±9	32±1	23±8

[a]Based on total sample.
[b]Mean values in parts per billion with standard deviation.
[c]INF = unchlorinated influent liquid sludge; EFF = chlorinated effluent liquid sludge.
[d]T = trace.

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mine the extent of their sorption by the solids in activated sludge and raw wastewater. The Freundlich adsorption isotherm relationship was used to describe the sorption capacity and intensity of the solid for each of the radiolabeled compounds. Measurable sorption capacities (K) were detected for each of the compounds. Sorption studies conducted over several different time periods indicated large variations in K values (e.g., for chloroform it ranged from 0.62 to 3.54). The sorption intensity (n) for several chemicals varied by as much as a factor of 3. The results indicated that sorption of volatile chemicals to the solid phase in activated sludge cannot be ignored when attempting to predict their concentration in the off-gas by measuring liquid phase concentrations. The sorption capacity for the same chemicals to solids in raw wastewater was deemed negligible.

A pilot study and two experiments were conducted on different days to determine the levels of volatile priority pollutants in the off-gas from aeration basins in activated sludge and raw wastewater at the Northside Treatment Plant in Durham, North Carolina. In general, the concentrations of priority pollutants in the off-gas were higher at the front end of the aeration basin than at either the middle or end of the basin— a decrease by a factor of 2 to 3. In contrast, the levels of priority pollutants measured in the activated sludge did not appear to decrease at the same three points along the aeration basin. The concentrations of priority pollutants in raw wastewater were higher, however, than in the activated sludge itself, indicating that the priority pollutants were partially lost at other points in the treatment facility or that a dilution had occurred before reaching the aeration basin. Because of a significant sorption for the priority pollutants to the solids in activated sludge and the lack of a concentration gradient across an aeration basin, it was concluded that a simple Henry's Law relationship cannot be used to accurately predict the off-gas concentrations of a priority pollutant from its concentration in the liquid phase.

The emission rate from the entire composite aeration tank area for the Northside Treatment Plant in Durham, North Carolina, was determined for a number of priority pollutants. The highest rates were observed for chloroform and tetrachloroethylene with emission reaching 5.7 and 7.0 kg/hr, respectively.

Sampling and analysis for chlorinated compounds in superchlorinated sludge revealed the presence of several hundred chlorinated constituents; the superchlorinated sludge effluent contained 2% to 5% organic chlorine. The organic chlorine content for the unchlorinated influent sludge solids was at the limit of detection using the Schöniger method. The use of negative ion chemical ionization/mass spectrometry (NICI/MS) made the specific and sensitive detection of chlorinated compounds easier. Quantification of purgeable priority pollutants before and after chlorination of sludge indicated increased concentrations. Chloroform increased from about 6 ppb before chlorination to over 1,000 ppb after; carbon tetrachloride was not detected in the influent but was measured at levels up to 989 ppb in the effluent. Increases of almost three orders of magnitude were also observed for p-chlorotoluene, in some cases from only

trace levels to 1,620 ppb. When using the priority pollutant method for sludge analysis, acid, base, and neutral fractions yielded only a few chlorinated nonpriority pollutants. In contrast, NICI/MS examination of the discard fraction generated by this method indicated that the majority of the chlorinated compounds amenable to gas chromatography were contained in these fractions. Even though the chlorinated compounds detected by NICI/MS were not quantified, it was evident that a major portion of the chlorinated organics was not detected by this method since the presence of up to 5% organic chlorine in the solid component of the chlorinated sludge had been demonstrated.

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James J. Westrick and H. Paul Warner are the EPA Project Officers (see below).
The complete report, entitled "Volatile Organics in Aeration Gases at Municipal Treatment Plants," (Order No. PB 82-227 760; Cost: $18.00, subject to change) will be available only from:
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