Preliminary assessment of the removal of volatile organic compounds in a biological selector process

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ABSTRACT: The fate of selected volatile organic compounds (VOCs) in anoxic or anaerobic selectors was investigated at pilot scale. Tetrachloroethylene, 1,4-dichlorobenzene, and 1,3,5-trimethylbenzene were consistently removed at efficiencies in excess of 30%. The removals observed in this study were highly compound specific. Compounds with similar chemical structures such as toluene and 1,3,5-trimethylbenzene displayed substantially different behavior. The selector biomass concentration and hydraulic retention time were found to have little apparent effect on the VOC removal efficiencies. However, the results were confounded by a change in wastewater temperature that also influenced the loading of nitrate on the selector. The results of these experiments demonstrate the potential of selector technologies for reducing the mass loading of VOCs to aeration basins. The lower mass loadings should reduce the mass of aerobically recalcitrant VOCs that will be stripped to the atmosphere. *Water Environ. Res.*, **67**, 798 (1995).

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In an activated sludge plant, selectors are processes that are located upstream of the aeration basin and provide a high localized food:microorganism (F:M) ratio by maintaining relatively short hydraulic retention times (HRTs). The high F:M ratio and the lack of aeration in these processes commonly result in either anoxic or anaerobic conditions. The practice of sequentially exposing contaminated streams to alternating oxidation-reduction potentials has been suggested as a means to degrade compounds that are generally recalcitrant in the aerobic treatment process (Zitomer and Speece, 1993). The use of anoxic and anaerobic selectors in wastewater treatment presents such an opportunity. Highly chlorinated organic compounds, in particular, have proven to be poorly degraded in aerobic environments but readily degraded in anaerobic environments (Vogel *et al.*, 1987).

A class of compounds that are of particular concern in wastewater treatment are the VOCs because they tend to volatilize and strip from aerated processes. This report documents a preliminary study that was undertaken to assess the potential for enhanced biodegradation of VOCs in wastewater treatment by the use of selector technology. The experiments, which were conducted at pilot scale, assessed the impact of selector HRT and volatile suspended solids concentration on the removal of selected VOCs.

Materials and methods

Pilot plant description. The pilot plant employed in the study was located at the Wastewater Technology Centre in Burlington, Ontario, and was treating degritted municipal wastewater from the Burlington Skyway wastewater treatment plant. The sequence of unit processes consisted of a primary clarifier, selector tank, aeration tank, and secondary clarifier. The process flowsheet is detailed in the figure. The aeration tank has a volume of 5 m^3, whereas the clarifiers each have a volume of 3.5 m^3. The pilot plant was operated with a 10-day solids retention time and a 6-hr HRT in the aeration basin. This portion of the pilot plant has been described in greater detail elsewhere (Parker *et al.*, 1993). The selector tank has been installed more recently, and the process conditions for this tank for each experiment are summarized in Table 1. The tank was mechanically agitated to maintain biomass in suspension and sealed from the atmosphere to minimize losses due to volatilization. Volatile suspended solids concentrations in the selector were adjusted by varying the recycle flow rate and maintaining the total flow rate through the selector constant at 24 L/min. The HRT in the selector was adjusted by varying the liquid level in the selector.

Selector dosing and sampling. The municipal wastewater that is received from the Burlington wastewater treatment plant contains negligible quantities of VOCs. Therefore, it was necessary to dose the pilot plant with a selection of candidate compounds to ensure a constant and detectable flow of VOCs to the selector. The candidate compounds were chosen on the basis of one or more of the following criteria:

- presence on the U.S. EPA Priority Pollutant List
- frequency of detection in municipal wastewaters
- broad range of physical properties including volatility and partitioning to biomass solids
- broad range of chemical properties including aliphatic and aromatic, chlorinated and nonchlorinated.

The selected compounds are summarized along with their relevance to the previously specified criteria in Table 2.

The candidate compounds were solubilized in methanol and dosed directly into the selector contents. The mass loading to the selector of each candidate compound was equivalent to that which would be obtained if the influent wastewater concentration of each candidate compound was 100 μg/L. That is:

$$Q_{methanol}C_{methanol} = Q_0C_0$$

Where

$Q_{methanol}$ = methanol dosing flow
Q_0 = total flow to selector, approximately 24 L/min
$C_{methanol}$ = concentration of VOC in methanol
C_0 = simulated concentration of VOC in selector influent, approximately 100 μg/L

Table 1—Selector process conditions in each experiment.

Experiment	Liquid volume, L	Recycle flow, L/min	Selector HRT, min	Volatile suspended solids concentration, mg/L	Temperature, °C	Dissolved oxygen, mg/L	Nitrate concentration, mg/L	
							Influent	Effluent
1	330	10	14	2 830	13	<0.3	BDL[a]	BDL
2	330	5.33	14	1 890	11	<0.3	1.38	0.4
3	670	5.33	28	1 925	13	<0.3	0.16	BDL
4	670	10	28	2 535	18	<0.3	3.6	0.6
5	670	10	28	2 580	18	<0.3	2.0	0.5

[a] BDL, below detection limit of 0.1 mg/L.

The methanol solution was pumped through a fine aperture that dispersed the dosing solution as it entered the selector to ensure that the candidate compounds were solubilized and did not remain in a separate phase. Dosing was maintained at a constant rate for a period of four selector HRTs, ensuring hydraulic steady state of the candidate compounds in the selector effluent. This dosing approach ensured that there were minimal VOCs returning from the aeration basin in the return activated sludge and is believed to produce results under conditions of unacclimated biomass.

Liquid samples of the dosing solution, the selector influent, and the selector effluent were taken in the experiments. Grab samples for liquid VOC analysis were taken in 40-mL amber vials that contained 0.5 mL of 80 g/L $CuSO_4$ solution for preservative. Samples of the selector influent and dosing solution were taken at the midpoint and end of the dosing period, whereas duplicate samples of the selector effluent were taken after dosing of the selector for four HRTs. Samples of the selector influent and effluent were also collected for analysis of nitrate. A grab sample of the selector headspace was taken in a 6-L passivated stainless steel canister to assess losses of the candidate compounds to the headspace. The dissolved oxygen concentration of the selector contents was measured during the dosing period.

Analysis. Liquid samples were analyzed for VOCs with a Tekmar model LSC 2000 concentrator with a Tekmar 2016 autosampler coupled to a Hewlett-Packard 5890 gas chromatograph (GC). The GC was interfaced to a Hewlett-Packard model 5970B mass selective detector (MSD). The gas chromatographic column was a 30-m long DB-624 with an internal diameter of 0.32 mm. The isotope dilution technique was employed to correct for losses through the analytical procedure.

Gas samples were analyzed using a cryogenic gas sample concentrator joined to a Hewlett-Packard 5890 GC with a Hewlett-Packard model 5970 MSD. The chromatographic column was a DB1 with a length of 60 m and an inside diameter of 0.32 mm. Nitrate analyses were performed as per *Standard Methods* (1989). Dissolved oxygen concentrations were measured with YSI dissolved oxygen probes.

Results and analysis

A total of five experiments were conducted in this preliminary survey of the fate of VOCs in selectors. Experiments 1 through

Table 2—Properties of candidate compounds.

Compound	EPA priority pollutant list	EPA 40 publicly owned treatment works study,[a] % detect	Henry's law coefficient, m^3/m^3	Log K_{ow} partition coefficient	Aliphatic/ aromatic	Halogen substituted
Chloroform	Y	91	0.150[b]	1.97[c]	Aliphatic	Y
1,1,1-Trichloroethane	Y	85	0.703[b]	2.47[c]	Aliphatic	Y
Trichloroethylene	Y	90	0.392[b]	2.53[c]	Aliphatic	Y
Tetrachloroethylene	Y	95	0.723[b]	2.53[c]	Aliphatic	Y
1,1,2,2-Tetrachloroethane	Y	7	0.011[d]	2.56[c]	Aliphatic	Y
Bromoform	Y	2	0.018[e]	2.30[f]	Aliphatic	Y
Toluene	Y	96	0.277[d]	2.69[c]	Aromatic	N
o-Xylene	N	NA[g]	0.210[d]	3.12[f]	Aromatic	N
1,3,5-Trimethylbenzene	N	NA	0.290[d]	3.42[c]	Aromatic	N
1,4-Dichlorobenzene	Y	17	0.137[d]	3.39[c]	Aromatic	Y

Note: All Henry's law coefficients at 25°C.
[a] Burns and Roe (1982).
[b] Gosset (1987).
[c] U.S. EPA WERL Database (1990).
[d] Ashworth *et al.* (1988).
[e] Munz and Roberts (1989).
[f] Howard (1990).
[g] NA, not available.

3 were conducted under relatively low liquid temperatures (11° to 13°C); however, Experiments 4 and 5 were substantially delayed because of excessively dilute feed that resulted from the spring thaw. The dilute feed resulted in very low biomass yields, and it was, therefore, difficult to maintain the desired biomass concentrations in the selector. As a consequence of the experimental delay, Experiments 4 and 5 were performed at warmer wastewater temperatures than the previous three experiments. The warmer temperatures had an impact on the extent of nitrification occurring in the aeration basin and, hence, the concentration of nitrate recycled to the selector in the return activated sludge. The concentrations of nitrate in the selector influent and effluent are presented in Table 1. Dissolved oxygen concentrations measured in the selector are also presented in Table 1.

To assess the extent of biodegradation of the candidate VOCs in the selector, it was necessary to perform a mass balance on each candidate compound as it entered and exited the selector. At the time of effluent sampling, the selector had been continuously dosed for four HRTs. Because the system was well mixed, it was assumed that hydraulic steady state of the candidate compounds had been achieved at this time. Accumulation of the candidate compounds in the selector was, therefore, assumed to be negligible, and the percentage removed was calculated as:

$$\text{Percent Removed} = \frac{Q_{\text{methanol}}C_{\text{methanol}} - Q_0C_e}{Q_{\text{methanol}}C_{\text{methanol}}} \times 100$$

Where

C_e = measured effluent concentration of candidate compound

The results of this analysis are presented as removal efficiencies for each compound in each experiment in Table 3.

The previously described calculations ignored any losses to the headspace of the reactor that was essentially stagnant during the experiment. In a separate calculation, the percent of the influent mass flow of a candidate VOC that was present in the selector headspace was calculated as:

$$\text{Percent Volatilized} = \frac{V_gC_g}{(Q_{\text{methanol}}C_{\text{methanol}})t} \times 100$$

Where

V_g = head-space volume
C_g = head-space concentration of candidate compound
t = duration of dosing

In all cases, the percent volatilized was less than 2% of the total mass that flowed into the selector over the duration of the dosing. The contribution of volatilization to the overall removal described in the previous section was assumed to be negligible. Therefore, the removal efficiencies that were computed previously were attributed to biodegradation.

It is apparent from Table 3 that the removal efficiencies of VOCs in the selector were compound specific. The compounds that were removed to the greatest extent were 1,4-dichlorobenzene, 1,3,5-trimethylbenzene, and tetrachloroethylene with overall average removal efficiencies of 43%, 53%, 40%, respectively. The compounds that displayed the lowest removal efficiencies were 1,1,1-trichloroethane, chloroform, trichloroethylene, toluene, and 1,1,2,2-tetrachloroethane with removal efficiencies 13%, 10%, 18%, 17%, and 14%, respectively.

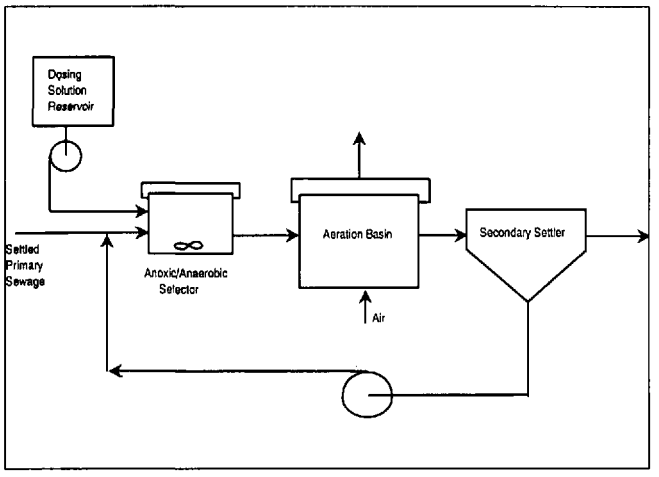
The removal of VOCs in the selector did not appear to follow any trends with respect to chemical structure. Although both chlorinated and nonchlorinated compounds were significantly removed, other compounds with similar chemical compositions were not substantially removed. For example, tetrachloroethylene was substantially removed, whereas trichloroethylene and 1,1,2,2-tetrachloroethane were removed to lesser extents. The degradation of highly chlorinated compounds in environments with reduced oxygen concentrations has been attributed to reductive dechlorination (Vogel *et al.*, 1987). If this is the case in the selector environment, these results indicate that the reductive degradative pathways might be quite specific in nature. The mechanisms responsible for removal of nonchlorinated aromatic VOCs are unclear because compounds with similar formulation (1,3,5-trimethylbenzene, toluene) exhibited substantially different behaviours. These mechanisms might include anaerobic fermentation or anoxic respiration.

It should be noted that some of the candidate compounds examined are potential metabolic breakdown products of other candidate compounds. For example, reductive dechlorination of tetrachloroethylene can result in the formation of trichloroethylene. This may explain the relatively poor removals of trichloroethylene as compared with tetrachloroethylene. Further research with individual compounds would be required to determine if breakdown products were accumulating in the selector.

The selector process parameters that were varied in the experiments were HRT and biomass concentration. It would appear that, over the ranges varied in this study, there was no direct relationship between these parameters and removal of VOCs in the selector. These results are, however, confounded

Table 3—VOC removal efficiencies.

	Removal efficiencies observed in selector, %				
Compound	Exp 1	Exp 2	Exp 3	Exp 4	Exp 5
Chloroform	14.0	19.1	12.1	5.8	0.3
1,1,1-Trichloroethane	22.6	22.4	12.7	5.2	3.2
Trichloroethylene	23.1	26.2	17.5	12.9	8.4
Tetrachloroethylene	46.8	44.8	40.4	33.0	34.4
1,1,2,2-Tetrachloroethane	19.6	21.5	15.0	8.9	7.3
Bromoform	14.0	28.9	13.8	15.8	12.6
Toluene	22.5	27.7	21.1	5.8	8.6
o-Xylene	40.9	28.9	13.8	15.8	12.6
1,3,5-Trimethylbenzene	61.8	53.7	49.8	49.8	51.5
1,4-Dichlorobenzene	53.9	42.8	46.2	36.0	38.5



Process flow sheet.

because the experiments were performed at different temperatures, and there was a significant variation in the amount of nitrate being returned to the selector.

Previous studies have indicated that the extent of degradation achieved by reductive dechlorination is influenced by the concentration of intracellular electron carriers such as reduced nicotinamide adenine denucleotide or reduced metalloenzymes. The concentrations of these substances are controlled by the concentration of the primary electron donor (biochemical oxygen demand) and the primary electron receiver (O_2, NO_3, SO_4, CO_2) (Bae and Rittmann, 1990; Wrenn, 1992). Because the concentrations of dissolved oxygen were negligible in all experiments, it seems quite likely that the introduction of nitrate into the selector in the latter experiments would have had an effect on any reductive dechlorination reactions in the selector. The results of this research appear to confirm these prior observations. In the latter two experiments, with elevated loading of nitrate to the selector, reduced removal efficiencies of virtually all the chlorinated compounds were observed. Further research is required to more accurately define the relationship between nitrate loading and removal of toxics in selectors.

If the results of the first three experiments that were conducted at the same temperature are examined alone, it would appear that the experiment that was performed with the longer HRT (Experiment 3) also had the lowest removal efficiencies. The longer HRT would result in a reduced F:M ratio, which would tend to reduce the availability of electrons that would be available for reductive reactions. The differences in removal efficiencies between the experiments were, however, relatively small for most compounds, and, therefore, the significance of these differences is questionable. Significantly more research is required to determine the impacts of HRT and biomass concentration on the removal of VOCs in selectors.

The high removal efficiencies observed for the some of the chlorinated compounds are significant with respect to reducing atmospheric emissions from the aeration basin. These compounds are generally recalcitrant aerobically and, hence, tend to be stripped from the aeration basin (Parker *et al.*, 1993). The degradation of 1,3,5-trimethylbenzene will likely have less impact on air emissions because it is easily degraded aerobically and does not tend to be stripped.

Conclusions

Substantial removals of tetrachloroethylene, 1,4-dichlorobenzene and 1,3,5-trimethylbenzene were observed in a pilot-scale anaerobic or anoxic selector. Other chlorinated and non-chlorinated compounds with similar chemical structures demonstrated substantially lower removals. The selector HRT and biomass concentration did not appear to have a substantial impact on the extent of removals observed. However, the results were confounded by a change in wastewater temperature that also influenced the loading of nitrate to the selector. Increased reactor F:M ratios may result in a enhanced removal of some VOCs.

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