# Odor and Volatile Organic Compound Removal from Wastewater Treatment Plant Headworks Ventilation Air Using a Biofilter

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ABSTRACT: Laboratory-scale experiments and field studies were performed to evaluate the feasibility of biofilters for sequential removal of hydrogen sulfide and volatile organic compounds (VOCs) from wastewater treatment plant waste air. The biofilter was designed for spatially separated removal of pollutants to mitigate the effects of acid production resulting from hydrogen sulfide oxidation. The inlet section of the upflow units was designated for hydrogen sulfide removal and the second section was designated for VOC removal. Complete removal of hydrogen sulfide (H2S) and methyl tert-butyl ether (MTBE) was accomplished at loading rates of 8.3 g  $H_2S/(m^3 \cdot h)$  (15-second empty bed retention time [EBRT]) and 33 g MTBE/(m<sup>3</sup>·h) (60-second EBRT), respectively. In field studies performed at the Hyperion Treatment Plant in Los Angeles, California, excellent removal of hydrogen sulfide, moderate removal of nonchlorinated VOCs such as toluene and benzene, and poor removal of chlorinated VOCs were observed in treating the headworks waste air. During spiking experiments on the headworks waste air, the percentage removals were similar to the unspiked removals when nonchlorinated VOCs were spiked; however, feeding high concentrations of chlorinated VOCs reduced the removal percentages for all VOCs. Thus, biofilters offer a distinct advantage over chemical scrubbers currently used at publicly owned treatment works in that they not only remove odor and hydrogen sulfide efficiently at low cost, but also reduce overall toxicity by partially removing VOCs and avoiding the use of hazardous chemicals. Water Environ. Res., 75, 444 (2003).

**KEYWORDS:** waste air treatment, publicly owned treatment works, headworks, biofilter, odor, hydrogen sulfide, volatile organic compounds, methyl *tert*-butyl ether.

## Introduction

Federal and local air quality regulations require publicly owned treatment works (POTWs) to quantify and control volatile organic compounds (VOCs) and toxic air pollutants emitted from wastewater and solids handling processes. In Southern California, the 1990 New Source Review regulations for air toxics requires establishment of Maximum Achievable Control Technology (MACT) standards for POTWs as outlined in the Federal Clean Air Amendments of 1990. Furthermore, POTWs in Southern California are required to meet facility-based standards for existing sources as imposed by proposed regulations from the South Coast Air Quality Management District (SC-AQMD).

Contaminated air at POTWs contains two major groups of pollutants: reduced sulfur species and a variety of VOC species. Hydrogen sulfide, the predominant reduced sulfur compound, is the principal cause of odor nuisance, and is usually present at concentrations up to 300 ppm<sub>v</sub> (Iranpour et al., 2001). Volatile organic compounds that are commonly encountered include both nonhalogenated (e.g., benzene and toluene) and halogenated (e.g.,

dichlorobenzene and methylene chloride) compounds (Iranpour et al., 2001). Total VOC concentrations in POTW exhaust air is typically less than 10  $ppm_v$ . Odor control at POTWs typically involves the use of chemical scrubbers. However, they are relatively expensive to operate because of their high rates of chemical consumption. Additionally, chemical scrubbers are ineffective for the removal of VOCs.

In Europe, biological treatment using biofilters has rapidly been gaining ground as a relatively simple, economical, and efficient technology for emission reductions at POTWs (Devinny et al., 1998; Kennes and Veiga, 2001). A similar trend is now observed in the United States. Biological treatment involves the use of microorganisms that convert air pollutants into harmless end products. Treatment costs are relatively low compared with those of alternatives such as incineration, chemical scrubbing, and absorption because the process is performed at ambient temperature and pressure with minimum or no chemical consumption. Traditionally, biological waste air treatment at POTWs has focused on odor abatement. Many studies discuss hydrogen sulfide removal by biofiltration as effective and efficient (Iranpour et al., 2001). However, less information is available regarding the simultaneous removal of odorous sulfur species and VOCs (Converse et al., 2001; Cox et al., 2001, 2003; Ergas et al., 1992; Schroeder et al., 2000; Webster et al., 1996; Wolstenholme and Finger, 1994).

The objective of the present research was to determine the feasibility of biofilters in treating POTW waste air containing a mixture of odorous sulfur species and toxic VOCs. Because sulfuric acid production from hydrogen sulfide oxidation potentially interferes with VOC biodegradation, the biofilter in the present study was designed for spatially separated sections for the removal of hydrogen sulfide and VOCs. This principle was first demonstrated and investigated in a laboratory-scale biofilter receiving an air stream with hydrogen sulfide and methyl *tert*-butyl ether (MTBE) as model pollutants. In a second phase, pilot-scale experiments were conducted at the Hyperion Treatment Plant (HTP) in Los Angeles, California, and biofilter performance in treating waste air from the headworks was evaluated.

## **Materials and Methods**

Laboratory-Scale Experiments. Simultaneous removal of hydrogen sulfide and MTBE was investigated in a laboratory-scale biofilter, as shown in Figure 1. The first section of the biofilter was designed for hydrogen sulfide removal, followed by four sections for MTBE removal. Based on previous experiments by Ergas et al. (1994), hydrogen sulfide removal rates were expected to be



Figure 1—Schematic of laboratory biofilter for simultaneous removal of hydrogen sulfide and MTBE.

sufficiently high for complete removal in the first section without penetration of hydrogen sulfide into sections 2 to 5, which would then be dedicated to MTBE removal. The unit was constructed of plexiglass in five 15-cm i.d. sections. Each section was 30 cm in length and packed with 25 cm of a compost, perlite, and oyster shell mixture in a 2:2:1 volume ratio. A 5-cm plenum separated the sections. Nutrients were supplied as an aerosol into the air stream entering the biofilter. The nutrient composition and concentrations are listed in Table 1. The aerosol also provided water to the biofilter preventing the unit from drying. Methyl tert-butyl ether was injected to a portion of the main air stream using a syringe pump. Hydrogen sulfide was added to the air stream by passing the air through a hydrogen sulfide generation bottle containing hydrogen chloride solution into which a monosodium sulfide (Na2S) solution (variable concentration) was continuously fed at predetermined rates to obtain the desired hydrogen sulfide gasphase concentrations. This system was used with the saturated gas rather than hydrogen sulfide supplied from a cylinder to prevent hazardous concentrations in case of leaks.

The hydrogen sulfide removal section of the biofilter was seeded with recycle liquid obtained from a working hydrogen sulfideremoving biotrickling filter, operated at the Joint Water Pollution Control Plant of the Los Angeles County Sanitation Districts. The MTBE removal sections were seeded with an MTBE-degrading culture maintained by the University of California at Davis.

The hydrogen sulfide and MTBE removal sections were initially operated as separate, independent units receiving either hydrogen sulfide or MTBE as single pollutants for periods of 124 and 236 days, respectively. Separate start-up was done to study the removal of hydrogen sulfide and MTBE as single pollutants without potential cross-inhibition by the presence of the other pollutants. Day 0 of the experiment run was the day the MTBE removal sections were seeded and started. Using the same time scale, the hydrogen sulfide section was seeded and started on day 112, and all sections were combined on day 236 to investigate simultaneous treatment of a mixture of MTBE and hydrogen sulfide. The gas flowrate was measured in the combined air stream prior to entering

# Table 1—Nutrient solution for laboratory tests.

| Nutrient                                                       | Concentration (mg/L) |
|----------------------------------------------------------------|----------------------|
| Monobasic potassium phosphate, KH <sub>2</sub> PO <sub>4</sub> | 3470                 |
| Dibasic potassium phosphate, K <sub>2</sub> HPO <sub>4</sub>   | 4267                 |
| Sodium nitrate, NaNO <sub>3</sub>                              | 2335                 |
| Magnesium sulfate, MgSO <sub>4</sub> ·7H <sub>2</sub> O        | 460                  |
| Calcium chloride, CaCl <sub>2</sub> ·2H <sub>2</sub> O         | 18                   |
| Ferrous sulfate, FeSO <sub>4</sub> ·7H <sub>2</sub> O          | 1                    |
| Boric acid, H <sub>3</sub> BO <sub>3</sub>                     | 0.3                  |
| Cobaltous chloride, CoCl <sub>2</sub> ·6H <sub>2</sub> O       | 0.2                  |
| Zinc sulfate, ZnSO <sub>4</sub> .7H <sub>2</sub> O             | 0.1                  |
| Manganese chloride, MnCl <sub>2</sub> .4H <sub>2</sub> O       | 0.03                 |
| Sodium molybdate, Na2MoO4·2H2O                                 | 0.03                 |
| Nickel chloride, NiCl <sub>2</sub> ·6H <sub>2</sub> O          | 0.02                 |
| Cupric chloride, CuCl <sub>2</sub> ·2H <sub>2</sub> O          | 0.01                 |

the biofilter unit. The MTBE removal performance was determined at empty bed retention times (EBRTs) of 15 to 60 seconds and inlet concentrations ranging between 20 and 180 ppm<sub>v</sub> (73 to 660 mg/m<sup>3</sup>). The hydrogen sulfide section was operated at an EBRT of 15 seconds and hydrogen sulfide inlet concentrations of up to 70 ppm<sub>v</sub> (99 mg/m<sup>3</sup>). Simultaneous treatment of hydrogen sulfide and MTBE by the combined biofilter sections, as indicated in Figure 1, was investigated during days 236 to 260.

**Pilot-Scale Experiments.** The Hyperion Treatment Plant is the primary wastewater treatment facility in Los Angeles, covering a service area of 1600 km<sup>2</sup> that is inhabited by approximately 3.8 million people. The flow to the plant averages approximately  $1.4 \times 10^6$  m<sup>3</sup>/d, all of which receives primary and secondary treatment, the secondary being a high-purity oxygen activated-sludge system. Experiments with the pilot biofilter were performed at the headworks building of the plant, where  $1.7 \times 10^5$  m<sup>3</sup>/h of ventilation air is currently being treated in chemical scrubbers that use sodium hydroxide and hypochlorite.

The pilot biofilter (diameter of 0.61 m and a height of 1.8 m) was constructed based on the results obtained from laboratory-scale experiments (Figure 2). The first section (bottom) was 0.25-m deep and designated for removal of hydrogen sulfide. The second section (top), for VOC removal, was 0.75-m deep. Both sections



Figure 2—Schematic of pilot biofilter at Hyperion Treatment Plant (S1, S2, and S3 are sample locations).



Figure 3—Removal of MTBE in the laboratory at EBRTs of 15 to 60 seconds (days 160 to 236, operation as single unit for removal of MTBE only; days 236 to 260, operation as a combined unit for removal of hydrogen sulfide and MTBE).

contained a mixture of compost, perlite, and crushed oyster shells as the packing material, similar to the packing material in the laboratory-scale biofilter previously described. Seeding of the packing was with the recycle liquid of a hydrogen sulfidedegrading biotrickling filter. The two sections were separated by a plenum and each section had an independent, timer-controlled system for supply of secondary effluent water through permeable soaker hoses on top of each section. Secondary effluent was supplied once a day for a period of approximately 10 minutes to provide moisture and nutrients at an approximate rate of 2 L/min to each of the hydrogen sulfide and VOC removal sections. Excess water was drained from the biofilter through an outlet port located at the bottom of the first section.

The available pressure in the headworks ventilation air discharge line was sufficient to provide an initial average slip-stream of 42.5 m<sup>3</sup>/h to the bottom of the biofilter (up-flow configuration) out of a total of  $1.7 \times 10^5$  m<sup>3</sup>/h generated by the headworks facility. A gas flowrate of 42.5 m<sup>3</sup>/h corresponds to an overall EBRT in the biofilter of 25 seconds. Actual gas flowrates to the biofilter during the course of the experiments were measured with an anemometer positioned in the inlet air stream of the biofilter. During 10 months of operation of the biofilter, increasing pressure drops over the



Figure 4—Steady-state MTBE elimination capacity of 25-cm sections (EBRT of 15 seconds per section) of biofilter as determined over days 177 to 236 (solid line for complete removal).



Figure 5—Hydrogen sulfide removal in the first section of the laboratory biofilter at an EBRT of 15 seconds (seeding on day 112, after which operation was as a separate unit for removal of hydrogen sulfide only; in-line placement of this unit with MTBE removal sections on day 236).

biofilter caused a reduction of the gas flowrate and a gradual increase of the average EBRT to 52 seconds ( $20.4 \text{ m}^3/\text{h}$ ). The waste air to the biofilter contained between 10 to 50 ppm<sub>v</sub> of hydrogen sulfide as the principal odor-causing agent as well as a broad variety of chlorinated and nonchlorinated VOCs in concentrations ranging from 0 to 150 ppb<sub>v</sub>. Performance of the biofilter was determined during 10 months of operation, with frequent analysis of the inlet and outlet air for VOCs and hydrogen sulfide and VOCs was increased to once every few hours to determine the short-term performance. In addition to routine

operations with unmodified gas from the headworks, several brief tests were conducted regarding biofilter performance on gas spiked with higher concentrations of various pollutants. One test used toluene; another used gasoline, which provided a mixture of benzene, toluene, and xylenes; and a third test used a combination of gasoline, dichloromethane, and trichloroethylene.

Analytical Methods. Gas-phase MTBE concentrations in laboratory-scale experiments were determined by analysis using a gas chromatograph (model 14A, Shimadzu Scientific Instruments, Columbia, Maryland) equipped with a 0.5-mL gas sampling loop, a 30-m-long (0.53-mm i.d.) megabore column (model DB-



Figure 6—Concentration profiles of MTBE before and after introduction of hydrogen sulfide oxidation system.



Time (hour)

Figure 7—Long- and short-term hydrogen sulfide removal performance in pilot tests.

624, S & W Scientific, Folsom, California), and a flame-ionization detector. Hydrogen sulfide concentrations in laboratory- and pilot-scale experiments were directly determined in inlet and outlet air streams by using a Jerome 631-X hydrogen sulfide analyzer (Arizona Instruments, Tempe, Arizona). Volatile organic compound removal in the pilot biofilter was determined on a semi-weekly basis by sampling the inlet and outlet air in 10-L Tedlar bags for approximately 4 minutes. Samples were typically analyzed within 24 hours according to U.S. Environmental Protection

Agency method TO-14 using a gas chromatograph equipped with photoionization and electrolyte conductivity detectors. Concentrations of organic reduced sulfur compounds were determined (Performance Analytical, Inc., Simi Valley, California) after 253 days of operation of the pilot biofilter. Analyses were done in triplicate using a gas chromatograph with a chemiluminescence detector. Grab samples were taken the same day and analyzed by an eight-member panel (Odor Science & Engineering, Bloomfield, Connecticut) for odor dilution-to-threshold (D/T) ratios and odor

|                                      | Mean $\pm$ standard deviation |                      |                        |  |
|--------------------------------------|-------------------------------|----------------------|------------------------|--|
| Pollutant                            | Inlet concentration           | Outlet concentration | Removal efficiency (%) |  |
| Hydrogen sulfide (ppm <sub>v</sub> ) |                               |                      |                        |  |
| Long-term                            | 23 ± 9                        | 0.14 ± 0.31          | 99 ± 2                 |  |
| Short-term                           | 26 ± 8                        | 0.37 ± 0.34          | 98 ± 1                 |  |
| Volatile organic compounds (ppk      | o <sub>v</sub> )              |                      |                        |  |
| Short-term                           |                               |                      |                        |  |
| Benzene                              | 8 ± 3                         | 2 ± 2                | 74 ± 23                |  |
| Toluene                              | 68 ± 18                       | 12 ± 10              | 79 ± 20                |  |
| Xylenes                              | 79 ± 35                       | 31 ± 21              | 56 ± 28                |  |
| Dichlorobenzenes                     | $14 \pm 4$                    | 11 ± 4               | 18 ± 17                |  |
| Dichloromethane                      | 42 ± 27                       | 38 ± 24              | 5 ± 21                 |  |
| Chloroform                           | 74 ± 19                       | 74 ± 20              | $0 \pm 4$              |  |
| Tetrachloro ethylene                 | 79 ± 24                       | 80 ± 24              | $-1 \pm 2$             |  |
| Trichloro ethylene                   | 9 ± 2                         | 9 ± 2                | 0 ± 6                  |  |

## Table 2—Summary of performance during pilot tests at the Hyperion Treatment Plant (see Figures 7 and 8).

intensity. Gas flowrates to the biofilter were regularly determined with an Omega anemometer (model HHF300A, Stamford, Connecticut).

## Results

**Laboratory-Scale Experiments.** *Removal of MTBE as Sole Pollutant.* Removal of MTBE was poor during the first 2 months of operation, presumably because of a nutrient limitation. Additional nitrogen supply and reseeding of the biofilter after 2 months increased the performance, until an elimination capacity of 8.2 g/(m<sup>3</sup>·h) was observed after 108 days of operation. Subsequent experiments focused on variation of the gas flowrate and MTBE inlet concentration to determine the maximum performance.

Biofilter performance from days 160 to 260 is shown in Figure 3. During this period the EBRT was maintained at 60 seconds and the MTBE inlet concentration was varied between 20 and 180  $ppm_v$  to determine the elimination capacity. Removal of MTBE was complete under most conditions and breakthrough of MTBE was only observed between days 206 and 210 when the MTBE inlet concentration was increased to 180 ppm<sub>v</sub>. Figure 4 shows the mass of MTBE removed in the various 0.25-m sections of the biofilter during steady-state operation as a function of the sectional MTBE mass loading. The EBRT in each section was 15 seconds. Removal of MTBE was complete up to a loading rate of 12.5 g/( $m^3 \cdot h$ ). Higher loading rates resulted in higher elimination capacities, but only at reduced removal efficiency. A maximum elimination capacity of 62.5 g/( $m^3 \cdot h$ ) was observed at a loading rate of 167 g/( $m^3 \cdot h$ ), corresponding to 37.5% removal.

*Removal of Hydrogen Sulfide as Sole Pollutant.* The hydrogen sulfide removal section was operated for approximately 4 months as a separate unit before this section was plumbed to precede the MTBE removal sections. The hydrogen sulfide removal performance at an EBRT of 15 seconds is shown in Figure 5 (days 112 to 236). The initial inlet hydrogen sulfide concentration was 9 ppm<sub>v</sub> and was increased to 25 ppm<sub>v</sub>, which is, in most cases, the approximate concentration expected in POTW waste air. Nine days after start-up, removal of hydrogen sulfide was complete with no detectable hydrogen sulfide in the outlet air (less than 1 ppb<sub>v</sub>). Hydrogen sulfide removal was consistently greater than 99% during 4 months of operation. In addition, complete removal of hydrogen sulfide spikes up to a concentration of 70 ppm<sub>v</sub> (not

shown) indicated that higher hydrogen sulfide loads can be effectively treated at a residence time of 15 seconds.

Removal of a Mixture of Hydrogen Sulfide and MTBE. On day 236, the MTBE and hydrogen sulfide sections were plumbed together. Examination of Figure 5 (days 236 to 260) reveals that the presence of 70 ppm<sub>v</sub> of MTBE had no effect on hydrogen sulfide removal in the first section. Similarly, there was little or no effect on MTBE removal when the hydrogen sulfide removal unit was placed in line with MTBE removal sections (days 236 to 260) in Figure 3). Concentration profiles of MTBE for VOC removal through the four sections remained essentially the same (Figure 6). This would be expected because hydrogen sulfide was completely removed in the first section (Figure 5) and no significant breakthrough of hydrogen sulfide to the MTBE-degrading sections was observed.

**Pilot-Scale Experiments.** Gas Flowrate and Empty Bed Retention Time. Large fluctuations in the gas flowrate through the biofilter were observed, with rates varying between 15 and 73 m<sup>3</sup>/h and an overall average of 31 m<sup>3</sup>/h. These variations resulted from increasing pressure drops across the biofilter packing (long-term effect) as well as by accumulation of water and loose packing material in the inlet air duct (short-term effect). On a few occasions (days 177 to 184, ~ day 211, ~ day 235), the inlet air duct became clogged causing large reductions of the gas flowrate through the biofilter. As a consequence of variable gas flowrates, similar fluctuations were seen for the EBRT. The average EBRT in the lower hydrogen sulfide removal section was 10 seconds (range of 3.6 to 17 seconds). The average EBRT based on the total packed bed volume (first and second sections) was 42 seconds (range of 14 to 69 seconds).

*Hydrogen Sulfide Removal.* Long-term performance of hydrogen sulfide removal in the pilot biofilter is shown in Figure 7a. As in the laboratory study, a rapid start-up was observed with greater than 99% removal within 2 weeks of operation. During the experiment, the average hydrogen sulfide removal efficiency was 99.3% at hydrogen sulfide inlet concentrations fluctuating between 10 and 50 ppm<sub>v</sub>. The hydrogen sulfide outlet concentration averaged 0.14 ppm<sub>v</sub>. The removal efficiency temporarily dropped to 95% during days 60 to 66. An interruption of water supply to the biofilter during this period may have caused a relatively poor performance. Measurements of hydrogen sulfide in the plenum between the hydrogen sulfide and VOC removal sections indicated



Figure 8—Short-term performance of VOC removals in pilot tests.



Figure 8—(Continued)

|                            |          | Inlet concentration (                | Inlet concentration (ppb <sub>v</sub> ) |                           | Removal efficiency (%) |  |
|----------------------------|----------|--------------------------------------|-----------------------------------------|---------------------------|------------------------|--|
| voc                        | n        | Mean ± standard deviation            | Range                                   | Mean ± standard deviation | Range                  |  |
| Spiking with toluene, day  | s 133–1  | 36                                   |                                         |                           |                        |  |
| Benzene                    | 7        | 6 ± 3                                | 3–12                                    | 27 ± 22                   | 3–59                   |  |
| Toluene                    | 6        | 24 921 ± 15 466                      | 4817–41 617                             | 59 ± 37                   | 14–99                  |  |
| Xylenes                    | 7        | 77 ± 31                              | 40-118                                  | 55 ± 28                   | 19–93                  |  |
| Dichlorobenzenes           | 7        | 6 ± 5                                | 2–14                                    | $58 \pm 36$               | 18–100                 |  |
| Dichloromethane            | 7        | 31 ± 14                              | 17–49                                   | $59 \pm 44$               | -12-95                 |  |
| Chloroform                 | 7        | 70 ± 18                              | 53-100                                  | 6 ± 15                    | -9-36                  |  |
| Tetrachloro ethylene       | 7        | 49 ± 17                              | 24-72                                   | 20 ± 36                   | -11-90                 |  |
| Trichloro ethylene         | 7        | 4 ± 2                                | 2–7                                     | 13 ± 24                   | -9-62                  |  |
| Spiking with gasoline, da  | ys 196–  | 204                                  |                                         |                           |                        |  |
| Benzene                    | 7        | 330 ± 144                            | 16–483                                  | 73 ± 11                   | 54–88                  |  |
| Toluene                    | 7        | 1778 ± 721                           | 163-2472                                | 75 ± 14                   | 49–97                  |  |
| Xylenes                    | 7        | 2339 ± 875                           | 378-3298                                | 50 ± 16                   | 26-68                  |  |
| Dichlorobenzenes           | 7        | 16 ± 4                               | 10–21                                   | 30 ± 17                   | 8–50                   |  |
| Dichloromethane            | 7        | 46 ± 19                              | 24–70                                   | 81 ± 7                    | 68–92                  |  |
| Chloroform                 | 7        | 76 ± 12                              | 54–86                                   | $4 \pm 5$                 | -4-12                  |  |
| Tetrachloro ethylene       | 7        | 122 ± 60                             | 43-226                                  | $1 \pm 5$                 | -7-10                  |  |
| Trichloro ethylene         | 0        |                                      |                                         |                           |                        |  |
| Spiking with gasoline, did | chlorome | ethane, and trichloro ethylene, days | s 217–226                               |                           |                        |  |
| Benzene                    | 5        | 216 ± 29                             | 183–246                                 | $17 \pm 11$               | 5–33                   |  |
| Toluene                    | 6        | 1093 ± 202                           | 900-1311                                | 26 ± 11                   | 9–39                   |  |
| Xylenes                    | 6        | 1425 ± 265                           | 1116–1710                               | 41 ± 9                    | 28–53                  |  |
| Dichlorobenzenes           | 2        | 9 ± 0.2                              | 8–9                                     | 4 ± 0.1                   | 3–4                    |  |
| Dichloromethane            | 6        | 7097 ± 2527                          | 4064–9881                               | $-31 \pm 12$              | -5017                  |  |
| Chloroform                 | 2        | 62 ± 16                              | 51–73                                   | $-2 \pm 4$                | -5-1                   |  |
| Tetrachloro ethylene       | 3        | 97 ± 26                              | 75–125                                  | $-13 \pm 19$              | -34-4                  |  |
| Trichloro ethylene         | 5        | 3191 ± 1047                          | 1905–4199                               | $-49 \pm 11$              | -6533                  |  |

## Table 3—Volatile organic compound removal with spiking during pilot tests at the Hyperion Treatment Plant.

that hydrogen sulfide removal occurred in the first section; hence, penetration of hydrogen sulfide to the section designated for VOC removal was negligible. The hydrogen sulfide concentration after the first section was often less than 0.1 ppm<sub>v</sub>. The short-term performance data, presented in Figure 7b, show a general pattern of increasing hydrogen sulfide inlet concentrations as the day progressed. Despite these large fluctuations, the dynamic response of the biofilter proved adequate by consistently removing hydrogen sulfide to an average and relatively constant outlet concentration of 0.37 ppm<sub>v</sub> during these short-term experiments. The short- and long-term performance of hydrogen sulfide removal is summarized in Table 2.

Volatile Organic Compound Removal. Air streams were routinely analyzed for 15 VOCs, of which only toluene, benzene, xylenes, dichlorobenzenes, methylene chloride, chloroform, trichloro ethylene, and tetrachloro ethylene were present in concentrations consistently higher than the detection limit (0.5, 1, or 2 ppb<sub>v</sub>). Vinylchloride, vinylidenechloride, carbontetrachloride, 1,1dichloroethane, 1,2-dichloroethane, chlorobenzene, and methylchloroform were always below the detection limit. Volatile organic compound removal was evaluated on a semiweekly basis and more frequently on selected days at intervals of 3 hours. Representative examples of VOC removal over a period of 1 month are presented in Figure 8, whereas average VOC removal efficiencies are summarized in Table 2. Aromatic VOCs such as benzene, toluene, and xylenes were removed at average efficiencies of 74, 79, and 56%, respectively. Similar performance was observed throughout the 10-month experiment.

Removal was low to nil for chlorinated VOCs depending on the particular compound. No removal was observed for chloroform, trichloro ethylene, and tetrachloro ethylene. Moderate removal of dichlorobenzenes was observed intermittently so that the average removal of 18% does not seem statistically significant. Highly fluctuating removal of dichloromethane (25 to 75%) was observed, but only after 200 days of operation; the table shows that the mean removal percentage for this compound for the whole period is also low.

*Spiking Experiments.* In addition to the observations of filter performance in treating unmodified headworks waste air, during several periods that lasted a few days each the air was spiked with much higher concentrations of several VOCs to test filter response to a wider range of gas compositions. Results are shown in Table 3.

The first test consisted of 4 days of spiking with a high concentration of toluene on days 133 to 136. As shown, the removal percentages of benzene and toluene decreased, although greatly increased removal percentages of dichlorobenzenes and dichloromethane were observed. It must be noted that the reduced removal percentage for toluene represents a much higher absolute removal than in the unspiked measurements.

When gasoline was spiked on days 196 to 204, a lower concentration was used than in the toluene spiking test, and the removal percentages for the compounds in gasoline (benzene, toluene, and xylenes) were not much different from the percentages in Table 2. However, the removal of dichloromethane was even better than in the toluene spiking test. Combining dichloromethane and trichloro ethylene with the gasoline during the third spiking

Table 4—Performance during pilot tests on day 253 (range values are data from morning, afternoon, and evening determinations).

| Pollutant                                                                                                                               | Inlet                                                                                                                                                                             | Removal<br>efficiency (%)                                      |
|-----------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|
| Sulfur compounds                                                                                                                        |                                                                                                                                                                                   |                                                                |
| Hydrogen sulfide<br>Carbonyl sulfide<br>Methyl mercaptan<br>Dimethyl sulfide<br>Carbon disulfide<br><i>tert</i> -Butyl mercaptan        | 15–24 ppm <sub>v</sub><br>19–52 ppb <sub>v</sub><br>149–165 ppb <sub>v</sub><br>8–12 ppb <sub>v</sub><br>6–8 ppb <sub>v</sub><br><2–3 ppb <sub>v</sub>                            | 99–99.8<br>30–33<br>91–94<br>0–21<br>32–36<br>>31 <sup>a</sup> |
| VOCs<br>Benzene<br>Toluene<br>Xylenes<br>Dichlorobenzene<br>Dichloromethane<br>Chloroform<br>Tetrachloro ethylene<br>Trichloro ethylene | 0.5–1 ppb <sub>v</sub><br>20–60 ppb <sub>v</sub><br>40–150 ppb <sub>v</sub><br>4–8 ppb <sub>v</sub><br>NA <sup>b</sup><br>50–75 ppb <sub>v</sub><br>50–140 ppb <sub>v</sub><br>NA | 0–50<br>42–86<br>40–75<br>43–60<br>NA<br>0–17<br>0–9<br>NA     |
| Odor                                                                                                                                    |                                                                                                                                                                                   |                                                                |
| Odor reduction                                                                                                                          | 35 000-46 000 D/T                                                                                                                                                                 | 99–99.4                                                        |

<sup>a</sup> This compound was present in a concentration close to the detection limit. An accurate estimation of the removal efficiency is not possible.

<sup>b</sup> NA = not available.

test on days 217 to 226 resulted in poor performance for all of the VOCs. When the concentration of a VOC was higher in the outflow than in the inflow, causing negative removal efficiencies, the biofilter was either producing the VOC or releasing some that was absorbed earlier. In the case of chlorinated VOCs, desorption is generally more plausible than synthesis. However, this study did not attempt to determine the details of the processes performed by the culture on any of the detected compounds.

Overall Performance. Table 4 presents an overview of the overall performance of the pilot biofilter with simultaneous measurement of the removal of hydrogen sulfide, organic sulfur compounds, VOCs, and odor. This experiment was performed 253 days after start-up, at which time the overall EBRT was 33 seconds. Removal of hydrogen sulfide was greater than 99%. As hydrogen sulfide was present in concentrations up to three orders of magnitude higher than most other pollutants, it was the principal odorous compound. Hence, odor removal correlated with hydrogen sulfide removal, and an odor reduction of greater than 99% was observed. For organic sulfur compounds, good removal was also observed for methyl mercaptan and possibly tert-butyl mercaptan, but removal of dimethyl sulfide and carbon disulfide was less than 40%. Removal of nonchlorinated VOCs was approximately 40 to 86%, whereas, in general, removal of chlorinated VOCs was in agreement with the results presented in Figure 8.

## Discussion

The results demonstrate that a mixture of MTBE and hydrogen sulfide can be effectively removed by passing the waste air through a biofilter. Methyl *tert*-butyl ether is a compound that for a long time has been considered poorly biodegradable. However, Fortin and Deshusses (1999) recently demonstrated its biodegradation and removal from contaminated air. In addition, the University of California at Davis recently succeeded in isolating a pure species that can use MTBE as the sole source of carbon and energy. This species was used to seed our laboratory biofilter. Although a relatively long adaptation period was required for start-up of the biofilter, the final maximum MTBE elimination capacity of 62 g/(m<sup>3</sup>·h) is comparable to the observed elimination capacities for other, more biodegradable VOCs (Devinny et al., 1998). This demonstrates the feasibility of biofilters for MTBE treatment when the packing is seeded with pure cultures capable of MTBE biodegradation.

Effective treatment of a mixture of hydrogen sulfide and VOCs may require a biofilter with separate sections for removal of each class of pollutants. The reason for this is potential inhibition of VOC removal by low pH resulting from sulfuric acid production from hydrogen sulfide oxidation. Although VOC biodegradation in low-pH biofilters has been observed (Webster et al., 1997), significant removal was only observed after a long adaptation period and the removal efficiencies obtained were not always optimum. A possible solution is a two-stage system consisting of an acid biotrickling filter for hydrogen sulfide removal followed by VOC treatment in a biofilter (Chitwood et al., 1999). The biofilter design presented here is based on a similar principle of spatially separated removal of hydrogen sulfide and VOCs. However, by housing the sections for hydrogen sulfide and VOC in one bioreactor, significant reductions in capital costs and process complexity can be achieved. For both the laboratory and pilot biofilter, no cross interference between hydrogen sulfide and MTBE or VOC removal was observed. Because hydrogen sulfide removal in biofilters is fast, it is removed first in the biofilter. Biodegradation of MTBE in the first section is unlikely to occur because low pH inhibits MTBE biodegradation. Complete MTBE removal is achieved in the sections following the hydrogen sulfide oxidation section without interference by the preceding hydrogen sulfide removal section, as demonstrated by the MTBE concentration profiles presented in Figure 6. A crucial aspect in the design is that the hydrogen sulfide removal section should be large enough for complete removal of hydrogen sulfide to prevent its penetration into VOC removal sections. Separation of hydrogen sulfide and MTBE removal also allows for independent water control of each section. Using an upward flow and positioning the hydrogen sulfide removal section below the VOC removal section also prevents acidic leachate from trickling into the VOC removal section.

Hydrogen sulfide removal performance data from the pilot test at the Hyperion Treatment Plant were consistent with that of the laboratory biofilter. The pilot biofilter removed 10 to 50 ppm<sub>v</sub> of hydrogen sulfide at greater than 99% efficiency and at a sectional EBRT of 3.7 to 17 seconds, depending on the actual gas velocity. During both short- and long-term experiments, outlet concentrations were always less than 1 ppm, which is the limit set by the SC-AQMD at that site. Biofilters are, therefore, an attractive alternative to chemical scrubbers because comparable hydrogen sulfide and odor removal can be achieved but at a lower cost and with less chemical consumption. As summarized by Iranpour et al. (2001), the number of biofilters deployed at POTWs is rapidly increasing. However, there is concern about the stability of biofilters when treating high loads of hydrogen sulfide over several months or years. During this study, increasing pressure drops over the biofilter, which is an indication of packing deterioration and air channeling, were observed. This may be due to sulfuric acid production and, hence, biotrickling filters with inert packing may

be preferred for treating high hydrogen sulfide loads (Cox et al., 2002), although the maximum hydrogen sulfide load for costeffective biofilter use remains to be defined.

In addition to the near complete reduction of odor and hydrogen sulfide, significant removal of nonchlorinated VOCs was observed. Removal of dichloromethane and dichlorobenzenes was observed when spiking raised the concentrations of nonchlorinated VOCs. This difference may be tentatively attributed to a change in culture resulting from the additional nonchlorinated VOCs. Other chlorinated VOCs were not significantly removed. Volatile organic compound removal primarily depends on the biodegradability of the species. Laboratory studies with biofilters and biotrickling filters by other researchers have shown high removal rates of toluene, benzene, xylenes, dichlorobenzenes, and dichloromethane, which is consistent with the results of the present study. Treatment of chloroform, trichloro ethylene, and tetrachloro ethylene remains a challenge. Although Devinny et al. (1996), Webster et al. (1996), and Wolstenholme and Finger (1994) demonstrated removal of these compounds in biofilters, removal requires either co-metabolism or anaerobic conditions, which are difficult to control in biofilters.

## Conclusions

The design of the biofilter with separate sections for hydrogen sulfide and VOC removal allowed for effective treatment of waste air containing mixtures of hydrogen sulfide and VOCs in a single bioreactor. This was observed both in laboratory tests in which the VOC was MTBE and in pilot tests at the Hyperion Treatment Plant, where the headworks air contained several chlorinated and nonchlorinated VOCs. Thus, the biofilter not only reduces odor nuisance by near complete removal of hydrogen sulfide, but also reduces the emission of air toxics and VOCs. The removal of nonchlorinated VOCs and some of the chlorinated VOCs could be significant to POTWs as they could get credit toward overall removal of cumulative VOCs by regulatory agencies. This is particularly true because similar removal efficiencies for nonchlorinated VOCs are observed over several orders of magnitude in the concentrations of these compounds as long as incoming chlorinated VOC concentrations are modest. The removal of VOCs is a clear advantage of biofilters over chemical scrubbers that only remove hydrogen sulfide; hence, the use of biofilters may help in further reducing air emissions from POTWs.

## Acknowledgments

**Credits.** This project was funded by the Water Environment Research Foundation (project # 98-CTS-4). In-kind contribution was provided by the City of Los Angeles, California, Environmental Monitoring Division laboratories, Hyperion Treatment Plant staff, and, in particular, the Applied Research Group of the Wastewater Engineering Services Division.

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Submitted for publication October 1, 2001; revised manuscript submitted July 16, 2002; accepted for publication January 13, 2003.

The deadline to submit Discussions of this paper is January 15, 2004.

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