

# **Single-Stage H<sub>2</sub>S and VOC Removal in Biotrickling Filters and Biofilters: A Comparative Study at the Hyperion Treatment Plant**

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## **ABSTRACT**

The present paper compares a pilot-scale biofilter and biotrickling filter for the combined removal of H<sub>2</sub>S and VOCs at a wastewater treatment plant. The results obtained over a six-month period demonstrate that both technologies removed H<sub>2</sub>S with >98% efficiency at inlet concentrations ranging between 10 and 50 ppm<sub>v</sub>. The influent waste gas also contained trace concentrations (10-150 ppb<sub>v</sub>) of toluene, benzene, xylenes, dichlorobenzene, chloroform and perchloroethylene. From these, toluene, benzene and xylenes were removed at efficiencies ranging from 50 to 80%. No significant removal was observed of the chlorinated VOCs in either reactor. Overall, the biofilter seemed to perform better in removing low concentrations of VOCs, whereas the biotrickling filter may be more efficient for removal of high H<sub>2</sub>S concentrations.

While H<sub>2</sub>S removal is relatively fast at the concentrations prevailing at wastewater treatment plants, research to enhance VOC removal should be considered, where emissions of trace concentrations or VOCs and air toxics is a concern.

## **INTRODUCTION**

Apart from odorous compounds such as reduced sulfur compounds, waste air from publicly owned treatment works (POTWs) contains a broad variety of volatile organic compounds (VOCs). Because of stricter federal and local air quality regulations, POTWs have been focusing their attention on quantifying and controlling VOCs and toxic air pollutants emitted from wastewater and solids handling processes. The effort has been greatest in the Southern California Air Basin, where New Source Review regulations for toxics have been effective since 1990. The upcoming regulations include the establishment of Maximum Achievable Control Technology (MACT) standards for POTWs as mandated under the Federal Clean Air Act Amendments of 1990. In addition, new regulations proposed by the South Coast Air Quality Management District (SCAQMD) include the requirement for POTWs to meet facility-based standards for existing sources.

Current practice of waste air treatment at POTWs is treatment in wet scrubbers. Though effective in removing odorous compounds such as H<sub>2</sub>S, scrubbers do not remove VOCs from the waste air, and, in fact, they even may generate certain chlorinated VOCs (Witherspoon, 1995). Treatment in biofilters or biotrickling filters, on the other hand, holds promise for efficient and cost-effective removal of both H<sub>2</sub>S and VOCs.

Odor removal in biofilters and biotrickling filters has been extensively studied (Webster, Iranpour *et al.*, 2001). Laboratory studies have demonstrated removal of many of the VOCs often found in POTWs' waste air (Webster *et al.*, 1996; Iranpour *et al.*, 2001). Most of these studies dealt with the treatment of single compounds. However, much less is known on the combined biological treatment of VOCs and odorous compounds such as H<sub>2</sub>S. In a demonstration project funded by the Water Environment Research Foundation, a comparative study was performed at the Hyperion Treatment Plant in Los Angeles to evaluate biofilters and biotrickling filters in their performance to reduce odor and VOC emissions. Previous studies have used two bioreactors in series (Chitwood *et al.*, 1999). In the first one, H<sub>2</sub>S is removed at a low pH in general by acid-tolerant *Thiobacillus* species. VOCs are removed by heterotrophic microorganisms in the second bioreactor, operated at a neutral pH. The challenge of the project at the Hyperion Treatment Plant is to combine H<sub>2</sub>S and VOC treatment in one bioreactor, and to determine the overall effectiveness of biotrickling filters and biofilters for this purpose.

## **MATERIALS & METHODS**

### **Site Description**

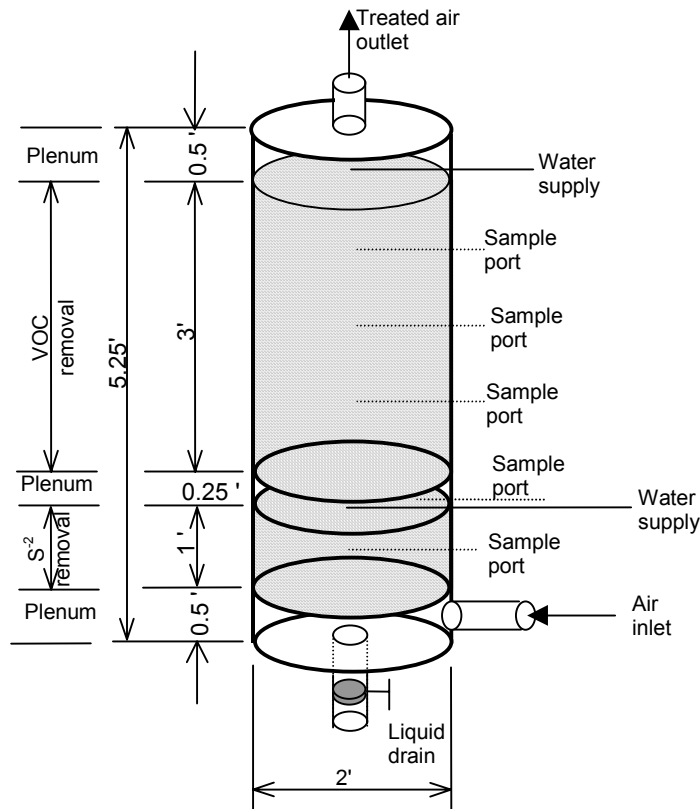
The Hyperion Treatment Plant (HTP) facility is approximately 15 miles southwest of downtown Los Angeles, California, along the coastline of the Santa Monica Bay. HTP treats about 330 mgd (1,250,000 m<sup>3</sup> per day) of raw sewage collected from four major sewer interceptors. HTP also receives solids discharged to the wastewater collection system by upstream plants. The plant is a full secondary facility, in which all effluent receives secondary treatment using the high purity oxygen activated system.

The first process step at HTP is screening of the wastewater through automatically raked bar screens at the Headworks facility. The entire Headworks' process air and building ventilation air at a total flow rate of 177,000 m<sup>3</sup>/h (104,000 cfm) is routed through single-stage packed tower chemical scrubbers. For this project, a small part of the Headworks' air is diverted to the pilot-scale units and after treatment routed back to the scrubbers. The available differential pressure was about 13 cm of water column. No blowers were required to operate the biofilter and biotrickling filter at the design empty bed residence times of 20 to 50 s.

### Design and Operation of the Pilot-Scale Biofilter and Biotrickling Filter

The biofilter (diameter 0.61 m; height 1.8 m) was designed for spatially separated removal of H<sub>2</sub>S and VOCs, as shown in Figure 1. The first section (bottom) was 0.25 m deep and designated for removal of H<sub>2</sub>S. The second section (top) for VOC removal was 0.75 m deep. The two sections were separated by a plenum and each section had an independent, timer-controlled system for water supply, consisting of permeable soaker hoses. Secondary effluent was supplied once a day for a period of about 10 min. Both sections contained a mixture of compost, crushed oyster shells and perlite as the packing material.

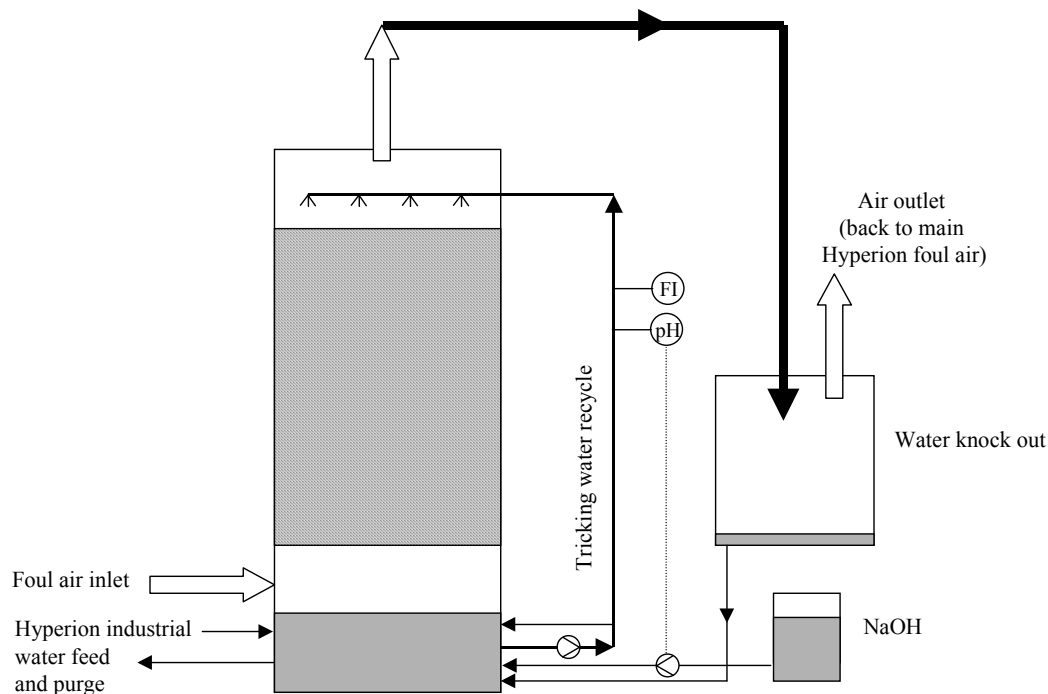
**Figure 1.** Schematic of the pilot-scale biofilter.



The biotrickling filter was constructed of 304 stainless steel with a diameter of 1.5 m and a height of 3.4 m (Figure 2), containing seven layers of a PVC COOLdek™ Munters 12060 structured packing with a specific surface area of 230 m<sup>2</sup>/m<sup>3</sup> and a porosity of 90-95%. The packing height was 2.1 m, resulting in a packed bed volume of 3.8 m<sup>3</sup>. A 0.75 HP pump was

used for continuous trickling of recycle liquid at a rate of approximately 1.4 m<sup>3</sup>/h (superficial liquid velocity of 0.8 m/h). The liquid was collected at the base of the reactor, containing approximately 0.6 m<sup>3</sup> of recycle liquid. The dynamic liquid hold-up in the packed bed section was estimated to be approximately 0.05 m<sup>3</sup>. Secondary effluent water was supplied as a source of nutrients and to purge produced sulfate. The feed rate was 6-12 L/min. A constant recycle liquid volume was maintained by an overflow outlet. Effluent feed and purge rates were comparable, indicating that evaporation losses were negligible. pH control was via a stand-alone Cole-Parmer pH controller, which actuated the metering of 0.75 M NaOH to the base of the reactor. Previous experiences with the biotrickling filter unit at a bathtub manufacturing facility and details on construction and economics have been presented elsewhere (Webster *et al.*, 1999; Deshusses and Webster, 2000).

**Figure 2** Schematic of the biotrickling filtration system.



## Experimental Set-Up

Experiments with the pilot-plant units started on April 3, 2000 (day 0 in graphs), on which day the biotrickling filter was inoculated with a mixture of raw influent sewage and recycle liquid of a H<sub>2</sub>S-degrading biotrickling filter. The bottom section of the biofilter was inoculated with recycle liquid from an H<sub>2</sub>S degrading biotrickling filter operated at the Joint Water Pollution Control Plant in Carson, California while the top section was not inoculated. Results are presented over a period of 180 days of continuous operation. The biofilter and biotrickling filter treated the same air from the Headworks' building at empty bed gas residence times (EBRT) of 20-50 s and 15-25 s, respectively. The fluctuations observed in the gas flow rates were probably due to slight variations of the pressure in the inlet air, and for the biofilter also to increasing headlosses across the packed bed. The biotrickling filter was initially operated without pH control. After 46 days, automatic pH control was initiated to maintain a pH of about 7.0. Due to

the poor buffering capacity of the recycle liquid at this pH, actual pH values were in general between 7 and 9.

Long-term performance of the reactors was determined on a (semi)-daily basis with determination of the gas flow rate and the pressure drop and analysis of H<sub>2</sub>S inlet and outlet concentrations. For the biotrickling filter, the recycle liquid pH, the secondary effluent feed rate and the purge rate were also recorded. VOC removal was determined on 4 selected days after 4 and 8 weeks of operation. VOCs as well as H<sub>2</sub>S were sampled at 3-hour intervals to determine the influence of fluctuating inlet concentrations on the removal efficiencies (short-term performance).

### **Analytical Procedures**

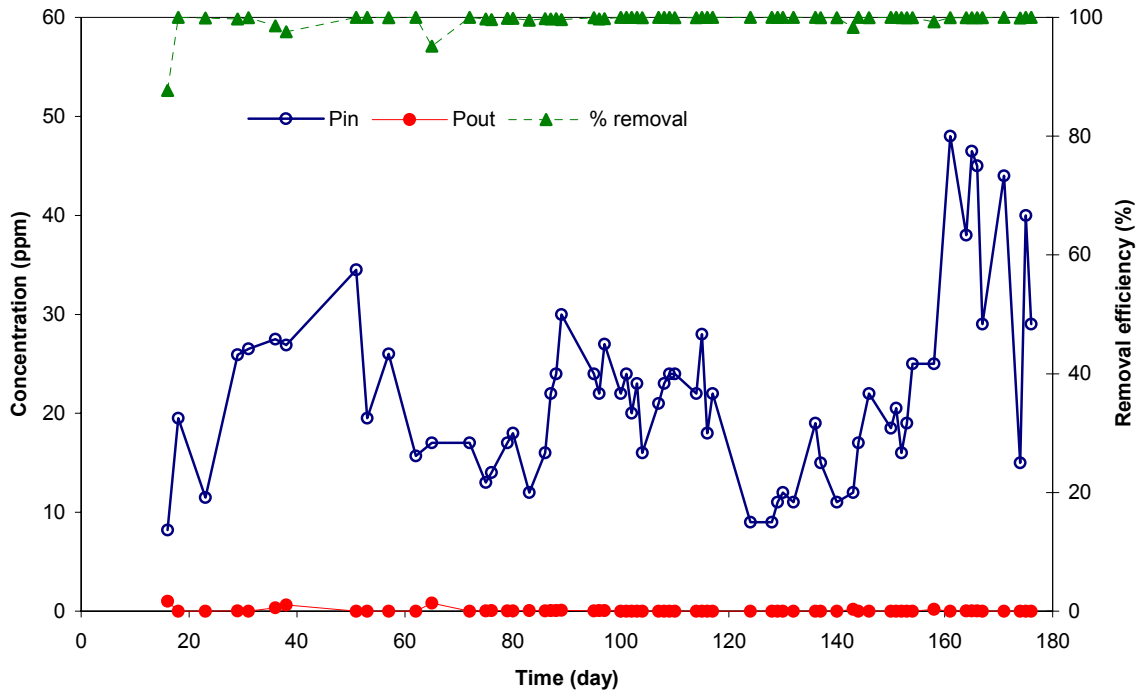
H<sub>2</sub>S was measured directly in inlet and outlet ducts with a model 621-X Jerome meter (Arizona Instruments, Phoenix, AZ) with a detection range of 0.001-50 ppm<sub>v</sub>. For VOC analyses, gas samples were collected in 10 L Tedlar bags and analyzed the same day by HTP's analytical department according to EPA method TO-14 using PID/ELCD. Each sample was analyzed for thirteen different VOCs. The following compounds in the inlet gas were always present in concentrations below or close to the method detection limit of 0.5-2 ppb<sub>v</sub>: vinyl chloride, 1,1-dichloroethene, trichloroethylene, 1,2-dichloroethane, and methyl chloroform. Removal efficiencies are reported for toluene, benzene, xylenes, methylene chloride, chloroform, perchloroethylene, and p-dichlorobenzene, which were present in concentrations substantially above the detection limit. Gas flow rates were determined at the inlet duct with a 1" Omega anemometer.

## **RESULTS**

### **H<sub>2</sub>S and VOC Removal in the Biofilter**

H<sub>2</sub>S samples were taken once a day, usually in the morning when the inlet concentration appeared to be the lowest of the day (see short-term performance). Apart from variations over the day, also seasonal variations in the H<sub>2</sub>S inlet concentration were observed (Figure 3), which were tentatively attributed to weather conditions and ambient temperatures. Figure 3 demonstrates close to 100% H<sub>2</sub>S removal in the biofilter at H<sub>2</sub>S inlet concentrations ranging between 10 and 50 ppm<sub>v</sub>. The start-up was fast, and complete removal was observed within 20 days. Outlet concentrations were in general below 0.05 ppm<sub>v</sub>. Periodical measurements of H<sub>2</sub>S between the two packing sections indicated that removal occurred in the first section designated for H<sub>2</sub>S removal and that penetration of H<sub>2</sub>S into the second section was minimal.

**Figure 3.** Long-term H<sub>2</sub>S removal in the biofilter (P=Pollutant=H<sub>2</sub>S)



The short-term performance of H<sub>2</sub>S removal in the biofilter on six selected days is presented in Figure 4. On most days, the inlet concentration was lowest in the morning and it increased during the day. No effect was observed on H<sub>2</sub>S outlet concentration, illustrating the immediate response of the biofilter to a rapid increase of the H<sub>2</sub>S inlet concentration.

**Figure 4.** Short-term H<sub>2</sub>S removal in the biofilter (P=Pollutant=H<sub>2</sub>S)

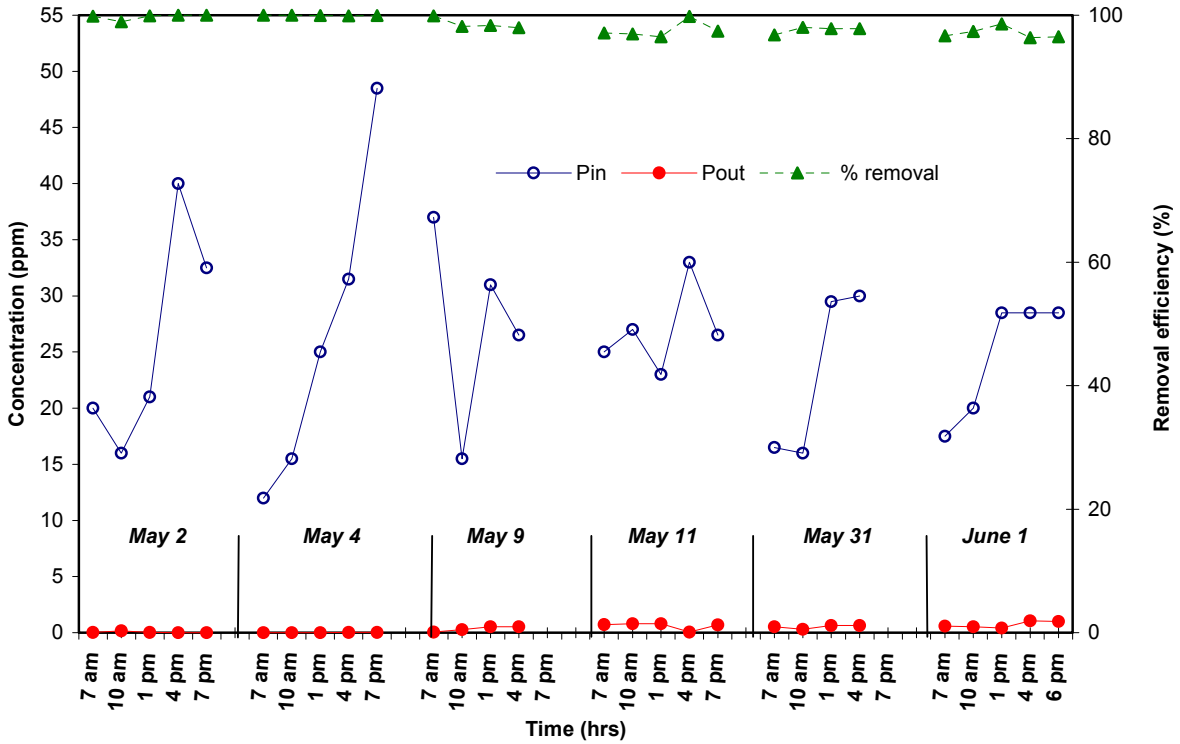


Figure 5. Short-term performance of VOC removal in the biofilter (May 2 to June 1 corresponds to days 29-59). Figure A, benzene; B, toluene; C, xylenes.

Figure 5a. VOC removal (P=Benzene) in the biofilter

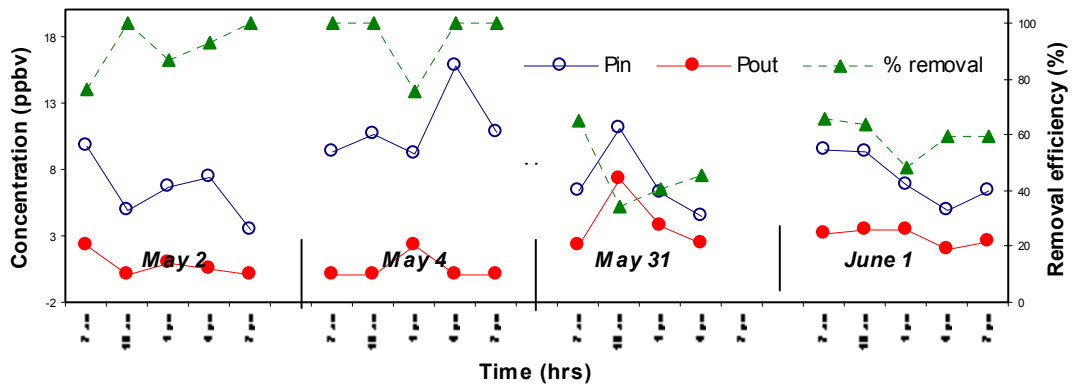


Figure 5b. VOC removal (Toluene) in the biofilter

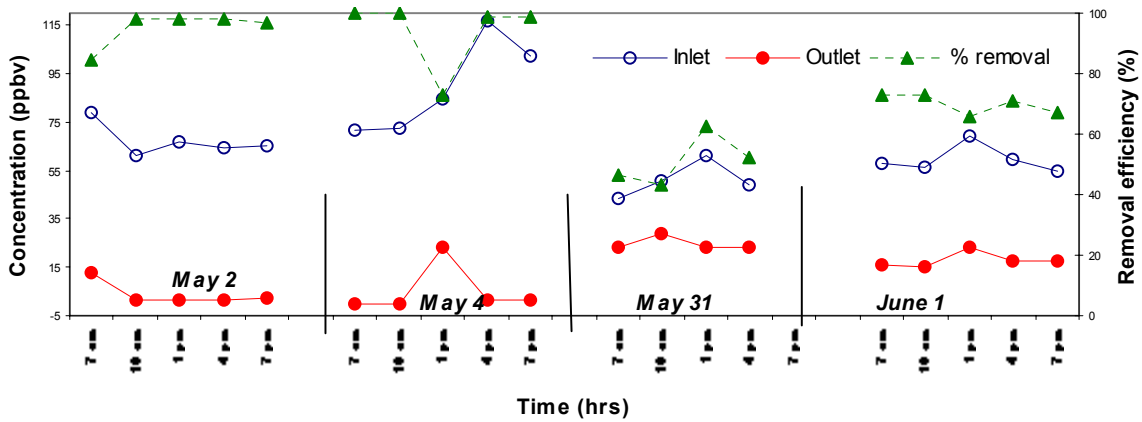
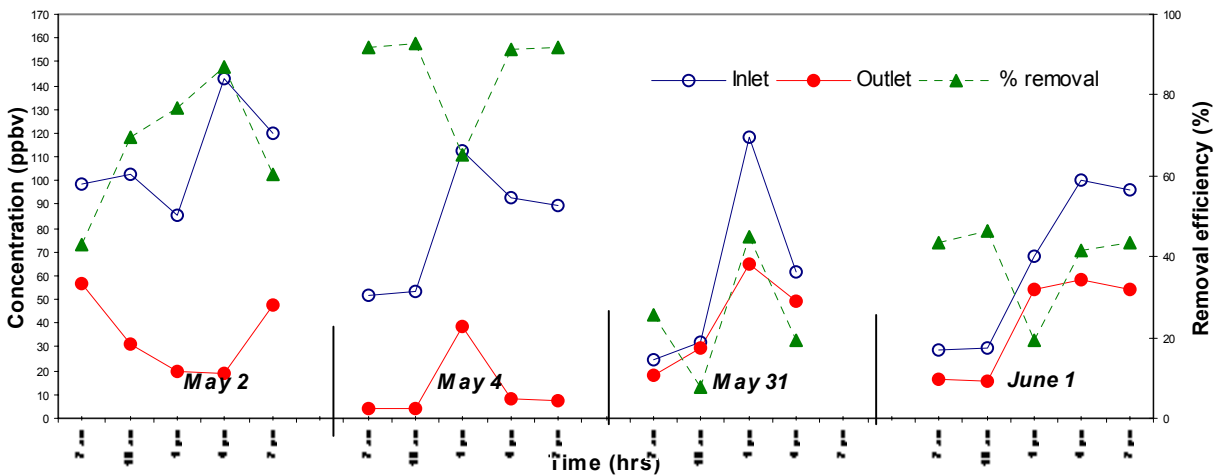


Figure 5c. VOC removal (Total Xylenes) in the biofilter

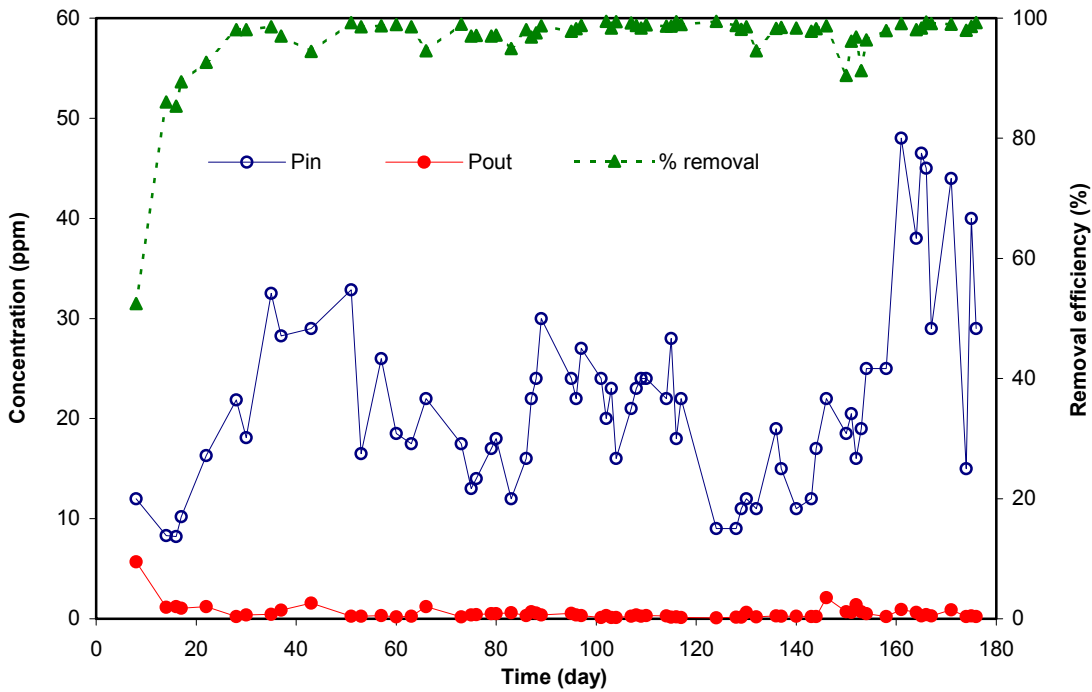


The major VOCs detected in HTP's Headworks waste air were toluene, benzene, xylenes, methylene chloride, chloroform, perchloroethylene and dichlorobenzene. Concentrations were in general between 5 and 150 ppb<sub>v</sub>, with large fluctuations observed for individual compounds and without any apparent correlation to the concentration of other VOC species or H<sub>2</sub>S. Non-chlorinated VOCs such as benzene, toluene and xylenes were removed at greater than 60% removal efficiencies during the first week of May, i.e., after 30 days of operation (Figures 5A to C). However, a substantial decrease of removal of these compounds was observed in the final week of May. Since the EBRT was the same during both sampling periods, we believe that the decline in the removal of aromatics was due to the failure of the water supply system and the partial drying of the packing material. The removal of the aromatic compounds increased after proper watering of the bed resumed. Removal of chlorinated VOCs (10-20 ppb<sub>v</sub> dichlorobenzene, 15-80 ppb<sub>v</sub> methylene chloride, 40-100 ppb<sub>v</sub> chloroform, 50-120 ppb<sub>v</sub> perchloroethylene) was not detected during either sampling period.

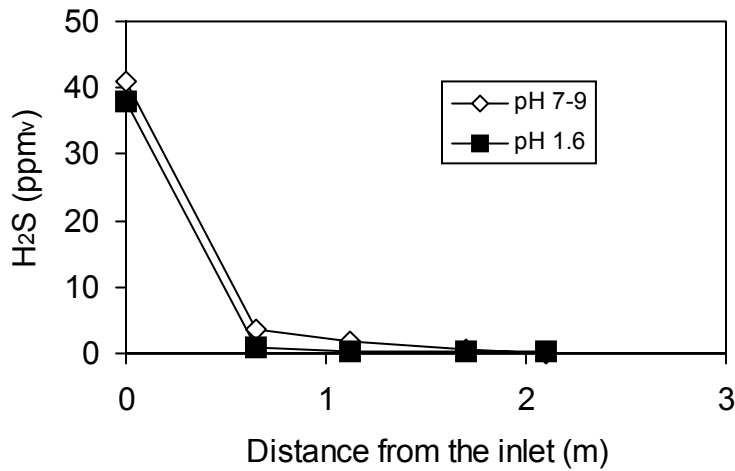
### **H<sub>2</sub>S and VOC Removal in the Biotrickling Filter**

Figure 6 presents the long-term H<sub>2</sub>S removal in the biotrickling filter. Removal started rapidly after inoculation on day 0, but it took 30 days before removal greater than 98% was observed. H<sub>2</sub>S outlet concentrations were always below 0.5 ppm<sub>v</sub> at inlet concentrations ranging from 10 to 50 ppm<sub>v</sub>. Initially, the biotrickling filter was operated without pH control and the recycle liquid pH was on average 1.5 for the first 46 days of operation. After this time, a pH control was implemented in order to maximize the removal of VOCs. Interestingly, although most *Thiobacillus* species have a pH optimum in the acidic range, maintaining a pH of 7-9 after day 46 did not affect H<sub>2</sub>S removal. This is more clearly illustrated in Figure 7, which shows concentration profiles of H<sub>2</sub>S along the reactor height at neutral pH operation, and at pH 1.6 (the low pH was caused by a temporary breakdown of the pH controller). Both profiles are almost identical, indicating that H<sub>2</sub>S removal in this biotrickling filter was not affected by the recycle liquid pH in the range of 1.6 to 9. Figure 7 also demonstrates that over 95% of the ingoing H<sub>2</sub>S was removed in the first bottom section of the biotrickling filter, but removal of low concentrations of H<sub>2</sub>S (<~1 ppm<sub>v</sub>) was poor in the second, third and fourth section. It was not determined if the latter was due to insufficient biomass growth in the upper sections, or to mass transfer or biological limitations at low H<sub>2</sub>S concentrations in general. As was found with the biofilter, the biotrickling filter was fast in responding to changing H<sub>2</sub>S concentrations. The short-term performance shown in Figure 8 illustrates that the removal efficiency was consistently greater than 98% during H<sub>2</sub>S fluctuations observed over the day. This was expected, since at an EBRT of 16 s, the H<sub>2</sub>S elimination capacity is larger than required for removal of 10-50 ppm<sub>v</sub> H<sub>2</sub>S (Figure 7).

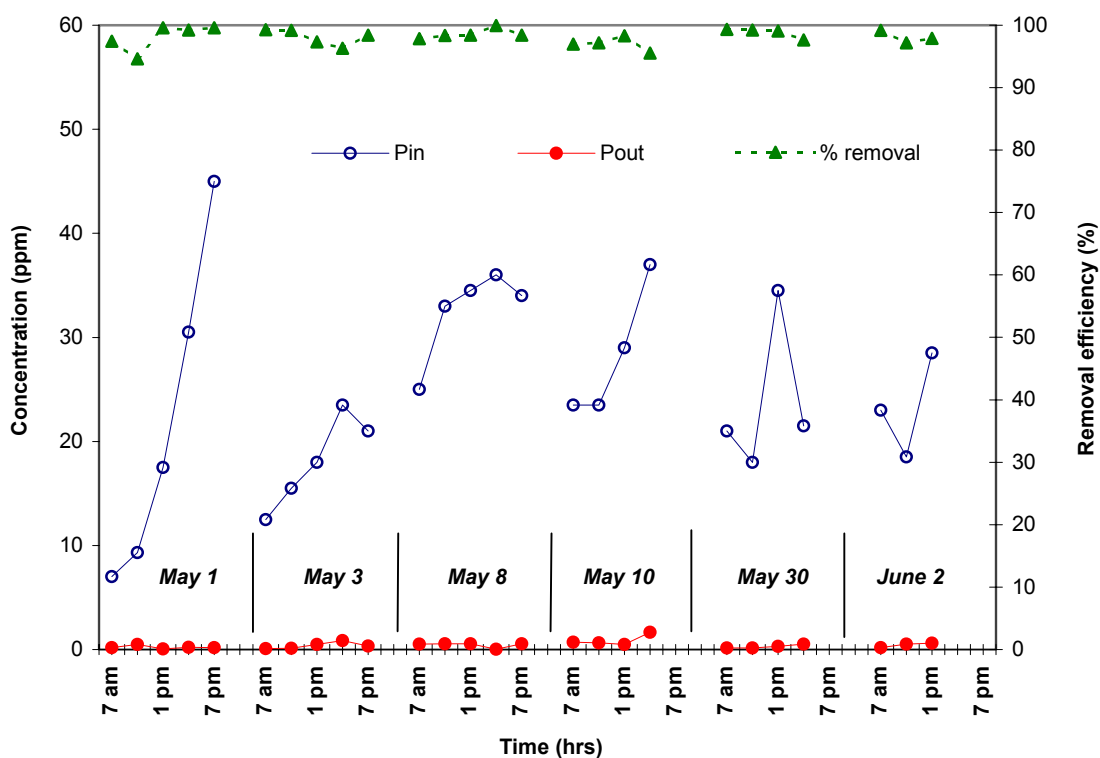
**Figure 6.** Long-term H<sub>2</sub>S Removal in the biotrickling filter (P=Pollutant=H<sub>2</sub>S)



**Figure 7.** Concentration profiles of H<sub>2</sub>S over the height of the biotrickling filter, operated at low and neutral pH; EBRT = 16 s.



**Figure 8.** Short-term H<sub>2</sub>S Removal in the biotrickling filter (P=Pollutant=H<sub>2</sub>S)



Removal of VOCs required control of the pH at a neutral value. As illustrated in Figures 9A to C, easily biodegradable VOCs such as benzene, toluene and xylenes were not removed during the first sampling round in May, i.e., when the pH was allowed to drop and the recycle liquid pH was on average 1.5. Removal of benzene and toluene and to a lesser extent xylenes improved however in the last of week of May, i.e., two weeks after operation at a neutral pH. pH-control did not improve the removal of the chlorinated VOCs dichlorobenzene, methylene chloride, chloroform and perchloroethylene and average removal efficiencies of these compounds were close to zero irrespective of the pH of the recycle liquid.

Figure 9a. VOC removal (P=Benzene) in the biotrickling filter

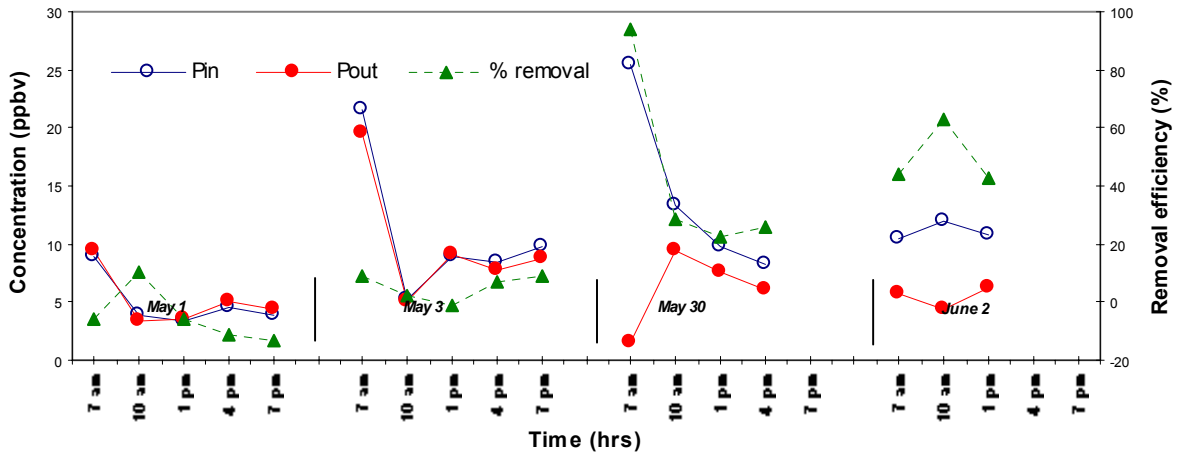


Figure 9b. VOC removal (Toluene) in the biotrickling filter

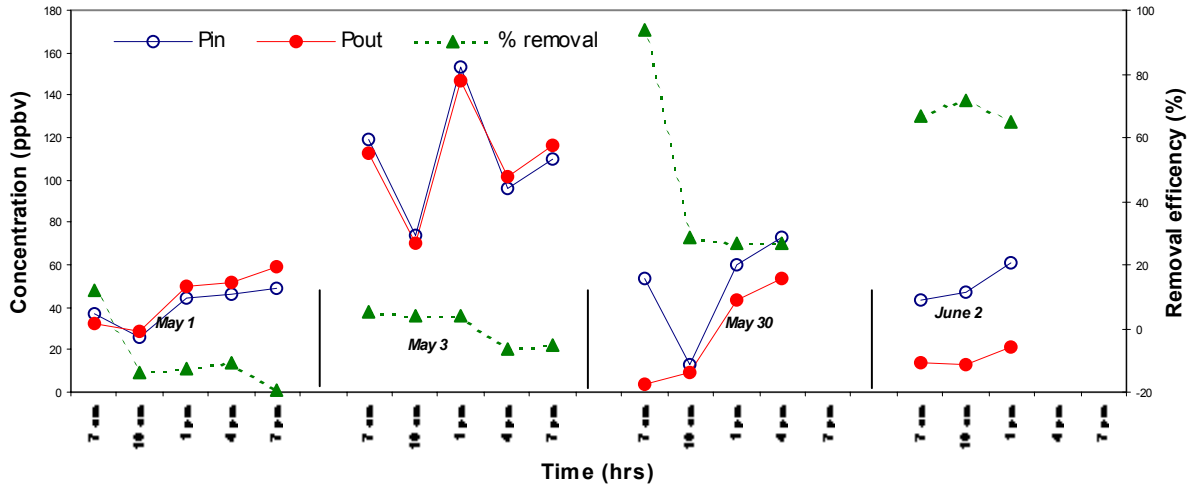
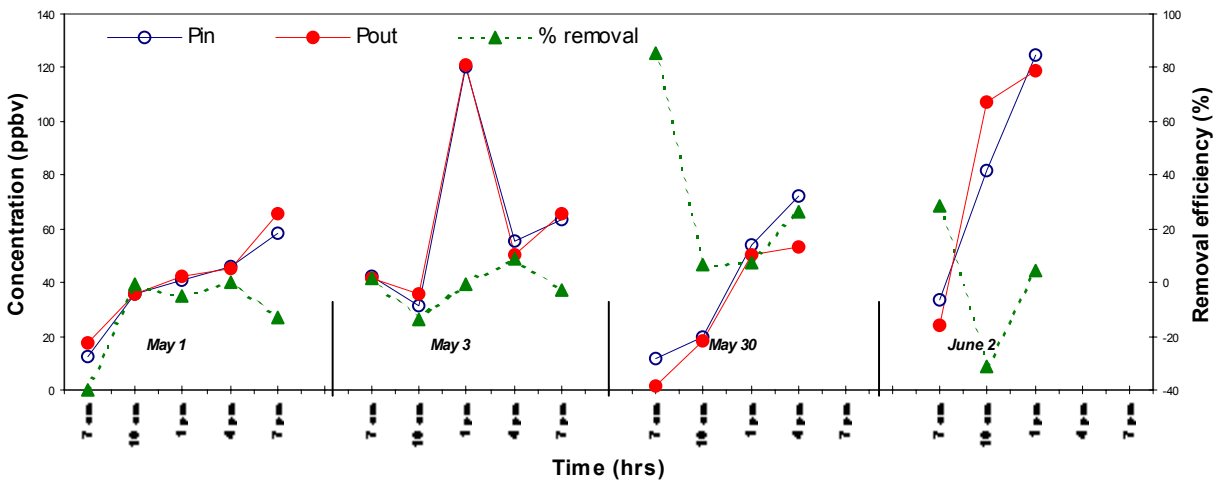


Figure 9c. VOC removal (Total Xylenes) in the biotrickling filter



## DISCUSSION

Biofilters and biotrickling filters are becoming established techniques for H<sub>2</sub>S and odor removal at wastewater treatment plants and other facilities (Leson and Winer, 1991; Williams, 1994; Van Lith *et al.*, 1997; Devanny *et al.*, 1999). In the present research, both the biofilter and biotrickling filter showed excellent removal of H<sub>2</sub>S over the long-term as well as during short-term fluctuations of the H<sub>2</sub>S inlet concentration during the day. When comparing both technologies, it appears that the strength of biotrickling filters lies in removing high H<sub>2</sub>S concentrations at a relatively short EBRT. H<sub>2</sub>S elimination capacities of up to 100-150 g H<sub>2</sub>S/m<sup>3</sup>.h have been observed for biotrickling filters (Kraakman *et al.*, 1998). Such high capacities can probably not be maintained in biofilters, due to rapid acidification and accelerated packing deterioration. Biofilters appear especially useful when a high degree of H<sub>2</sub>S removal is required. Thus, the expected H<sub>2</sub>S inlet concentration and total load, as well as the required removal efficiency or the maximum allowable outlet concentration, should be considered when selecting the most appropriate technology. In the present research, both the biofilter and the biotrickling filter removed up to 50 ppm<sub>v</sub> H<sub>2</sub>S to less than 1 ppm<sub>v</sub>, which is the present SCAQMD limit for the wet scrubbers currently used at HTP. The results indicate that the EBRT in the biotrickling filter can be further reduced to about 5-10 s without exceeding this limit. Reduction of the EBRT may also be feasible for the biofilter, which was operated at a relatively long EBRT (30-50 s) during these studies. However, increasing headlosses across the packing (after 8 months of operation, 8 cm of water column at an EBRT of 50 s) may be the limiting factor for increasing the gas velocity.

Table 1 presents a summary of the average VOC removal efficiencies observed in the biofilter and biotrickling filter. Both technologies removed easily biodegradable compounds such as aromatic hydrocarbons, but removal of chlorinated VOCs was not observed. VOC removal was in general slightly better in the biofilter, which was probably due to a longer EBRT. Nevertheless, VOC removal was incomplete in both reactors, although individual loads of VOC species were much smaller than the elimination capacities commonly observed in the laboratory (see e.g., Deshusses and Johnson, 2000 or Iranpour *et al.*, 2001). This suggests that further improvement of VOC removal is possible, especially since removal of the VOCs listed in Table 1 (except chloroform) has been demonstrated in pilot or full-scale studies (Iranpour *et al.*, 2001). In addition, we have previously shown that H<sub>2</sub>S does not have an inhibitory effect on the removal of toluene and MTBE in biotrickling filters (Cox and Deshusses, 2000). Therefore, co-treatment of H<sub>2</sub>S and VOCs in biofilters or biotrickling filters may become a feasible and attractive technology for POTWs once an explanation is found for the low VOC removal efficiencies. Present research focus on the stimulation of the growth and activity of the heterotrophic microbial population to improve biodegradation of the VOCs.

**Table 1.** Average VOC removal efficiencies in H<sub>2</sub>S degrading biofilters (EBRT = 30-50 s) and biotrickling filters (EBRT = 16 s).

VOC	Removal in the Biofilter	Removal in the Biotrickling filter	
		Without pH control	pH 7-9
Benzene	74 %	4 %	46 %
Toluene	79 %	3 %	51 %
Xylenes	56 %	1 %	8 %
Dichlorobenzene	18 %	2 %	1 %
Methylene chloride	5 %	1 %	1 %
Chloroform	0 %	0 %	0 %
Perchloroethylene	2 %	1 %	5 %

## ACKNOWLEDGMENTS

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