### ODOROUS COMPOUNDS EMISSIONS FROM BIOTRICKLING FILTERS AT WASTEWATER TREATMENT PLANTS

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### ABSTRACT

This paper evaluates treatment of odorous compounds (hydrogen sulfide, reduced sulfur compounds, VOCs, ammonia, and total odor) in wet chemical scrubbers that were converted to biotrickling filters at the Orange County Sanitation District (OCSD), California. Results of over two years of continuous operation in five biotrickling filters are discussed. The biotrickling filters were usually operated at a gas contact time of 1.6 to 2.2 seconds (nominal gas contact time) or up to 10 seconds during specific experiments with various effects on odor removal. In all cases outlet concentrations of sulfur compounds (calculated as H<sub>2</sub>S) were well below the emissions permit limits (24 h average of 1 ppm) while total odor exhaust concentrations depended on the particular biotrickling filter. The biotrickling filters were resilient to temporary changes in inlet gas composition, including a highly-fluctuated hydrogen sulfide concentration. Overall, the study results indicate that there is a significant benefit in converting chemical scrubbers to biotrickling filters for odor control. Improvement of the odor removal performance should focus on the treatment of residual total odor which, in many but not all cases, is believed to originate from trace reduced sulfur and organic compounds.

### **KEY WORDS**

Biotrickling filters, odor control, wastewater treatment

#### **INTRODUCTION**

From the wide range of technologies available for odorous air treatment, physico-chemical processes have been the most widely used. Presently, chemical scrubbing in packed-towers is leading the world market for odor control in publicly owned treatment works (POTWs)(Stuetz and Frechen, 2001). This is because chemical scrubbing is reliable and has historically had the

lowest cost, especially at low concentrations and for the treatment of foul air for applications over  $50,000 \text{ m}^3 \text{ h}^{-1}$  ( $30,000 \text{ ft}^3 \text{min}^{-1}$ ) (Card, 2001). However, wet scrubbing is expensive when operating and investment costs are compared to emerging biotreatment techniques such as biofiltration and biotrickling filtration (Devinny et al., 1999). In the case of foul air treatment at POTWs, biotrickling filtration appears to be the most promising development, as it allows for very effective and compact reactors (Gabriel and Deshusses, 2003a).

Biotrickling filters are configured in a similar manner to reactive chemical scrubbers except that the reaction is mediated by microorganisms. Foul or contaminated air is passed through a packed bed on which pollutant degrading bacteria are allowed to grow. Liquid containing essential inorganic nutrients is trickled over the packed bed, so that optimum conditions (pH, salt and nutrient concentration) can be maintained for the process culture. Biotrickling filters require low maintenance and are particularly effective for the treatment of H<sub>2</sub>S and other odorous compounds, such as ammonia, though residual odor can sometimes be an issue. Biotrickling filters are increasingly used in industrial applications (Cox and Deshusses, 1998; Devinny et al., 1999). The advantage of biological treatment over physicochemical techniques is the savings accrued from the absence of chemicals. Other benefits of biological techniques, such as environmental health and safety and decreased liability are real. Biotrickling filters, unlike chemical scrubbers, do not use chemicals representing risk to the public in case of their accidental release.

In this paper, the treatment of odors in chemical scrubbers converted to biotrickling filters is evaluated. In this new development, the vessel of the chemical scrubber is kept, but modification of the operation and of the packing material allows for operation as a biological scrubber. In all cases, the original gas contact time of 1.6 to 2.2 seconds was kept. The biotrickling filters achieved similar or superior  $H_2S$  removal performance compared to the previously installed chemical scrubbers (Gabriel and Deshusses, 2003a). The present paper focuses on the treatment of total odor and low concentrations of sulfur compounds in the converted scrubbers, evaluated over a period of about two years.

# MATERIALS AND METHODS: FULL-SCALE SCRUBBER CHARACTERISTICS AT OCSD

OCSD manages two different wastewater treatment facilities (Plant 1 and Plant 2) that treat a total average flow of 910,000 m<sup>3</sup> (240 million gallons) of wastewater per day. The District has implemented many measures to control and reduce odors, and the plants now have extensive odor control facilities. Dosage of chemicals into the trunklines and a total of 34 packed tower chemical scrubbers are used for treatment of odor emissions from both facilities. Ferric chloride is added to the trunklines to lower sulfide concentrations and  $H_2S$  emissions. Chemicals used at OCSD in wet scrubbers are sodium hydroxide and either hydrogen peroxide or sodium hypochlorite.

Most of OCSD scrubbers are constructed following a similar design. The main differences among them are in the foul air composition and the chemical feeds. The characteristics of the scrubbers considered in this paper are provided in Table 1 and a picture of one of the scrubbers is shown in Figure 1. All chemical scrubbers at OCSD are made of fiberglass reinforced plastic

(FRP) shells, with a foul air fan to blow the gases upward through the scrubber by forced draft. Fans are typically fixed speed or two-speed floor mounted FRP centrifugal blowers. The scrubber towers contain a multi-beam type packing support, a packed bed contact section, a liquid distribution system (see Table 1 for kind of system), and a demisting section (usually made of packing of smaller nominal size than installed in the bed). All scrubbers have U type overflow pipe, a liquid reservoir at the bottom with a plenum for air inlet, make-up water and chemical reagents feed points. All scrubbers are connected to a supply of plant water, which is used in the case of the converted scrubbers to both control pH and as nutrient supply to the process culture. The scrubbers were converted following a procedure described elsewhere (Gabriel and Deshusses, J. Environ. Eng.-ASCE in press). Most relevant to the conversion was the replacement of the original plastic packing material by foam packing (manufactured by Zander or EDT AG, both in Germany) which is suitable for high performance biotrickling filtration. The packing (4 cm cubes) is made of open-pore polyurethane foam with 10-15 pores per linear inch (PPI) (4-6 pores per cm), and has a specific surface area of  $600 \text{ m}^2 \text{ m}^{-3}$ , a density of 35 kg m<sup>-3</sup>, and a porosity of 0.97. All reactors were inoculated with activated sludge at the time of the startup.

| Parameter                               | Scrubber 10                  | Scrubber I                   | Scrubber Q           | Scrubber G                      | Scrubber J                   |
|---|------------------------------|------------------------------|----------------------|---------------------------------|------------------------------|
| Location                                | Plant 1                      | Plant 2                      | Plant 2              | Plant 2                         | Plant 2                      |
| Scrubber duty                           | Pretreatment                 | Pretreatment                 | End-of-pipe          | End-of-pipe                     | End-of-pipe                  |
| Air source                              | Influent sewer<br>trunkline  | Influent sewer<br>trunkline  | Primary<br>treatment | DAFT off-<br>gases <sup>a</sup> | Dewatering off-<br>gases     |
| Packed height (m)                       | 3.9                          | 3.3                          | 3.3                  | 3.1                             | 4.9                          |
| Diameter (m)                            | 2                            | 2                            | 3.3                  | 2                               | 3.3                          |
| Bed volume (m <sup>3</sup> )            | 12                           | 10                           | 27.7                 | 15                              | 41.6                         |
| Liquid distributor                      | Parting box and weir troughs | Parting box and weir troughs | Nozzles              | Nozzles                         | Parting box and weir troughs |
| Fan power low / high (kW)               | 30                           | 30                           | 33/75                | 30                              | 28                           |
| Liquid recycle (m <sup>3</sup> /h)      | 136                          | 79                           | 136                  | 168                             | 150                          |
| Air flow low / high (m <sup>3</sup> /h) | 17,000 <sup>b</sup>          | 17,000 <sup>b</sup>          | 40,800 / 68,000      | 47,000 <sup>b</sup>             | 39,000 <sup>b</sup>          |
| EBRT high / low (s) <sup>c</sup>        | 2.03 <sup>b</sup>            | 2 <sup>b</sup>               | 1.96 / 1.18          | 0.93 <sup>b</sup>               | 3.07 <sup>b</sup>            |
| Average inlet H <sub>2</sub> S (ppm)    | 10-40                        | 40-100                       | 2-10                 | 0-10                            | 0-1 <sup>d</sup>             |

<sup>a</sup>Dissolved Air Flotation Thickeners.

<sup>b</sup>High flow not available, single speed blower.

<sup>c</sup>Empty Bed Retention Time = bed volume/air flow.

<sup>d</sup>Usually H<sub>2</sub>S concentration is below detection level

Figure 1. Photo of a bank of eight wet scrubbers at Plant 2 of OCSD. The second from the left has been converted to biotrickling filter Q.



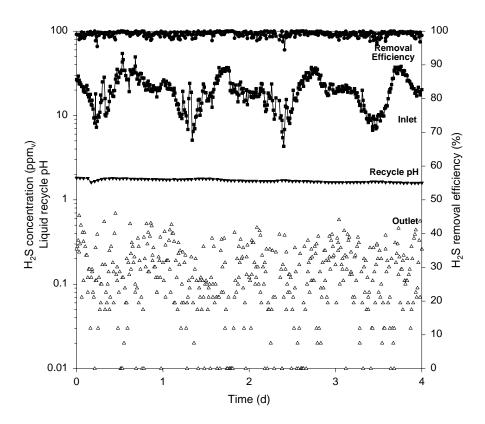
Chemical scrubbers at OCSD are highly instrumented systems, thus, after conversion, good monitoring of the operating conditions could be accomplished. At the time of the study, scrubber #10, scrubber Q, and scrubber I each had on-line separate H<sub>2</sub>S meters (Vapex Sentinel System, Vapex Inc., Florida) with independent sensors connected for the air inlet and outlet of the scrubber. These Vapex units were configured to display H<sub>2</sub>S inlet and outlet concentrations every 4 seconds and to store the average of 12 minute segments. The units were regularly calibrated by the manufacturer and checked against H<sub>2</sub>S determinations made using a Jerome 631X series meter (Arizona Instruments, Tempe, AZ) or gas chromatograph with flame photometric detector (GC/FPD). Also, each scrubber has an in-line pH sensor connected to the SCADA system of OCSD used for continuous monitoring. pH control was achieved by supplying only plant water to the biotrickling filter. The scrubbers also include a water-filled U-tube manometer to measure the pressure drop across the bed, on-line rotameters for measuring water make-up supply, low liquid level alarms, and a low pressure switch for recycle pump shut-down. Odor dilution to threshold (D/T) was measured off-line after taking grab samples and analyzed following standard techniques by an odor panel at Los Angeles County Sanitation District. Details of the operation or equipment not mentioned here can be found in other papers by co-author Deshusses.

### **RESULTS AND DISCUSSION** Control of Low Concentrations of H<sub>2</sub>S

Each converted scrubber at OCSD was exposed to different  $H_2S$  concentrations. Biotrickling filter I (roughing scrubber) was exposed to the highest concentrations, followed by biotrickling filter 10 (also a roughing scrubber), Q, and G, while influent  $H_2S$  concentrations to biotrickling filter J are minimal. Thus operation of those biotrickling filters covers a wide range of influent  $H_2S$  conditions.

Typical  $H_2S$  removal in Biotrickling Filter #10 subject to medium to high  $H_2S$  concentrations is shown in Figure 2, where time 0 corresponds to 12:00 AM on September 5, 2001. Inlet concentrations fluctuated daily between 5 and 40 ppm, while outlet concentrations were always maintained well below the 24 h average discharge limit of 1 ppm. Such performance is representative of long term operation of converted scrubbers exposed to medium  $H_2S$ concentrations.

Figure 2. Typical H<sub>2</sub>S removal in Biotrickling Filter #10 at gas contact times of 1.8-2.2 seconds. The performance shown is representative of long-term operation of biotrickling filters exposed to medium to high concentrations of H<sub>2</sub>S at OCSD. H<sub>2</sub>S measured by Vapex sensor; non-detect shown as 0.01 ppm.

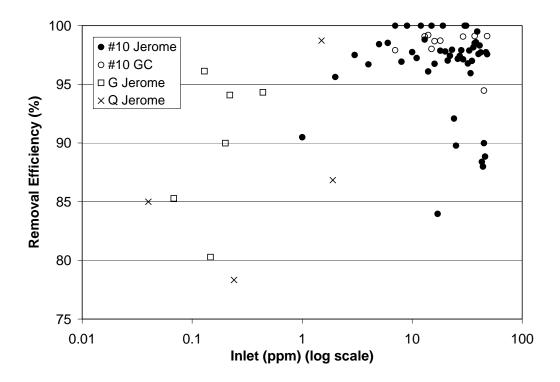


Evaluation of one year of operation of biotrickling filter #10 reveals that the biotrickling filter successfully treated H<sub>2</sub>S at rates comparable to those of chemical scrubbers (Gabriel and

Deshusses, 2003a). On average,  $H_2S$  removal was about 97.5% for  $H_2S$  inlet concentrations of up to 25 ppm (N~15,000 data points), and for many of the 12-minute average samples,  $H_2S$  removal exceeded 98% for inlet  $H_2S$  concentrations as high as 30 to 50 ppm. A means for comparison between biotreatment system is the so called elimination capacity. The elimination capacity is the amount of a given pollutant that can be removed by a unit volume of bioreactor bed. The above removal corresponds to  $H_2S$  elimination capacities of 95 to 105 g  $H_2S$  m<sup>-3</sup> h<sup>-1</sup>. This is exceptionally high compared with other biofilters or biotrickling filters removing low concentrations of  $H_2S$ , even at higher gas contact times (Gabriel and Deshusses, 2003a).

In Figure 3, the removal of low concentrations of  $H_2S$  is illustrated. When dealing with low concentrations, it is important to ensure that the monitoring technique is capable of accurately quantifying ppb levels of  $H_2S$ . Therefore, electrochemical sensors are generally inappropriate. As mentioned earlier, the removal of  $H_2S$  at concentrations above 10 ppm was on average 97.5% with some outliers around 85-90% shown in Figure 3. As the inlet concentration decreased, a decreasing trend was observed for the removal. At 0.1 ppm inlet, the removal ranged from 80 to 95%, i.e., outlet concentrations ranging from 5 ppb to 20 ppb. These are very low values, slightly above the odor detection threshold.

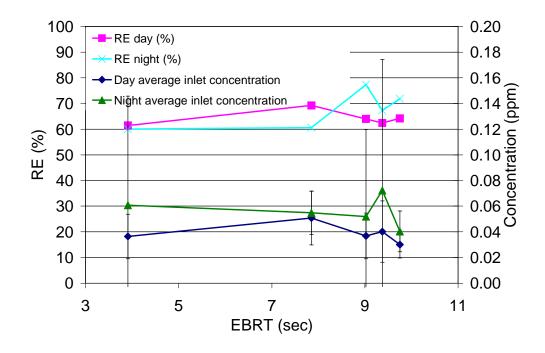
Figure 3.  $H_2S$  removal in the three converted scrubbers at OCSD that treat average to low concentrations of  $H_2S$ . Biotrickling Filters I and J are not shown (too high concentration for I and too low concentrations for J). The log scale emphasizes the removal at low concentration. The legend (Jerome or GC) denotes the method for analysis of  $H_2S$ .



The question arises whether  $H_2S$  and odor could be effectively treated at much lower concentrations, even in biotrickling filters that do not routinely experience high spikes, such as biotrickling filter 10, shown in Figure 3. Thus, one focus of the study was on the performance of biotrickling filter J, which is treating mostly non- $H_2S$  odors. The results are reported in Figures 4 and 5. In this experiment, the air flow was varied so that the effect of the gas contact time on the removal of  $H_2S$  and total odor could be quantified. The experiment lasted three months, during which time intense monitoring of the biotrickling filter performance was implemented.

As shown in Figure 4, the influent  $H_2S$  concentrations were extremely low, ranging from 30 to 70 ppb. Unlike in other scrubbers exposed to higher concentrations,  $H_2S$  levels were relatively constant throughout the day and there were no significant differences between sampling during the day and at night. The removal of  $H_2S$  ranged from 60 to 80%, resulting in outlet concentrations of  $H_2S$  in the low ppb range. As shown in Figure 4, the removal was not influenced by changes in the gas contact time from 4 to 10 seconds. This may seem counterintuitive, but is most probably because of the extremely low concentrations treated. As the treated concentrations decrease, the common rule of thumb valid at higher concentrations that greater contact time leads to greater treatment does not necessarily apply. The reasons for this still remain to be elucidated.

# Figure 4. Average inlet $H_2S$ concentrations (error bars indicate standard deviations) and removal efficiencies (RE) determined for various EBRTs. $H_2S$ measurements were made using the Jerome 631X.



## **Control of Organic Compounds**

As shown in Table 2, 35 to 70% removal of reduced sulfur compounds (RSCs), including carbonyl sulfide, methyl mercaptans and carbon disulfide, ammonia (>99% not shown in Table 2), and volatile organic compounds (e.g., toluene 29%, xylenes 45%, chloroform 30%) was also observed. Table 2 also reports the removal for some reduced sulfur compounds (RSCs) in chemical scrubbers reported in one of the recent studies. The very wide range of performance of chemical scrubbers (e.g., 16 to 97% removal for carbonyl sulfide) suggests that chemical scrubbers are not consistently treating those compounds. Usually, removal efficiencies for RSCs, VOCs, and odor by chemical scrubbers are lower than those from biotrickling filters (Card, 2001; Easter, 2003). Further comparison of the removal of air toxics and RSCs in biotrickling filters and chemical scrubbers is warranted.

| Compound           | Inlet concentration,<br>ppb <sub>v</sub> | Removal<br>efficiency, % | Reported removal observed<br>in chemical scrubbers<br>(Easter, 2003) |
|--------------------|--|--------------------------|--|
| Carbonyl sulfide   | $67.2\pm7.7$                             | $44 \pm 11$              | 16-97%   |
| Methyl mercaptan   | $192.5\pm34.1$                           | $67 \pm 11$              | 65-99%   |
| Carbon disulfide   | $70.3\pm20.5$                            | $35 \pm 5$               | 16-97%   |
| Methylene chloride | $132\pm93$                               | $36 \pm 25$              |  |
| Chloroform         | $326\pm263$                              | $30 \pm 21$              |  |
| Benzene            | $147\pm105$                              | $32 \pm 21$              |  |
| TCE                | $16 \pm 15$                              | $46 \pm 28$              |  |
| PCE                | $224\pm257$                              | $28 \pm 20$              |  |
| Toluene            | $753\pm2144$                             | $29 \pm 14$              |  |
| Ethyl benzene      | $148\pm221$                              | $41 \pm 27$              |  |
| p and m-xylene     | $480\pm852$                              | $41 \pm 19$              |  |
| o-xylene           | $110\pm210$                              | $44 \pm 30$              |  |
| Odor               | $1980\pm480~\text{D/T}$                  | 65 ±21                   | 70-90%   |

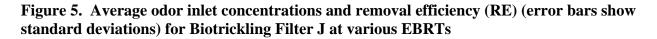
| Table 2. Inlet concentrations and removal efficiencies of VOCs and RSCs from |  |
|--|--|
| Biotrickling Filter 10.  |  |

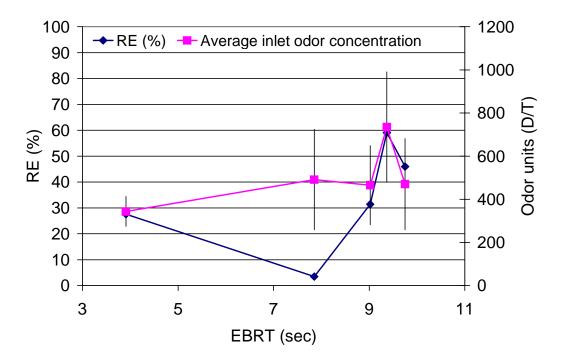
Data are mean  $\pm$  standard deviation, n=21 for RSCs, n=19 for VOCs, and n=9 for odor panels, and are representative of about 8 months of operation at gas contact times between 1.6 and 3.4 seconds.

# **Control of Total Odor**

Odor treatment performance during the course of the experiment with biotrickling filter J is reported in Figure 5. Again, inlet levels are plotted, as it is important to ensure that conditions were comparable at the gas contact time tested. Here a larger scattering of both inlet and removal performance is observed. Inlet odor ranged from 300 to 700 D/T, which are relatively low values for process air at a POTW, and compared to other samples collected at OCSD. Odor removal was scattered, with an apparent low removal at 8 s gas contact time and better removal at either 4 s or above 9 s gas contact time. While the results are believed to be significant, it is difficult to

find an explanation to such inconsistent behavior. It may be due to the lifting of some mass transfer limitations at low gas contact time, as discussed elsewhere (Kim and Deshusses, 2003) though it remains to be proved. Alternate explanations include temporal changes in the process air, or subtle changes in the makeup of the biotrickling filter process culture. Some residual odor (150 to 300 D/T) is always expected in the exhaust air from a biotrickling filter. At this time, it is not clear what compounds causes this residual odor, neither is the exact makeup of the influent odor to biotrickling filter J known. In most other scrubbers three RSC were commonly reported: carbonyl sulfide, methyl mercaptan and carbon disulfide. In biotrickling filter J, no RSC's were detected. It may be explained by the relatively high detection limits for these compounds during our experiments. Further detailed analysis of possible nitrogen compounds should be conducted to complete the list of possible odorants.





A compilation of all odor removal measurements for all biotrickling filters operated at their nominal gas contact time is shown in Figure 6. Note that the results presented in this figure include different scrubbers, and therefore the character and makeup of the odor is different for each scrubber. Large scattering of the data is observed. One important reason is the subjective nature of sensory measurements, which leads to large variations in the odor levels that were observed both in the inlet and in the outlet of the biotrickling filter. Another important reason is that a POTW is, by nature of its operation, functioning under transient conditions with rapid changes in key parameters. Therefore, grab samples, though collected simultaneously from the scrubbers' inlet and outlet, are merely a snapshot of a given condition. It suggests that methods that enable integrated sampling should be considered, in order to quantify the performance of odor control equipment. Even so, Figure 6 presents some highly promising results, with odor removal sometimes exceeding 80%, over a wide range of conditions.

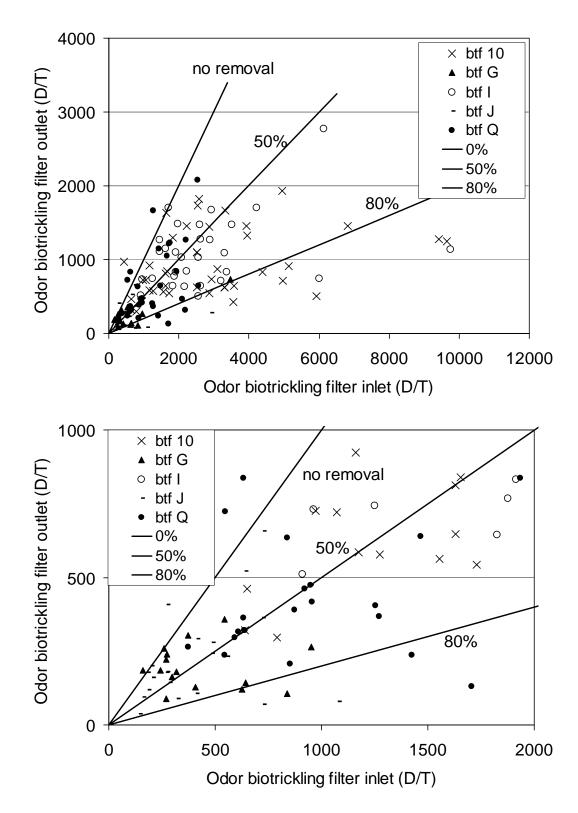


Figure 6. Total Odor removal in the different biotrickling filters at OCSD. The bottom graph shows a magnification of the 0-1000 D/T inlet conditions.

### CONCLUSION

As the deployment of high performance biotrickling filters increases, an operator's perspective on this new development is warranted. For plant operators, biotrickling filters present substantial advantages over chemical scrubbers. For operating and monitoring, the lack of chemicals being added to the system simplifies the process control. Essentially only one parameter (pH) must be controlled. When  $H_2S$  is the primary concern, controlling the pH at its optimum value of 1.8-2.2 for  $H_2S$  removal is relatively easy, as it involves only one setting (makeup water flow rate). Safety also is increased greatly when operations and maintenance staff no longer work with the hazardous chemicals used in conventional scrubbers.

There are certain challenges inherent in using biological systems. While the biotrickling filters have been found to handle even substantial sudden inlet loading changes (Gabriel and Deshusses, 2003b), there are limits to their short-term reaction capabilities; it is possible to overwhelm them with sufficiently large increases that exceed their removal capacity, resulting in breakthrough of contaminants in the treated gas. Also, as with any biological system, exposing the biotrickling filters to toxic substances, either in the inlet gas stream or in the makeup water, can harm the biological population and impair the filters' performance. When the possibility of such poisoning incidents is reasonably foreseeable, precautions can be taken to minimize their impacts (e.g., by dechlorinating makeup water to guard against inadvertent overchlorination incidents). Finally, unlike a chemical scrubber, there is an initial acclimation period before a biotrickling filter shows appreciable removal capability. Through redundancy or other means, the system must be designed to provide adequate treatment during these startup periods. One can reasonably predict that over the next few years, with further experience using high performance biotrickling filters, these challenges may very well become a matter of routine.

### REFERENCES

- Card T. (2001). Chemical odour scrubbing systems. In: Odours in Wastewater Treatment: Measuring, Modelling and Control. R. Stuetz & F.B. Frechen (ed.). IWA Publishing, London. pp. 309-344.
- Cox H.H.J. and Deshusses, M.A. (1998). Biological waste air treatment in biotrickling filters. Current Opinion in Biotechnology **9**(3), 256-262.
- Devinny, J.S., Deshusses, M.A., and Webster, T.S. (1999) *Biofiltration for Air Pollution Control*; CRC-Lewis Publishers: Boca Raton, FL.
- EPA, (1996). U.S. EPA, Office of Air Quality Planning and Standards, OAQPS Control Cost Manual, Fifth Edition, EPA 453/B-96-001, Research Triangle Park, NC.
- Easter, C. (2003). Odor control prevention, strategies, technologies, and approaches overview. Presented at the 2<sup>nd</sup> IWA International Workshop and Conference on odour and VOCs. Singapore, September 14-17, 2003.

- Gabriel D. and Deshusses M.A. (2003a). Retrofitting Existing Chemical Scrubbers to Biotrickling Filters for H<sub>2</sub>S Emission Control. *Proc. Natl. Acad. Sci. USA*, **100**(11), 6308-6312
- Gabriel D. and Deshusses M.A. (2003b). Performance of a full-scale biotrickling filter treating H<sub>2</sub>S at a gas contact time of 1.6-2.2 seconds. *Environ. Prog.*, **22**, 111-118.
- Gabriel D., Cox H.H.J. and Deshusses M.A. (in press). Conversion of full-scale wet scrubbers to biotrickling filters for H<sub>2</sub>S control at POTWs. *J. Environ. Eng.-ASCE*
- Kim, S., Deshusses, M.A. (2003). Development and experimental validation of a conceptual model for H<sub>2</sub>S biotrickling filtration. *Environ. Prog.*, **22**, 119-128.
- Stuetz R. and Frechen F.B. (2001) ed.. Odours in Wastewater Treatment, London. IWA Publishing.