Transient Behavior of Biofilters: Start-Up, Carbon Balances, and Interactions Between Pollutants

By Marc A. Deshusses[1]

ABSTRACT: The work describes the aerobic biodegradation of volatile organic compound (VOC) mixtures from effluent air streams in laboratory-scale compost based biofilters. A rapid start-up of the system (3–5 d) was observed and 82% of the carbon in the influent pollutant (methyl ethyl ketone) was recovered as carbon dioxide in the exhaust air after this period. Biofilter performance and carbon dioxide production were also investigated during and after 0.5–1-h step inputs of 2–10 g m^{-3} of hexane, acetone, 1-propanol, and/or methyl isobutyl ketone (MIBK) during steady methyl ethyl ketone (MEK) treatment. Carbon dioxide patterns suggest that pulsed pollutants were first sorbed onto the packing material and subsequently degraded within 2–5 h. Hexane was not sorbed, and thus not degraded to a significant extent. Little effect was observed of the step inputs on the overall MEK removal process, mainly because the reactors were operated well below MEK breakthrough loading. However, the analysis of MEK profiles within the biofilter bed showed that significant inhibition did indeed occur. An even more important inhibition was observed between 1-propanol, MIBK, and acetone, when such a mixture was injected into the reactor. Practical design of biofilters should consider the possibility of reduced performances due to the presence of multiple VOCs in the waste air stream.

INTRODUCTION

Industrial biofilters are often exposed to waste air streams from discontinuous processes in which highly variable conditions occur. Therefore, a major need exists to obtain reliable information and develop conceptual understanding of the phenomena that occur during transients in biofilters, particularly when multiple pollutants are treated. Clearly, extended studies of transient behavior of biofilters are needed to provide the basic empirical knowledge necessary for plant design, scale-up, and performance evaluation under real conditions. In addition, the study of transient behavior offers a genuine basis for the development of a conceptual explanation of the complex phenomena that occur in biofilters during pollutant elimination, thereby providing an opportunity for further progress in establishing fundamental understanding of such reactors (Shareefdeen et al. 1994; Deshusses et al. 1995b).

Very few publications report details concerning the start-up period of biofilters. This situation probably exists because start-up is usually thought not to influence the future performances of biofilters. However, most biofilters are limited by reaction rather than by mass transfer. Hence, optimization of active biomass density, through better understanding of the initial colonization of support material by growing biomass may alter such views. Investigations on acclimation time (Deshusses et al. 1996), start-up, and carbon balances (Deshusses 1995) are one means to access some fundamental information on the rate of biomass buildup and/or on the rate of synthesis of degradation key enzyme. Experiments on the start-up and carbon balances are presented and discussed in the first part of the results section. Regarding the understanding of microscopical principles of biofiltration, further research regarding the relationship between active and inactive biomass densities and biofilter removal efficiency is needed.

As far as industrial biofiltration is concerned, pollutant concentration and loading, packing moisture content and temperature are the main operational variables influencing process efficiency. If the latter parameters are essentially control variables, the former are usually governed by the pollutant emission process. In addition to such influences, transient conditions and the presence of multiple pollutants have been shown to affect significantly the performance of biofilters. Only a limited number of papers deal with the transient response of biofilters to changes in operating conditions (Hodge et al. 1992; Shareefdeen et al. 1994; Tang et al. 1995; Deshusses et al. 1996). It has been emphasized (Shareefdeen et al. 1994; Deshusses et al. 1996) and modeled (Deshusses et al. 1995a) that pollutant sorption plays a major role during transient operation. Further, interactions between multiple pollutants undergoing treatment, such as described earlier between methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) (Deshusses 1994), or between hexanal and sulfur dioxide (SO$_2$) (Van Langenhove et al. 1987), have demonstrated a tremendous influence on the removal process. From an industrial point of view, these phenomena can result in significant pollutant emissions, which are unpredictable a priori. The experiments described in the second part of the results section illustrate the combined effect of transients and exposure to multiple pollutants. As far as practical applications are concerned, major differences between systems are expected depending on pollutant/packing affinity and on both biodegradability and degradation pathways of all pollutants undergoing treatment.

MATERIALS AND METHODS

Material and methods were similar to previously used (Deshusses et al. 1996). A schematic diagram of the equipment used is shown in Fig. 1.

Biofilter and Packing Material

The biofilter was constructed from clear polyvinyl chloride (PVC) tubing and was 1.5 m in length and 152 mm in internal diameter. Operating temperatures were maintained between 20° and 25°C. The biofilter was filled with a mixture of horse manure and yard waste compost, and redwood chips provided by The Reynolds Group (Tustin, Calif.). It was buffered to near neutral pH with a mixture of mono- and dibasic potassium phosphate. The voidage of the packing material was not determined. The active filter bed height was about 1 m, split in four sections allowing reproducible air sampling at intermediate heights. The packing density (55–60% water content) was between 450 and 500 g of packing per liter of bed volume. As before (Deshusses 1994), the packing material was inoc-

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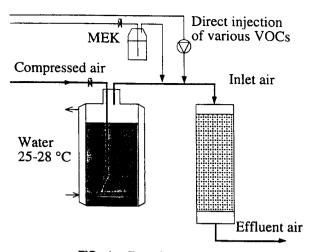
FIG. 1. Experimental Setup

ulated with a concentrated enrichment culture. No additional mineral nutrient source or pH buffer was added after beginning the experiments.

Pollutant Containing Humid Air Stream

Compressed oil-free air was saturated with water vapor by sparging the air through water at 25–28°C. One smaller compressed air stream was sparged into 0.5-L bottles, containing MEK and subsequently mixed with the major humidified air stream. As required, a metered flow of hexane, MIBK, acetone, 1-propanol or mixtures of these compounds was injected into the main air stream by a metering pump (by FMI, Inc., New Jersey), where it was evaporated. All chemicals were of high purity grade (Fisher Scientific), except for the hexane, which was a mixture of several branched hexanes. Downward gas flow rates of 0.7–0.8 m^3 h^{-1} were used in most experiments, giving surface or volumetric loadings of about 40 m h^{-1}. The gas had a relative humidity greater than 95%, and the pressure drop over the filter was less than 50 mm water gauge.

Analysis

The concentrations of volatile organic compounds (VOCs) in the gas phase were determined by gas chromatography. Air samples, selected by a 16-stream injection valve (Valco, Houston, Tex.), were pumped through 0.1 mL and 0.25 mL sampling loops for automatic injection into a Hewlett-Packard type 5890A Series II gas chromatograph operated isothermally at 65°C. The VOC separation was performed with a 30 m Supelcowax 10 column (0.53 mm, 1 µm film, Supelco, Bellefonte, Pa.) and detection was with a flame ionization detector. Carbon dioxide was analyzed with a 2.4 m 80/100 Chemosorb 1/4 in. packed column (Supelco, Bellefonte, Pa.) and detection was with a thermal conductivity detector.

RESULTS AND ANALYSIS

Biofilter Start-Up and Carbon Balances

The start-up of the biofilter degrading methyl ethyl ketone (MEK) vapors is shown in Fig. 2. After an initial sorption phase (not shown) of about 8–12 h during which MEK vapors were removed by physical sorption only, inlet and outlet concentration remained the same until the onset of biological activity at about 60 h. At this point the endogenous respiration was measured and corresponded to a CO_2 production of 0.13 ± 0.02 gC m^{-3}. A progressive increase in reactor efficiency was observed that resulted in complete pollutant elimination after 75 h. As reported in Fig. 2, this correlated with an in-

crease in carbon dioxide production. After 100 h operation, the MEK inlet concentration was approximately doubled. Even so, no breakthrough could be detected. The analysis of carbon dioxide production in Fig. 2 shows consistent increases with the increases in MEK removal. Interestingly, 2–5 h were needed to establish a steady state with respect to carbon dioxide. One plausible explanation is that MEK was essentially removed by sorption after the step increase, and that a few hours were necessary for the dormant or inactive biomass, located in the unexposed part of the biofilter, to turn on pollutant degrading mechanisms.

Reported in Fig. 3, is the carbon recovery defined as

$$\text{Carbon recovery} = \frac{\text{moles of } CO_2 \text{ produced}}{\text{moles of C pollutant consumed}} \quad (1)$$

Initially high (>1) values are obtained due to endogenous respiration. Later, lower values are observed corresponding with the increase of pollutant removal. In none of the cases, were these values comparable to the 0.5–0.6 observed in liquid suspended culture of MEK degraders (Deshusses 1994). This indicates that the biofilter process culture is subject to a significant stress, and is required to convert a larger fraction of the pollutant to carbon dioxide to satisfy its maintenance requirement. Carbon recovery is expected to approach unity after several weeks when the microbial growth equals its decay, and steady state, as strictly defined, is established. In the experiments reported here, when steady state was reached, an average of ca 82 ± 10% of the degraded MEK was recovered in carbon dioxide. The temporary low value observed at 100 h is due essentially to extended sorption after the increase in the inlet concentration.
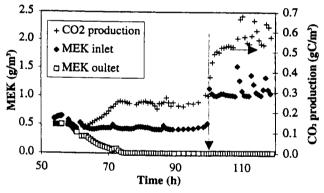

FIG. 2. Initial Start-Up Time Course—Initial Conditions: Inlet Concentration of MEK 0.45 g·m^{-3}, Air Flow 760 L·h^{-1} (42 m^3·m^{-2} h^{-1})—Reported Are MEK Inlet (♦) and Outlet (□) Concentrations, and Carbon Dioxide Production (+)
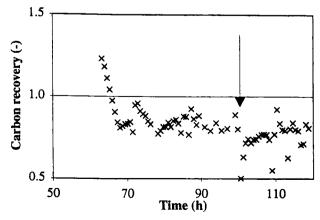

FIG. 3. Carbon Recovery During Start-Up of Biofilter; Arrow Corresponds to Step Increase of MEK Inlet Concentration From 0.45 g m^{-3} to 1.1 g m^{-3} (Conditions as in Fig. 2)

It is difficult to account for the missing carbon. Although the formation of organic by-products has been reported by others during treatment of VOCs such as ethanol or ethyl acetate (Devinny and Hodge 1995; Johnson and Deshusses 1996), it is an improbable explanation here, since neither metabolites nor degradation by-products other than carbon dioxide were ever detected during biotreatment of MEK. Tautz et al. (1992) found that in a biofilter degrading toluene, carbon recovery was consistently higher than one for inlet concentration lower than 0.2 g m^{-3}, and decreased to recoveries close to 0.6 when the biofilter was exposed to higher toluene concentration. The missing carbon was assumed to be incorporated in biomass. However, using the conditions of Fig. 2 and assuming 1.1 g MEK m^{-3}, 42 m^3 m^{-3} h^{-1}, and 50% C content in dry biomass, it is calculated that the missing 10% carbon represents an hourly formation of 6.1 g of dry biomass per cubic meter of reactor. This figure indicates that if the missing carbon fraction would be incorporated in biomass, the reactor would rapidly be clogged. This is not the case however, most probably because other nutrients become limiting. A possible explanation for the fate of missing carbon is the formation of carbonate that leaves the reactor unaccounted in a minimum of leaching water. Further analysis would be needed to close the carbon balance.
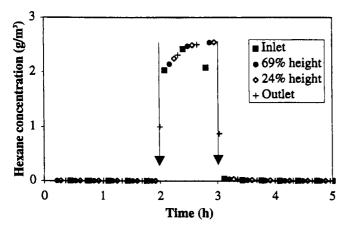

FIG. 4. Dynamic Response of Biofilter to 1-h Step of 2.2 g m^{-3} Hexane in Inlet Air; Air Flux = 740 L h^{-1}; Inlet Feed of MEK = 1.55 g m^{-3}; Inlet, Intermediary Heights and Outlet Concentrations are Reported

Interactions between Pollutants Undergoing Treatment

In Fig. 4, the dynamic response of a biofilter degrading a constant load of MEK, and exposed to a one-hour step of a mixture of hexanes is presented. The concentrations at different heights in the reactor are reported. It is obvious from Fig. 4 that hexane was not sorbed to a significant extent onto the packing material, hence no markedly different responses were observed at the different locations in the reactor. No influence of the hexane presence on MEK removal was observed and the carbon dioxide production pattern (not shown) confirmed that virtually no degradation of hexane occurred. This result is most probably due both to the unfavorable air/water partition coefficient (high Henry coefficient) of hexane, and to the fact that the reactor was never exposed to hexane before this experiment. Previously reported values for hexane elimination capacity in biofilters are, not unexpectedly, as low as 0.1–2.5 g m^{-3} h^{-1} (Sabo 1991; Knuth 1994). Nevertheless, the effect of repeated step injections still needs to be investigated to determine if bacterial adaptation occurs after a certain number of steps.

In a similar experiment, a total of 4.0 g of 1-propanol was fed over 30 min to a biofilter degrading a steady load of MEK. This corresponds to an inlet concentration of 1-propanol of about 10 g m^{-3}, or a transient load of 440 g m^{-3} h^{-1}. As indicated by the attenuation of the signal in the consecutive ports in Fig. 5, important biodegradation of the pulsed propanol occurred. The integration of the different responses showed that out of the 4 g injected, 1.5 g were recovered at the first sampling port at 69% height, 0.5 g at the second port, and only 0.1 g at the outlet. Overall, this represents 98% biodegradation. Lower concentration steps of 1-propanol (not shown) resulted in complete removal.

Although significant inhibition of MEK biodegradation was observed during the propanol step at the 69% height (see Fig. 6), the overall MEK removal remained higher than 99.6% over the entire time course. The carbon dioxide pattern for the propanol experiment reported in Fig. 7 is consistent with the temporary inhibition of MEK at mid height (mid-height decreases at 10–14 h) and with the biodegradation of the 1-propanol signal (increased overall CO$_2$ production). Apparently, a delay of 2–4 h exists between the introduction of 1-propanol and the observed rise in CO$_2$ production. A possible explanation for this is that under such conditions, the discontinuously in-
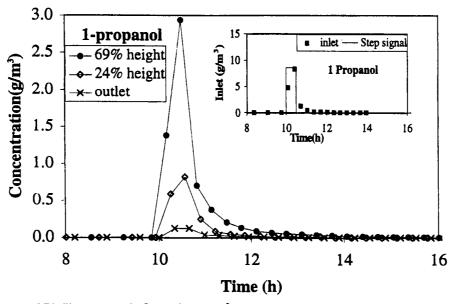

FIG. 5. Dynamic Response of Biofilter to 30 min Step of 10 g m^{-3} 1-Propanol in Inlet Air (Time = 10–10.5 h); Volumetric Loading 43 m^3 m^{-3} h^{-1}, Constant Inlet Feed of MEK = 1.3 g m^{-3}; 1-Propanol Time Course: (■) Inlet (Inset); (●) 69% Height; (◇) 24% Height; (×) Outlet

jected VOC is essentially sorbed to the packing prior to biodegradation, with subsequent release of CO_2.

When the same experiment was repeated with a step pulse of MIBK, the high removal of the base feed of MEK observed before could no longer be sustained as reported in Fig. 8. A much higher inhibition was observed resulting in a 2-h long MEK breakthrough. Also, MIBK was much less degraded than
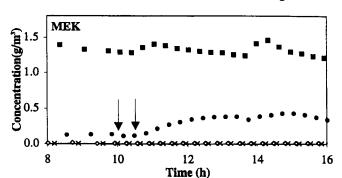
1-propanol under the same conditions: overall only 26% of the injected MIBK was biodegraded. Interestingly, there seems to be no evident correlation between the extent of inhibition of the base pollutant degradation (MEK here), and the amount of pulsed pollutant removed. The exact phenomena involved during such steps of multiple pollutants need to be further inves-
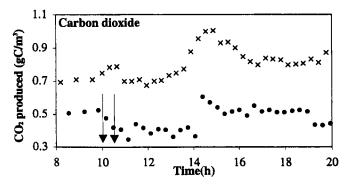

FIG. 6. Time Course for MEK during 1-Propanol Signal (Symbols as in Fig. 5)

FIG. 7. Carbon Dioxide Production Time Course during 1-Propanol Signal: Extended Scale, (●) 69% Height; (×) Outlet
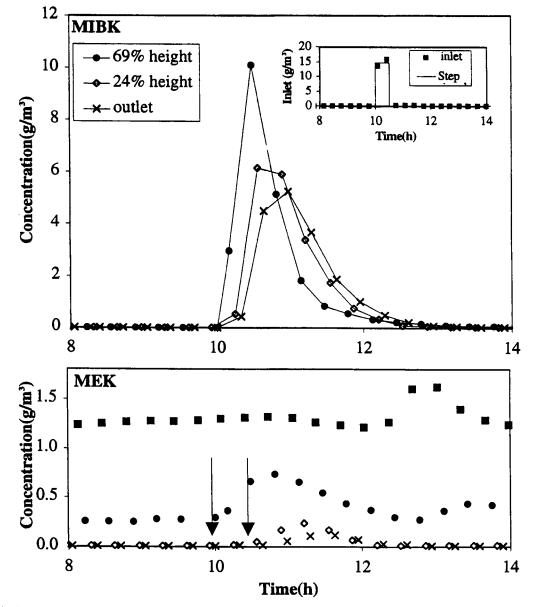

FIG. 8. Dynamic Response of Biofilter to 30 min Step of 10 g m⁻³ MIBK in Inlet Air (Time = 10–10.5 h); Volumetric Loading 42 m³ m⁻³ h⁻¹, Constant Inlet Feed of MEK = 1.3 g m⁻³; Upper Graph MIBK Time Course (Inset is Inlet MIBK), Lower Graph MEK Time Course: (■) Inlet; (●) 69% Height; (◊) 24% Height; (×) Outlet

TABLE 1. Result of Recovery of Acetone, or Mixture of Acetone, 1-Propanol, and MIBK, when Injected as Step Signal over 30 min; (Base Feed of MEK = 1.37 g m⁻³; Volumetric Loading 43 m³ m⁻³ h⁻¹)

Data Inlet signal (1)	Acetone Only Acetone 4 g m⁻³ (2)	Acetone, 1-Propanol, MIBK Injected as Mixture			
		Acetone 4 g m⁻³ (3)	1-propanol 4 g m⁻³ (4)	MIBK 4 g m⁻³ (5)	Total 12 g m⁻³ (6)
Injected at the inlet	1.5 g	1.5 g	1.5 g	1.5 g	4.5 g
Recovered 69% height	1.2 g	1.5	1.0 g	1.5 g	4.0 g
Recovered 24% height	0.2 g	0.6 g	0.9 g	1.2 g	2.7 g
Outlet	0.01 g	0.5 g	0.4 g	0.8 g	1.7 g
Overall removal	99%	67%	75%	47%	51%
Amount degraded	1.49 g	1.0 g	1.1 g	0.7 g	2.8 g
MEK removal	>99.6%	—	—	—	99.4ᵃ–98.2%ᵇ

ᵃBefore the step.
ᵇMinimum during the step.

Acetone injected alone

Acetone injected simultaneously with MIBK and 1-propanol

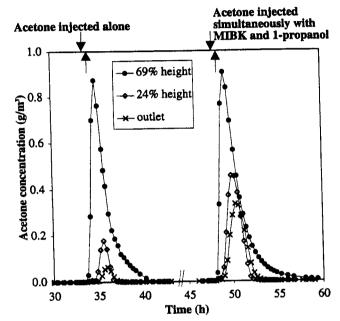- 69% height
- 24% height
- outlet

FIG. 9. Dynamic Response of Biofilter to 30 min Step of 4 g m⁻³ Acetone in Inlet Air (Left Side), and Acetone Mixed with 1-Propanol and MIBK, 4 g m⁻³ Each (Right Side); Volumetric Loading 42 m³ m⁻³ h⁻¹; Constant Inlet Feed of MEK = 1.3 g m⁻³; Acetone Time Course (Inlet Shown by Arrows Only): (●) 69% Height; (◊) 24% Height; (×) Outlet

tigated. However, the comparison of hexane and propanol or MIBK experiments suggests that, in addition to some specific pollutant toxicity effects, cross inhibition following shock loading is more likely to occur for biofilters equipped with packing with high sorption capacity and treating pollutants with low Henry coefficients.

In a similar manner, acetone was fed for 30 min to the biofilter operating under the same conditions and the experiment compared to an identical signal of acetone mixed with methyl isobutyl ketone (MIBK) and 1-propanol. The results, presented in detail for acetone in Fig. 9 and summarized for all pollutants in Table 1, clearly show that the VOCs considered were not degraded independently of one another. Comparison of acetone time courses in Fig. 9 shows that when pulsed alone to a biofilter degrading MEK, the outlet concentration of acetone never exceeded 0.07 g m⁻³, whereas when mixed with others, concentrations as high as 0.3 g m⁻³ were detected. Similar conclusion could be made for 1-propanol and MIBK.

Although, the total amount of VOC degraded was higher in the case of multiple pollutant injection, the removal percentage of the individual components was affected by the presence of the other VOCs. This effect was particularly important for 1-propanol, for which up to 98% could be degraded when injected alone at 10 g m⁻³ (see the experiment reported in Fig. 5), and only 75% of 4 g m⁻³ were removed when injected with other VOCs at a total concentration of 12 g m⁻³. For acetone, the presence of 1-propanol and MIBK resulted in a 50% increase in the amount released to the atmosphere (see Table 1). This stresses the significant influence that pollutants can have on one another when treated simultaneously in biofilters.

Plausible explanations to the observed phenomena are that the VOCs considered are probably degraded by the same consortia and competitive inhibitions occur. This is supported by the fact that seven pure cultures of MEK degraders, isolated from the biofilters considered here, could grow on acetone, 1-propanol, and MIBK as sole carbon and energy substrates. Also it has been observed that mixtures of solvents exhibit an enhanced toxicity. This effect was particularly pronounced for ketones, in conjunction with other VOCs (O'Donoghue 1984; World Health Organization 1993). Further experiments will seek to better quantify the inhibitions occurring when mixtures of pollutants are treated, and to develop appropriate kinetic relationships.

CONCLUSIONS

The results of a start-up of a compost based biofilter were shown and discussed. Inoculation of the packing with specific enrichment cultures was most probably a reason for rapid start-up (3–5 d). Carbon dioxide production was shown to correlate well with the pollutant elimination and within a few days from the start-up, a stable value of 82 ± 10% carbon recovery in CO_2 was observed in the exhaust air. Future efforts will be directed towards closing the mass balance with a better accuracy.

When hexane, acetone, MIBK, 1-propanol, or mixtures of these solvents were introduced in a step pulse manner to a biofilter degrading MEK, very different responses were observed. Hexane was neither sorbed to the packing nor biodegraded to a significant extent. Acetone was subject to important sorption and well degraded. 1-propanol was even better removed even though the biofilter had never been exposed to 1-propanol vapors before the experiment. During 30-min transients, loadings of 1-propanol up to 440 g m⁻³ h⁻¹ were handled with only minor breakthrough. Interestingly carbon dioxide emission usually peaked 2–5 h after the step injection of VOC suggesting that during a transient state, pollutants are first sorbed to the packing material, and subsequently degraded. This would explain why hexane was not degraded. MIBK showed the most inhibitory effect on the degradation of the base feed of MEK. So far no explanation other than a competitive inhibition exists, for the cross interaction between multiple pollutant biodegradation. This is corroborated by ob-

servation of cultures extracted from the biofilter being able to grow on both MEK, MIBK, 1-propanol, and acetone. The differences observed between the biodegradation and inhibition rates of the different VOCs can mainly be attributed to differences in packing affinities, in Henry coefficients, in intrinsic biodegradation rates, and affinity with the degradation key enzymes.

The phenomena involved during transient operation of biofilters with multiple pollutants need to be further investigated since these experiments provide information on the behavior under real operating conditions. They also help in establishing a fundamental description of pollutant removal in biofilters and permit the development of conceptual explanations presently missing in the literature.

APPENDIX. REFERENCES

Deshusses, M. A. (1994). "Biodegradation of mixtures of ketone vapours in biofilters for the treatment of waste air," PhD thesis, Swiss Fed. Inst. of Technol., Zurich, Switzerland.

Deshusses, M. A. (1995). "Operation of compost based biofilters under transient and multiple VOC conditions." *Proc., 1995 Conf. on Biofiltration*, D. S. Hodge and F. E. Reynolds Jr., eds., Tustin, Calif., 45–52.

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1995a). "Behavior of biofilters for waste air biotreatment. II: Experimental evaluation of a dynamic model." *Envir. Sci. and Technol.*, 29(4), 1059–1068.

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1995b). "Behavior of biofilters for waste air biotreatment. I: Dynamic model development." *Envir. Sci. and Technol.*, 29(4), 1048–1058.

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1996). "Transient state behavior of a biofilter removing mixtures of vapors of MEK and MIBK from air." *Biotechnol. Bioengrg.*, 49(5), 587–598.

Devinny, J. S., and Hodge, D. S (1995). "Formation of acidic and toxic intermediates in overloaded ethanol biofilters." *J. Air and Waste Mgmt. Assn.*, 45(2), 125–131.

Hodge, S. H., Medina, V. F., Wang, Y., and Devinny, J. S. (1992). "Biofiltration: Application for VOC emission control." *Proc., 47th Purdue Industrial Waste Conf.*, Lewis Publishers, Chelsea, Mich., 609–619.

Johnson, C. T., and Deshusses, M. A. (1996). "Evaluation of a rapid methodology to determine elimination capacities in biofilters for VOC treatment." *Proc., 2nd Conf. on Biofiltration*, F. E. Reynolds Jr., ed., Tustin, Calif., 223–230.

Knuth, M. (1994). "Beseitiqung von Riechstoffen und Hexan im Abgas einer Olmühle mit einem Biofilter." *VDI Berichte 1104*, VDI Verlag, Düsseldorf, Germany (in German), 333–341.

O'Donoghue, J. L., Krasavage, W. J., Divincenzo, G. D., and Katz, G. V. (1984). "Further studies on ketone neurotoxicity and interractions." *Toxicology Appl. Pharmacol.*, 72(2), 201–209.

Sabo, F. (1991). "Behandlung von Deponiegas im Biofilter," PhD thesis, Univ. of Stuttgart, Germany, Stuttgarter Berichte zur Abfallwirtschaft, Band 47, Stuttgart, Germany (in German).

Shareefdeen, Z., and Baltzis, B. C. (1994). "Biofiltration of toluene vapor under steady-state and transient conditions—theory and experimental results." *Chemical Engrg. Sci.*, 49(17), 4347–4360.

Tang, H. M., Hwang, S. J., and Hwang, S. C. (1995). "Dynamics of toluene degradation in biofilters." *Haz. Waste and Haz. Mat.*, 12(3), 207–219.

Tautz, H., Bronnenmeier, R., Frank, P., and Zeller, B. (1992). "Hochleistungsbiofilter." *Vortragsunterlagen zum Seminar Mikrobiologische Verfahrenstechniken zur Umweltsanierung*, Linde AG, Höllriegel skreuth, Germany (in German).

Van Langenhove, H., Lootens, A., and Schamp, N. (1987). "Inhibitory effects of SO2 on biofiltration of aldehydes." *Proc., Biol. Treatment of Industrial Waste Gases*, Dechema, Heidelberg, Germany.

World Health Organization. (1993). "Methyl ethyl ketone." *Envir. Health Criteria 143*, World Health Organization, Geneva, Switzerland.