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Development and Validation of a Simple Protocol To Rapidly Determine the Performance of Biofilters for VOC Treatment

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A protocol has been developed for the rapid determination of complete elimination characteristics of target pollutants in waste air biofilters. The protocol involves the determination of two pollutant concentration profiles along the height of a three-segment biofilter under carefully chosen conditions. The combination of the data results in 12 points on the elimination capacity vs load curve which is sufficient to fully characterize a system. The protocol conditions were chosen to enable characterization of biofiltration systems with VOC elimination capacities ranging from 20 to 120 g m^{-3} h^{-1}. The protocol was then applied to 18 different VOCs, and the results compared well with previously published data, when available. Maximum removal performance of classes of compounds in the biofilter followed the sequence alcohols > esters > ketones > aromatics > alkanes. An attempt was made to correlate the pollutant elimination with Henry's coefficient, and the octanol/water partition coefficient and trends were obtained. The results suggest that biodegradation of VOCs in biofilters is influenced both by the pollutant availability (Henry's Law coefficient) and to a lesser extent by the hydrophobicity of the treated compounds (octanol/water partition).

Introduction

Biofiltration is an emerging technology to control odor and volatile organic compound (VOC) emissions from contaminated air streams (*1*−*4*). It is particularly well suited for the treatment of large air streams with low concentrations of pollutants. Biofilters work by passing humidified polluted air through a bed of porous material, generally a mixture of compost and wood chips. On the packing, microorganisms are naturally immobilized and biodegrade the absorbed pollutants. Under optimum conditions, biodegradable contaminants are rapidly converted to carbon dioxide and water without the formation of intermediates or dead-end metabolites. Sulfur, chlorine, or nitrogen containing pollutants will generate sulfate, chloride, and nitrate, respectively, and their applicability in biofilters might be limited because of the difficulty to leach these metabolites out of the packing. In these cases, biotrickling filters might be better suited (*5*).

Biofilters have been used for more than 20 years in industrial applications. Significant progress has been made in the past decade in the design of biofilters (*1*). However, in most cases, full-scale reactor design is still based on the results of bench or pilot-scale tests performed either on-site with the actual air stream or in laboratories with a synthetic air stream. The reason is often that data on the elimination of a given pollutant or of a given combination of pollutants are either not available or were acquired under different conditions. Hence they cannot be trusted for full-scale reactor design. Also, although a large body of empirical data has been published, the fundamental knowledge necessary for biofilter design based on theoretical concepts or on mathematical models is still missing. Hence, there is a need for the establishment of both standard biofilter test protocols and the establishment of databases for pollutant removal rates in biofilters. Particularly useful are data acquired under similar conditions. This will help designing biofilters and understanding the factors that influence the elimination of pollutants in biofilters.

To generate an extended database of elimination capacities, a large number of experiments needs to be conducted. Typically, for each pollutant, a complete curve for the elimination capacity of the biofilter as a function of the pollutant loading as shown in Figure 1 is desired. The pollutant elimination capacity (EC) is defined in eq 1 as a function of the inlet and outlet gas concentrations ($C_{g,in}$ and $C_{g,out}$), the air flow rate (Q), and the biofilter bed volume (V). The elimination capacity represents the amount of substrate degraded per unit of trickling filter volume and time and is often reported as a function of the pollutant loading L (eq 2).

$$\mathrm{EC} = \frac{(C_{g,in} - C_{g,out}) \times Q}{V} (\mathrm{g\ m^{-3}\ h^{-1}}) \qquad (1)$$

$$L = \frac{C_{g,in} \times Q}{V} (\mathrm{g\ m^{-3}\ h^{-1}}) \qquad (2)$$

Of particular interest for reactor design are the maximum performance (EC_{max}) of the biofilter and the maximum loading called "critical loading" before the removal deviates significantly from the 100% removal line (Figure 1). In this study the critical loading was defined as the loading at which 95% removal occurred. It should be mentioned here that it is usually assumed that the performance of a biofilter depends only on the pollutant load, hence, that low concentrations−high flowrates conditions lead to similar elimination capacities than high concentrations−low flowrates. This assumption is generally valid because the pollutant concentrations commonly encountered in biofilters are high enough for the biofilter to operate in the zero-order kinetic regime. This is no longer true at very low pollutant concentrations (typically below 0.05−0.01 g m^{-3}), in particular for pollutant with high Henry's law coefficients, because first-order kinetics will prevail in the biofilter resulting in a reduction of the maximum elimination capacity.

Obtaining complete data for one pollutant usually represents 2−3 months of work with daily analyses of biofilter influent and effluent concentrations. Consequently, the establishment of a database for a large number of pollutants is a large investment in time, effort, and resources. Hence, the primary objective of the present work was to develop and validate a protocol to rapidly determine complete elimination characteristics of a pollutant in a biofilter. The target was a result within a 20% error margin obtained in 48 h or less. A second objective was to apply this protocol to various VOCs and to establish a minidatabase. This database was then used to evaluate the relationship between the

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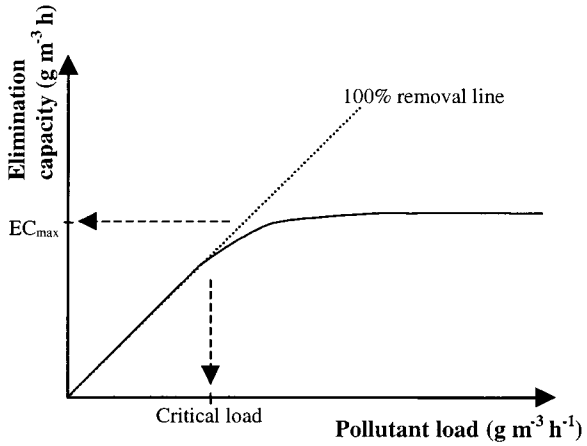

FIGURE 1. Typical elimination capacity vs load characteristic in a biofilter. EC_{max} is the maximum elimination capacity; the critical load is the maximum loading at which the removal efficiency starts to deviate significantly from the 100% removal line.

removal of the tested VOCs and selected properties of the pollutants in order to search for trends and correlations. Such a discussion helps in understanding of the factors influencing the elimination of pollutants in biofilters. An obvious extension of this work will be the development of quantitative structure−activity relationships (QSARs) for biodegradation of VOCs in biofilters (*6*−*8*) so that the elimination of any pollutant in biofilters can be theoretically predicted from previous experiments. When structure activity relationships are fully developed and validated, reactor design will be greatly simplified.

Experimental Approach

To reduce the time of experimentation, a protocol was developed where a tested VOC was injected in a three-segment biofilter over 35 h. The concentration profile in the biofilter, determined for two different concentrations, was then used to calculate the elimination capacity of each segment, and each combination of segments. Hence six data points were obtained per concentration profile. Two concentration profiles, i.e., 12 points per VOC, are sufficient to determine a complete elimination capacity vs load characteristic. The application of this protocol allows one to obtain removal performance data for about 10 different compounds over a month. This is an impossible task with conventional protocols.

Several obstacles exist for such a short protocol to be valid. First, it is unlikely that process culture population shifts will occur within 35 h after exposure to a new VOC, so that no or low pollutant elimination is observed. This would underestimate the biofilter performance for the given pollutant. It was hypothesized that this effect could be reduced if the biofilter was exposed to a selection of VOCs between the different tests. This is supported by the fact that biofilter acclimation is generally shortened in systems that are either inoculated with a competent culture or that have received a continuous supply of a similar compound (*9*−*11*). The selected VOCs for this purpose were methyl isobutyl ketone (MIBK), isopentane, and toluene (1:1:1 mixture) as model pollutants for oxygenates, aliphatics, and aromatics, respectively. Although it is probable that some biological competition/inhibition occurred between the elimination of these three compounds in the biofilter, it is likely that their simultaneous presence in the air stream between each experiments maintained an appropriate biodiversity and stimulated various metabolisms in the biofilter. The fact that simultaneous removal of the three compounds occurred indicated that several common VOC cleavage mechanisms

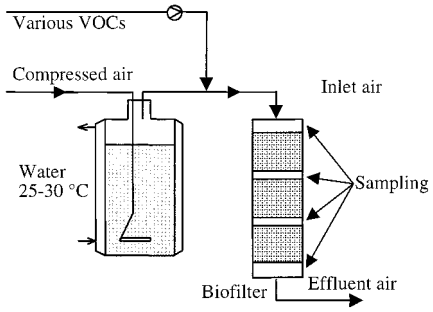

FIGURE 2. Schematic of the experimental setup.

such as ortho or meta cleavage of aromatics, β-elimination for aliphatics, etc. were indeed active.

Another concern during such short term experiments are sorption effects commonly observed during transients (*9*, *10*, *12*). Such effects could be mistakenly considered as biodegradation leading to overestimation of biofilter performance. Hydrophilic pollutants are of greater risk, because their sorption to the damp support is significant. Hydrophobic compounds are less problematic as gas/biofilm equilibrium was shown to occur within minutes (*12*). Thus, to limit the effect of sorption, high air flow rate and low concentrations were preferred in the test protocol to favor quick establishment of sorption equilibrium. Still, packing materials that include activated carbon should not be tested with the proposed protocol, since sorption is known to take much longer on those supports. As a possible screening tool to differentiate sorption from biodegradation, it was attempted to compare VOC elimination with carbon dioxide production. Any disappearance of VOC not correlated with CO_2 production would be considered as sorption. However, this approach failed. Carbon dioxide production was lower than expected, and the response to changes was slow. Problems with closing the carbon balance in biofilters have been reported before (*12*, *13*).

It is difficult to estimate the extent of uncertainty introduced by the phenomena discussed above. It will clearly depend on the pollutant undergoing treatment, in particular its biodegradability and its hydrophobicity. As mentioned, failure to wait for culture adaptation will result in underestimation of performance, whereas misinterpretation of sorption will result in overestimation of performance. Altogether, given that biofiltration experiments are prone to some degree of variation, a result within 10−20% uncertainty will be considered as acceptable.

It should be mentioned that long-term effects such as bed plugging or poisoning, packing acidification, nutrient shortage, etc. exist in biofilters (*1*). They usually occur after 6 months to a year operation and will clearly not be detected by the protocol discussed herein. Their cause and influence clearly fall outside of the scope of this work. In fact, these long term effects are often not fully identified during conventional pilot or laboratory scale experiments either. When such problems arise during conventional testing, a significant effect on the pollutant removal performance is observed which will in turn influence the quality of the data obtained. Hence, an advantage of the protocol developed herein is that it takes a snapshot of the process performance at a given time, under a given set of operating conditions.

Materials and Methods

A schematic diagram of the equipment used is shown in Figure 2.

Biofilter and Packing Material. The biofilter was constructed from clear PVC tubing 1.5 m in length and 0.15 m in internal diameter. Operating temperatures were maintained between 20 and 25 °C. The biofilter was filled with a

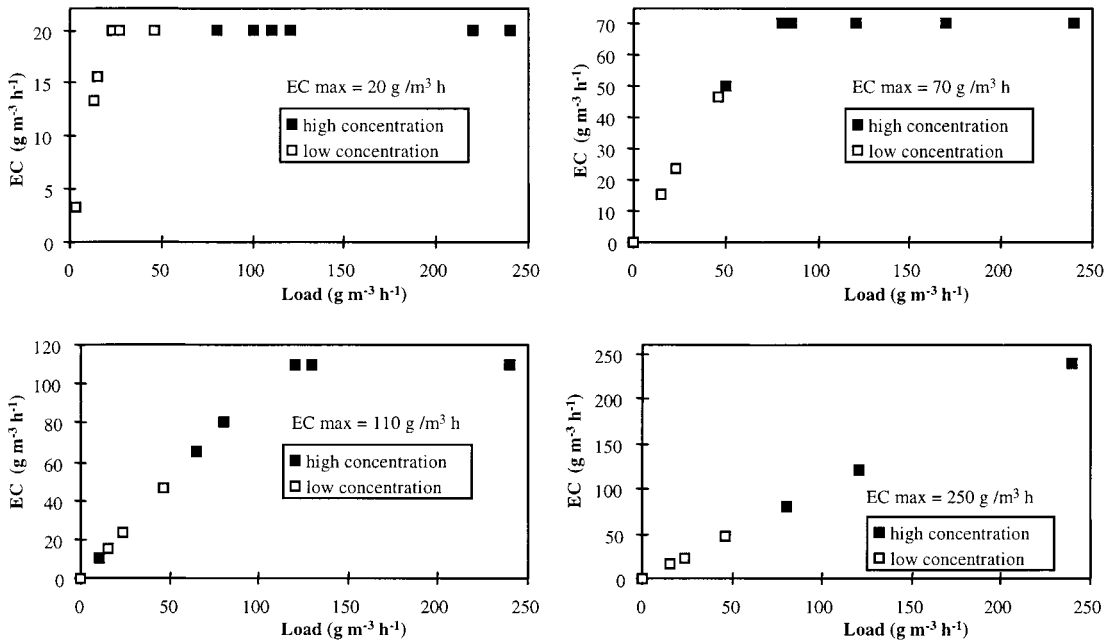

FIGURE 3. Computed elimination capacity vs pollutant load plots for the proposed protocol assuming simple kinetics (see text for details) for four different maximum elimination capacities. Conditions: air flow rate of 1 m^3 h^{-1} (surface loading of 55 m^3 m^{-2} h^{-1}); inlet pollutant concentration of 0.35 g m^{-3} (open symbols) and 1.8 g m^{-3} (closed symbols).

mixture of mushroom compost and wood chips (irregular shape, approximately 1−4 cm length, ratio compost to wood chips was about 20:80 vol. basis). The packing was buffered to near neutral with lime (25 kg m^{-3}) and initially amended with slow release nutrients (25 kg of blood and bone meal and 25 kg of 4-4-2 N-P-K compost activator per cubic meter of finished packing) to prevent medium acidification and nutrient limitation, respectively. After the beginning of the experiments, neither nutrient nor pH buffer was added. The void volume of the packing material was approximately 40−50%. The filter bed was split into three separate sections of 40 cm height each, to allow reproducible air sampling at intermediate bed depth. Only with this setup could concentration profiles be reliably determined. Prior to the experiments presented herein, the same biofilter medium was used for a 3-month long study involving toluene and ethyl acetate vapor removal (*14*). The packing had been initially inoculated with concentrated enrichment cultures and was not modified for these experiments.

Pollutant Containing Humid Air Stream. Compressed oil-free air was saturated with water vapor by sparging the air through water thermostated at 25−30 °C. VOCs were injected into the air stream by a metering pump (FMI, Inc. Oyster Bay, NY), where they subsequently evaporated. All chemicals were of high purity grade (Fisher Scientific, Pittsburgh, PA), except for hexane (a mixture of n- and branched hexanes; Fisher Scientific) and xylenes (o, m, p, with traces of ethylbenzene; Fisher Scientific). A constant downward gas flow rate of 1 m^3 h^{-1} was metered with a mass flow controller (Porter instruments, Hatfield, PA), giving volumetric loadings of about 138, 69, and 46 m^3 m^{-3} h^{-1} (empty bed retention times of 26, 52, 78 s, respectively), for one, two, and three segments of biofilters, respectively. During standard conditions, a mixture of toluene, methyl isobutyl ketone (MIBK), and isopentane was injected at a concentration of 0.2 g m^{-3} each. The synthetic waste air had a relative humidity greater than 95%. Under the test conditions, the pressure drop over the filter remained low (below 3 cm water gauge) for about a month and then slowly increased up to 11.2 cm water column as a result of packing compaction.

Analyses. The VOC concentrations in the gas phase were determined by gas chromatography. Air samples, selected by a 16 stream injection valve (Valco, Houston, TX), were pumped via heated sampling lines through 0.1 and 0.25 mL sampling loops for automatic injection into a Hewlett-Packard type 5890A Series II gas chromatograph (Wilmington, DE) operated initially at 65 °C. A pressure and a temperature program was necessary to analyze VOCs and carbon dioxide under 10 min. VOCs and potential metabolites were separated on a 30 m Supelcowax 10 column (0.53 mm, 1 μm film, Supelco, Bellefonte, PA) and detected with a flame ionization detector. Carbon dioxide was analyzed with a 2.4 m 80/100 Chemosorb 1/4" packed column (Supelco, Bellefonte, PA) and detected with a thermal conductivity detector.

Experimental Protocol. For the selection of the most appropriate biofiltration experimental protocol, hypothetical elimination capacity versus load characteristics were constructed. This was done assuming that the elimination capacity equaled the loading at loadings below the maximum elimination capacity and that it equaled the maximum elimination capacity at higher loadings. In doing so, the effect of diffusion limitation was neglected, but a relatively good projection of the results could be obtained (Figure 3). The objective of this design exercise was to select experimental conditions that enabled detailed elimination characteristics to be obtained for a wide range of systems, based on concentration profiles for two different inlet concentrations only. By trial and error, a constant air flow rate of 1 m^3 h^{-1} (surface load of 55 m^3 m^{-2} h^{-1}) and inlet pollutant concentrations of 0.35 g m^{-3} first and then 1.8 g m^{-3} were selected as the most optimum test conditions. As shown in Figure 3, the protocol allows good characteristics to be obtained for maximum elimination capacity ranging from 20 to approximately 120 g m^{-3} h^{-1}. Another protocol would be needed for lower or higher elimination capacities.

To determine elimination characteristics for one VOC over a short time span (48 h), the protocol listed in Table 1 was followed. VOC concentrations were analyzed continuously and averaged at the end of each test phase to determine the reactor performance. In an earlier protocol, the tested VOC was injected in a similar manner but over 8 h only. This was later extended to 35 h to allow more time for the biofilter to adapt and to minimize artifacts due to sorption. Nevertheless, neither protocols are appropriate for biofilters equipped with

TABLE 1: Experimental Protocol To Determine a Complete Elimination Characteristic over 48 h in a Three-40 cm Segment Biofilter[a]

time (h)	treatment condition	concn(s)
0−10	tested VOC, low concn, analysis at 9.5−10 h	0.35 g m^{-3}
10−35	tested VOC, high concn, analysis at 34−35 h	1.80 g m^{-3}
35−39	no VOC	
39−46	standard conditions: 1:1:1 mass, isopentane, toluene, MIBK; the mixture was continued until 2 h prior to next test if no test is performed at 48 h.	0.2 g m^{-3} each
46−48	no VOC; the biofilter is ready for another test at 48 h.	

[a] A constant air flow rate of 1 m^3 h^{-1} was used (volumetric loadings of 138, 69, and 46 m^3 m^{-3} h^{-1}, for one, two, and three segments of biofilters, respectively).

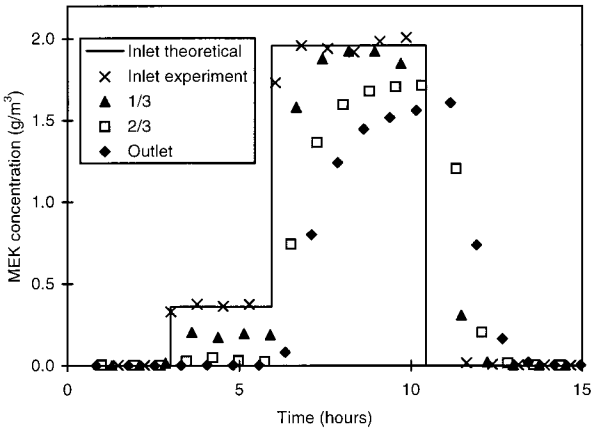

FIGURE 4. Typical results of the test protocol (MEK shown): concentrations of MEK at different heights in the biofilter vs time.

activated carbon packing because of the slow sorption dynamics (*15, 16*).

Results and Discussion

Approximately 7 days after the 1:1:1 mixture of isopentane, toluene, and MIBK was first injected, the biofilter displayed nearly complete MIBK degradation. Isopentane and toluene were degraded as well but to a lesser extent. Such a short acclimation period was expected since the biofilter packing had been used before for tests with toluene and ethyl acetate for approximately 3 months (*14*). Proper inoculation and acclimation for about 2−4 weeks would be recommended for fresh biofilter packing. After the acclimation phase, a random test sequence of VOCs was performed, with two or sometimes three different compounds tested per week. Between the tests, standard operating conditions were maintained (Table 1).

Figures 4−6 represent typical test results for a pollutant. Here, methyl ethyl ketone (MEK) is shown as tested by the earlier protocol (same concentrations, injection over 8 h only). The transient response shown in Figure 4 is typical for the treatment of hydrophilic compounds in compost based biofilters (*10, 12*). For the determination of steady-state elimination capacity, only the data shortly before the step-change were utilized. Detailed examination of Figure 4 shows that the concentrations were not fully steady at that time where the MEK concentration was either increased or turned off. This motivated the change in the duration of the test protocol extending it to 48 h (35 h of VOC injection), as described in Table 1, which allowed the establishment of

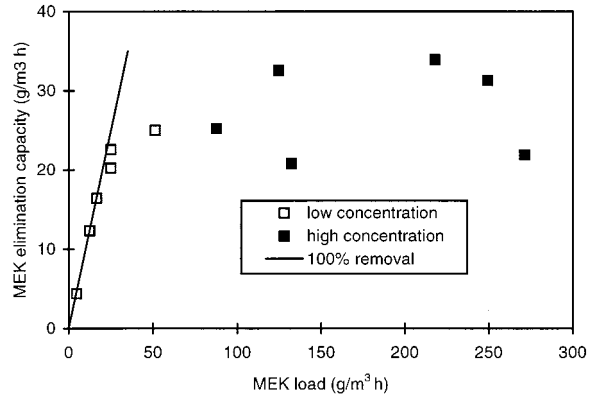

FIGURE 5. Typical results of the test protocol: MEK elimination capacity as a function of the loading.

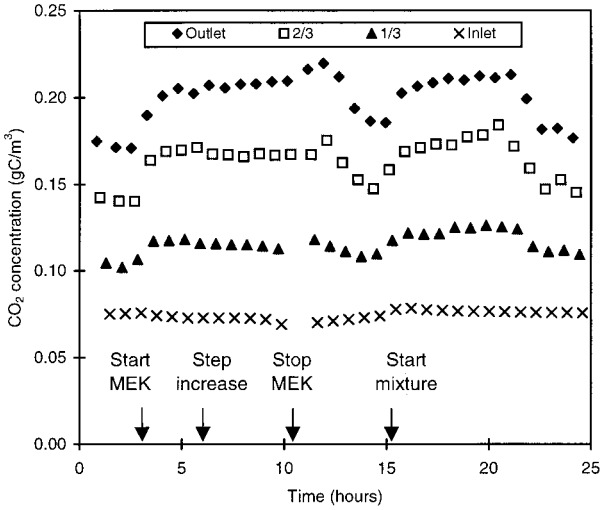

FIGURE 6. Typical results of the test protocol: concentrations of CO_2 at different heights in the biofilter vs time during the MEK run. Note the extended scale.

more reliable pseudo-steady state. In general, hydrophilic compounds such as MEK, methanol, or ethyl acetate were relatively slow to reach steady performance, but reasonable steady performance (±10%) was obtained within the 35 h duration of each VOC injection. When hydrophobic compounds were treated, sorption effects were very minor. Since biofilter performance is generally reported with a ±10−15% uncertainty, such sorption effects were not considered to be a major drawback.

The data of Figure 4 allows a good elimination capacity vs load characteristic to be obtained (Figure 5). The maximum elimination capacity for MEK was about 30−35 g m^{-3} h^{-1}, while the critical loading ranged from 20 to 23 g m^{-3} h^{-1}. Analysis of carbon dioxide patterns (Figure 6) clearly shows a marked increase in CO_2 production after MEK was introduced in the system, but no clear change was observed after the MEK concentration was raised to 1.8 g m^{-3}. After the end of the experiment, when MEK was stopped and before the standard VOC mixture was resumed, a decrease in CO_2 production was observed. It would have reached levels corresponding to endogenous respiration if VOC supply had not been resumed at 15 h. Overall, a low recovery (30−80%) of the degraded pollutant as CO_2 was observed in most experiments. This prevented the use of CO_2 data for further calculations. The fact that poor (CO_2 formed)/(degraded carbon) ratios were obtained has been reported before, especially during transient state (*12*). It can be attributed to several phenomena, including the probable formation of carbonates, and in rare cases, the formation of partially

TABLE 2. Summary of Maximum Elimination Capacities and Critical Loadings Obtained and Comparison with Previously Values Observed by Others

no.	compound	EC max ($g\ m^{-3}\ h^{-1}$)	critical load ($g\ m^{-3}\ h^{-1}$)	EC_{max} reported by others (ref) ($g\ m^{-3}\ h^{-1}$)	critical load reported by others (ref) ($g\ m^{-3}\ h^{-1}$)
1	hexane	3−8	1	1.5[h] (*17*); 21[c,f] (*18*); 2.5[c,e] (*19*)	<0.5[h] (*17*); 21[f] (*18*)
2	isopentane	7−8	1−2	18−28[l] (*20*), 2−3.5[j] (value for pentane) (*21*)	8−15[l] (*20*); <1.5[j] (value for pentane) (*21*)
3	MEK	30−35	20−22	120[g] (*22*), 22−43[p] (*23*)	75−100[g] (*22*), 2−10[p] (*23*)
4	MIBK	40−50	13−15	25−30[g] (*22*)	15−18[g] (*22*); <15[e] (*24*)
5	acetone	65−70	21−23	40−45[c,g] (*25*); 100−150[g] (*26*)	120[g] (*27*)
6	ethyl acetate	140−240	175−180	150−250[e] (*28*); 79−96[g] (*15*); 170−200[d,e] (*14*); 280−350[k] (*29*)	40−60[e] (*28*); 130−180[d,e] (*14*); 180−200[k] (*29*)
7	butyl acetate	32−34	28−32	40[g] (*30*)	8−10[g] (*30*)
8	isobutyl acetate	74−76	44−48	NF[q]	NF[q]
9	methanol	135−150	32−34	30−65[h] (*17*), 100−120[f] (*31*)	25−40[h] (*17*); 50−80[f] (*31*); 42[g] (*32*)
10	ethanol	148−150	78−80	20−40[l] (*33*); 90−130[m] (*34*); 18−40[o] (*35*)	40[o] (*35*)
11	1-propanol	150	115−120	NF[q]	NF[q]
12	2-propanol	120[a] (*25*[b])	78−80	58−78[g] (*15*)	NF[q]
13	*sec*-butanol	140[ac] (*20*[d])	80−85	NF,[q] values for butanol reported: 70[h] (*17*); 24−26[o] (*35*); 70−76[h] (*36*)	NF,[q] values for butanol reported: 55-60[h] (*17*); 20−22[o] (*35*); 30−40[h] (*36*)
14	benzene	7−8	1	2−5[f] (*37*); 23[h] (*36*); 31−47[j] (*38*)	<5[f] (*37*)
15	toluene	8−20	6−8	5−18[h] (*17*); 10−40[e] (*28*); 20−25[g] (*30*); 45−55[f] (*13*); 25[l] (*39*); 23−32[f] (*40*); 20[d,e] (*14*)	5−8[e] (*28*); <10[g] (*30*); 30−40[f] (*13*); 10−15[l] (*39*); 6−10[f] (*40*); 11−20[f] (*9*)
16	xylene	15−20	2	25−27[h] (*36*); 25−42[n] (*41*)	10−15[n] (*36*)
17	ethylbenzene	30−32	2	NF[q]	NF[q]
18	methyl *tert*-butyl ether (MTBE)	0	0	8[j] (*42*); 38−57[p] (*43*)	no biofilter data, 15−20[p] (*43*)

[a] Significant metabolite formation was observed; value is for pollutant disappearance. [b] Value is pollutant disappearance minus metabolite formed. [c] Limited data, maximum elimination capacity may not have been reached in these experiments. [d] In a mixture with other VOCs. [e] Biofilter media: compost + wood chips. [f] Biofilter media: compost + perlite. [g] Biofilter media: compost + polystyrene beads. [h] Biofilter media: compost + expanded clay. [i] Biofilter media: peat moss mixture. [j] Biofilter media: synthetic medium (biotrickling filter operated as a biofilter). [k] Biofilter media: compost + bark. [l] Biofilter media: peat. [m] Biofilter media: compost. [n] Biofilter media: peat + bark + wood chips. [o] Biofilter media: peat + perlite. [p] Biofilter media: biotrickling filter. [q] NF, no reference found.

oxidized metabolites. Still, further research to elucidate the dynamics of carbon in biofilters is warranted.

The results for all 17 VOCs tested are summarized in Table 2 and compared to previously published values, when available. Although direct comparison may sometimes be difficult because of the differences in biofilter setup or because of the presence of copollutants in the air stream, a good agreement between the values determined herein and those reported previously is observed. Note that the previously published data for toluene and ethyl acetate of ref *14* were from the same biofilter but for a conventional long term protocol. The results are comparable. Table 2 also presents biodegradation data for some pollutants (e.g., 2-butanol, isobutyl acetate, 1-propanol, MEK, ethylbenzene) that have not been widely studied in biofilters. Overall, the combined data presented in Figures 4−6 and in Table 2 and the good agreement with previously reported values demonstrate that the developed protocol is well suited for the rapid determination of biofilter performance.

The average maximum elimination capacities that were obtained herein are reported by classes of compounds in Figure 7. The data illustrate that the pollutant removal performance in biofilters follows the sequence alcohols > esters > ketones > aromatics > alkanes. Contrary to common belief, there seems to be no clear correlation between the maximum elimination of the VOC undergoing treatment and its molecular weight. The only ether tested was methyl *tert*-butyl ether (MTBE) for which biodegradation is possible but requires a much longer acclimation than accomplished during the experiments (*42*, *43*). Thus, the MTBE data obtained herein are not representative of either other ether removal or of long term biofilter performance for MTBE. In fact ethers are relatively well degraded in vapor phase bioreactors (*43*−*45*).

In an attempt to correlate biofilter performance with physicochemical properties of the treated pollutants, all data

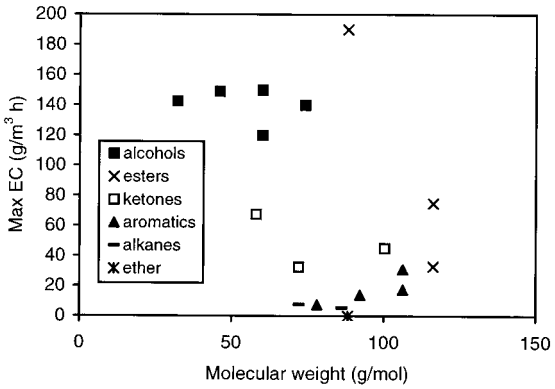

FIGURE 7. Average of experimentally determined maximum elimination capacities of VOCs by classes of compounds and molecular weight.

listed in Table 2 were reported as a function of the logarithm of their Henry's Law coefficients and logarithm of their octanol/water partition coefficients in Figure 8. General trends were sought, either for the entire set of data of each graph in Figure 8, or for subsets of the data when only part of the graph was found to be linear. The resulting correlations coefficients r are reported in Table 3. Statistical analysis reveals that the best correlations were between the logarithm of Henry's Law coefficient and the logarithm of the maximum elimination capacity or of the critical loading (r ranging from 0.67 to 0.88). Correlations with log $K_{o/w}$ was less significant, in particular for the data reported by others (Table 3). In all cases, the correlation was better for the data obtained herein than for the combination of the data reported by others (Table 3). One reason for this is the greater variation of biofilter systems used by others. Overall, the fact that low to medium correlation coefficients were obtained suggests that the trends

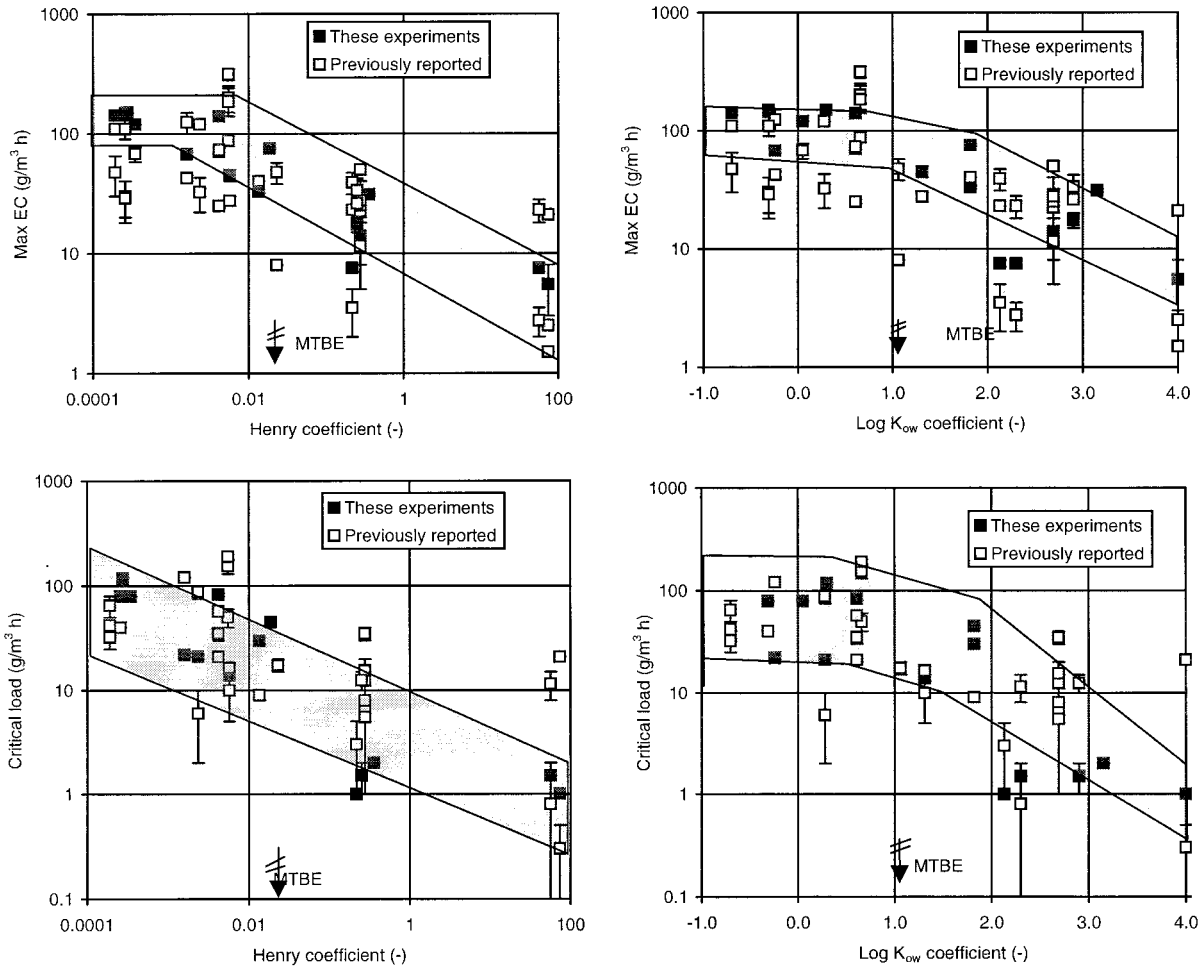

FIGURE 8. Experimentally determined and previously published maximum elimination capacities of the tested VOCs as a function of their dimensionless Henry and logarithm of octanol/water partition coefficients. All values of Table 2 are reported. Henry and octanol/water partition coefficients were obtained from refs 46−51. The gray area represents the general trend.

TABLE 3. Correlation Coefficients for the Regression of Biofilter Performance with Either the Logarithm of Henry's Law Coefficient or This of the Octanol/Water Partition Coefficients of the Treated VOCs

	correlated with log *H*		correlated with log $K_{o/w}$	
parameter correlated	these data	data by others	these data	data by others
	Log EC_{max}			
entire data set	0.88	0.70	0.81	0.66
partial data set[a]	0.82	0.75	0.79	0.70
	Log Critical Load			
entire data set	0.84	0.67	0.79	0.64
partial data set[a]	ND[b]	ND[b]	0.84	0.59

[a] Data with $H > 0.001$, or data with log $K_{o/w} > 0$. [b] ND = not determined.

were significant but that other factors should also be considered for better quantitative description of biofilter performance.

Figure 8 and Table 3 quantify what others have suggested, i.e., that pollutants with high Henry's Law coefficients are difficult to eliminate in a biofilter. The reason is that these pollutants have an unfavorable gas−liquid partition, and the pollutant concentration in the biofilm is too low to sustain a high biodegradation rate. For example, the equilibrium liquid concentration with a gas-phase concentration of 0.5 g m^{-3} of hexane is 7×10^{-3} mg L^{-1}, while the liquid concentration of ethanol would be 2 g L^{-1} under the same conditions. This will not only affect the biodegradation kinetics but also the rate of pollutant interphase mass transfer.

The data of Figure 8 also suggest that there is a limit to the maximum biodegradation rate in biofilters at about 200−300 g m^{-3} h^{-1} for hydrophilic compounds. A possible explanation for this is a diffusion limitation of oxygen in the biofilm. While experimental demonstrations of oxygen limitation in biofilters have not been conclusive, biofilm diffusion-reaction modeling shows that oxygen limitation should occur for hydrophilic compounds at high concentration (*31*). Further examination of the trends in Figure 8 reveals that pollutant with high octanol/water partition coefficients were not well removed although, as discussed above, the trend is less significant, especially for the data reported by others (*r* ranging from 0.59 to 0.7). A reversed trend was expected, since the growth of *Pseudomonas sp*. was found to be slowed in the presence of solvents with log K_{ow} lower than 2.5−3.0 (*50*). However, in the absence of more detailed experiments, it is difficult to separate the effect of the toxicity of the VOCs to the process culture and the effect of physicochemical parameters represented by log K_{ow} values.

Overall, the data of Figure 8 and the correlation coefficients of Table 3 show that both Henry and water/octanol partition coefficients play an important role in the elimination of VOCs in biofilters. Obviously, these are not the only factors affecting biodegradation in biofilters. Therefore, future development of quantitative structure biodegradation relationships for biofilter should further consider molecular structure de-

scriptors such as connectivity indices and physicochemical properties other than Henry's Law or octanol/water partition coefficients.

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