Removal of selected ozonation by-products in pilot scale drinking water biofilters: compound interactions and mass transfer considerations

S. D. J. Booth, P. M. Huck, R. M. Slawson, B. J. Butler and S. Ndiongue

ABSTRACT

Biofilters are finding increasing use in drinking water treatment. Among the substances they remove are ozonation by-products such as low molecular weight aldehydes and carboxylic acids. Because a number of these compounds also participate in or are produced by major bacterial metabolic pathways, their behaviour in biofilters may be complex. This pilot scale study investigated biodegradation relationships between methylglyoxal and pyruvate. A second objective was to determine the impact of mass transfer on removals.

The formation of pyruvate was observed when methylglyoxal was the sole easily biodegradable compound fed in the filter influent. The removal rates of formaldehyde and methylglyoxal were found to be comparable when each was the sole easily biodegradable compound fed. When fed alone, complete removals of methylglyoxal were obtained under steady-state conditions. When fed alone, the removal rate of pyruvate was more than twice than that of either formaldehyde or methylglyoxal. The removal rate of pyruvate was reduced by more than 50% when it was fed together with methylglyoxal. The reduced rate was probably due both to competition and to the formation of pyruvate from methylglyoxal. Backwashing was shown to have essentially no effect on removals of the compounds investigated.

The mass transfer investigations showed that neither external nor internal mass transfer was limiting. Therefore removals were governed by biodegradation rates. The lack of importance of mass transfer is significant because it simplifies modelling for the removal of easily biodegradable substances in drinking water biofilters.

Key words | biodegradation, biofiltration, drinking water, easily biodegradable substances, mass transfer, ozonation by-products

S. D. J. Booth
Carollo Engineers,
12592 West Explorer Drive—Suite #200,
Boise, Idaho 83713,
USA

P. M. Huck (corresponding author)
S. Ndiongue
University of Waterloo,
NSERC Chair in Water Treatment,
Department of Civil Engineering,
200 University Avenue West,
Waterloo, Ontario N2L 3G1,
Canada
E-mail: *pm2huck@uwaterloo.ca*
http://www.civil.uwaterloo.ca/watertreatment

R. M. Slawson
Department of Biology,
Wilfrid Laurier University,
75 University Avenue West,
Waterloo, Ontario N2L 3C5,
Canada

B. J. Butler
University of Waterloo,
Department of Biology,
200 University Avenue West,
Waterloo, Ontario N2L 3G1
Canada

INTRODUCTION

The pool of organic substrates in water typically consists of humic substances, combined amino acids, proteins, carbohydrates, and other compounds. It has been documented that ozonation increases the biodegradability of the natural organic matter (NOM) of waters (e.g. van der Kooij *et al.* 1989). This can be accomplished in several ways which include cleaving larger molecules into smaller, more bioavailable ones, by modifying the chemical structure of the NOM, and by producing compounds known to be easily degraded, such as acetate (Huck 1994). In drinking water treatment, the reaction of ozone with NOM can produce a large number of compounds, such as organic peroxides, hydrogen peroxide, various free radicals, aldehydes, and organic acids (Weinberg *et al.* 1992). Specifically, the low molecular weight aldehydes have been acknowledged as ubiquitous ozonation by-products

(Weinberg *et al*. 1993). Several low molecular weight keto–acids may be produced in relatively high concentrations (Xie & Reckhow 1992), and a number of carboxylic acids have been measured in a full-scale plant (Gagnon *et al*. 1997). These compounds represent the three major identified groups of biodegradable organic ozonation by-products.

The aldehydes and organic acids are of interest for several reasons. The keto-acids, pyruvate and glyoxylate, readily promote the growth of the bacterial *Spirillum* strain NOX (van der Kooij & Hijnen 1984). Pyruvate has also been shown to be an efficient trihalomethane precursor (Reckhow & Singer 1985). The aldehydes glyoxal and methylglyoxal have been shown to exert carcinogenic tumour promoting activity (Takahishi *et al.* 1989). Furthermore, formaldehyde is a suspected human carcinogen (Sax 1981).

Various studies have examined the removal of biodegradable ozonation by-products. For example, Krasner *et al*. (1993) showed that formaldehyde was typically readily removed in biologically active filters, while glyoxal and methyglyoxal usually appeared to be less biodegradable. Gagnon *et al*. (1997) provided formation and removal data for several carboxylic acids. Prévost *et al.* (1995) investigated the removal of formaldehyde, glyoxal and oxalate, formed by post sedimentation ozone, with the dosage adjusted to maintain a residual of 0.4 mg/l during disinfection. In biologically activated carbon/sand filters operated at an empty bed contact time (EBCT) of about 13 min, formaldehyde removal at 10°C was over 80%.

A number of the low molecular weight aldehydes and organic acids that are common ozonation by-products are also naturally occurring microbial substrates or metabolites (Gottschalk 1986). This implies not only that these compounds will be readily biodegraded, as discussed above, but also that they may be released by microbes as part of normal metabolism, or as a result of cell death and lysis.

Booth (1998) considered bacterial metabolic pathways that involve ozonation by-products of interest and prepared a simplified conceptual model (Booth *et al*. 1995; Booth 1998) that indicated potential interactions among these compounds in biological filters. The model summarizes a combination of metabolic capabilities which a mixed microbial community, such as those present in biologically active filters, could be expected to possess.

Metabolic processes may have an impact on biofilter performance, due to phenomena such as a preference for one compound over another, or the production of one compound by the metabolism of another. The classical bacterial metabolic pathways on which the model is based pertain to reactions within bacterial cells. In order to have an effect on filter effluent quality, formed compounds would have to accumulate outside the cells, i.e. in the bulk water.

Non-steady state or upset conditions may result in a shift in a biofilm population, and therefore a change in its overall metabolic capabilities. This may lead to the temporary appearance of some substrates in the effluent of filters.

Booth (1998) used his conceptual model to choose compounds for evaluation in batch experiments. These experiments involved groups of compounds whose metabolism appeared to be related, according to the model. Analysing for aldehydes and carboxylic acids, the only transformation product detected in the bulk water in these experiments was pyruvate, formed from methylglyoxal. Thus these two compounds were chosen for investigation in the filter experiments described in this paper. The objective was to investigate how the biodegradation of each of these compounds was influenced by the presence of the other, to assist in interpreting removals observed in practice. A second objective was to determine the extent to which mass transfer limitations might influence the removal rates of easily biodegradable compounds in drinking water biofilters.

MATERIALS AND METHODS

Physical configuration of the filters

Figure 1 shows a schematic of the experimental set-up. The details (media, flowmeter, etc.) shown for the first filter were the same for all the filters. The filters were operated with a constant head, with the flow rate controlled by a flowmeter (Gilmont Instruments, Cole Parmer

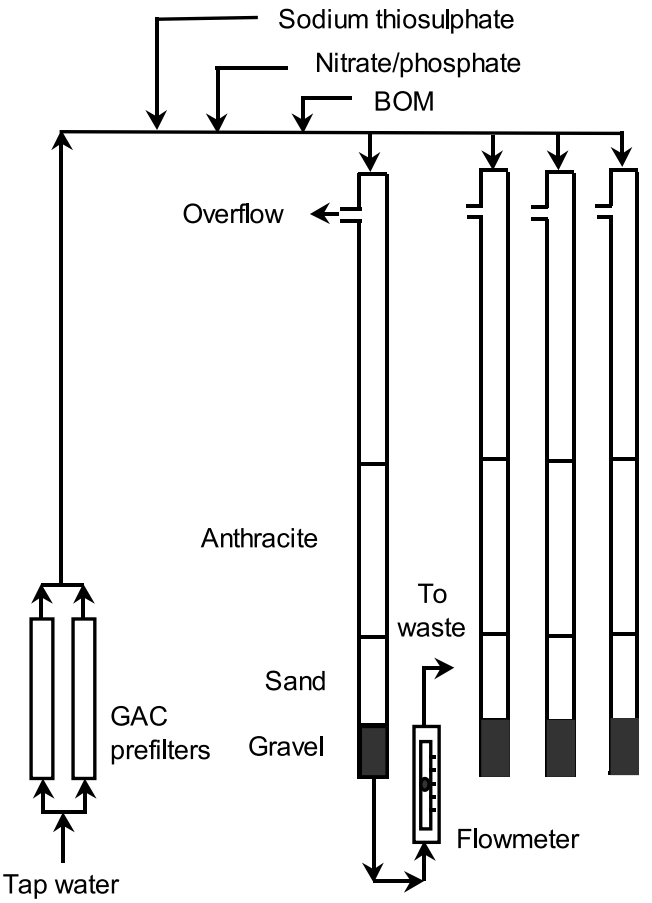

Figure 1 | Schematic of filter apparatus (configuration shown is for Experiment 2).

Instrument Company, Niles, Illinois) with a valve on the effluent line. Due to the low turbidity of the influent water the flow rate could usually be maintained at the target level throughout the filter run.

The filter columns were glass (Namdar Custom Glass-blowing Production, Mississauga, Ontario) with an inside diameter of 5 cm (2 in.). The columns were filled with 25 cm of fresh sand and 50 cm of fresh anthracite at the start of each experiment, providing a total bed depth of 75 cm. The effective size and uniformity coefficients were 1 mm and 1.6 for the anthracite, and 0.5 mm and 1.5 for the sand, respectively. The media rested on about 15 cm of graded support gravel.

Wall effects and channelling are considered to be negligible when the ratio of the filter diameter to the media particle size is equal to or greater than 50 (Perry *et al.* 1984). The anthracite used in this research had an effective size of 1 mm, therefore this criterion was satisfied.

Feed water

The feedwater was tapwater from a ground water source, with a high alkalinity (300 to 325 mg/l as $CaCO_3$) and hardness (325 to 350 mg/l as $CaCO_3$), a total organic carbon concentration of about 1.0 to 1.5 mg C/l, and a pH of about 7.5. The feedwater was fed from the tap through Teflon® tubing (Johnson Industrial Plastics, Toronto, Ontario) and stainless steel valves and fittings. The water then passed through one of two parallel glass GAC pre-filters, which provided an EBCT of 1.5 to 2 min. The GAC had been exhausted with respect to TOC removal. The pre-filters were primarily designed to remove any free chlorine residual, although they may have also removed a small amount of biodegradable organic matter (BOM), if it was present. Normally a negligible chlorine residual (<0.05 mg Cl_2/l) was measured in the pre-column effluent.

After the pre-filters, sodium nitrate ($NaNO_3$), potassium phosphate (K_2HPO_4), and BOM were added. The feed bottles containing deionized water were autoclaved (Castle Autoclave, MDT Biologic Company, Rochester, New York). After the bottles had cooled to room temperature the calculated quantity of pure component was added aseptically to the bottles and mixed well. The nitrogen and phosphorus-containing compounds were combined in one bottle, while separate bottles were used for each organic component. The C:N:P ratio was targeted at 100:20:5 on a molar basis. Camper (1994) found that the required C:N:P ratio for microbial growth in drinking water distribution systems was 100:10:1. The ratio selected for the present research provided excess nitrogen and phosphorus, and thus ensured that growth was carbon-limited. The concentrations of BOM (i.e. the easily biodegradable compounds) used in each experiment are discussed later.

The feed cocktails were pumped with peristaltic pumps (Masterflex, Cole Parmer Instrument Company, Niles, Illinois) using PharMed® tubing (Norton Co.). New tubing was used for each experiment. It was autoclaved prior to the start of an experiment, and thereafter every two to three weeks.

During the second filter experiment the tapwater typically contained 0.5 mg/l monochloramine. About half of this was removed in the GAC pre-filters, with the remainder being quenched by sodium thiosulphate ($Na_2S_2O_3$). Both the residual monochloramine and thiosulphate were monitored during this experiment.

Backwashing

In the first stage of backwashing water was pumped at 40% of the fluidization velocity, or 12 m/h. Air was also passed upwards through the filter at 50 m/h (at standard temperature and pressure), such that conditions termed 'collapse-pulsing' (Amirtharajah *et al.* 1991) occurred. Collapse-pulsing was maintained for 3 min, following which the air was turned off and the water flow was increased to 35 m/h for 4 min, to achieve a 20% bed expansion. Each filter was backwashed with its own effluent, which had been previously collected and stored in glass carboys. Backwashing was performed every three to four days.

Sampling

Each filter had eight sample ports, the uppermost of which served as the filter influent sample port. Samples were collected by piercing the sample port with a stainless steel needle attached to a 50 ml glass syringe and extracting a sample from the centre of the filter. The septa were lined with teflon on the inside, and silicon on the outside. Effluent samples were obtained via a plug valve located on the effluent line, just below the filter.

Analytical procedures

All chemical products were purchased from Aldrich Chemical Company Inc. (Milwaukee, WI). Further details of all methods may be found in Booth (1998).

Carboxylic acids

Samples for carboxylic acid determinations were preserved with 0.1% (v/v) chloroform ($CHCl_3$), stored at 4°C immediately after sampling, and measured within 2 weeks of their collection. An ion chromatographic (IC) method (Peldszus *et al.* 1996, 1998) was used for analysis. Samples were injected directly into the IC, without any sample preparation. Utilizing a sodium hydroxide gradient, the organic acids were separated on an anion exchange column (AS 10, Dionex, Sunnyvale, CA) followed by conductivity detection. The acids were identified by their retention time. The minimum reporting limits for the most common acids were: acetate (5 μg/l), formate (2 μg/l), pyruvate (3 μg/l) and oxalate (9 μg/l). Standards and method blanks were included in every sample queue.

Aldehydes

Aldehydes were derivatized at room temperature overnight by oximation with o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA), and extracted with hexane, as described by Sclimenti *et al.* (1990) and *Standard Methods for the Examination of Water and Wastewater* (APHA *et al.* 1995). The extracted samples were stored at −10°C for up to 30 days. The samples were analysed by gas chromatography with electron capture detection (Model HP 5890 series II, Hewlett-Packard, Sunnyvale, CA). The aldehydes were identified by their retention time. One day prior to analysis fresh standards and method blanks were prepared. Standards and blanks were run after every eight injections. The aldehydes contained in the standard (with their reporting limits in parentheses) were formaldehyde (1.6 μg/l), glyoxal (3.5 μg/l), methylglyoxal (2.5 μg/l) and acetaldehyde (2.0 μg/l). The hexane used for extracting the derivatized aldehydes contained an internal standard (dibromopropane).

Non-purgeable organic carbon (NPOC)

Non-purgeable organic carbon (NPOC) was measured using a Xertex Dohrman DC-180 Total Carbon Analyser using Method 5310C in *Standard Methods for the Examination of Water and Wastewater* (APHA *et al.* 1995). Each reported value was typically the average of three determinations. The coefficient of variation for replicate

measurements was normally less than the value of 2% cited for the method.

Chlorine

Chlorine was measured using the colorimetric version of the N,N-diethyl-p-phenylenediamine (DPD) method (APHA *et al.* 1995). Measurements were made with a DR-200 UV-Visible spectrophotometer (Hach Co., Loveland, Co) at a wavelength of 530 nm. The detection limit was 0.02 mg Cl_2/l.

Sodium thiosulphate

The thiosulphate concentration was monitored using the carboxylic acid method described above, without any modifications. Using this method the minimum reporting limit was 0.025 mg $Na_2S_2O_3$/l.

Biomass (phospholipid method)

The amount of living biomass on the filter media was quantified by determining its phospholipid content using the method of Findlay *et al.* (1989), with minor modifications. Briefly, between 0.1 and 1.0 g of media was transferred to a 20 ml screw cap vial. The phospholipids contained in the cell membranes of the biofilm cells were extracted into a chloroform-methanol-water mixture, in a volumetric ratio of 1:2:0.8. This mixture was allowed to stand overnight, then separated into a lipid-containing chloroform phase and a methanol-water phase by the addition of chloroform and water, such that the final volumetric ratio of chloroform-methanol-water was 1:1:0.9. The chloroform was transferred to another vial and evaporated using nitrogen gas. The remaining lipids were then digested using potassium persulphate to liberate inorganic phosphate. The phosphate was quantified using ammonium molybdate and malachite green, as described by VanVeldhoven & Mannaerts (1987). The absorbance of the sample at 610 nm was measured using a UV-Visible spectrophotometer (model HP 8453, Hewlett-Packard; Sunnyvale, CA). The absorbance was related to the inorganic phosphate concentration by the use of a standard curve, prepared as described by Booth (1998). Duplicate samples were always obtained, with each being analysed once. Blank samples were analysed in order to monitor for possible phosphate contamination. The results were reported as nmol lipid-P per g dry filter media, or per cm^3 of filter bed. The minimum reporting limit for this method was 2 nmol lipid-P/g media.

Experimental design

The first experiment described in this paper examined the removal of methylglyoxal fed as the sole substrate. This was done under pseudo steady-state conditions at two different hydraulic loading rates (5 and 10 m/h), and when various perturbations were applied to the filters (backwashing, a step increase in influent BOM concentration, and a period out of service). An additional objective was to determine whether measurable pyruvate concentrations would be observed in the filter. The operating conditions of the three filters used in this experiment are given in Table 1. The first filter, which was not fed any BOM, was operated as a control.

The second experiment was conducted to further investigate the formation of pyruvate from methylglyoxal. In this experiment, one filter was fed only methylglyoxal, a second only pyruvate and a third both methylglyoxal and pyruvate. A fourth filter was included, which was fed only formaldehyde, to provide a direct comparison of methylglyoxal and formaldehyde removals. This comparison was performed because methylglyoxal removals have often been reported as being lower than those of formaldehyde (e.g. Krasner *et al.* 1993).

In order to study the interactions between methylglyoxal and pyruvate, other organic substances that would normally be present in natural waters, such as humic substances, carbohydrates, other microbial metabolites and other ozonation by-products, were excluded from the experiment. The compounds under investigation are generally readily biodegradable. Therefore, it was considered that the exclusion of the natural compounds, many of which are much less readily biodegradable than the compounds of interest, would not have a substantial effect on the trends observed. In full-scale biofilters, however, the removal rates of the studied compounds could be affected

Table 1 | Experimental conditions

	Experiment # 1			Experiment # 2			
	Filter 1	Filter 2	Filter 3	Filter 1	Filter 2	Filter 3	Filter 4
BOM (μg/l):							
methylglyoxal	0	150	150	200		100	
pyruvate					290	145	
formaldehyde							250
Th.OD (mg O_2/l)[a]	0	0.20	0.20	0.267	0.267	0.267	0.267
HLR (m/h)	5	5	10	8	8	8	8
Bed depth (mm):							
anthracite	490	490	490	500	500	500	500
sand	250	250	250	250	250	250	250
EBCT (min)	8.9	8.9	4.4	5.6	5.6	5.6	5.6
DO (mg/l):[b]							
influent	6.10	6.11	6.00	7.08	7.00	7.11	7.12
effluent	6.05	5.89	5.80	6.60	6.62	6.81	6.70
Temperature (°C)	16.4[c]	16.4[c]	16.2[c]	15.3[d]	15.3[d]	15.3[d]	15.4[d]

[a]Th.OD = theoretical oxygen demand.
[b]The given dissolved oxygen (DO) measurements refer to steady-state conditions.
[c]The average of the influent and effluent temperatures is given. The water temperature rose by 0.4 to 1.3°C through the filters.
[d]The average of the influent and effluent temperatures is given. The water temperature rose by about 0.6°C through the filters.

by the presence of other aldehydes and organic acids that are common ozonation by-products. Therefore, although information on removal rates was obtained for methylglyoxal and pyruvate under the conditions of these experiments, the main objective of these investigations was to evaluate how biodegradation of these two compounds in biofilters was influenced by the presence of the other, rather than to determine removal rates that might be observed in full scale practice.

Data from both experiments described in this paper were used to assess the extent to which mass transfer limitations might influence the removal rates of the studied compounds in drinking water biofilters. The approach to evaluating mass transfer is described in the next section.

MASS TRANSFER CONSIDERATIONS

In their steady-state model, Rittmann & McCarty (1980*a*) included the major processes which are expected to be important in substrate removal by biofilms. These are: the flux of the substrate to the outer surface of the biofilm and

the simultaneous utilization and diffusion of substrate within the biofilm. The transfer of BOM from the bulk solution to the biofilm surface is a diffusion process, referred to as external mass transfer, and occurs through a diffusion layer having an effective thickness L. The diffusion of BOM within the biofilm is referred to as internal mass transfer. Measured BOM removal rates are controlled by whichever process is slower: mass transfer or utilization (biodegradation). Through the use of moduli, it is possible to determine which process controls the removal rate.

External mass transfer modulus

An external mass transfer modulus, designated herein as φ_{ext}, has been suggested (Karel *et al.* 1985), and is defined as:

$$\varphi_{ext} = \frac{R_{obs} L_c}{k_L S_b} \quad (1)$$

Where,
R_{obs} is the observed reaction rate, $M_{BOM} L^{-3} T^{-1}$,
L_c is a characteristic length, L,
k_L is the external mass transfer coefficient, LT^{-1}, and
S_b is the bulk BOM concentration, $M_{BOM} L^{-3}$.

If the value of this modulus is much less than unity, utilization kinetics control the rate of substrate removal, and if the value approaches or exceeds unity, mass transfer becomes limiting (Karel *et al.* 1985). The advantage of this modulus is that it does not require prior knowledge of specific kinetic parameters. A more rigorous approach would require prior determination of the kinetic parameters for which the chosen modulus is defined, and the determination of specific mass transfer parameters.

The thickness of the external diffusion layer, L, can be selected as the characteristic length, L_c. An empirical formula presented by Jennings (1975) can be used to provide an estimate of L:

$$L = \frac{D\, N_{Re}^{0.75}\, Sc^{0.667}}{5.7\, HLR} \quad (2)$$

Where $N_{Re} = \dfrac{2\rho\, D_p\, HLR}{(1-\varepsilon)\mu}$, and

$$Sc = \frac{\mu}{\rho D},$$

in which,
L is the external diffusion layer thickness, L,
D is the diffusivity, $L^2 T^{-1}$,
ρ is the density of water, $M_{water} L^{-3}$,
D_p is the diameter of the filter media, L,
ε is the porosity of the filter bed, and
μ is the dynamic viscosity of water, $M_{water} L^{-1} T^{-1}$.

The diffusivity of acetate ($D = 1.24 \times 10^{-9}$ m^2/s, Perry *et al.* 1984) was used for the BOM components used in the present research. The effective size of the anthracite media, 1 mm, was used for D_p, and the other values were known or obtained from appropriate handbooks. Booth (1998) calculated a value of 3.91×10^{-5} m for L, which agrees closely with that calculated for AOC (Zhang & Huck 1996) in a dual media filter. Since k_L is equal to D/L, Booth (1998) obtained a value for k_L of 3.17×10^{-5} m/s. This value is also in good agreement with values calculated by Zhang & Huck (1996) of 9.65×10^{-6} and 1.47×10^{-5} m/s, for AOC in a dual media filter. Also, Rittmann & McCarty (1980*b*) calculated a value of approximately 1×10^{-5} m/s, for acetate. The compounds investigated in this research are components of AOC, and are likely to have similar mass transfer characteristics. Because both k_L and L are in good agreement with literature values, the assumed value for D must also be reasonable.

In the present paper, L and k_L were calculated for the actual conditions of each experiment (temperature and HLR).

Internal mass transfer modulus

An internal mass transfer modulus, designated herein as φ_{int}, has been suggested by Weisz (1973), and is defined as follows:

$$\varphi_{int} = \frac{R_{obs} L_c^2}{D_f S_b} \quad (3)$$

where D_f is the diffusivity of the BOM within the biofilm, $L^2 T^{-1}$

As for the external mass transfer modulus φ_{int}, if the value of this modulus is much less than unity, utilization

kinetics control the rate of reaction, and if the value exceeds unity, mass transfer is limiting. This modulus also does not require prior knowledge of specific kinetic parameters.

The biofilm thickness, L_f, was selected for L_c, because it represents the distance over which mass transfer occurs. Choosing a value for the biofilm thickness was complicated by the fact that it could not be directly measured and few values are available in the literature. Rittmann & McCarty (1980*a*) reported calculated values in the range of 25 to 320 μm, for filter influent concentrations of 500 to 4,400 μg acetate/l, where the lowest calculated value corresponded to the lowest influent concentration. These influent concentrations are approximately 2 to 15 times greater than those employed in the present research, based on the theoretical oxygen demand. Also, L_f is expected to be greatest at the top of the filter and diminish with filter depth, as the bulk substrate concentration, and hence flux, also reduces with depth. Therefore, an average value for L_f must be chosen. A conservative estimate of 25 μm was chosen for these calculations. This value is reasonable based on values reported by Lu (1993), who estimated biomass thickness from scanning electron micrographs. A large majority of her reported thicknesses were less than 5 μm, with only one value exceeding 20 μm.

The value of D_f was assumed to be half the value of D, as suggested by Zhang & Huck (1996), which is 5×10^{-10} m^2/s. D_f may actually be closer to the diffusivity of the bulk liquid, given that the biofilm is probably a collection of small, sparse clusters (Costerton *et al.* 1994). However, this assumption was considered to be conservative: a lower value of D_f is more likely to result in internal diffusion limitations.

As mentioned previously, data from both filtration experiments were used to calculate the external and internal mass transfer moduli for the compounds being studied. The data used are from filters for which the compound in question was the only one fed. R_{obs} (the observed reaction rate) was calculated by dividing the amount of BOM removed by the corresponding EBCT. The data used were measured at the filter influent and the sample port which corresponded, as closely as possible, to the point at which complete removal of the BOM component occurred. S_b was taken as the average of these two values, which is approximately the average concentration exposed to the biofilm. The porosity of the filter bed was assumed to be 0.45. This represents a conservative assumption in the present context because calculations performed with an assumed porosity of 0.40 led to slightly lower calculated values of φ_{ext}.

The highest external mass transfer modulus calculated for methylglyoxal, pyruvate, and formaldehyde was 0.0187, 0.0407, and 0.0165 respectively. Since the value of the modulus was much less than unity in each case, it is very unlikely that external mass transfer limits the removal of BOM, under these conditions. (It should be noted that if the actual contact time rather than EBCT had been used to calculate R_{obs}, the values of φ_{ext} would have been at most a factor of 3 higher, which would not have changed the conclusion.)

The values obtained for the internal mass transfer modulus, φ_{int}, are also shown in Table 2. This modulus uses the values of R_{obs} and S_b that have already been calculated for the external mass transfer modulus.

The highest values of the internal mass transfer modulus calculated for methylglyoxal, pyruvate and formaldehyde were 0.0147, 0.0389, and 0.0157 respectively. Since the value of the modulus was much less than unity in each case, it is very unlikely that internal mass transfer limits the removal of BOM under these conditions.

Thus, neither internal nor external mass transfer limited the removal of BOM in this experimental system. This conclusion is supported by the work of several others. Wang (1995) showed that the rate of removal of BDOC in biological filtration was controlled by reaction rate, and not mass transfer. Urfer-Frund (1998) demonstrated that both external and internal mass transfer were of only minor importance for the removal of easily biodegradable compounds in his pilot scale biofilters. Gagnon & Huck

RESULTS AND DISCUSSION

Evaluation of mass transfer

Table 2 presents calculations for the external mass transfer modulus, for each of the three compounds investigated.

Table 2 | Calculation of the external and internal mass transfer moduli*

Exp.	Day	Filter No.	Temp. °C	*HLR* m/h	μ N.s/m^2	ρ kg/m^3	*Sc*	N_{Re}	*L* m	k_L	$S_{inf.}$ µg/l	S_{final} µg/l	EBCT min	R_{obs} µg/(l · min)	S_b µg/l	φ_{ext}	φ_{int}
Methylglyoxal																	
´1	23	2	16.4	5	1.101E-03	998.8	888.97	4.58	4.55E-05	2.73E-05	121	2.5	6.48	18.3	61.9	0.0082	0.0062
	43								4.55E-05	2.73E-05	152	2.5	2.88	51.9	77.2	0.0187	0.0140
´1	23	3	16.2	10	1.106E-03	998.9	892.92	9.12	3.82E-05	3.25E-05	130	2.5	4.44	28.7	66.2	0.0085	0.0090
	43								3.82E-05	3.25E-05	149	14.4	2.34	57.7	81.9	0.0138	0.0147
´2	75	1	15.3	8	1.131E-03	999.0	913.01	7.14	4.03E-05	3.08E-05	211	50.2	1.80	89.1	130.4	0.0149	0.0142
Pyruvate																	
´2	59	2	15.3	8	1.131E-03	999.0	913.01	7.14	4.03E-05	3.08E-05	302	3	1.13	264.9	152.7	0.0379	0.0361
	64								4.03E-05	3.08E-05	309	3	1.05	291.1	155.9	0.0407	0.0389
	75								4.03E-05	3.08E-05	293	3	1.05	276.4	148.1	0.0407	0.0389
Formaldehyde																	
´2	64	4	15.4	8	1.128E-03	999.0	910.59	7.16	4.03E-05	3.07E-05	244	23.3	2.93	75.4	133.8	0.0123	0.0117
	75								4.03E-05	3.07E-05	256	48.7	1.80	114.9	152.1	0.0165	0.0157

*The external mass transfer modulus is calculated for an assumed bed porosity of 0.45.

(2001), examining the removal of easily biodegradable compounds in model drinking water distribution systems, showed that neither external nor internal mass transfer limited removals.

The fact that neither external nor internal mass transfer was found to limit the removal of the compounds studied is significant. It means that modelling for the removal of these compounds in biofilters can be considerably simplified, as only biodegradation need be considered. The phospholipid biomass values in this research are in the general range of those measured in full-scale biofilters (Huck *et al.* 2000). Although the possibility of mass transfer limitations in a given situation should always be investigated, it would be reasonable to consider that, as a first approximation, such limitations could be neglected for all easily biodegradable substances in drinking water biofilters. (Comprehensive models, which also considered the simultaneous removal of less readily biodegradable materials such as humic substances, would however probably not be able to ignore mass transfer effects.)

Experiment 1

Control filter

Sampling of Filter 1, the control filter, indicated insignificant concentrations of most carboxylic acids and aldehydes. Formate concentrations in the range of 4.2 to 26 µg/l and formaldehyde concentrations of 2.2 to 12 µg/l were observed in the filter influent. Background concentrations in this range were also observed in the other filter influents. There was no significant difference between the

average influent and effluent concentrations of these compounds, at the 1% level, by comparing paired influent and effluent values, from day 43 onward (Booth 1998). Also, negligible biomass accumulation was measured on the media (<4 nmol lipid-P/cm^3 filter) in Filter 1, after 81 days of operation. Much higher biomass values were measured in the filters with added BOM in the influent, as discussed below. Thus the control filter served to show that low levels of the added compounds were present as background in the tap water, and that these levels led to very low biomass accumulation.

NPOC removal

NPOC was measured in the influent and effluent of all filters several times throughout the experiment. The NPOC of the tap water was about 1.3 mg/l. It was not possible to demonstrate a significant difference between the influent and effluent concentrations for any of the three filters, at the 1% level (Booth 1998). A difference might have been expected for Filters 2 and 3, which accumulated a measurable biomass, but not Filter 1, the control filter. The difference between influent and effluent values would consist of whatever added BOM and background NPOC was removed. One explanation for the lack of an observed difference is the low concentration of added BOM. The added methylglyoxal was approximately 0.075 mg C/l or about 6% of the NPOC of the tap water. Even if all of the added methylglyoxal were removed, it would be difficult to reliably detect this by NPOC measurements. The lack of NPOC removal indicates that the background NPOC was highly stable, as expected for a high quality groundwater.

Steady-state removals

Complete removal of methylglyoxal was observed in Filters 2 and 3 after about 20 days. Figure 2a shows the concentration profile of methylglyoxal in Filter 2 (operated at 5 m/h), on day 43. Pyruvate was observed at a depth of 4 cm, or about 0.5 min of EBCT. Figure 2b shows the corresponding data for Filter 3, which was operated at 10 m/h. In this filter pyruvate was also observed, although at lower concentrations and at three different EBCTs. On

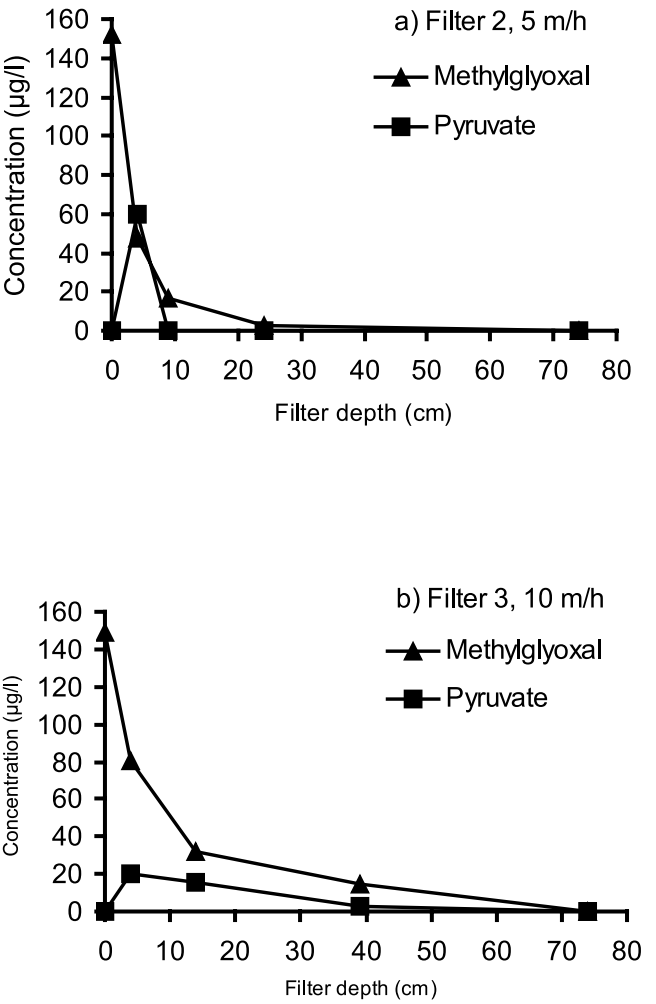

Figure 2 | Methylglyoxal and pyruvate concentration profiles on day 43 of Experiment 1.

day 6 pyruvate was not observed in either filter, but was observed on day 23, in a similar pattern as shown in Figure 2 (Booth 1998). It was therefore concluded that the formation of pyruvate coincided with the development of biomass and the utilization of methylglyoxal, as observed in batch experiments (Booth 1998).

The methylglyoxal concentration profiles for the two filters appear generally similar when plotted versus EBCT as in Figure 2. Servais *et al.* (1992) showed that any combination of HLR and depth which provide a given EBCT, will give the same BDOC removal. It is reasonable to extend this to the removal of specific BOM components. Since pyruvate formation is linked to methylglyoxal

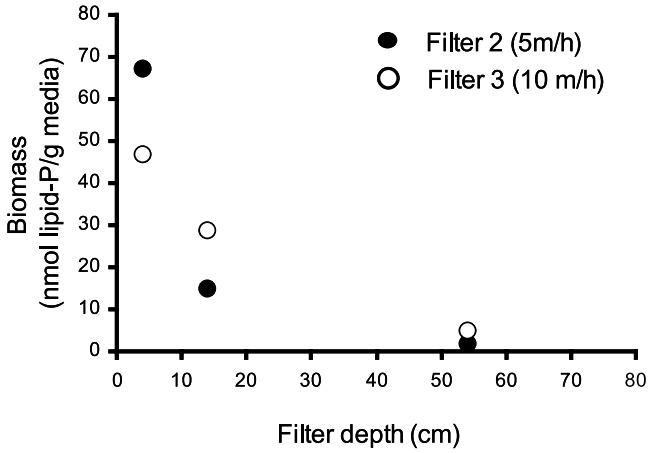

Figure 3 | Biomass profiles in Filters 2 and 3 on day 43 of Experiment 1.

utilization, the higher remaining methylglyoxal concentrations at a given depth in Filter 3 lead to lower pyruvate values at these depths.

Biomass (phospholipid) data for Filters 2 and 3 on day 43 are shown in Figure 3. Booth (1998) reported that these biomass profiles could be described by an exponential decay function. He used these results in a model that was zero order in substrate to determine rate constants for substrate removal. Although this model gave a good qualitative description of observed substrate profiles, there was some systematic lack of fit. The modelling, however, does suggest that a major contributing factor to the observed first order behaviour for substrate removal in drinking water biofilters (e.g. Huck *et al*. 1994) may be the biomass profile within the filter.

As noted above, neither methylglyoxal nor pyruvate were observed in the effluent of either Filter 2 or 3, under steady-state conditions.

Table 3 shows calculated rates of removal ($\mu g/l \cdot min$) from the top of the media to various depths of Filters 2 and 3. This allows for quantitative comparisons without tying the results to a specific kinetic model. For example, the lack of effect of hydraulic loading rate can be seen by comparing the initial removal rates (i.e. in the top sections of the filters) for Filters 2 and 3. In Filter 2, an EBCT of 0.48 min gave a methylglyoxal removal rate of 218 $\mu g/(l \cdot min)$. Although data are not available for the same EBCT in Filter 3, interpolation indicates that the removal rate would be roughly similar.

Table 3 also shows results for samples taken prior to and just after backwashing. The results indicate that backwashing essentially did not affect removal rates, although exact comparisons for Filter 2 are not possible because of the different sampling depths used before and after backwashing. Backwashing did not have a measurable effect on the methylglyoxal and pyruvate concentration profiles within the filter, except that small quantities of methylglyoxal (below the minimum reporting level of the method) were observed in the effluents (Booth 1998).

Effect of step increase in influent concentration

In order to evaluate the effect of a sudden increase in influent concentration, a step increase of approximately four times the normal methylglyoxal concentration, lasting for 24 h, was introduced to Filters 2 and 3. Methylglyoxal removal dropped from complete removal to about 60% at the beginning of the step increase (Table 4). Both filters had the same overall removal percentage, despite being operated at different HLRs. The methylglyoxal concentration profile within Filter 2 appeared to follow an exponential decay, with most of the removal occurring in the first 4 min of EBCT. Very little biomass had accumulated in the bottom half of Filter 2, since very little BOM was normally available in that portion of the filter. In contrast, the methylglyoxal concentration profile in Filter 3 was essentially linear, because more biomass had accumulated at lower depths of this filter (Figure 3). Since most of the removal in each filter occurred in the first 4 min of contact time, the overall performance of the filters was similar. This 4 min occupied only about half of the depth of Filter 2, but the entire depth of Filter 3.

At the end of the 24-h step, nearly complete removals of methylglyoxal were observed in both filters, as shown in Table 4. A measurable quantity of pyruvate continued to be present in the effluent of Filter 3, which was operated at the higher HLR. The excellent removals of methylglyoxal are noteworthy, since it was not expected that nearly complete recovery of BOM removal would be obtained after only 24 h. This was because the formation of additional biomass would not necessarily be complete in

Table 3 | Rate of removal* of methylglyoxal

Event	Filter	Depth (cm)	EBCT (min)	Methyglyoxal concentration (μg/l)	Rate of removal (μg/l · min)
Steady state conditions					
before backwashing	2 (5 m/h)	0	0.00	152	
		4	0.48	47.5	218
		9	1.08	16.8	125
	3 (10 m/h)	0	0.00	149	
		4	0.24	80.2	288
		14	0.84	32.2	139
		39	2.34	14.4	58
following backwashing	2 (5 m/h)	0	0.00	141	
		14	1.68	22.3	71
	3 (10 m/h)	0	0.00	138	
		39	2.34	17.0	52
Perturbed conditions					
4 h after 24 h step**	2 (5 m/h)	0	0.00	149	
		4	0.48	30.8	246
		9	1.08	13.4	126
	3 (10 m/h)	0	0.00	150	
		4	0.24	71.4	328
		9	0.54	14.8	250
after 48 h shutdown	2 (5 m/h)	0	0.00	128	
		4	0.48	58.8	144
		9	1.08	29.6	91
	3 (10 m/h)	0	0	123	
		4	0.24	97.5	104
		9	0.54	46.5	141

*Calculated from top of media to indicated depth.
**i.e. 4 h after concentration returned to normal.

Table 4 | BOM concentrations during and following step increases in Experiment 1

Time of sampling	Filter	Methylglyoxal (μg/l)			Pyruvate (μg/l)	
		Influent	Effluent	Percent removal	Influent	Effluent
Start of 24 h step increase	Filter 2 (5 m/h)	523	203	61.2	0	28.6
	Filter 3 (10 m/h)	487	180	63.0	0	109
End of 24 h step increase	Filter 2 (5 m/h)	644	12.0	98.1	0	0
	Filter 3 (10 m/h)	615	23.8	96.1	0	5.8
End of 3 day step increase	Filter 2 (5 m/h)	646	2.5	99.6	0	0
	Filter 3 (10 m/h)	634	41.5	93.5	0	13.3

that time. In Filter 2 the biomass at a depth of 4 cm was significantly higher, but only at the 10% level, at the end of the step increase compared to that observed prior to the step (Figure 4). The biomass difference at the 4 cm depth was not statistically significant in Filter 3, however, the biomass at a depth of 14 cm was found to be significantly higher after the step, at the 10% level. There was little additional biomass observed in the lower half of Filter 2 (data not shown).

About 4 h after the normal influent concentration of methylglyoxal was re-established, superior removals were observed in both filters, compared to the steady-state values observed on day 43. This is evident in the higher initial removal rates calculated for both filters (Table 3). Values for k_0, the zero-order substrate removal rate constant, were determined but were not significantly different than those calculated for day 43, at the 5% level (Booth 1998). Thus the results indicate that, as expected, it was the higher biomass levels that led to the better removals.

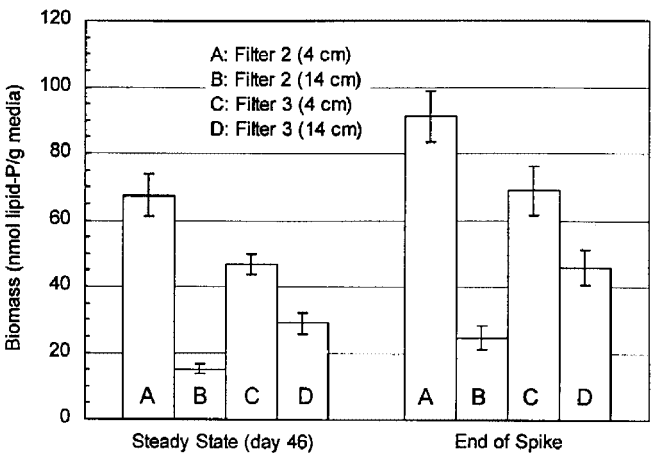

Figure 4 | Biomass comparison prior to and at the end of a 24 h spike in the influent methylglyoxal concentration (error bars represent±standard deviation).

The step increase was repeated after allowing the filters to run at normal conditions for about 2 weeks. In this second trial the higher concentration was maintained for 3 days. Table 4 includes a summary of these results. The improvement in the methylglyoxal removals in the first 24 h was not followed by any additional improvement after the next 2 days (Booth 1998). The fact that pyruvate remained in the effluent of Filter 3 even after 3 days indicates that recovery of BOM removal took longer at the higher HLR. Alternatively, it may be that the presence of pyruvate in the effluent of Filter 3 would be unavoidable, even under pseudo steady-state conditions, at the hydraulic and organic loading applied in the step experiment. This hypothesis would need to be confirmed in an experiment of greater duration. Sampling at intermediate depths indicated that the methylglyoxal concentration profiles in Filters 2 and 3 had the appearance of exponential decay curves. About 66% removal was achieved at a depth of 9 cm, or 0.5 min of EBCT, in Filter 3, and 75% removal had occurred at this depth in Filter 2, which

corresponded to 1 min of EBCT. This was an indication that additional biomass development occurred in the top portion of the filters, with less new growth in the bottom portions.

Effect of period out of service

The filters were shut down for 48 h after 81 days of operation and about 10 days after returning to the normal influent methylglyoxal concentration. The water level was maintained at the level of the overflow during shutdown. Just prior to re-starting the filters the dissolved oxygen of the water in the filters had dropped to about 2.0 mg/l in Filters 2 and 3, and about 4.8 mg/l in Filter 1. Samples for BOM analysis were taken within an hour of re-starting the filters. In terms of overall filter performance, methylglyoxal removals were not strongly affected by the shutdown. A concentration of methylglyoxal less than the method detection limit of 2.5 μg/l was observed in the effluent of Filter 3. However, Table 3 shows that the removal rates in the uppermost section of each filter were appreciably lower. This suggests that, for substances such as methylglyoxal, measurable effects of a period out of service might be observed in filters with shorter contact times.

Pyruvate profiles following the shutdown were generally similar to what had been observed at steady-state, although pyruvate was detected about 5 cm deeper in both filters. Pyruvate was not observed in the filter effluents.

Experiment 2

As noted previously, the objective of Experiment 2 was to further investigate methylglyoxal and pyruvate removal relationships by feeding them separately and together (Table 1). For comparison, formaldehyde was fed to Filter 4. A control filter without BOM addition was not operated.

For about the first 30 days of this experiment a monochloramine residual, of about 0.5 mg Cl_2/l, was present in the tap water. Approximately half of this was removed in the GAC pre-filters, leaving a residual of about 0.25 mg Cl_2/l in the influent of the filters. This residual was sufficient to prevent any significant removal of BOM in all filters in the first 18 days of operation. It was expected, based on the results of filter experiment 1, that removals of 90% would be established for methylglyoxal and formaldehyde, after about 20 days of operation.

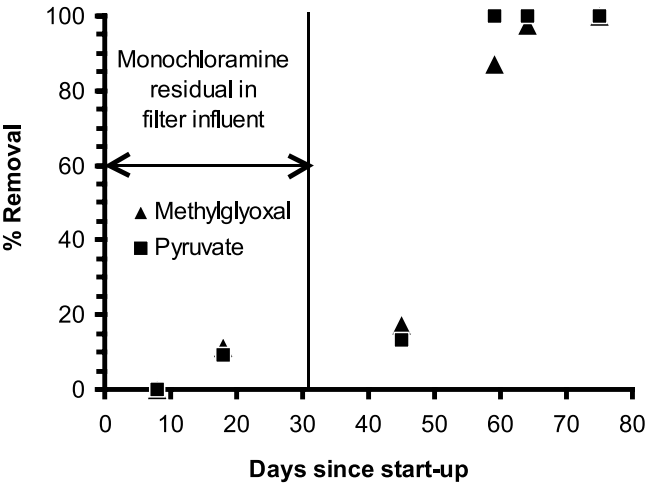

Figure 5 | Removal of pyruvate and methylglyoxal in Filter 2, over the duration of Experiment 2.

Therefore, beginning on day 31, sodium thiosulphate was introduced to the feed water, after the GAC pre-filters, to quench the monochloramine residual. The feed rate of thiosulphate was increased step-wise, from day 31 to 37, to obtain a concentration which would provide essentially complete quenching, while also minimizing the thiosulphate residual that remained in the influent water. After quenching began, the BOM removals in the filters steadily improved, and steady-state values were obtained in about the same time as expected from the other filter experiments, as shown for Filter 2 in Figure 5. Filter influent thiosulphate concentrations ranged from approximately 0.1 to 0.14 mg/l. Removals through the filters gradually improved and by day 64 no thiosulphate was detected in the filter effluents. Thiosulphate concentration profiles measured on day 75 for all four filters showed that the thiosulphate concentration decreased rapidly (to <0.05 mg/l) within the top 10 cm of the filter (Booth 1998).

The presence of thiosulphate may have slightly altered the composition of the biofilm community compared with

Table 5 | Methylglyoxal and pyruvate results after 64 days of operation (Experiment 2)

	Methylglyoxal			Pyruvate		
	Influent (μg/l)	Effluent (μg/l)	Percent removal	Influent (μg/l)	Effluent (μg/l)	Percent removal
Filter 1	203	46.6	77.1	—	18.7	—
Filter 2	—	—	—	309	0	100
Filter 3	96.6	2.5	97.4	145	0	100

the first experiment, by allowing chemolithotrophic thiosulphate oxidation as an additional means of cellular energy production. However, the thiosulphate represented only about 10 to 15% of the theoretical oxygen demand in the filter influent. It was thus assumed that comparisons with the results from Experiment 1 remained valid.

Results for day 64 (27 days after thiosulphate quenching began) indicated that essentially complete BOM removals had been achieved in Filters 2 and 3, but only partial removal in Filter 1 (Table 5). It is significant to note that pyruvate was detected in the effluent of Filter 1, which was only fed methylglyoxal. By day 75, complete removal of methylglyoxal occurred in Filter 1, and no pyruvate was detected in the effluent (Booth 1998). In Experiment 1, where the influent concentration of methylglyoxal was 25% lower, pyruvate was not observed in the filter effluents under steady-state conditions.

Sampling at intermediate ports of Filter 2 showed that nearly complete pyruvate removal occurred in just over 1 min of EBCT (results not shown). Complete pyruvate removal was also observed in Filter 3 (which was fed both compounds), confirming that it is more readily biodegradable than methylglyoxal. A comparison of the data for Filters 1 and 3 in Table 5 also indicates that methylglyoxal percentage removal over the entire filter depth was higher in the presence of pyruvate. This may be due to the fact that biomass was established more quickly, due to the utilization of pyruvate. However, the actual amount of methylglyoxal removed in Filter 3 was lower, because the influent concentration was lower. This is discussed further below. The possibility of observing pyruvate formation from methylglyoxal in Filter 3 was limited because both compounds were essentially completely removed at the same filter depth.

By day 75 good removals had been well established in all four filters (Figure 6). For comparison purposes, the rates of removal in the first 4 cm of bed depth were calculated (Table 6). When pyruvate was present on its own, its rate of removal at the top of the filter was nearly three times as high as that for methylglyoxal on its own, and more than twice that of formaldehyde, even though the theoretical oxygen demand (Th OD) was the same in all cases (Table 1). The removal rates ($\mu g/l \cdot min$) in the top of the filter of both methylglyoxal and pyruvate were substantially reduced when they were fed together, although this might be partly due to the fact that the initial concentrations were lower (Table 1). The percentage removals for methylglyoxal were the same in the first 4 cm of Filters 1 and 3 (Table 6), which would be expected if removals followed a first order process and if the presence of pyruvate did not adversely affect the removal of methylglyoxal. In the case of pyruvate, the percentage removal in the top 4 cm of Filter 3 was lower. This is likely due both to competition and to formation from methylglyoxal. The percentage removals for methylglyoxal and formaldehyde in the top of the filter were similar. The mass removal rate of formaldehyde was somewhat higher, due in part to its higher influent concentration.

Direct comparisons of initial removal rates for methylglyoxal alone between Experiments 1 and 2 (Tables 3 and 6) are difficult because neither EBCTs nor hydraulic

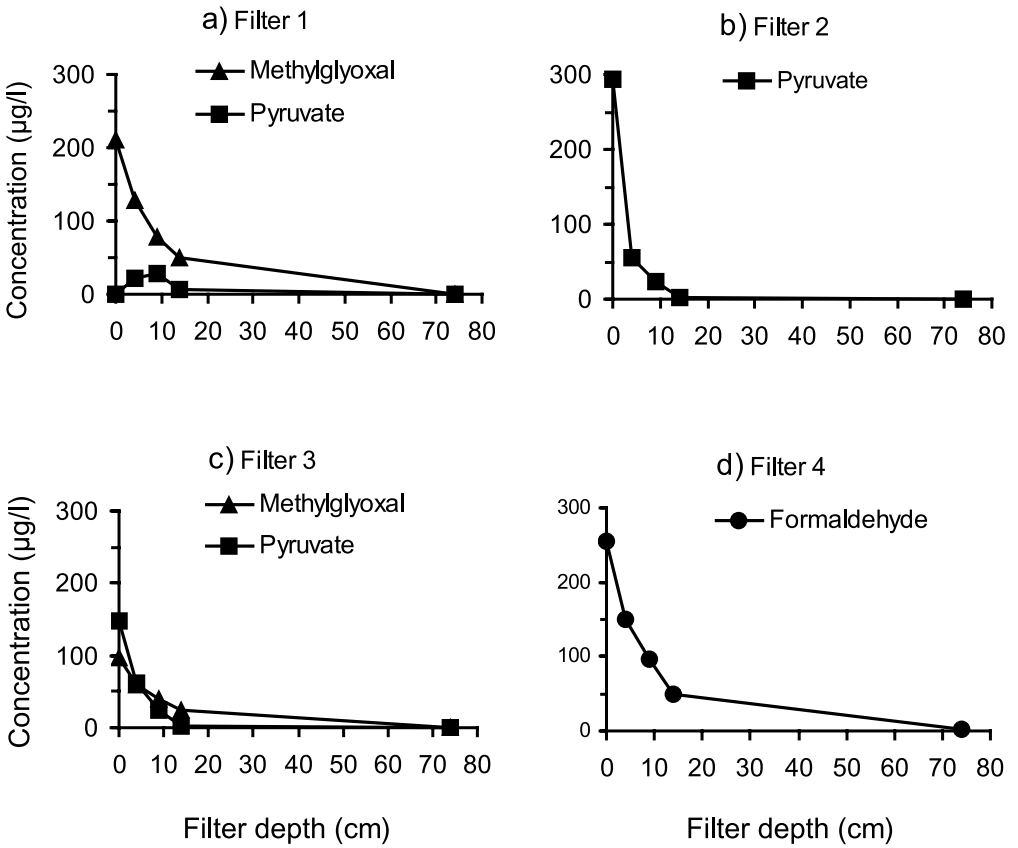

Figure 6 | Concentration profiles in filters on day 75 in Experiment 2 (38 days after quenching began): (a) Filter 1, (b) Filter 2, (c) Filter 3, (d) Filter 4.

Table 6 | Removal rates in the top of the filters in Experiment 2*

Filter number	HLR (m/h)	Compound	Concentration (µg/l) Depth 0 cm	Depth 4 cm (EBCT=0.30 min)	Rate of removal (µg/l · min) (top 4 cm)	Percentage removal (top 4 cm)
1	8	Methylglyoxal	211	129	272	39
2	8	Pyruvate	293	55.3	793	81
3	8	Methylglyoxal	97.5	59.6	126	39
		Pyruvate	149	62.0	289	58
4	8	Formaldehyde	256	149	354	42

*On day 75 following startup.

loadings were the same. However, the rate of 288 μg/(l · min) in Filter 3 in Experiment 1 under steady-state conditions at an EBCT of 0.24 min is just slightly higher than the rate of 272 μg/(l · min) in Filter 1 at an EBCT of 0.30 min. This suggests that the removals observed were reproducible.

It was expected that pyruvate would be very readily biodegradable, as demonstrated for it and other carboxylic acids at a full-scale installation (Gagnon *et al.* 1997). The similarity between formaldehyde and methylglyoxal removal rates was consistent throughout the present study. Others researchers have observed that formaldehyde tends to be more easily removed than methylglyoxal (Weinberg *et al.* 1993; Krasner *et al.* 1993; Niquette *et al.* 1998). However, in those studies the methylglyoxal resulted from ozonation, while in the present study it was added from a feed solution. This may account for some of the difference, however, Wang *et al.* (1995) reported removals similar to those reported here, for methylglyoxal in a pilot-scale study.

The results over the complete filter depth in the present study indicate that, at least under certain conditions, it is possible to obtain good removals of methylglyoxal. In batch investigations (Booth 1998) related to the column experiments reported herein, BIOLOG® results (Biolog, Inc.; Hayward, CA) suggested that methylglyoxal utilization resulted in a considerable shift in the composition of the microbial community, compared to the starting population (i.e. the inoculum). This result provides a possible explanation for the observation by some investigators that methylglyoxal is less readily biodegradable than other ozonation by-products.

CONCLUSIONS

The major conclusions of this study, which examined the removals of selected easily biodegradable compounds fed to pilot scale drinking water biofilters, are:

1. Neither external nor internal mass transfer was found to limit the removal rate of the compounds investigated: methylglyoxal, formaldehyde, and pyruvate. This is significant because it indicates that for typical drinking water biofilter operating conditions, modelling the removals of easily biodegradable substances need only consider biodegradation. This considerably simplifies the modelling.
2. When methylglyoxal was the sole BOM component in the influent, pyruvate formation within the filters was observed. Pyruvate appeared in the filter effluents under the following conditions: in Experiment 1 following step increases in influent methylglyoxal concentration, and in Experiment 2 during the time that methylglyoxal removal was becoming established.
3. The removal rates of formaldehyde and methylglyoxal were found to be comparable, when each was the sole BOM component in the filter influent. Complete removals of methylglyoxal (when fed as the sole BOM component) were obtained under steady state conditions in Experiment 1 and by the end of Experiment 2 (day 75).
4. When fed alone, the removal rate of pyruvate was far higher than that of either formaldehyde or methylglyoxal. The removal rate of pyruvate was measurably reduced when it was fed together with methylglyoxal. The reduced rate was probably due both to competition and to the formation of pyruvate from methylglyoxal.
5. Samples taken just before and just after backwashing showed that backwashing had essentially no effect on BOM removals.
6. When a three- to four-fold step increase in influent concentration was provided to the filters being fed only methylglyoxal, excellent removals of that compound were regained after an acclimation period. However at the end of the step period, pyruvate continued to be observed in the filter effluent at the higher (10 m/h) hydraulic loading.
7. A 48-h shutdown did not have a strong effect on overall filter performance (this condition was imposed only on the filters being fed methylglyoxal alone). However, removal rates in the uppermost sections of the filters were appreciably lower when the filters were restarted. This suggests that, for substances such as methylglyoxal, measurable effects

on effluent concentration might be observed in filters with relatively short contact times (i.e. only several minutes).

8. A relatively small monochloramine residual (approximately 0.25 mg/l) in the filter influents impaired the biological removal of the compounds investigated (methylglyoxal, pyruvate and formaldehyde).

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