Riverbank filtration: Effect of ground passage on NOM character

W. Joshua Weiss, Edward J. Bouwer, William P. Ball, Charles R. O'Melia, Ramon Aboytes and Thomas F. Speth

ABSTRACT

Research was conducted to explore the effect of underground travel on the character of the natural organic matter (NOM) originating from river water sources during riverbank filtration (RBF) at three Midwestern US drinking water utilities. Measurements of biodegradable dissolved organic carbon (BDOC) and assimilable organic carbon (AOC) showed significant reductions (50 to 90%) in the biodegradable portion of NOM at two of the sites. Specific UV-absorbance (SUVA) values suggested preferential reduction (26% reduction in SUVA) in UV-absorbing NOM at one of the sites but negligible changes in SUVA were observed at the other two sites. XAD-8 characterization was carried out on the river and well waters to investigate possible changes in the character of the NOM. The distribution of dissolved organic carbon (DOC) between the XAD-8 adsorbing ('hydrophobic') and non-adsorbing ('hydrophilic') fractions was similar between the river and well waters (40 to 70% hydrophilic and 30 to 60% hydrophobic), indicating no significant, consistent, preferential removal of either fraction upon ground passage. SUVA measurements on the separate XAD-8 fractions similarly showed no significant change during bank filtration. Disinfection by-product (DBP) formation testing was performed on the various fractions, keeping the ratio of chlorine:DOC:bromide constant. DBP formation testing showed no preferential formation between the hydrophobic and hydrophilic fractions in either the river or well waters. While the overall concentrations of organic DBP precursors are effectively reduced during bank filtration, the reductions appear to be largely the result of the reduction in NOM concentration rather than a consistent change in NOM character.

Key words | disinfection by-products, filtration, NOM, riverbank, XAD-8

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INTRODUCTION

Riverbank filtration (RBF) has shown much promise as a process for removing a variety of constituents in water, among them natural organic matter (NOM) and disinfection by-product (DBP) precursor material (Miettinen *et al.* 1994, 1998; Cosovic *et al.* 1996; Kivimaki *et al.* 1998; Kuehn & Mueller 2000; Ray *et al.* 2002*a*, 2002*b*; Weiss *et al.* 2002, 2003*a*, *b*; Wang 2002). The character of the NOM in a water source can have a substantial effect on its reactivity with chlorine, the speciation of the DBPs formed as a result of this reaction, and the treatability of the NOM (Aiken & Cotsaris 1995; Croué *et al.* 1999). The objective of this work was to determine whether RBF preferentially removes specific portions of NOM, resulting in a change in its overall character. In particular, XAD-8 resin chromatography was used to separate the NOM in river and bank-filtered water samples into operationally defined hydrophilic and hydrophobic fractions that were then subjected to DBP formation testing. Of the two possible DBP precursors, NOM and bromide, bromide concentrations between the river and well waters were similar (Weiss *et al.* 2003*a*). Therefore, in this paper, the term 'DBP precursors' refers specifically to the NOM precursor material.

NOM characterization

NOM is composed of a wide variety of functional groups and molecules with different characteristics. Numerous methods are available to characterize NOM in water (Leenheer 1985; Amy *et al.* 1987; Logan & Jiang 1990; Aiken & Leenheer 1993; Frimmel 1998; Croué *et al.* 1999; Muller *et al.* 2000; Wong *et al.* 2002). A commonly used approach for NOM characterization is to separate the NOM into operationally defined subgroups of material that are more chemically and/or physically homogeneous as a result of the separation, as controlled by the mechanisms of the method and by the sample conditions. The various fractions of NOM often comprise different functional groups whose properties can help provide insight into the behaviour or reactivity of overall NOM in a system.

For this study, NOM was characterized using an established XAD-8 resin fractionation method (Leenheer 1981; Thurman & Malcolm 1981). Water containing dissolved NOM was acidified and passed through a column of XAD-8 resin, and NOM in the initial column effluent was operationally defined as the 'hydrophilic' fraction. NOM adsorbed on the resin was eluted in reverse direction to isolate the NOM operationally defined as the 'hydrophobic' fraction. Elution was carried out first with strongly acidic water to remove the 'hydrophobic bases' and then with strongly basic water to remove the 'hydrophobic acids' (both of these fractions were combined as simply the 'hydrophobic' fraction). The hydrophobic material represents that fraction of NOM that affiliates more strongly with the XAD-8 resin under acidic conditions and which has operationally been defined by others (Thurman & Malcolm 1981; Owen *et al.* 1995; Krasner *et al.* 1996) to represent the so-called aquatic humic substances (humic acids, fulvic acids and a 'hydrophobic neutral' fraction). 'Hydrophobic neutrals' can be isolated by soxhlet extraction of the XAD-8 resin following the elutions. In general, studies have shown the hydrophobic fraction to be the major contributor to trihalomethane (THM) formation upon chlorination, although the reactivity of the hydrophilic fraction with chlorine can also be significant (Collins *et al.* 1986; Croué *et al.* 1999). In addition, the hydrophobic fraction is typically more easily removed during conventional treatment than the non-adsorbing fraction (Collins *et al.* 1986; Owen *et al.* 1995; Singer 1999).

Characterization studies in the literature

In early studies involving XAD resin fractionations, Leenheer (1981) characterized a S. Platte River water sample as being evenly split between hydrophilic and hydrophobic material. Thurman & Malcolm (1981) noted that for typical uncoloured surface water, 30 to 50% of the DOC is adsorbed to the XAD-8 resin (as the hydrophobic fraction). Collins *et al.* (1986) characterized natural water sources at four drinking water treatment plants and the corresponding treated waters using XAD-8 fractionation. The non-volatile (NV) total organic carbon (TOC) generally comprised a slightly higher fraction of hydrophobic relative to hydrophilic material. In addition, the hydrophobic fraction often produced significantly higher THM concentrations upon chlorination. Two river and one reservoir source waters were treated by conventional treatment or direct filtration and one groundwater source was treated using lime softening. Upon treatment at three of the facilities (two rivers and the groundwater), reductions in the NV TOC and THM formation potential (FP) of the hydrophobic fraction were higher than those of the hydrophilic fraction. THM FP reductions were significantly higher than the corresponding NV TOC reductions, indicating the preferential removal of chlorine-reactive NOM.

Martin-Mousset *et al.* (1997) used XAD-8 and XAD-4 resin columns to characterize NOM in four reservoir and four river waters in France. The authors found that in all waters, the hydrophilic and hydrophobic material each contributed approximately half of the DOC, although they note that the hydrophobic fraction was slightly more abundant in the reservoir waters (approximately 50 to 60% of the DOC) than in the river waters (40 to 50% of the DOC). No direct correlation was observed between hydrophilic/hydrophobic character and biodegradable dissolved organic carbon (BDOC) or THM FP measurements. Singer (1999) described work involving chlorination testing of hydrophobic and hydrophilic fractions of

NOM from different source waters. Under two pH conditions, the chlorinations resulted in higher THM and haloacetic acid (HAA) concentrations from the hydrophobic material compared with the hydrophilic material. The two fractions were normalized to the same TOC concentration prior to chlorination.

A complicating factor in XAD-8 characterization studies of natural waters involving DBP testing is the presence of bromide. Bromide has been shown to contribute to the formation of DBPs upon chlorination, with a larger percentage of brominated DBP species formed as bromide concentrations increase relative to the amount of DOC present (Summers *et al.* 1993; Shukairy *et al.* 1994; Chang *et al.* 2001; Kampioti & Stephanou 2002). During XAD-8 characterization, bromide present in the water passes through the XAD-8 column and remains with the hydrophilic fraction, with the subsequent elution of the hydrophobic fraction usually occurring in water that is devoid of bromide. If chlorination of these two fractions is conducted without correction of this issue (as in some prior work), then observed differences in DBP quantity and speciation may result primarily from the differences in bromide concentrations and thus not be solely a result of differences in the character of the NOM. In the research presented here, the authors have taken measures to ensure that the ratio of chlorine:DOC:bromide was held constant for all XAD-8 fractions subjected to chlorination for a given set of river and corresponding well water samples.

Biodegradability of NOM

Biological processes in drinking water treatment, such as biologically active filters, provide a means of removing NOM from source water (Bouwer & Crowe 1988; Hozalski *et al.* 1995). In addition to being a source of DBP precursor material, biodegradable organic matter in drinking water sources has received particular attention because of its contribution to bacterial regrowth in distribution systems (Huck 1990; Escobar & Randall 2001). Because of biological activity in the subsurface, RBF has the potential to remove the biodegradable portion of NOM. Miettinen *et al.* (1994) observed a decrease in the ratio of the chemical oxygen demand (COD) to TOC upon bank filtration of a high-NOM Finnish lake water, indicating a preferential reduction in the reduced and reactive fraction of NOM.

Preferential removal of the more biodegradable (or assimilable) fractions is not always observed, however. For example, Lehtola *et al.* (2002) recently demonstrated an average 60% removal of overall TOC, along with a 53% removal of assimilable organic carbon (AOC) and a 64% removal of microbially available phosphorus during soil infiltration at several Finnish waterworks. Volk *et al.* (2000) measured BDOC and AOC during jar-scale enhanced coagulation experiments using a number of surface waters. The authors found that the AOC fraction was more difficult to remove than the BDOC fraction and suggested that the BDOC fraction may contain some humic material and larger molecules that can be removed by coagulation while the AOC fraction represents the more rapidly assimilable, small, non-humic molecules that are more difficult to remove by coagulation.

Specific UV-absorbance

The specific UV-absorbance (SUVA) is defined as the ratio of UV-absorbance at 254 nm (UV-254) to the DOC concentration (typically reported in units of $l\,mg^{-1}\,m^{-1}$). A reduction in SUVA upon removal of NOM generally indicates a preferential removal of UV-absorbing material. SUVA has been shown to be a good predictor of the aromatic content of aquatic NOM (Croué *et al.* 1999; Singer 1999). The hydrophobic fraction of NOM, as isolated by XAD chromatography, has been found to comprise material with higher values of SUVA than the corresponding hydrophilic fraction (Martin-Mousset *et al.* 1997; Singer 1999). Typically, NOM with a higher SUVA value is more reactive with chlorine, more readily adsorbed by inorganics and less biodegradable (Reckhow *et al.* 1990; Aiken & Cotsaris 1995; Goel *et al.* 1995; Owen *et al.* 1995; Krasner *et al.* 1996; Singer 1999). In the study by Martin-Mousset *et al.* (1997), reservoir waters were found to have higher SUVA values than river waters, and this was shown to reflect a slightly more abundant hydrophobic fraction in the NOM of the reservoir waters. In a similar study, Krasner *et al.* (1996) observed a higher SUVA for the humic fraction of a reservoir water compared with the non-humic fraction.

Table 1 | Characteristics of the three study sites

Well	Distance from river	Depth to well screen	Well screen length	Estimated travel time	Approx. well capacity
Indiana American Water at Jeffersonville, Indiana					
Well #9	100 ft (30 m)	45 ft (14 m)	50 ft (15 m)	3 to 5 days	1,000–1,400 gpm (5,450–7,630 m^3 day^{-1})
Well #2	580 ft (177 m)	66 ft (20 m)	25 ft (8 m)	13 to 19 days	1,000–1,400 gpm (5,450–7,630 m^3 day^{-1})
Indiana American Water at Terre Haute, Indiana					
Horizontal Collector Well	90 ft (27 m)	80–90 ft (24–27 m) depth to arms	1,600 ft (480 m) of screened laterals	14 to 60 days	8,350 gpm (45,500 m^3 day^{-1})
Well #3	400 ft (122 m)	78 ft (24 m)	45 ft (14 m)	NA	690 gpm (3,760 m^3 day^{-1})
Missouri American Water at Parkville, Missouri					
Well #4	120 ft (37 m)	57 ft (17 m)	20 ft (6 m)	NA	1,150 gpm (6,270 m^3 day^{-1})
Well #5	120 ft (37 m)	59 ft (18 m)	30 ft (9 m)	NA	1,400 gpm (7,630 m^3 day^{-1})

NA=data not available.

MATERIALS AND METHODS

Site descriptions

The study sites have been described previously (Weiss *et al.* 2003*a*). The three sites (Indiana American Water at Jeffersonville, Indiana; Indiana American Water at Terre Haute, Indiana; and Missouri American Water at Parkville, Missouri) currently employ RBF and are owned and operated by American Water, with whom this research was conducted. The wells sampled at the Jeffersonville site were Well #9 and Well #2 (100 ft (30 m) and 580 ft (177 m) from the Ohio River, respectively). At the Terre Haute site, the Horizontal Collector Well and Well #3 (90 ft (27 m) and 400 ft (122 m) from the Wabash River, respectively) were sampled; on the Collector Well, screened horizontal arms extend out from centre at a depth of 80 ft (24 m) below the bottom of the river. Finally, at the Parkville site, Well #4 and Well #5 (both at a distance of 120 ft (37 m) from the Missouri River) were sampled. The geological characteristics of the three sites have been described in more detail elsewhere (Weiss *et al.* 2003*a*). Table 1 provides a summary of the characteristics of the wells at the three sites.

To characterize the potential dilution from groundwater at the three study sites, a number of inorganic parameters in the river and well waters were measured, including temperature, pH, major cations and major anions. For Jeffersonville, groundwater flow analysis was previously performed by Eagon & Associates, Inc. (Worthington, Ohio), using the USGS groundwater flow and particle tracking program, MODPATH (Pollock 1994). Analysis of the travel time and river water influx to the wells suggested that 96% of the total discharge from the entire modelled well field (which included the Babb well field and a proposed well field on an adjacent property for a total of 11 wells) was obtained from induced infiltration from the Ohio River. As described previously (Weiss *et al.* 2003*a*), inorganic analyses indicate that at Jeffersonville and Terre Haute, water from the closer well

at each site (Well #9 at Jeffersonville and the Collector Well at Terre Haute) comprises primarily bank-filtered river water, while the further wells (Well #2 at Jeffersonville and Well #3 at Terre Haute) are likely to be more significantly influenced by dilution from the local groundwater. For this reason, the XAD-8 characterization studies described herein were performed using the river waters and waters from the closer wells only (thus isolating the effects of ground passage from those of dilution). At Parkville, inorganic analyses indicate that both wells (located at equal distances from the Missouri River) largely comprise bank-filtered river water with only minor influences from dilution.

Biodegradable organic carbon measurements

BDOC and AOC measurements were made to evaluate changes in biodegradability of NOM during ground passage at the three sites. BDOC represents the fraction of organic carbon that can be mineralized by heterotrophic microbes, while AOC is the fraction that is converted into cell mass by specific strains or mixtures of bacteria (Huck 1990; Escobar & Randall 2001). For AOC, a water sample is incubated with a specific population of bacteria and the maximum level of bacteria (at the stationary phase of growth) is taken to be proportional to the limiting nutrient, which is assumed to be carbon under the nutrient-rich conditions of the test (LeChevallier *et al.* 1993). The limiting nutrient concentration is converted into carbon equivalents using an empirical cell yield coefficient for the bacteria and substrate. In general, AOC is a measure of the growth potential of a water sample and generally comprises the most readily degradable fraction of BDOC. BDOC was measured using a biofilm-coated sand method as described by Joret & Levi (1986) and Joret (1988). AOC was determined using the rapid ATP method of LeChevallier *et al.* (1993). Both measurements were made on seven bi-monthly samples.

DOC, UV-254 and SUVA measurements

River and well waters were filtered through pre-rinsed 0.45 μm filter papers (Durapore type HVLP, Millipore, Bedford, Massachusetts) to separate dissolved from particulate NOM. DOC concentrations were measured on the filtrate using a Phoenix 8000 TOC Analyser (Tekmar-Dohrmann, Mason, Ohio). The Phoenix 8000 TOC Analyser uses the ultraviolet/persulfate oxidation method as described in *Standard Methods* 5310 (1998) and a non-dispersive infrared (NDIR) detector. Standards were prepared using a commercially available 1000 ppm (1 ml = 1 mg C) potassium hydrogen phthalate carbon standard (Fisher Scientific, Pittsburgh, Pennsylvania). Each sample run included a blank (distilled, deionized water) and three standards, bordering the expected sample concentrations. For a given run, the raw data (instrument response) for the blank was subtracted from all standards to give a normalized instrument response (blanks and standards were prepared using the same distilled, deionized water). A standard curve using the normalized standard responses was then used to calculate sample DOC concentrations.

To test the reproducibility of the DOC measurements, eight sub-samples of a single standard (1.0 mg l^{-1}, near the DOC concentration of most well water samples) were run at the same time, yielding an average of 1.0 mg l^{-1} with a standard deviation of 0.02. UV-254 values for the filtered (DOC) samples were measured on a Shimadzu UV-160U spectrophotometer (Columbia, Maryland) using a 1 cm cell, with no additional sample manipulation prior to analysis. High nitrate concentrations can affect the measurement of UV-254; however, nitrate concentrations in the river and well waters were fairly low (less than 1.3 mg l^{-1} at Jeffersonville and Parkville and between 2 and 3 mg l^{-1} at Terre Haute). SUVA was calculated as the ratio of the UV-254 (cm^{-1}) of a particular sample to the DOC concentration (mg l^{-1}) of that sample, multiplied by 100 to give units of l mg^{-1} m^{-1}.

NOM fractionation

The XAD-8 fractionation method was chosen for this study because the method allows for the fractionation of large volumes of water, as required for the intended subsequent analyses. A number of studies in the literature have used the XAD-8 approach to characterize natural

waters as well as in treatment studies (Owen *et al.* 1995; Krasner *et al.* 1996; Martin-Mousset *et al.* 1997; Croué *et al.* 1999; Leenheer *et al.* 2001). In this study, the river and the well closest to the river at each of the three sites were sampled at approximately the same time (same date) on each sampling occasion. For operational reasons, at Jeffersonville, Well #9 and Well #10 were sampled alternately during different sampling events. The two wells are located at similar distances from the Ohio River and are of similar water quality. An XAD-8 resin column was used to separate the NOM in each water sample into its hydrophobic and hydrophilic fractions. The various fractions were subsequently analysed for DOC and UV-254, and subjected to THM and HAA formation testing as described later in this section. In addition, values of SUVA were calculated for the various fractions.

XAD-8 fractionation procedure

The XAD-8 fractionation procedure is based on the methods proposed by Leenheer (1981) and Thurman & Malcolm (1981). River water samples were pre-filtered through a 1.2 μm glass fibre filter (Whatman AH-234, Whatman Co., Kent, UK) to remove large particles. Pre-filtered river water samples and well water samples were filtered through a 0.45 μm filter (Durapore type HVLP, Millipore, Bedford, Massachusetts) to remove particulate organic carbon (POC). The filtrate was then acidified to pH 2.0 with concentrated H_3PO_4 and passed through the XAD-8 column at a rate of approximately 15 bed volumes per hour (column preparation as described in the following section). Organic material not retained on the resin (the hydrophilic fraction of the NOM) was collected in the column effluent. The fraction of NOM adsorbed onto the column (the hydrophobic fraction) was eluted in reverse direction with successive portions of 0.1 N HCl and 0.1 N NaOH at a flow rate of approximately 5 bed volumes per hour. The hydrophobic fraction (comprising the hydrophobic bases and the hydrophobic acids) was collected and diluted to 3.0 l with distilled, deionized water to provide enough volume for subsequent analyses.

As noted in the introduction, a 'hydrophobic neutral' fraction can also be isolated by extracting the XAD-8 resin following a sample run. However, this was not done in the current research because of the practical need to re-use the XAD-8 columns for a number of river and well water samples (the 'hydrophobic neutrals' were shown by mass balance to typically comprise less than 10% of the NOM in the river and well water samples—essentially at or below the detection limit of the DOC measurements).

XAD-8 column preparation

The XAD-8 resin was obtained from Supelco (Supelite DAX-8, Sigma-Aldrich, St Louis, Missouri). Supelite DAX-8 is an acrylic ester with a mesh size of 40–60 and a mean surface area of 160 $m^2\ g^{-1}$. The resin was first extracted in a beaker with 0.1 N NaOH. Each day for five days, the resin was rinsed with NaOH and fines were decanted off the top. The resin was then extracted in a Soxhlet apparatus for approximately 24 hours with acetone and hexane and stored in methanol. The resin was then packed into the column as a slurry. The column was rinsed with methanol to remove any remaining acetone and hexane. Distilled, deionized water was then pumped through the column until the DOC of the effluent was negligible. Preceding every sample application, the column was rinsed with 0.1 N NaOH, 0.1 N HCl, and distilled, deionized water.

The size of the column was based on the column-capacity factor k′, defined as the ratio of mass of solute sorbed on XAD-8 to the mass of solute dissolved in water (Leenheer 1981; Thurman & Malcolm 1981). The volume of the resin bed was determined by the effluent volume required for subsequent analyses. From a mass balance, the effluent volume is:

$$V_e = 2V_o(1 + k'), \quad (1)$$

where V_o is the total void volume (interparticle and intraparticle) of the XAD-8 resin and V_e is the effluent volume at which 50% of the solute mass added is retained and 50% of the solute mass has eluted (Thurman & Malcolm 1981). Thurman & Malcolm (1981) have recommended that for separation of aquatic humic substances the column size be chosen such that a solute with a k′ of 100 is 50% retained

by the column for a given effluent volume, V_e, and this recommendation was followed in this study.

Two glass columns (53 ml total volume, 15 mm inside diameter) were prepared, one of which was used only for characterization of the river waters and one of which was used only for well waters. As specified by the resin manufacturer, the column was packed approximately half-full with XAD-8 resin to provide room for expansion as the resin swells (Supelco 1998). Leenheer (1981) and Supelco technical representatives estimated that the total void volume of the XAD-8 resin is approximately 65% of the total resin bed volume in the column. V_o was then calculated by multiplying the bed volume of the resin column by 0.65. The bed volume was calculated as $V_{bed} = \pi R^2 L$, where R is the inside radius of the column and L is the length of the bed (the height of resin in the column). The above calculations were made for each column after preparation to determine the amount of sample that could be passed through the column (V_e) to maintain a retained material with the appropriate approximate average value of k′ ($= 100$). For both columns, V_e for the characterization experiments was approximately 3.5 l.

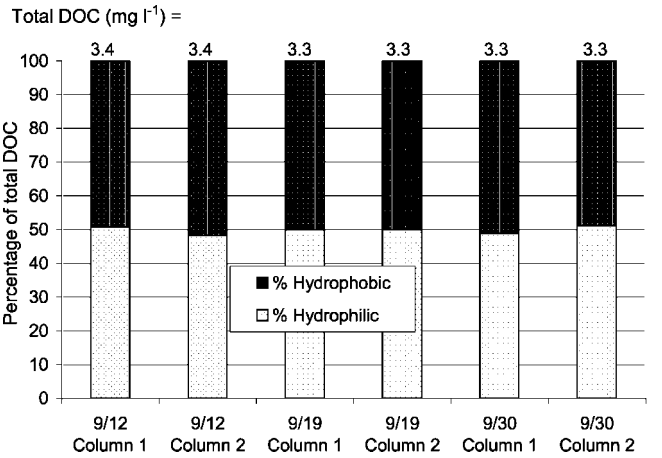

Figure 1 | Reproducibility of XAD-8 column results with Potomac River water

Reproducibility of XAD-8 columns

A single large water sample from the Potomac River in western Maryland was fractionated several times through both XAD-8 columns to evaluate the variability of the XAD-8 fractionation method. The results show very good reproducibility of the method as well as good agreement between the two XAD-8 columns (Figure 1).

Preparation of samples for DBP formation testing

Upon chlorination, the Cl_2:DOC:Br ratio among all samples from a particular site and sampling event was manipulated to maintain a constant value between samples. Prior to DBP formation testing for a given site and sampling event, a portion of the original (unfractionated) river and well waters and the hydrophobic and hydrophilic fractions of each were brought to neutral pH through addition of acid or base as necessary and then normalized to a constant DOC concentration by dilution with distilled, deionized water. This was done in order to ensure that differences in DBP formation arose from differences in the character of the fractions rather than differences in the amounts of organic matter in each fraction. In addition to adjusting the DOC concentrations, sodium bromide was added to the waters such that the DOC:Br ratio was constant between river and well water NOM fractions for a given site and sampling round.

Bromide concentrations were measured in a portion of the unfractionated river and well waters set aside prior to column testing. Because the bromide concentrations in the river and well waters were typically very small (Table 2), samples of the water were concentrated by evaporation prior to bromide measurement. Bromide measurements were conducted on a Dionex DX-600 Ion Chromatograph (IC; Sunnyvale, California). Each sample set was run along with five standards bordering the expected sample bromide concentrations. The addition of strong acid for passage through the XAD-8 column prevented the measurement of bromide in the acidified samples due to swamping of the IC signal. Similarly, the concentrations of bromide in the hydrophilic and hydrophobic samples could not be measured due to the addition of strong acid or base. The assumption was made that all

Table 2 | UFC test conditions (DOC, chlorine and bromide concentrations) and results (free chlorine residual, THM4 and HAA9 concentrations) for all sampling rounds at the three sites

Sample	Date	DOC (mg l^{-1})	Chlorine (mg l^{-1})	Bromide (mg l^{-1})	Free chlorine residual (mg l^{-1})	THM4 (μmol l^{-1})	HAA9 (μmol l^{-1})
Jeffersonville							
Ohio R. unfract.	May 2001	1.0	2.5	0.23	1.7	0.31	0.29
Ohio R. h-philic	May 2001	1.0	2.5	0.23	1.7	0.17	0.34
Ohio R. h-phobic	May 2001	1.0	2.5	0.23	1.7	0.23	0.34
Well #10 unfract.	May 2001	1.0	2.5	0.23	2.0	0.11	0.16
Well #10 h-philic	May 2001	1.0	2.5	0.23	2.0	0.09	0.19
Well #10 h-phobic	May 2001	1.0	2.5	0.23	2.2	0.06	0.17
Ohio R. unfract.	Sep 2001	1.0	2.5	0.2	1.7	0.11	0.19
Ohio R. h-philic	Sep 2001	1.0	2.5	0.2	1.0	0.15	0.29
Ohio R. h-phobic	Sep 2001	1.0	2.5	0.2	1.6	0.16	0.15
Well #10 unfract.	Sep 2001	1.0	2.5	0.2	1.8	0.14	0.15
Well #10 h-philic	Sep 2001	1.0	2.5	0.2	0.6	0.15	0.20
Well #10 h-phobic	Sep 2001	1.0	2.5	0.2	2.0	0.07	0.13
Ohio R. unfract.	Feb 2002	1.0	2.5	0.5	1.3	0.15	0.20
Ohio R. h-philic	Feb 2002	1.0	2.5	0.5	1.4	0.14	0.17
Ohio R. h-phobic	Feb 2002	1.0	2.5	0.5	1.7	0.17	0.16
Well #9 unfract.	Feb 2002	1.0	2.5	0.5	0.9	NA	0.14
Well #9 h-philic	Feb 2002	1.0	2.5	0.5	0.3	0.13	0.18
Well #9 h-phobic	Feb 2002	1.0	2.5	0.5	1.8	0.09	0.13
Ohio R. unfract.	Mar 2002	0.5	1.25	0.09	0.4	0.31	0.12
Ohio R. h-philic	Mar 2002	0.5	1.25	0.09	0.5	0.23	0.14
Ohio R. h-phobic	Mar 2002	0.5	1.25	0.09	NA	0.33	0.11
Well #9 unfract.	Mar 2002	0.5	1.25	0.09	0	0.16	0.10
Well #9 h-philic	Mar 2002	0.5	1.25	0.09	0.4	0.09	0.10
Well #9 h-phobic	Mar 2002	0.5	1.25	0.09	0.5	0.22	0.09

Table 2 | *continued*

Sample	Date	DOC (mg l^{-1})	Chlorine (mg l^{-1})	Bromide (mg l^{-1})	Free chlorine residual (mg l^{-1})	THM4 (μmol l^{-1})	HAA9 (μmol l^{-1})
Terre Haute							
Wabash R. unfract.	May 2001	1.3	3.3	0.03	2.3	0.19	0.15
Wabash R. h-philic		1.3	3.3	0.03	2.0	0.10	0.17
Wabash R. h-phobic		1.3	3.3	0.03	2.8	0.14	0.12
Collector Well unfract.	May 2001	1.3	3.3	0.03	2.5	0.15	0.20
Collector Well h-philic		1.3	3.3	0.03	2.6	0.10	0.21
Collector Well h-phobic		1.3	3.3	0.03	3.1	0.10	0.13
Wabash R. unfract.	Jul 2001	0.8	2.0	0.14	1.6	0.12	0.16
Wabash R. h-philic		0.8	2.0	0.14	1.2	0.14	0.20
Wabash R. h-phobic		0.8	2.0	0.14	2.0	0.12	0.16
Collector Well unfract.	Jul 2001	0.8	2.0	0.14	1.6	NA	0.13
Collector Well h-philic		0.8	2.0	0.14	1.5	0.10	0.18
Collector Well h-phobic		0.8	2.0	0.14	2.0	0.10	0.12
Wabash R. unfract.	Sep 2001	1.0	2.5	0.25	1.4	0.22	0.24
Wabash R. h-philic		1.0	2.5	0.25	0.9	0.16	0.25
Wabash R. h-phobic		1.0	2.5	0.25	1.7	0.13	0.20
Collector Well unfract.	Sep 2001	1.0	2.5	0.25	1.8	0.17	0.15
Collector Well h-philic		1.0	2.5	0.25	1.5	0.19	0.23
Collector Well h-phobic		1.0	2.5	0.25	1.9	0.11	0.19
Wabash R. unfract.	Feb 2002	NA	NA	NA	NA	NA	NA
Wabash R. h-philic		1.1	2.75	0.06	1.5	0.31	0.26
Wabash R. h-phobic		1.1	2.75	0.06	2.0	0.34	0.24
Collector Well unfract.	Feb 2002	1.1	2.75	0.06	1.5	0.25	0.15
Collector Well h-philic		1.1	2.75	0.06	1.5	0.24	0.24
Collector Well h-phobic		1.1	2.75	0.06	2.2	0.12	0.12
Wabash R. unfract.	Mar 2002	1.0	2.5	0.07	1.2	0.86	0.22

Table 2 | *continued*

Sample	Date	DOC (mg l^{-1})	Chlorine (mg l^{-1})	Bromide (mg l^{-1})	Free chlorine residual (mg l^{-1})	THM4 (μmol l^{-1})	HAA9 (μmol l^{-1})
Wabash R. h-philic		1.0	2.5	0.07	0.7	0.61	0.29
Wabash R. h-phobic		1.0	2.5	0.07	1.4	0.10	0.26
Collector Well unfract.	Mar 2002	1.0	2.5	0.07	1.3	0.52	0.15
Collector Well h-philic		1.0	2.5	0.07	0.2	0.47	0.21
Collector Well h-phobic		1.0	2.5	0.07	1.3	0.88	0.11
Parkville							
Missouri R. unfract.	May 2001	1.6	4.0	0.08	2.2	0.25	0.32
Missouri R. h-philic		1.6	4.0	0.08	2.5	0.17	0.39
Missouri R. h-phobic		1.6	4.0	0.08	2.4	0.17	0.39
Well #4 unfract.	May 2001	1.6	4.0	0.08	2.4	0.19	0.21
Well #4 h-philic		1.6	4.0	0.08	2.0	0.13	0.29
Well #4 h-phobic		1.6	4.0	0.08	3.2	0.16	0.28
Missouri R. unfract.	Jul 2001	1.2	3.0	0.1	2.1	0.21	0.21
Missouri R. h-philic		1.2	3.0	0.1	2.0	0.16	0.28
Missouri R. h-phobic		1.2	3.0	0.1	2.1	0.17	0.23
Well #4 unfract.	Jul 2001	1.2	3.0	0.1	2.5	0.18	0.17
Well #4 h-philic		1.2	3.0	0.1	2.0	0.17	0.24
Well #4 h-phobic		1.2	3.0	0.1	2.5	0.15	0.23
Missouri R. unfract.	Sep 2001	1.5	3.75	0.3	2.3	0.24	0.28
Missouri R. h-philic		1.5	3.75	0.3	2.0	NA	0.32
Missouri R. h-phobic		1.5	3.75	0.3	2.0	0.04	0.35
Well #4 unfract.	Sep 2001	1.5	3.75	0.3	2.2	0.18	0.22
Well #4 h-philic		1.5	3.75	0.3	2.0	0.20	0.30
Well #4 h-phobic		1.5	3.75	0.3	2.5	0.05	0.28
Missouri R. unfract.	Feb 2002	1.3	3.25	0.11	1.8	0.38	0.20
Missouri R. h-philic		1.3	3.25	0.11	0.9	0.34	0.27

Table 2 | *continued*

Sample	Date	DOC (mg l^{-1})	Chlorine (mg l^{-1})	Bromide (mg l^{-1})	Free chlorine residual (mg l^{-1})	THM4 (μmol l^{-1})	HAA9 (μmol l^{-1})
Missouri R. h-phobic		1.3	3.25	0.11	2.5	0.46	0.14
Well #4 unfract.	Feb 2002	1.3	3.25	0.11	1.0	0.25	0.14
Well #4 h-philic		1.3	3.25	0.11	0.7	0.16	0.13
Well #4 h-phobic		1.3	3.25	0.11	2.4	0.22	0.20
Missouri R. unfract.	Mar 2002	1.0	2.5	0.07	0.5	0.53	0.16
Missouri R. h-philic		1.0	2.5	0.07	0.4	NA	0.20
Missouri R. h-phobic		1.0	2.5	0.07	1.5	0.31	0.20
Well #4 unfract.	Mar 2002	1.0	2.5	0.07	NA	0.50	0.12
Well #4 h-philic		1.0	2.5	0.07	0	0.22	0.09
Well #4 h-phobic		1.0	2.5	0.07	1.1	0.45	0.15

NA=data not available.

bromide in the unfractionated waters passed through the column and ended up in the hydrophilic fraction; the bromide in the hydrophobic fraction was assumed to be zero.

Because all of the river and well water fractions (including the 'unfractionated' samples) for a given site and sampling round had to be diluted to the lowest DOC concentration (usually the well water hydrophilic or hydrophobic fraction), the samples had low concentrations of DOC when subjected to DBP formation testing, ranging from 0.5 to 1.6 mg l^{-1} among the three sites (Table 2). For a particular site, the lowest DOC concentration generally changed from one sampling round to the next, within the range just given. Therefore, as described later, the results for the different sampling rounds were normalized to the DOC concentration for comparison. In regard to bromide addition prior to chlorination, the fraction with the highest bromide concentration served as the baseline to which all other fractions were adjusted. The adjusted bromide concentrations upon DBP formation testing ranged from 0.03 to 0.5 mg l^{-1} (Table 2).

DBP formation testing

Formation of DBPs in the various fractions was evaluated by a modified uniform formation conditions (UFC) test (Summers *et al.* 1996). For a given site and sampling event, the unfractionated river and well waters and the hydrophilic and hydrophobic fractions for the river and well waters were subjected to UFC testing. Application of the UFC test to the river and well waters at the three sites was as described elsewhere (Weiss *et al.* 2003*b*); conditions included pH of 8.0 and a contact time of 1 day. Temperature was not strictly monitored during incubation; samples were incubated at room temperature. For application to the fractionated NOM samples, this test was further modified as described in the earlier section of this paper; that is, in a manner that maintained a constant Cl_2:DOC:Br ratio for all river and well fractions for a particular sampling event. Typically the chlorine dose for UFC testing is determined using a chlorine demand test with three different chlorine doses, corresponding to Cl_2:DOC ratios of 1.2:1, 1.8:1 and 2.5:1. The dose giving a

free chlorine residual between 0.6 and 1.4 mg l^{-1} after the 24-h incubation time is chosen as the appropriate dose for UFC testing. In order to keep the Cl_2:DOC ratio constant among all samples for a particular site and sampling round, however, only one chlorine dose was used for all such samples, regardless of the individual chlorine demands. To be conservative, the chlorine dose for a given sampling event was chosen such that the Cl_2:DOC ratio was 2.5:1. The free chlorine residual concentrations at the end of the UFC testing incubation period ranged from 0 to 3.2 mg l^{-1} among samples from the three sites (Table 2). In the two cases where the residual went to zero during the incubation period (Jeffersonville, March 2002, Well #9 unfractionated; and Parkville, March 2002, Well #4 hydrophilic), the data represent underestimates in DBP formation due to inadequate chlorine dosing for these samples. Therefore, these data were not included in the subsequent discussion. Concentrations of DOC, chlorine and bromide during UFC testing for the various sampling rounds at the three sites are given in Table 2.

Following UFC testing, THM samples were taken and quenched with sodium thiosulfate, and concentrations of four THM species (chloroform, bromodichloromethane, chlorodibromomethane and bromoform) in the chlorinated water were measured according to *Standard Methods* 6232 B, liquid–liquid extraction gas chromatograph (GC) Method (*Standard Methods* 1998) at Johns Hopkins University. Samples were extracted with pentane (containing 30 μg l^{-1} 1,2-dibromopropane as an internal standard) and separated and analysed on a GC equipped with a linearized electron capture detector (ECD). Each set of samples was run with five THM standards (containing the four measured species) bordering the expected concentrations. THM results are reported as the sums of the four individual species measured here, referred to hereafter as THM4. HAA samples were quenched with ammonium chloride and sent to EE&T Laboratories (Environmental Engineering & Technology, Inc., Newport News, Virginia) for measurement of nine HAA species (trichloroacetic acid, dichloroacetic acid, chloroacetic acid, bromodichloroacetic acid, bromochloroacetic acid, chlorodibromoacetic acid, bromoacetic acid, dibromoacetic acid and tribromoacetic acid) using US EPA method 552.2 (US EPA 1995). Results are reported as the sums of the ninespecies measured here, referred to hereafter as HAA9.

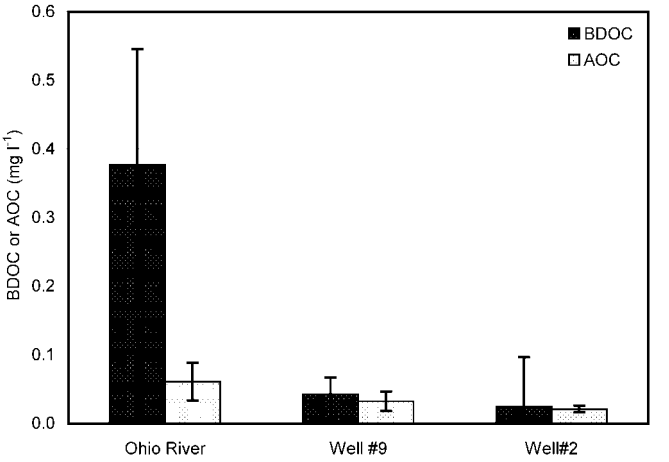

Figure 2 | Average BDOC and AOC concentrations at Jeffersonville (n=7; error bars indicate standard deviations of the averages)

RESULTS

Reduction in BDOC and AOC concentrations

Average BDOC and AOC data for Jeffersonville indicate that the Ohio River water contained close to 0.4 mg l^{-1} BDOC compared with less than 0.05 mg l^{-1} BDOC in the well waters (Figure 2). Average AOC was present at significantly lower concentration in the Ohio River and a 50% lower value was observed in the well water. BDOC and AOC data are compared for all three RBF sites in Table 3. The Wabash River water had an average concentration of 0.9 mg l^{-1} BDOC compared with less than 0.2 mg l^{-1} BDOC in the well water (Table 3). The reduction in average AOC between the river and well at Terre Haute (85%) was higher than that observed for Jeffersonville. At Parkville, the reduction in average BDOC was not statistically significant (Table 3). Average AOC concentrations in the Missouri River and the well waters at Parkville were similar (Table 3).

Table 3 | Average BDOC and AOC concentrations and SUVA (±standard deviations of the averages) at the three sites; percentage reductions relative to river waters given in brackets (n=7 for BDOC and AOC datasets; n=16 for Ohio River SUVA, n=17 for Well #9 and Well #2 SUVA; n=16 for Terre Haute SUVA; and n=14 for Missouri River SUVA, n=15 for Well #4 and Well #5 SUVA)

	BDOC ($mg\ l^{-1}$)	AOC ($mg\ l^{-1}$)	SUVA ($l\ mg^{-1}\ m^{-1}$)
Jeffersonville			
Ohio River	0.38 ± 0.17	0.061 ± 0.028	2.7 ± 1.2
Well #9	0.043 ± 0.024 [89%][1]	0.032 ± 0.014 [48%][1]	2.0 ± 0.7 [26%][1]
Well #2	0.025 ± 0.072 [93%][1]	0.021 ± 0.005 [66%][1]	1.7 ± 0.8 [37%][1]
Terre Haute			
Wabash River	0.90 ± 0.59	0.19 ± 0.095	2.7 ± 0.8
Collector Well	0.18 ± 0.19 [80%][1]	0.028 ± 0.011 [85%][1]	2.6 ± 0.8 [4%]
Well #3	0.092 ± 0.22 [90%][1]	0.021 ± 0.013 [89%][1]	2.0 ± 1.5 [26%]
Parkville			
Missouri River	0.41 ± 0.29	0.25 ± 0.093	2.3 ± 1.1
Well #4	0.29 ± 0.22 [29%]	0.25 ± 0.15 [0%]	2.7 ± 1.5 [− 17%]
Well #5	0.25 ± 0.19 [39%]	0.21 ± 0.11 [16%]	2.8 ± 2.0 [− 22%]

[1]Differences significant at 95% or higher confidence interval.

Change in SUVA upon RBF

The average calculated SUVA value was 26% less at Well #9 than in the Ohio River at Jeffersonville (Table 3). At Terre Haute, there was no significant change in SUVA from the Wabash River to the Collector Well (Table 3). At Parkville, average SUVA in the well waters was higher than that in the Missouri River (Table 3), although these averages were largely affected by a single monthly monitoring round during which a difference was observed, and were not statistically significant. The remainder of the data set indicates similar SUVA values between the Missouri River and the well waters. Thus the SUVA values were highly variable and no universal change upon bank filtration was observed.

XAD-8 fractionations

Over four sampling events at Jeffersonville, the composition of the Ohio River NOM as determined by XAD-8 fractionation was approximately 50–60% hydrophilic material and 40–50% hydrophobic material (Figure 3). The composition of the Well #9 (or Well #10) water was approximately 40–55% hydrophilic material and 45–60% hydrophobic material. Over six sampling events at Terre Haute, the Wabash River and the Collector Well both comprised approximately 50–65% hydrophilic and 35–50% hydrophobic material (Figure 4). Over five sampling rounds at Parkville, the Missouri River composition ranged from 60 to 70% hydrophilic and 30–40% hydrophobic NOM while the Well #4 water comprised 50–60% hydrophilic and 40–50% hydrophobic NOM (Figure 5).

SUVA of river and well water XAD-8 fractions

Values of SUVA for each of the river and well water hydrophilic and hydrophobic fractions at the three sites,

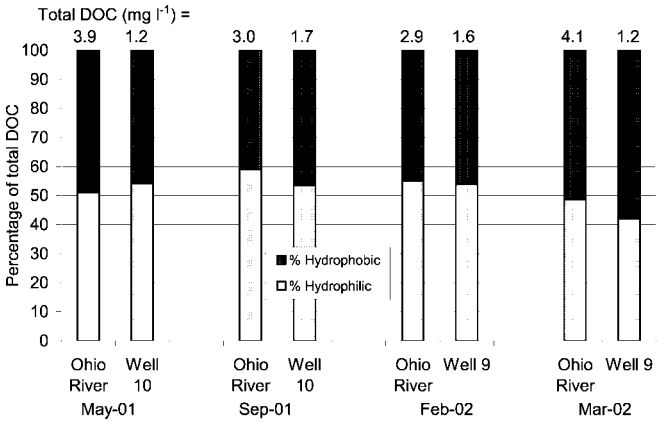

Figure 3 | XAD-8 fractionation of Jeffersonville samples

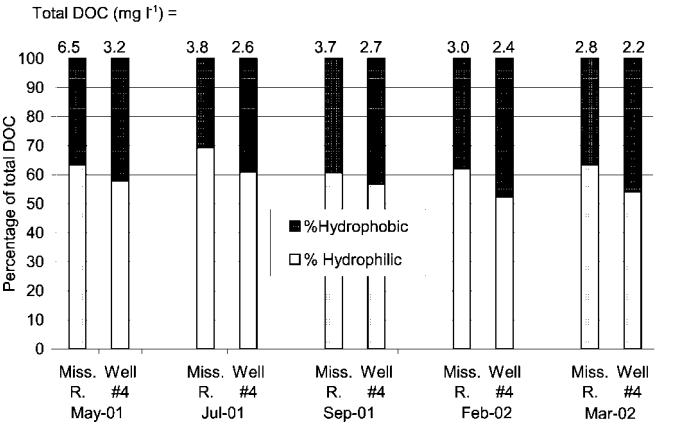

Figure 5 | XAD-8 fractionation of Parkville samples

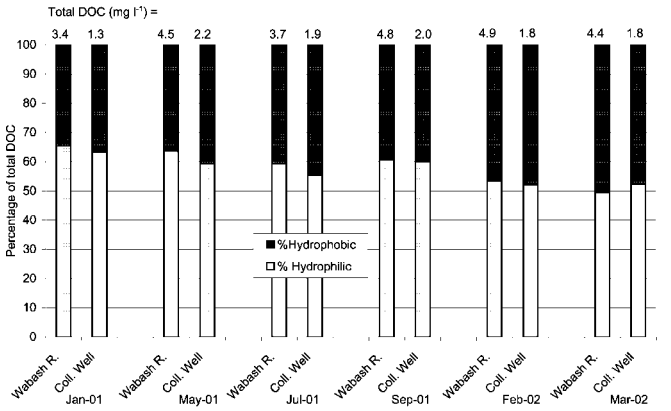

Figure 4 | XAD-8 fractionation of Terre Haute samples

averaged over the sampling rounds, are given in Table 4. At all three sites, the differences in SUVA between the river and well water fractions were found not to be statistically significant. At Jeffersonville, the SUVA data for the raw river and well waters discussed above indicated a statistically significant reduction in SUVA upon ground passage from the Ohio River to Well #9. The SUVA values for the fractionation results were not consistent with this observation; the average SUVA for the Ohio River water was lower for the samples taken during the fractionation studies while the average SUVA for the Well #9 water was similar for both data sets. However, the fractionation data consisted of significantly fewer samples ($n = 5$ for Jeffersonville) than the previously discussed SUVA data for the raw river and well water samples ($n = 16$ and 17 for the Ohio River and Well #9, respectively).

UFC testing of river and well water fractions

As described above, the ratio of Cl_2:DOC:Br was held constant among river and well water fractions for each sampling round, and the Cl_2:DOC ratio was always 2.5:1, irrespective of sampling round. Because the intrinsic Br:DOC ratio of the 'controlling' sample varied with time and location, however, it was not possible to hold the relative bromide concentration constant among all sampling events. For purposes of comparison, THM4 and HAA9 UFC concentrations for each sampling event have been presented in molar units to account for the higher mass associated with the brominated compounds and normalized to the corresponding initial DOC concentrations present at the time of chlorination. Additional bromide effects, even on a molar basis, are possible due to the faster reaction of hypobromous acid with NOM relative to hypochlorous acid. However, these effects are likely to be minor at the low bromide concentrations in these samples. The conditions of the UFC testing (DOC, chlorine and bromide concentrations) and the raw results (free chlorine residual, THM4 and HAA9 concentrations) are given in Table 2. DBP mass balances (not shown here)

Table 4 | Average SUVA (±standard deviations of the averages) for Jeffersonville, Terre Haute and Parkville XAD-8 fractions ($n=5$ for Jeffersonville; $n=6$ for Terre Haute and Parkville); differences between corresponding river and well water values were not significant at the 95% confidence interval

	Unfractionated SUVA (l mg-m^{-1})	Hydrophilic SUVA (l mg-m^{-1})	Hydrophobic SUVA (l mg-m^{-1})
Jeffersonville			
Ohio R.	2.2 ± 0.8	1.6 ± 0.4	2.4 ± 0.4
Well #9/10	1.9 ± 0.3	2.3 ± 0.6	2.0 ± 0.5
Terre Haute			
Wabash R.	2.6 ± 0.6	2.0 ± 0.3	3.0 ± 0.6
Collector Well	2.3 ± 0.4	2.1 ± 0.4	2.6 ± 0.7
Parkville			
Missouri R.	2.0 ± 0.7	1.8 ± 0.2	3.0 ± 0.4
Well #4	2.1 ± 0.6	1.9 ± 0.1	2.6 ± 0.2

between the unfractionated samples and the corresponding hydrophilic and hydrophobic fractions, using the results shown in Figures 3–5, indicated generally good agreement between the measured and calculated (based on the hydrophilic and hydrophobic UFC concentrations) THM4 and HAA9 UFC concentrations in the unfractionated samples.

At Jeffersonville, THM4 and HAA9 data from four sampling rounds are available. Molar UFC concentrations of THM4, normalized to DOC, were highly variable among sampling rounds (Figure 6). For the Ohio River, normalized THM4 UFC concentrations were higher for the hydrophobic fraction compared with the hydrophilic fraction. The opposite trend was observed for the normalized THM4 UFC concentrations in the Well #9/10 water during three of the sampling events (May 2001, September 2001 and February 2002). For the March 2002 sampling round, the normalized THM4 UFC concentration in the hydrophobic fraction was significantly higher than that in the hydrophilic fraction. Higher normalized concentrations of HAA9 UFC were observed in the hydrophilic fractions compared with the hydrophobic fractions for the Ohio River and well waters over all sampling rounds at Jeffersonville (Figure 7). Often, higher normalized THM4 and HAA9 concentrations were observed in the Ohio River fractions compared with the corresponding Well #9 or 10 fractions.

At Terre Haute, normalized THM4 UFC concentrations were generally similar between the hydrophilic and hydrophobic fractions with the exception of the March 2002 sampling round, during which the normalized THM4 UFC was much higher in the hydrophilic fraction of the Wabash River and higher in the hydrophobic fraction for the Collector Well water (Figure 8). However, by mass balance, for this sample, the normalized THM4 UFC concentration for the unfractionated sample should approximately equal the average of the THM4 UFC concentrations for the hydrophilic and hydrophobic fractions (from Figure 4, the hydrophilic and hydrophobic fractions each comprise approximately 50% of the unfractionated NOM). This is not the case, indicating a THM4 UFC mass balance problem for these two samples. In general, the normalized HAA9 concentrations were higher in the hydrophilic fraction compared to the hydrophobic fraction for both the Wabash River and Collector Well waters (Figure 9). As was the case with the Jeffersonville data,

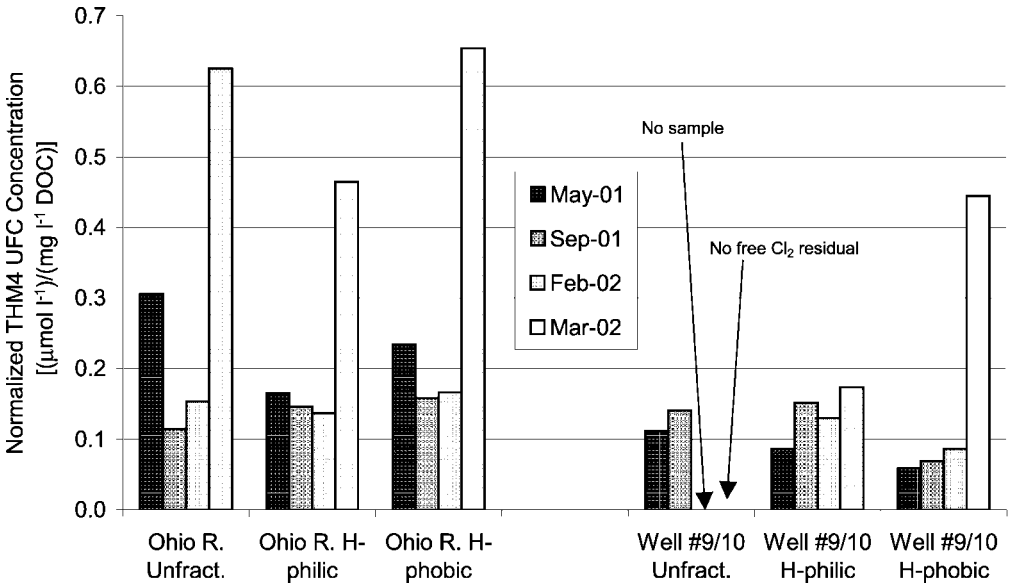

Figure 6 | THM4 UFC molar concentrations (normalized by initial DOC concentrations) for all sampling events at Jeffersonville

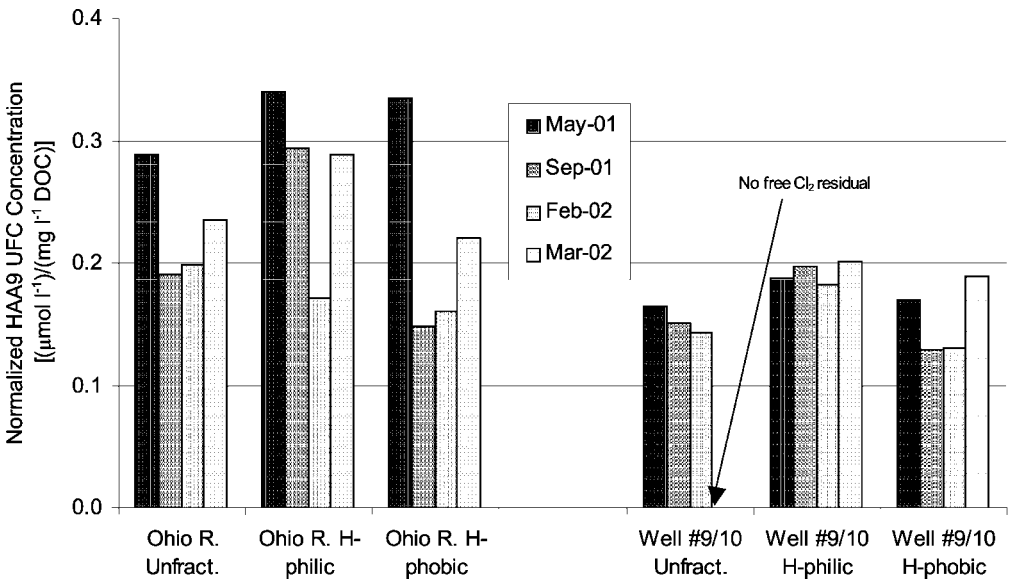

Figure 7 | HAA9 UFC molar concentrations (normalized by initial DOC concentrations) for all sampling events at Jeffersonville

normalized THM4 and HAA9 UFC concentrations were often higher for the Wabash River water compared with the Collector Well water. The normalized THM4 and HAA9 UFC concentrations were highly variable between sampling rounds.

At Parkville, normalized THM4 UFC concentrations were similar between fractions for the May 2001, July 2001 and September 2001 sampling rounds, but higher in the hydrophobic fraction for the February 2002 sampling round (Figure 10). A similar trend was observed for

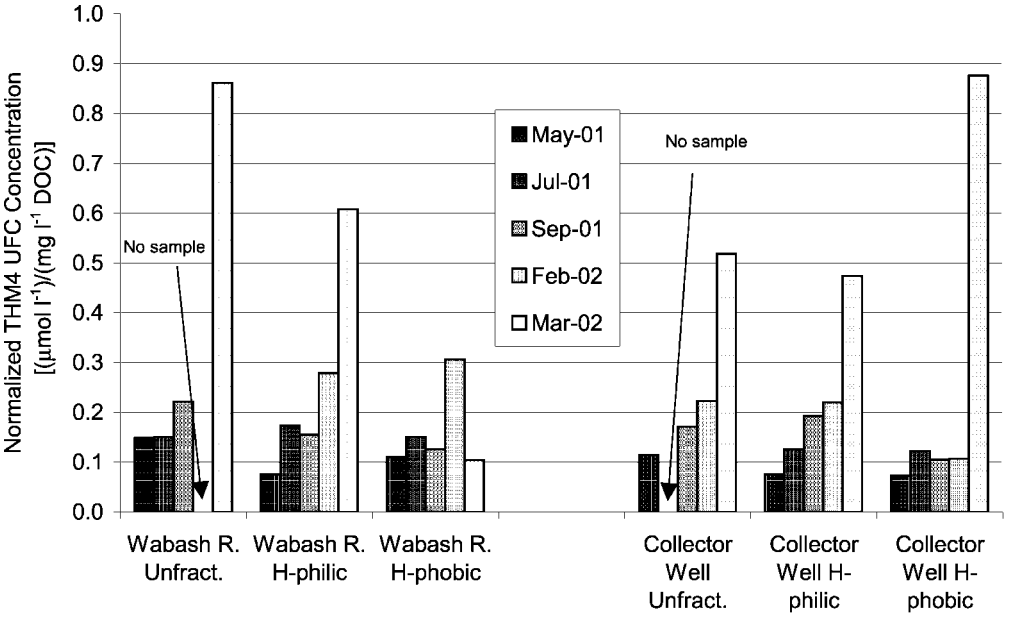

Figure 8 | THM4 UFC molar concentrations (normalized by initial DOC concentrations) for all sampling events at Terre Haute

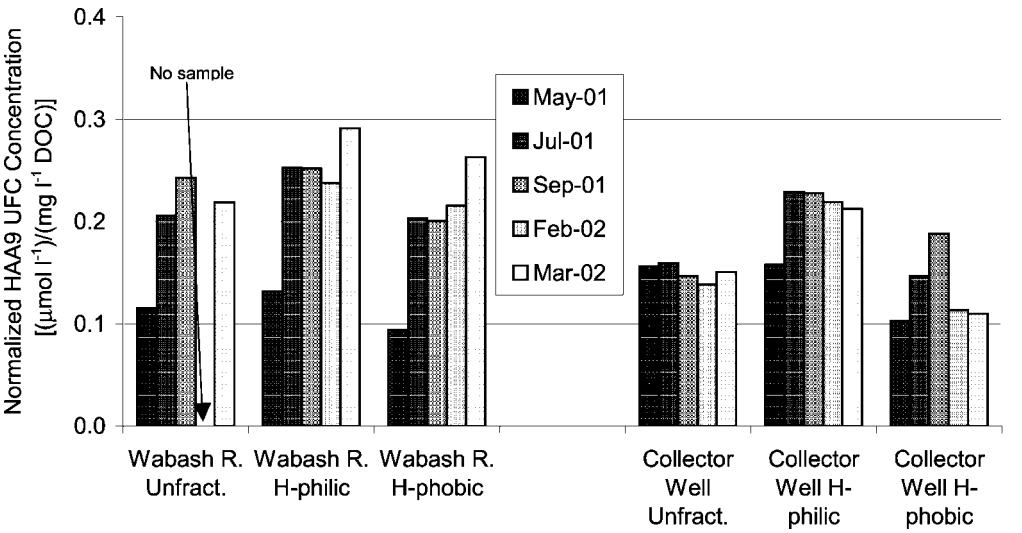

Figure 9 | HAA9 UFC molar concentrations (normalized by initial DOC concentrations) for all sampling events at Terre Haute

the normalized HAA9 UFC concentrations at Parkville, with the exception that for one of the sampling rounds (February 2002), the normalized concentration in the hydrophilic fraction of the Missouri River water was higher than that in the hydrophobic fraction (Figure 11). With some exceptions, the normalized THM4 and HAA9 concentrations were typically higher for the Missouri River fractions relative to the Well #4 fractions. As with the other two sites, the THM4 and HAA9 UFC data were highly variable among sampling events.

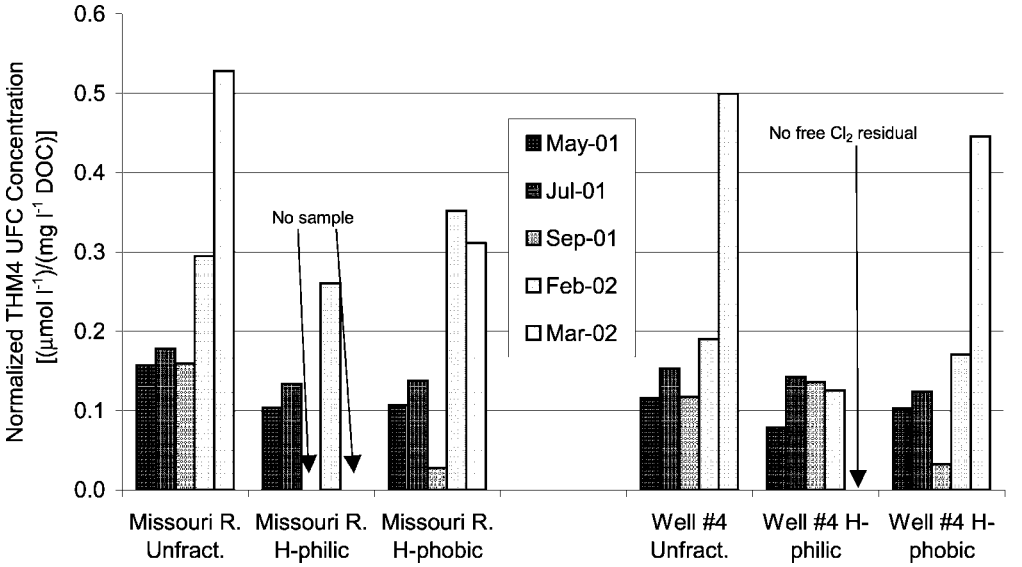

Figure 10 | THM4 UFC molar concentrations (normalized by initial DOC concentrations) for all sampling events at Parkville

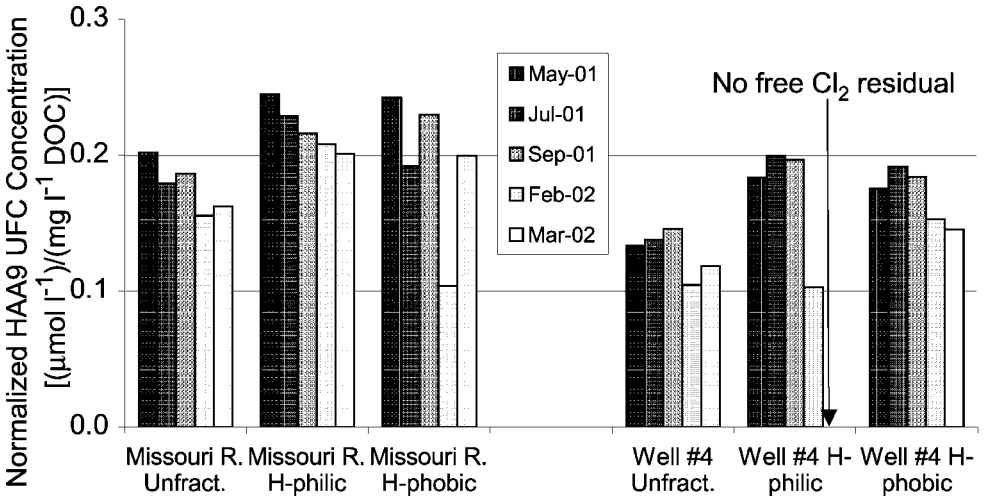

Figure 11 | HAA9 UFC molar concentrations (normalized by initial DOC concentrations) for all sampling events at Parkville

Bromine incorporation factors were calculated for the river and well water chlorinated fractions (Table 5). The bromine incorporation factor is defined as ratio of the total molar concentration of THM4 bromine ($1 \times CHCl_2Br + 2 \times CHClBr_2 + 3 \times CHBr_3$) to the overall THM4 molar concentration ($CHCl_3 + CHCl_2Br + CHClBr_2 + CHBr_3$) (Symons *et al.* 1993). The average bromine incorporation factors for the rivers and wells over the sampling rounds are similar between corresponding river and well water fractions (differences were not significant at the 95% confidence interval). Thus, with the Cl_2:DOC:Br held constant between river and well water fractions, there was no apparent significant change upon bank filtration in the distribution of the individual THM species over the average normalized THM4 UFC concentration at the three sites. Similarly, no significant changes

Table 5 | Average bromine incorporation factors (±standard deviations of the averages) for Jeffersonville, Terre Haute and Parkville XAD-8 fractions (n=4 for Jeffersonville; n=5 for Terre Haute and Parkville); differences were not significant at the 95% confidence interval

	Unfractionated	Hydrophilic	Hydrophobic
Jeffersonville			
Ohio R.	0.99 ± 0.52	0.61 ± 0.53	0.93 ± 0.46
Well #9/10	0.71 ± 0.28	0.84 ± 0.77	1.06 ± 0.58
Terre Haute			
Wabash R.	0.74 ± 0.46	0.59 ± 0.43	0.72 ± 0.47
Collector Well	0.63 ± 0.46	0.52 ± 0.31	0.52 ± 0.39
Parkville			
Missouri R.	0.43 ± 0.13	0.45 ± 0.18	0.41 ± 0.32
Well #4	0.52 ± 0.46	0.39 ± 0.37	0.47 ± 0.23

were observed in HAA speciation upon bank filtration when the DOC to bromide ratio was held constant.

DISCUSSION

Reduction in biodegradable and UV-absorbing NOM

Bank filtration has the potential to remove the biodegradable portion of the NOM from the river water, resulting in well water with a smaller fraction of biodegradable NOM. At the same time, adsorption processes in the subsurface could be expected to effectively remove the larger, humic molecules. In this context, one could expect combinations of adsorption and degradation processes during ground passage to provide removals of both the low-molecular weight, non-humic molecules and the higher-molecular weight humic molecules. The data support the conclusion that both biodegradation and adsorption processes are important in the removal of NOM upon bank filtration.

Significant reductions of both BDOC and AOC were observed upon ground passage at two of the sites (Jeffersonville and Terre Haute). Reductions of BDOC were somewhat higher than the previously reported reductions in DOC for the closer wells at these sites (50–70%) (Weiss *et al.* 2003*a*), which might seem to suggest a preferential removal of the biodegradable fraction of NOM. However, as noted by Volk *et al.* (2000), the portion of DOC captured by the BDOC test may contain some higher-molecular weight, humic material, while the AOC fraction represents the smaller, more rapidly assimilable DOC. The AOC reductions observed for Jeffersonville more closely match the DOC reductions, indicating similar removals of biodegradable and overall NOM. At Terre Haute, AOC reductions were greater than the previously reported DOC reductions, suggesting some preferential removal of the rapidly biodegradable fraction of DOC at this site. BDOC, AOC and DOC reductions at Parkville were all low compared with the other sites.

UV-absorbing NOM, as quantified by SUVA, generally consists of the higher-molecular weight, more aromatic, humic substances (Volk *et al.* 2000; Johnson *et al.* 2002); the lack of any significant changes in SUVA upon bank filtration at two of the sites (Terre Haute and Parkville) in

this study indicates no apparent preferential reduction of the more strongly UV-absorbing fraction. Presumably, as the larger, more aromatic materials are removed during ground passage, the smaller, non-humic materials are also being removed, probably through biochemical mechanisms. At Jeffersonville, the significant reduction in the SUVA from the Ohio River to Well #9 indicates a preferential reduction in the more strongly UV-absorbing fraction.

XAD-8 fractionations

In general, the river and well waters are of similar character (as defined by the XAD-8 characterization method), indicating that RBF is equally effective at removing the XAD-8 adsorbing (hydrophobic) and non-adsorbing (hydrophilic) portions of NOM at Jeffersonville and Terre Haute. At Parkville, the Well #4 water comprised a slightly higher fraction of hydrophobic (humic) material than the Missouri River water during all sampling rounds, suggesting a slight preferential removal of hydrophilic (non-humic) material upon ground passage at this site. The Parkville SUVA data do show a slight increase in the SUVA between the Missouri River and Well #4 (Table 3), which would be consistent with a preferential removal of the hydrophilic material, but this increase was largely affected by a single sampling round and was not found to be statistically significant. The data generally did not reflect this preferential removal, probably because of the imprecision of the relationship between SUVA and hydrophilic content.

SUVA and DBP formation testing on XAD-8 fractions

At Jeffersonville, a decrease in the SUVA of the hydrophobic fraction and a simultaneous increase in the SUVA of the hydrophilic fraction were observed upon RBF. At Terre Haute and Parkville, a reduction in the SUVA of the hydrophobic fraction was observed with no change in the SUVA of the hydrophilic fraction. However, in all three cases, the one standard deviation bars overlap and the statistics indicate that the differences were not significant at the 95% confidence interval. It appears that bank filtration is similarly capable of removing both the strongly UV-absorbing and non-UV-absorbing material, presumably through a combination of adsorption and biodegradation processes. The result is that no significant change upon ground passage was observed regarding the SUVA of the overall (unfractionated) water, as reflected by the data in Table 4. The Jeffersonville fractionation data is not entirely consistent with the SUVA data collected during earlier monitoring at this site (Table 3), which indicated a statistically significant reduction in the SUVA upon ground passage from the Ohio River to Well #9.

Although studies in the literature have generally shown higher DBP formation upon chlorination of hydrophobic NOM, there was no such consistent relationship here, either before or after RBF. Others have similarly failed to observe a direct correlation between hydrophobic content and DBP formation in natural surface waters (Martin-Mousset *et al.* 1997). No consistent changes were observed in the reactivity of the hydrophilic and hydrophobic fractions with chlorine upon bank filtration as measured by the UFC test. Thus, while the overall concentrations of DBP precursors are effectively reduced (Weiss *et al.* 2003*a*, *b*), the reductions appear to be largely the result of the reduction in NOM concentration rather than a consistent change in NOM character.

When UFC testing was performed with a constant Cl_2:DOC:Br ratio, no significant, consistent differences were observed in the distribution of the chlorinated and brominated species between the river and well water THM and HAA concentrations. Although the river fractions often had slightly higher THM4 and HAA9 UFC concentrations than the corresponding well waters, the difference was spread out among the chlorinated and brominated species. This finding confirms the authors' previously reported supposition that the earlier observations of a shift from chlorinated to brominated species upon bank filtration can be attributed primarily to the increasing bromide to DOC ratio as NOM is removed (Weiss *et al.* 2003*a*), rather than any preferential removal of precursor material for the chlorinated species. This result underscores the importance of the bromide level in DBP speciation and the need to consider the bromide concentration during treatment and characterization studies.

CONCLUSIONS

Riverbank filtration has been shown to effectively reduce the concentrations of DBP precursors in river water (Kuehn & Mueller 2000; Ray *et al.* 2002; Weiss *et al.* 2002, 2003*a*, *b*), potentially performing as well as or better than a conventional treatment train (Weiss *et al.* 2003*b*; Wang 2003). The purpose of this research was to determine whether such removals reflect a change in character of the NOM upon RBF. The data suggest that the different removal mechanisms applicable to subsurface transport and fate during RBF (e.g. sorption, biodegradation, filtration) combine to provide similar extents of removal of the XAD-8-adsorbable (hydrophobic) and less XAD-8-adsorbable (hydrophilic) components of NOM during ground passage. In addition, UFC testing with constant Cl_2:DOC:Br ratios indicates that there is no consistent preferential removal of precursor material responsible for chlorinated or brominated DBPs upon RBF.

ACKNOWLEDGEMENTS

We acknowledge the support of the US EPA Office of Research and Development (Project CR-826337) as well as the utility subsidiaries of American Water. We also thank the Environmental Engineering & Technology, Inc. Laboratories for the HAA testing and Anna Palazij for her help with operation of the XAD-8 columns. Finally, we acknowledge the valuable input from anonymous reviewers. The views expressed herein have not been subjected to Agency review and therefore do not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

ABBREVIATIONS

AOC	assimilable organic carbon
BDOC	biodegradable dissolved organic carbon
COD	chemical oxygen demand
DBP	disinfection by-product
DOC	dissolved organic carbon
EC	Delectron capture detector
GC	gas chromatograph
HAA	haloacetic acid
IC	ion chromatograph
k′	column capacity factor
L	height of XAD-8 resin in column
NDIR	non-dispersive infrared detector
NOM	natural organic matter
NV TOC	non-volatile total organic carbon
POC	particulate organic carbon
R	inside radius of XAD-8 column
RBF	riverbank filtration
SUVA	specific UV absorbance
THM	trihalomethane
TOC	total organic carbon
UV-254	UV absorbance at 254-nm wavelength
V_{bed}	bed volume of XAD-8 column
V_e	effluent volume of XAD-8 column
V_o	total void volume of XAD-8 column
UFC	uniform formation conditions

REFERENCES

Aiken, G. R. & Cotsaris, E. 1995 Soil and hydrology: Their effect on NOM. *J. Am. Wat. Wks Assoc.* **87**(1), 36–45.

Aiken, G. R. & Leenheer, J. 1993 Isolation and chemical characterization of dissolved and colloidal organic matter. *Chem. Ecol.* **8**, 135–151.

Amy, G. L., Collins, M. R. & Kuo, C. J. 1987 Comparing gel permeation chromatography and ultrafiltration for the molecular weight characterization of aquatic organic matter. *J. Am. Wat. Wks Assoc.* **79**(1), 43–49.

Bouwer, E. J. & Crowe, P. B. 1988 Biological processes in drinking water treatment. *J. Am. Wat. Wks Assoc.* **80**(9), 82–93.

Chang, E. E., Lin, Y. P. & Chiang, P. C. 2001 Effects of bromide on the formation of THMs and HAAs. *Chemosphere* **43**(8), 1029–1034.

Collins, M. R., Amy, G. L. & Steelink, C. 1986 Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: Implications for removal during water treatment. *Environ. Sci. Technol.* **20**(10), 1028–1032.

Cosovic, B., Hrsak, D., Vojvodic, V. & Krznaric, D. 1996 Transformation of organic matter and bank filtration from a polluted stream. *Wat. Res.* **30**(12), 2921–2928.

Croué, J-P., Debroux, J-F., Amy, G. L., Aiken, G. R. & Leenheer, J. A. 1999 Natural organic matter: Structural characteristics and reactive properties. In *Formation and Control of Disinfection By-Products in Drinking Water* (ed. P. C. Singer), American Water Works Association, Denver, Colorado.

Escobar, I. C. & Randall, A. A. 2001 Assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC): Complementary Measurements. *Wat. Res.* **35**(18), 4444–4454.

Frimmel, F. H. 1998 Characterization of natural organic matter as major constituents in aquatic systems. *J. Contam. Hydrol.* **35**, 201–216.

Goel, S., Hozalski, R. M. & Bouwer, E. J. 1995 Biodegradation of NOM: Effect of NOM source and ozone dose. *J. Am. Wat. Wks Assoc.* **87**(1), 90–105.

Hozalski, R. M., Goel, S. & Bouwer, E. J. 1995 TOC removal in biological filters. *J. Am. Wat. Wks Assoc.* **87**(12), 40–54.

Huck, P. M. 1990 Measurement of biodegradable organic matter and bacterial growth potential in drinking water. *J. Am. Wat. Wks Assoc.* **82**(7), 78–86.

Johnson, W. P., Bao, G. & John, W. W. 2002 Specific UV absorbance of aldrich humic acid: Changes during transport in aquifer sediment. *Environ. Sci. Technol.* **36**(4), 608–616.

Joret, J. C. 1988 Rapid methods for estimating bioeliminable organic carbon in water. In *Proceedings of the AWWA Annual Conference*, Orlando, Florida. American Water Works Assocaition, Denver, CO, USA.

Joret, J. C. & Levi, Y. 1986 Methode rapide d'evaluation du carbone eliminable des eaux par voie biologique. *Trib. Cebedeau* **510**(39), 3–9.

Kampioti, A. A. & Stephanou, E. G. 2002 The impact of bromide on the formation of neutral and acidic disinfection by-products (DBPs) in Mediterranean chlorinated drinking water. *Wat. Res.* **36**(10), 2596–2606.

Kivimaki, A-L., Lahti, K., Hatva, T., Tuominen, S. M. & Miettinen, I. T. 1998 Removal of organic matter during bank filtration. In *Artificial Recharge of Groundwater* (ed. J. H. Peters), A. A. Balkema, Rotterdam, Netherlands; Brookfield, Vermont.

Krasner, S. W., Croue, J-P., Buffle, J. & Perdue, E. M. 1996 Three approaches for characterizing NOM. *J. Am. Wat. Wks Assoc.* **88**(6), 66–79.

Kuehn, W. & Mueller, U. 2000 Riverbank Filtration: An Overview. *J. Am. Wat. Wks Assoc.* **92**(12), 60–69.

LeChevallier, M. W., Shaw, N., Kaplan, A. & Bott, T. L. 1993 Development of a rapid assimilable organic carbon method for water. *Appl. Environ. Microbiol.* **59**(5), 1526–1531.

Leenheer, J. A. 1981 Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environ. Sci. Technol.* **15**(5), 578–587.

Leenheer, J. A. 1985 Fractionation techniques for aquatic humic substances. In *Humic Substances in Soil, Sediment, and Water* (ed. G. R. Aiken, P. MacCarthy, R. L. Malcolm & R. S. Swift), Wiley-Interscience, New York.

Leenheer, J. A., Rostad, C. E., Barber, L. B., Schroeder, R. A., Anders, R. & Davisson, M. L. 2001 Nature and chlorine reactivity of organic constituents from reclaimed water in groundwater, Los Angeles County, California. *Environ. Sci. Technol.* **35**(19), 3869–3876.

Lehtola, M. J., Miettinen, I. T., Vartiainen, T. & Martikainen, P. J. 2002 Changes in content of microbially available phosphorus, assimilable organic carbon and microbial growth potential during drinking water treatment processes. *Wat. Res.* **36**(15), 3681–3690.

Logan, B. E. & Jiang, Q. 1990 Molecular size distributions of dissolved organic matter. *J. Environ. Engng* **116**(6), 1046–1062.

Martin-Mousset, B., Croue, J. P., Lefebvre, E. & Legube, B. 1997 Distribution and characterization of dissolved organic matter of surface waters. *Wat. Res.* **31**(3), 541–553.

Miettinen, I. T., Martikainen, P. J. & Vartiainen, T. 1994 Humus transformation at the bank filtration water plant. *Wat. Sci. Technol.* **30**(10), 179–187.

Miettinen, I. T., Martikainen, P. J. & Vartiainen, T. 1998 Mutagenicity and amount of chloroform after chlorination of bank filtered water. *Sci. Total Environ.* **215**(1), 9–17.

Muller, M. B., Schmitt, D. & Frimmel, F. H. 2000 Fractionation of natural organic matter by size exclusion chromatography—Properties and stability of fractions. *Environ. Sci. Technol.* **34**(23), 4867–4872.

Owen, D. M., Amy, G. L., Chowdhury, Z. K., Paode, R., McCoy, G. & Viscosil, K. 1995 NOM characterization and treatability. *J. Am. Wat. Wks Assoc.* **87**(1), 46–63.

Pollock, D. W. 1994 User's guide for MODPATH/MODPATH-PLOT, Version 3: A particle tracking post-processing package for MODFLOW, the US Geological Survey finite-difference ground-water flow model. USGS Open-file Report 94-464.

Ray, C., Grischek, T., Schubert, J., Wang, J. & Speth, T. 2002 A perspective of riverbank filtration. *J. Am. Wat. Wks Assoc.* **94**(4), 149–160.

Ray, C., Melin, G. & Linsky, R. B. 2003 *Riverbank Filtration: Improving Source-Water Quality*. Kluwer Academic Publishers, Dordrecht, the Netherlands.

Reckhow, D. A., Singer, P. C. & Malcolm, R. L. 1990 Chlorination of humic materials: Byproduct formation and chemical interpretations. *Environ. Sci. Technol.* **24**(11), 1655–1664.

Shukairy, H. M., Miltner, R. J. & Summers, R. S. 1994 Bromide's effect on DBP formation, speciation, and control: Part 1, ozonation. *J. Am. Wat. Wks Assoc.* **86**(6), 72–87.

Singer, P. C. 1999 Humic substances as precursors for potentially harmful disinfection by-products. *Wat. Sci. Technol.* **40**(9), 25–30.

Standard Methods for the Examination of Water and Wastewater 1998 20th edition, American Public Health Association/ American Water Works Association/Water Environment Federation, Washington, DC.

Summers, R. S., Benz, M. A., Shukairy, H. M. & Cummings, L. 1993 Effect of separation processes on the formation of brominated THMs. *J. Am. Wat. Wks Assoc.* **85**(1), 88–95.

Summers, R. S., Hooper, S. M., Shukairy, H. M., Solarik, G. & Owen, D. 1996 Assessing DBP yield: Uniform formation conditions. *J. Am. Wat. Wks Assoc.* **88**(6), 80–93.

Supelco 1998 Procedures for preparing and using columns of Amberlite XAD, Diaion, Dowex, MCI GEL, Sepabeads, and Supelite DAX adsorbent resins. Sigma-Aldrich Co, St Louis, MO, USA.

Symons, J. M., Krasner, S. W., Simms, L. A. & Sclimenti, M. 1993 Measurement of THM and precursor concentrations revisited:

The effect of bromide ion. *J. Am. Wat. Wks Assoc.* **85**(1), 51–62.

Thurman, E. M. & Malcolm, R. L. 1981 Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.* **15**(4), 463–466.

US EPA 1995 *Methods for the Determination of Organic Compounds in Drinking Water*. EPA/600/R-95/131.

Volk, C., Bell, K., Ibrahim, E., Verges, D., Amy, G. & LeChevallier, M. 2000 Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water. *Wat. Res.* **34**(12), 3247–3257.

Wang, J. 2003 Riverbank filtration case study at Louisville, Kentucky. In *Riverbank Filtration: Improving Source-Water Quality* (ed. C. Ray, G. Melin & R. B. Linsky), Kluwer Academic Publishers, Dordrecht, the Netherlands.

Weiss, W. J., Bouwer, E. J., Ball, W. P., O'Melia, C. R., Arora, H. & Speth, T. F. 2002 Reduction in disinfection byproduct precursors and pathogens during riverbank filtration at three Midwestern United States drinking-water utilitites. In *Riverbank Filtration: Improving Source-Water Quality* (ed. C. Ray, G. Melin & R. B. Linsky), Kluwer Academic Publishers, Dordrecht, the Netherlands.

Weiss, W. J., Bouwer, E. J., Ball, W. P., O'Melia, C. R., LeChevallier, M. W., Arora, H. & Speth, T. F. 2003a Riverbank filtration: Fate of disinfection by-product precursors and select microorganisms. *J. Am. Wat. Wks Assoc.* **95**(9).

Weiss, W. J., Bouwer, E. J., Ball, W. P., O'Melia, C. R., Arora, H. & Speth, T. F. 2003b Riverbank filtration: Comparison with lab-simulated conventional treatment for NOM and DBP precursor reductions. *J. Am. Wat. Wks Assoc.* **95**(12).

Wong, S., Hanna, J. V., King, S., Carroll, T. J., Eldridge, R. J., Dixon, D. R., Bolto, B. A., Hesse, S., Abbt-Braun, G. & Frimmel, F. H. 2002 Fractionation of natural organic matter in drinking water and characterization by ^{13}C cross-polarization magic-angle spinning NMR spectroscopy and size exclusion chromatography. *Environ. Sci. Technol.* **36**(16), 3497–3503.

First received 4 December 2002; accepted in revised form 14 July 2003