Seasonal variations in the disinfection by-product precursor profile of a reservoir water

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ABSTRACT

A sampling programme has been undertaken to investigate the nature and fate of natural organic matter (NOM) through a water treatment works (WTW). Specific focus has been given to the effect seasonal changes have on NOM. Water samples were collected from the reservoir inlet and after the filters at Albert WTW in Yorkshire. Samples were taken in January, June and November 2000. Changes in the dissolved organic carbon (DOC), ultra-violet (UV) absorbance at 254 nm, specific UV absorbance (SUVA) and trihalomethane formation potential (THM-FP) were measured for both the filtered and raw water. The waters were fractionated by XAD resin adsorption techniques into hydrophobic acid (HPO-A) and hydrophilic acid (HPI-A) fractions. The fractions were analysed for DOC, UV, SUVA and THM-FP.

The reactivity of the fractions changed throughout the year with the lowest reactivity (THM-FP) in January, increasing in June and reaching a maximum in November. This corresponded to the water being more difficult to treat in November and an increase in the proportion of hydrophobic acid. Information was obtained through the fractionation that would be impossible to predict from only the bulk water parameters.

Key words | characterisation, disinfection by-products, fractionation, natural organic matter

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INTRODUCTION

Natural organic matter (NOM) is described as an intricate mixture of organic compounds that occurs universally in ground and surface waters. NOM can cause major problems as it is converted into disinfection by-products (DBPs) when chlorine is used during water treatment (Krasner *et al.* 1989). These by-products can take the form of trihalomethanes (THMs), haloacetic acids (HAAs) and a host of other halogenated DBPs, a number of which have been shown to cause cancer in laboratory animals (Singer 1999; Rodriguez *et al.* 2000). Recent legislation has reduced the THM standard in the US from 100 to 80 μg l^{-1} (Crozes *et al.* 1995; Lin *et al.* 1999). A similar standard of 100 μg l^{-1} is in force in the UK and the European Commission has proposed standards for chloroform

(40 μg l^{-1}) and bromodichloromethane (15 μg l^{-1}) (Drinking Water Inspectorate UK 1998).

Isolation of aquatic NOM is widely used to study the different fractions that are inherent in NOM. The two different approaches used are: (1) concentration and fractionation, and (2) concentration only. A method was developed in 1992 for the concentration and fractionation of NOM using a two-column adsorption technique (Malcolm & MacCarthy 1992). It was based on the methods developed by Leenheer (1981) and Thurman & Malcolm (1981). The columns contained Amberlite XAD-8 and XAD-4 non-functional polymer resins and the method allowed for the isolation and separation of both the hydrophobic acid fraction and the hydrophilic acid fraction.

This fractionation process has been used here to investigate seasonal changes in NOM material and what effect these changes have on treatability.

It should be noted that the isolated materials are operationally defined based on the fractionation procedure. Operational definitions of the fractions obtained using the XAD-8/XAD-4 column pair are as follows (Aiken *et al.* 1992).

- *Hydrophobic acid fraction*–that portion of the DOC that sorbs on a column of XAD-8 at pH 2 and is eluted at pH 13. This fraction can contain aliphatic carboxylic acids of 5–9 carbons, one- and two-ring aromatic carboxylic acids, one- and two-ring phenols and aquatic humic substances.
- *Hydrophilic acid fraction*–that portion of the DOC contained in the XAD-8 effluent at pH 2 that sorbs on a column of XAD-4 resin and is eluted at pH 13. This fraction can contain polyfunctional organic acids and aliphatic acids of five or fewer carbons.

Following on from this, the fulvic and humic acid fractions can also be operationally defined (Malcolm & MacCarthy 1992). The eluate from the XAD-8 resin (hydrophobic acid fraction) is separated into fulvic and humic acid fractions at pH 1. At pH 1, the humic acid fraction precipitates and can be separated from the fulvic acid fraction by centrifugation.

NOM found in water consists of both hydrophobic and hydrophilic components where the largest fraction is generally hydrophobic acids, which makes up approximately 50% of the dissolved organic carbon (DOC) (Thurman 1985; Owen *et al.* 1993). These can be described as the aquatic acids or humic substances comprising of humic and fulvic acids. The humic substances are generally regarded as the main cause of natural colour and THM formation potential (THM-FP). For example it has been reported that the hydrophobic fraction produced 51 μg THM mg^{-1} DOC when compared to 21 μg THM mg^{-1} DOC for the hydrophilic acid fraction (Krasner *et al.* 1996). The reactivity of individual fractions has also been reported with values for the humic and fulvic acid fractions of 46 and 27 μg THM mg^{-1} DOC respectively, compared to a reactivity of 27 μg THM mg^{-1} DOC for the hydrophilic fraction (Croué *et al.* 1993).

Hydrophilic material has also been shown to be a cause for concern with regards to its THM-FP and it has been reported that 65% of the TOC and 56% of the THM-FP from the Colorado River was contributed by hydrophilic compounds (Owen *et al.* 1993). They showed that the hydrophilic fractions were exerting the largest chlorine demand when compared to the hydrophobic material (2.4 mg Cl$_2$ mg^{-1} hydrophilic vs. 0.32 mg Cl$_2$ mg^{-1} hydrophobic), leading to greater THM formation.

Several water treatment works (WTWs) in the Yorkshire and North West region in England have recently experienced difficulty in meeting THM limits (100 μg l^{-1}). This is unexpected given that the colour of the raw water has been reduced to two Hazen units or less. As the colour is being removed, it appears that residual organics are labile precursors to THMs. It is known that there are periods of the year where many treatment plants (typically those with low alkalinity, high SUVA source waters) are monitoring periods of high organic loading linked to heavy rainfall or snowmelt waters. It is during these periods of elevated dissolved organic carbon (DOC) that current treatment processes are failing and water quality is rapidly deteriorating with respect to DOC, colour and THM-FP. The work presented here has investigated the effect seasonal changes have on the character of NOM entering the WTW and the effect this has on their fate through the works.

METHODS

Albert WTW takes water from a reservoir. The treatment consists of coagulation using ferric sulphate, dissolved air flotation, rapid gravity filtration, chlorination, filtration through a manganese contactor and final chlorination before distribution. Water samples were collected from the reservoir inlet (75 l) and after the rapid gravity filters (300 l) at Albert WTW in the Yorkshire Water region in January, June and November 2000.

Measurements

The collected samples were analysed for dissolved organic carbon content (DOC), ultra-violet absorbance (UV) at
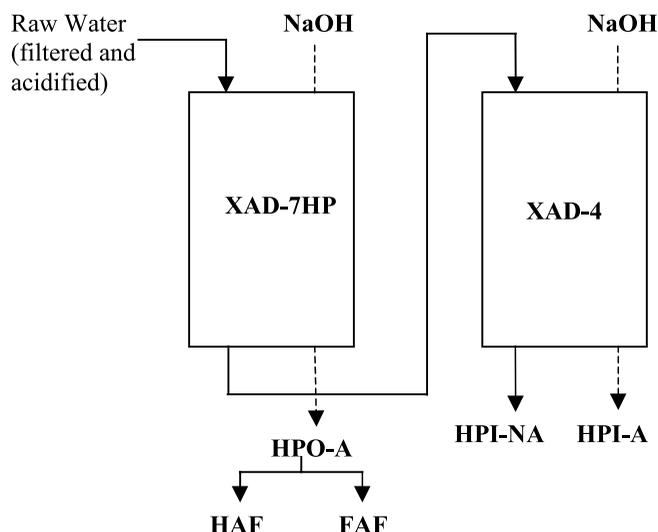
Figure 1 | Schematic of fractionation procedure. FAF—Fulvic acid fraction; HAF—Humic acid fraction; HPI-A—Hydrophilic acid fraction; HPI-NA—Hydrophilic non-acid fraction.

254 nm, specific UV absorbance (SUVA) and THM-FP. DOC was measured using a Shimadzu TOC-5000A analyser. UV absorbance at 254 nm was measured using a Jenway 6505 UV/VIS spectrophotometer. SUVA (m^{-1} l mg^{-1} C) was calculated as the ratio of UV absorbance at 254 nm (m^{-1}) to DOC (mg C l^{-1}). THM-FP was carried out using a method adapted from *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association 1992). The method involved buffering samples at pH 7, chlorinating samples with excess free chlorine and storing the sample at 20°C for 7 days to allow the reaction to approach completion. The total THM (chloroform, dichlorobromoform, dibromochloroform and bromoform) concentration was measured using a SRI 9300A gas chromatograph.

Fractionation

The waters were then fractionated by XAD resin adsorption techniques into their hydrophobic acid (HPO-A) and hydrophilic acid (HPI-A) fractions using a method adapted from Malcolm & MacCarthy (1992). A schematic of the procedure is shown in Figure 1. The resins used were Amberlite XAD-7HP resin and Amberlite XAD-4

resin (Rohm & Haas, PA, USA). Amberlite XAD-7HP is an acrylic ester polymer. It has been used in place of XAD-8 resin as its manufacture has been discontinued. Amberlite XAD-4 is a styrene divinylbenzene polymer. These resins were prepared by Soxhlet extraction for 24 h each with methanol, diethyl ether, acetonitrile and methanol again. The resins were each packed into glass columns of three different sizes and rinsed with reverse osmosis water until the column effluent DOC was <2 mg l^{-1}. Bio-Rad AG-MP-50 resin (Bio-Rad Laboratories Ltd., Herts, UK), a non-macroporous cation exchange resin, was used to hydrogen saturate the fractions produced. This resin was prepared by Soxhlet extraction for 24 h with methanol and packed into a small column and hydrogen saturated using 2 M hydrochloric acid (HCl). All the columns were wrapped in aluminium foil to prevent algal growth.

The water collected from Albert WTW was passed through a Whatman 1 μm pre-filter capsule and a Whatman 0.45 μm filter capsule and acidified to pH 2 using HCl. All of the acidified filtered water was put through the XAD-7HP/XAD-4 column pair. The XAD-7HP column was back eluted with 0.1 M sodium hydroxide (NaOH). The eluate was acidified to pH 2 and concentrated by passing it through another smaller XAD-7HP column to produce the hydrophobic acid fraction (HPO-A). After adjustment to pH 1 by adding concentrated HCl, the HPO-A was left to settle for 24 h and centrifuged. The supernatant (fulvic acid fraction—FAF) was decanted. The residue (humic acid fraction—HAF) was dissolved in the minimum required volume of 0.1 M NaOH. The HAF was hydrogen saturated by passing it through a column of Bio-Rad AG-MP-50 resin. The FAF was further concentrated on an even smaller column of XAD-7HP and desorbed with 0.1 M NaOH. The eluate was hydrogen saturated as described above.

The XAD-4 column was back eluted with 0.1 M NaOH. The eluate was acidified to pH 2 and concentrated by passing it through a smaller XAD-4 column to produce the hydrophilic acid fraction (HPI-A). The eluate was hydrogen saturated as described above. The effluent from both columns contained the non-acid hydrophilic fraction (HPI-NA). The fractions, which consisted of FAF, HAF,

Table 1 | Comparison of raw and filtered water from Albert WTW

Sample	pH	DOC (mg l^{-1})	UV absorbance at 254 nm (m^{-1})	SUVA (m^{-1}·l mg^{-1} C)	THM-FP (µg l^{-1})
Jan. raw water	6.0	7.5	34.0	4.5	632.2
Jan. filtered water	7.4	2.6	4.4	1.7	77.1
Jun. raw water	4.9	8.1	38.0	4.7	468.3
Jun. filtered water	6.8	2.6	4.5	1.7	29.6
Nov. raw water	5.0	10.2	60.2	5.9	907.5
Nov. filtered water	5.6	2.1	4.6	2.2	66.6

HPI-A and HPI-NA, were analysed for DOC, SUVA and THM-FP. The recovery of the DOC was quantified by measuring the influent DOC of the water and the DOC and volume of the fractions produced. Recoveries were in the range 87 to 110%. Unextracted material was assumed to be made up of the hydrophobic neutral fraction (HPO-N) as well as unrecovered material. This was not quantified.

RESULTS AND DISCUSSION

Bulk water

Samples of raw and filtered water collected in January, June and November 2000 were analysed for pH, DOC, UV and THM-FP. These results are summarised with calculated SUVA values in Table 1. SUVA is a useful parameter when assessing NOM as it allows us to classify water in terms of organic content, Table 2 (Edzwald & Tobiason 1999). Here the SUVA values tell us that the raw water is rich in humic material whilst the filtered water is more hydrophilic in nature and contains mainly low molecular weight organic compounds. This has been confirmed by High Performance Size Exclusion Chromatography—HPSEC (Parsons 2002). Over the year there are some variations in raw water DOC and UV observed, but little variation in the filtered water samples.

The results show a clear seasonal variation in SUVA in both the raw and filtered water and show that there is significantly more hydrophobic material in November than in January or June. There is also a corresponding increase in reactivity of both the raw and filtered water with chlorine in November in terms of THM-FP compared to June but the THM-FP in November and January are very similar. The November raw water has a THM-FP of 89 µg THM mg^{-1} C compared to 58 µg THM mg^{-1} C in June whilst the filtered water THM-FP increases from 11 µg THM mg^{-1} C in June to 31 µg THM mg^{-1} C in November. The THM-FP in January is also very similar to that in November–raw water 84 µg THM mg^{-1} C in January compared with 89 µg THM mg^{-1} C in November,

Table 2 | Guidelines for the nature of NOM (Edzwald & Tobiason 1999)

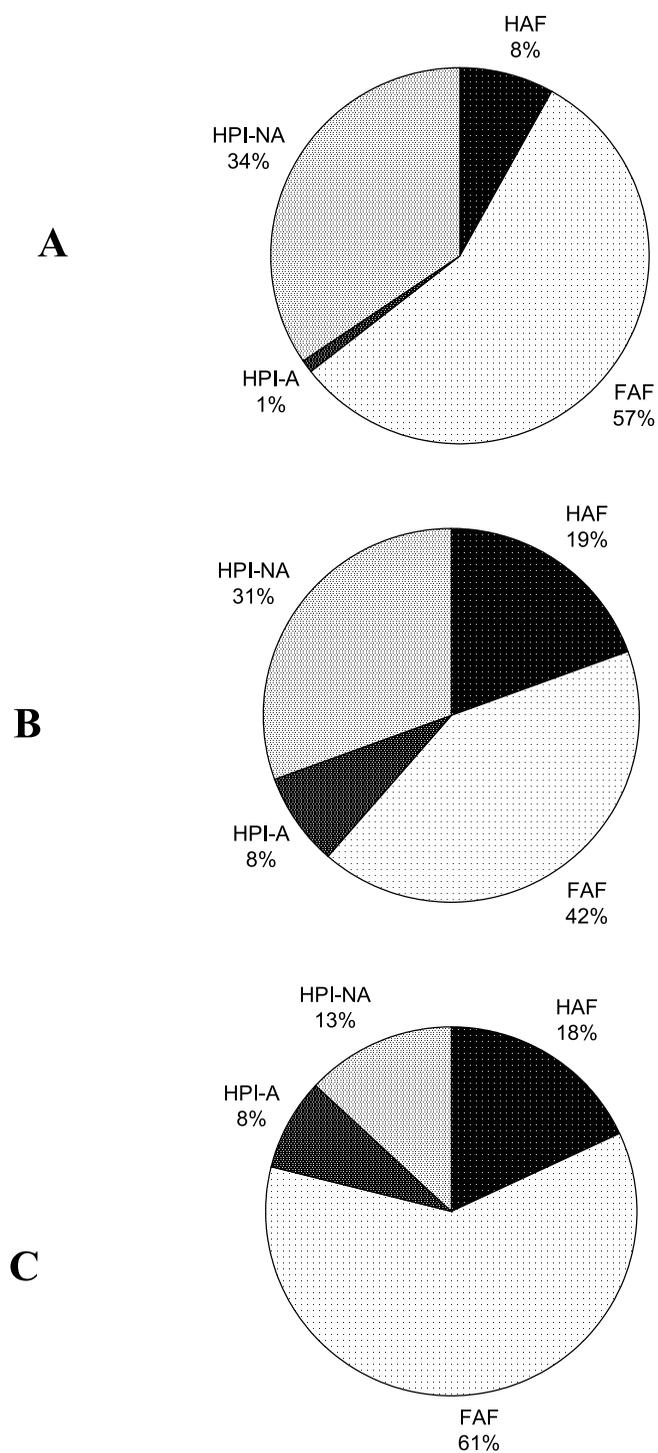| SUVA (m^{-1}·l mg^{-1} C)	Composition
>4	Mostly aquatic humics. High hydrophobicity. High MW.
2–4	Mixture of aquatic humics and other NOM. Mixture of hydrophobic and hydrophilic NOM, mixture of MWs.
<2	Mostly non-humics. Low hydrophobicity. Low MW.

filtered water 30 μg THM mg^{-1} C in January compared with 31 μg THM mg^{-1} C in November. To investigate what is causing the increased reactivity in January and November, we have assessed the nature of individual organic fractions.
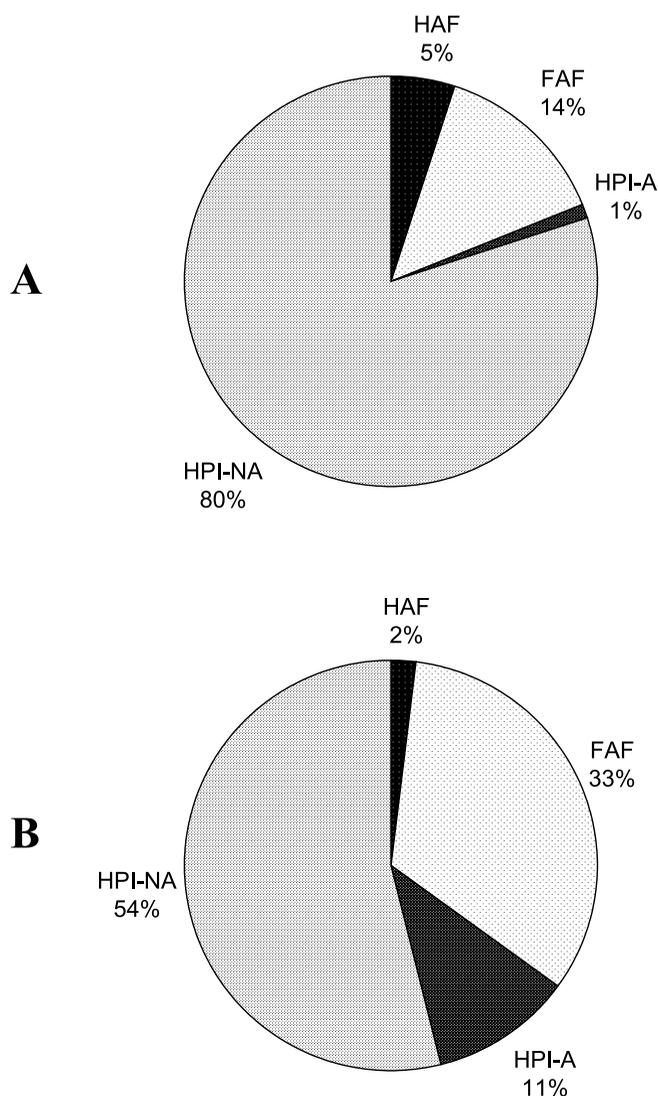
Fractionated water

Both raw and filtered water were fractionated to allow the content and fate of the individual fractions of DOC to be investigated (Figures 2 & 3). Here, it should be noted that the fractions will have been denatured. That is, structural changes will have resulted due to the extreme pH conditions used in the fractionation procedure. However, research has been carried out to validate the fractions produced by XAD resins, to prove that the fractions are not innate products of the procedure used to prepare them (Peuravuori & Pihlaja 1997). It has been found that the separation of organic matter at pH 1 has certain risks (Peuravuori & Pihlaja 1998). Considerable compositional and structural alterations take place, in addition to loss of organic matter, during the acid precipitation. This would be an important consideration if the structure of the NOM was being investigated.

The results show, as expected, that the raw water contains mainly hydrophobic material (here fractionated into humic and fulvic acids) whilst the filtered water contains mainly hydrophilic material. Seasonal changes can be observed in the distribution of the fractions. There was an increase from ~65% to ~80% in hydrophobic material from the water collected in November compared to the water collected in January and June, mainly due to an increase in the FAF. The filtered water also showed a significant increase in the FAF content in November.

Analysis of the SUVA values for each fraction gives further information on the types of organics found in each fraction (Tables 3 & 4). The high values of raw FAF SUVA in November are not expected as it is typically HAF that has higher values. As yet we have not been able to identify why this is. The SUVA of the raw HPI-A in November was particularly high compared with analysis of fractions taken in June, indicating a higher concentration of polar aromatic material than previously observed. Comparison of the raw and filtered SUVA values shows that, typically,

A

B

C

Figure 2 | Distribution of DOC of raw water fractions during January (A), June (B) and November (C) 2000.

A

HAF
5%

FAF
14%

HPI-A
1%

HPI-NA
80%

B

HAF
2%

FAF
33%

HPI-NA
54%

HPI-A
11%

Figure 3 │ Distribution of DOC of filtered water fractions during June (A) and November (B) 2000.

et al. 1999). At Albert WTW this trend reported in the literature was not observed and the reactivity of the hydrophobic and hydrophilic fraction was the same for 2 of the 3 samples. In June, the hydrophobic acid fraction formed 38 μg mg^{-1} C THM compared to 37 μg mg^{-1} C THM for the hydrophilic acid fraction. This continued in November where the hydrophobic and hydrophilic acid fractions formed 171 and 171 μg mg^{-1} C THM respectively. The values for the hydrophobic fraction have been taken as a weighted average of the HAF and FAF but the values for the hydrophilic fraction have been taken as the value for the HPI-A. This has been done to give a reasonable comparison with the literature values.

Relation to treatment

The fractionation data can provide considerable information on how the treatment processes are performing when compared with bulk water parameters. It is well known that traditional coagulation/flocculation processes are excellent at removing humic/fulvic acid material and an optimised process can successfully remove greater than 90% of the HAF and FAF (Crozes *et al.* 1995). It is clear from the results presented that the water treatment works investigated here is performing well and removing the majority of the hydrophobic fractions. During November the treatment processes are struggling to deal with the higher organic load and primarily the FAF. Although 90% removal of the FAF is being achieved, there is still a significant amount of FAF remaining due to the high initial organic load. It is also clear that the treatment processes are unable to remove the hydrophilic non-acid fraction (HPI-NA) which makes up 80% of the June filtered water and 54% of the November filtered water. This may be a cause for concern in the autumn as the reactivity of this fraction in January and June was <10 μg mg^{-1} C THM, whilst in November the reactivity of the raw and filtered HPI-NA was 85 and 70 μg mg^{-1} C THM respectively.

CONCLUSIONS

1.   The fractionation of raw and filtered water from Albert WTW showed that there was an increase in

higher molecular weight and hydrophobic molecules are being removed through treatment. This is true with the exception of the November HAF where the raw SUVA is less than the filtered SUVA. The reactivity of the fractions also varied considerably through the year although, for all samples, the hydrophobic acid fractions generally had the highest THM-FP.

Typically the hydrophilic fraction is less reactive than the hydrophobic fraction with chlorine in raw water samples (Collins *et al.* 1986; Krasner *et al.* 1996; Croue

Table 3 │ Summary of raw water fraction data

Fraction	January SUVA ($m^{-1} \cdot l\,mg^{-1}$ C)	January THM-FP ($\mu g\,mg^{-1}$ C)	June SUVA ($m^{-1} \cdot l\,mg^{-1}$ C)	June THM-FP ($\mu g\,mg^{-1}$ C)	November SUVA ($m^{-1} \cdot l\,mg^{-1}$ C)	November THM-FP ($\mu g\,mg^{-1}$ C)
HAF	5.8	32.4	6.1	64.0	4.9	118.9
FAF	3.9	40.8	5.3	26.7	6.1	186.5
HPI-A	1.1	17.7	2.3	37.4	3.7	171.3
HPI-NA	1.4	8.8	0.6	2.0	1.6	85.4

HAF—Humic acid fraction; FAF—fulvic acid fraction; HPI-A—hydrophilic acid fraction; HPI-NA—hydrophilic non-acid fraction.

the amount and proportion of hydrophobic material in autumn compared with winter and summer. This corresponded with an increase in the THM of both hydrophobic and hydrophilic fractions. This was not only due to the amount of each fraction but also a significant change in THM per mg of carbon for each fraction.

2. It is clear from the fractionation that even though there is around 90% removal of the hydrophobic FAF in autumn a significant proportion is going through the treatment works and contributes significantly to the THM-FP of the treated water.

3. There is little removal of the HPI-NA fraction through the existing treatment process. The THM-FP of this fraction is markedly increased in November, compared with January and June.

4. The information gleaned through fractionation of the water was far more in depth than the information obtained by just using bulk water parameters alone. The fractionation gives an insight into the seasonal effect on NOM and will allow improved treatment and removal of organic precursors of trihalomethanes and other disinfection by-products.

Table 4 │ Summary of filtered water fraction data

Fraction	June SUVA ($m^{-1} \cdot l\,mg^{-1}$ C)	June THM-FP ($\mu g\,mg^{-1}$ C)	November SUVA ($m^{-1} \cdot l\,mg^{-1}$ C)	November THM-FP ($\mu g\,mg^{-1}$ C)
HAF	4.2	11.7	6.5	154.0
FAF	2.5	84.3	2.9	92.0
HPI-A	2.1	11.9	2.0	43.9
HPI-NA	0.6	4.0	1.3	70.2

NOMENCLATURE

DBP	Disinfection by-product
DOC	Dissolved organic carbon (mg l^{-1})
FAF	Fulvic acid fraction

HAA	Halo acetic acid (μg l^{-1})
HAF	Humic acid fraction
HCl	Hydrochloric acid
HPI-A	Hydrophilic acid fraction
HPI-NA	Hydrophilic non-acid fraction
HPO-N	Hydrophobic neutral fraction
MW	Molecular weight
NaOH	Sodium hydroxide
NOM	Natural organic matter
SUVA	Specific ultra-violet absorbance at 254 nm (m$^{-1} \cdot$ l mg^{-1} C)
THM	Trihalomethane (μg l^{-1})
THM-FP	Trihalomethane formation potential (μg mg^{-1} C)
UV	Ultra-violet absorbance (m^{-1})
WTW	Water treatment works

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