

# **Sorptive removal of disinfection by-product precursors from UK lowland surface waters: impact of molecular weight and bromide**

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## **Abstract**

The current study compared the impact of three different unit processes, coagulation, granular activated carbon (GAC), and a novel suspended ion exchange (SIX) technology, on disinfection by-product formation potential (DBPFP) from two UK lowland water sources with medium to high bromide content. Specific attention was given to the influence of the organic molecular weight (MW) fraction on DBPFP as well as the impact of bromide concentration. While few studies have investigated the impact of MW fractions from Liquid Chromatography with Organic Carbon Detection (LC-OCD) analysis on dissolved organic carbon (DOC) removal by different processes, none have studied the influence of DOC MW fractions from this analysis on DBP formation. The impact of higher bromide concentration was to decrease the total trihalomethane (THM) and haloacetic acid (HAA) mass concentration, in contrast to previously reported studies. Results indicated that for a moderate bromide concentration source (135 µg/L), the THM formation potential was reduced by 22% or 64% after coagulation or SIX treatment, respectively. For a high bromide content source (210 µg/L), the THM formation potential removal was 47% or 69% following GAC and SIX treatment, respectively. The trend was the same for HAAs, albeit with greater differences between the two processes/feedwaters with reference to overall removal. A statistical analysis indicated

that organic matter of MW > 350 g/mol had a significant impact on DBPFP. A multiple linear regression of the MW fractions against DBPFP showed a strong correlation ( $R^2$  between 0.90-0.93), indicating that LC-OCD analysis alone could be used to predict DBP formation with reasonable accuracy, and offering the potential for rapid risk assessment of water sources.

**Keywords:** ion exchange; molecular weight; organic matter; LC-OCD; disinfection by-products

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**Declarations of interest**

Declarations of interest: none

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## 1. Introduction

Natural organic matter (NOM), or more generically dissolved organic carbon (DOC), if all organic matter is considered, can be substantially removed by coagulation/clarification in large-scale potable water treatment works (WTWs). Alternatively, granular activated carbon (GAC) can be employed at the start of the process as a “roughing” filter for organic matter removal [1,2]. However, GAC is limited in its efficacy with reference to the adsorptive capacity of the media [3] and its overall DOC removal capability [2,4].

In reality, neither conventional coagulation-clarification nor roughing GAC are usually capable of reliably meeting the regulated water quality standards for the more challenging of the DOC-laden surface waters. This relates to the DOC physicochemistry, and a very significant research effort has been dedicated to the correlation of disinfection by-product formation potential (DBPFP) with the physical and chemical fractional content of DOC. It is often the case that the DOC fraction contributing most significantly to DBPFP is the hydrophobic (HPO) fraction, which is also the fraction most extensively removed by conventional clarification [5–7]. Notwithstanding this, the concentration of the residual hydrophilic (HPI) fraction is often sufficient to generate levels of DBPs above the permitted limits [6]. For water sources containing a substantive amount of hydrophilic DOC, reducing the treated water DOC to acceptable levels can be challenging, particularly for coagulation processes. Lowland surface water sources in the UK would fit into this category.

Of the different technologies studied/implemented for supplementary DBP precursor removal, ion exchange (IEX) presents an alternative adsorptive process to activated carbon which provides a greater capacity for DOC on a mass basis [8,9]. Various IEX-based processes, including magnetic ion exchange (MIEX) and suspended ion exchange (SIX), and a wide range of other sorption media [10] have been successfully demonstrated to suppress formation of both THMs and HAAs [9,11–14] in treating of NOM or its analogues. Of the

published papers on the area, many have either been based on practical performance in terms of DOC removal [15,16] or DBP precursor removal [11,14,17], with many favouring physico-chemical fractionation for characterisation of the DOC [18–20].

Trihalomethanes (THMs) and haloacetic acids (HAAs) remain the most extensively studied of all halogenated DBPs in potable water treatment [21]. However, the most recent focus on brominated and iodinated DBPs has, as with HAAs over THMs, been prompted by evidence of the increased cytotoxicity and genotoxicity of these species compared with chlorinated equivalents. In addition, the drinking water guideline values from the World Health Organisation (WHO) tend to be lower for brominated DBPs when compared to fully chlorinated equivalents [22]. Studies of brominated DBPs pertaining to IEX technologies have included targeted removal of bromide [6,23] as a means of suppressing brominated DBP formation directly. Those in which impacts of raw water bromide concentration on treated water DBP speciation have been largely limited to bench-scale studies [11,13,24]. Reported outcomes across all studies have been inconsistent. Most authors have reported an increase in total DBP concentration with increasing bromine substitution (the proportion of brominated species making up the total DBP concentration) [25–27]. Conversely, and counter-intuitively, others [14,28] have reported a decrease, with some recent indication of the trend depending on the precise precursor [29].

Few of these papers have studied the impact of molecular weight (MW) fractions on DOC removal by novel and conventional processes [14,17], and studies of both DBPFP and DBP yield (FP/DOC concentration) have been largely based on chemical characterisation. Moreover, none have investigated the potential influence of DOC MW fractions from LC-OCD analysis on DBP formation, which could provide the Water Industry with an additional tool to characterise water sources and their potential risk for DBPFP. Lastly, no previous papers have combined the study of MW fractionation with bromide concentration impacts on the distribution of chlorinated and halogenated DBPs. The current study, based on real UK

surface waters, compares the impact of three different unit processes, GAC, and SIX technology, on DBPFP. Specific attention was given to the influence of the organic MW fraction on THM and HAA FP, the comparative efficacy of the conventional coagulation and GAC processes, and the possible impact of feedwater bromide concentration.

## **2. Methodology**

### **2.1 Water samples**

Water samples were collected from two WTWs in the UK. The samples from each WTW was collected within a six-week period to avoid seasonal impact on the results. One of the WTWs (Res) abstracts from a large reservoir, characterised as a “lowland reservoir”. The treatment train comprises primary ozonation, coagulation and pulsator-clarification and rapid gravity filtration for removal of bulk organic matter and suspended particles; secondary ozonation and GAC adsorption for pesticide removal; and chloramination (Fig S1). The other WTW (Riv) is considered to have a “lowland river” source. Treatment on site consists of roughing GAC adsorption and ultrafiltration membranes for bulk organic removal and suspended particles; UV/peroxide and GAC adsorption for pesticide removal; and UV disinfection and residual chlorination (Fig S1). The raw water was characterised (Table 1) and samples were taken downstream of the clarification process (Res) and GAC filter (Riv) (Fig S1) to allow comparison of treatment efficacy from these conventional processes to that of SIX. The coagulation process (Res) used ferric sulphate as coagulant at a concentration of 3.5 mg/L Fe. The GAC treatment (Riv) had an empty bed contact time of 20 min and used TL830 as media.

**Table 1.** Average and standard deviation of raw water characteristics for the lowland reservoir and river sources

Parameter	Lowland reservoir	Lowland river
	(Res)	(Riv)
DOC (mg/L)	5.6 ± 0.1	6.0 ± 0.1
pH	8.4 ± 0.1	8.3 ± 0.1
Alkalinity (mg/L)	192 ± 1	162 ± 1
Bromide (µg/L)	135.0 ± 0.2	210.0 ± 0.2

## 2.2 SIX jar tests and resin conditioning

The resin used was Lewatit® S 5128 (Lanxess, Germany), a Type 1 strong basic anion resin with an acrylic gel structure and an adsorption capacity of 1.8 eq/L, according to the manufacturer specifications. A previously presented methodology [24] was used for preparation (conditioning) of the virgin resin: prior to use and following each test the resin was first washed with deionised (DI) water, then regenerated with a 100 g/L sodium chloride solution for 30 min before rinsing with DI water. SIX jar tests were performed on 1L aliquots of raw and treated samples using a paddle jar tester and following the methodology of Finkbeiner et al. [24]. Three resin concentrations were tested, 10, 20 and 30 mL/L (7.3, 14.6, 21.9 g/L, respectively), with sampling times of 10, 20 and 30 min and duplicate tests for each test condition. The maximum concentration of resin tested was set at 30 mL/L as that is the operational limit at larger scale for high flows in the SIX process. All water samples were pre-filtered to 0.45 µm before analysis.

## 2.3 Analysis

### 2.3.1 Chemical

Chemical fractionation using non-ionic microporous resins [30] was carried out on both raw waters sampled over the same six-week period (June-July) to discount any seasonal

impacts. Two litres of water sample were passed through two 60 mL columns in tandem to determine the organic composition. The first column contained XAD7-HP resin, which preferentially adsorbs the hydrophobic fraction (HPO), and the second column with XAD4 resin, which adsorbs the transphilic (TPI) fraction. Organic compounds not adsorbed by either column were classified as the hydrophilic (HPI) fraction. Resins were back-eluted with 0.1M NaOH and cleaned with deionised water and HCl at 0.5%, yielding over 80% recovery. The resins were Soxhlet-extracted with methanol before first use and conditioned before each run by cleaning with water followed by 0.1M NaOH and 0.1 M HCl.

DOC was measured using a Shimadzu TOC-V analyser with a non-purgeable organic carbon (NPOC) method, where samples were acidified in the instrument with 2 M HCl and purged with carbon-free air to remove CO<sub>2</sub>-derived carbonates and bicarbonates. The method was calibrated to measure DOC in the 1-10 mg/L range. Blanks and quality control checks were analysed every five samples, with all analyses being duplicated. The limit of quantification (LOQ) was 1 mg/L.

DBP formation potential tests were performed on raw water and treated samples. Samples were diluted with ultrapure water to 1 mg/L DOC using a Cl<sub>2</sub>:DOC mass ratio of 5:1 (0.07:0.08 molar ratio and DOC as C), the free chlorine measured using DPD reagent [31]. The chlorinated samples were stored in 100 mL PTFE bottles with no headspace in the dark for 7 d, and the residual chlorine then quenched with sodium sulphite or ammonium chloride for THM or HAA analysis, respectively. The THMs species analysed comprised trichloromethane (TCM), tribromomethane (TBM), bromodichloromethane (BDCM) and chlorodibromomethane (CDBM). The HAAs analysed were monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and dibromochloroacetic acid (DBCAA). An Agilent GC-ECD 6890 with a capillary column (Phenomenex 30m x 0.25 mm x 0.25 µm) was used for



chromatographic analysis, following a modified USEPA extraction method (551.1 and 552), as used previously [32]. The LOQ for each DBP was 1 µg/L, with the exception of MCAA (LOQ 2 µg/L).

LC-OCD analysis by the Het Water Laboratorium (Netherlands) was conducted to determine organic matter MW distribution before and after treatment, following the method of [33]. The column used for this analysis had a separation range up to 10,000 g/mol, with the MW decreasing with elution time. The fastest-eluting compounds have a MW above 10,000 g/mol and are considered hydrophilic since they exhibit no interaction with the cation-exchanging column. The compounds in this group are not usually detectable by UV, and thus have few or no unsaturated chemical bonds. However, it has been reported [33] that they may show some response to the organic nitrogen detector, indicating polysaccharides with N material and possibly proteinaceous material. The second peak has been associated with humic-like substances (ca 1,000 g/mol) [33]. The third group has been identified as breakdown products from humic-like substances (300-500 g/mol). The next group eluted are low MW-acids (< 350 g/mol) followed by low MW neutrals (also < 350 g/mol).

### **2.3.2 Statistical Analysis**

Multiple linear regression analysis and analysis of variance was performed using MiniTab® statistical software (Minitab, LLC State College, Pennsylvania, USA) at a significance level of 0.05. The statistical analysis was expanded to include the dataset from this research and that published by Metcalfe et al. [14] and Finkbeiner et al. [17].

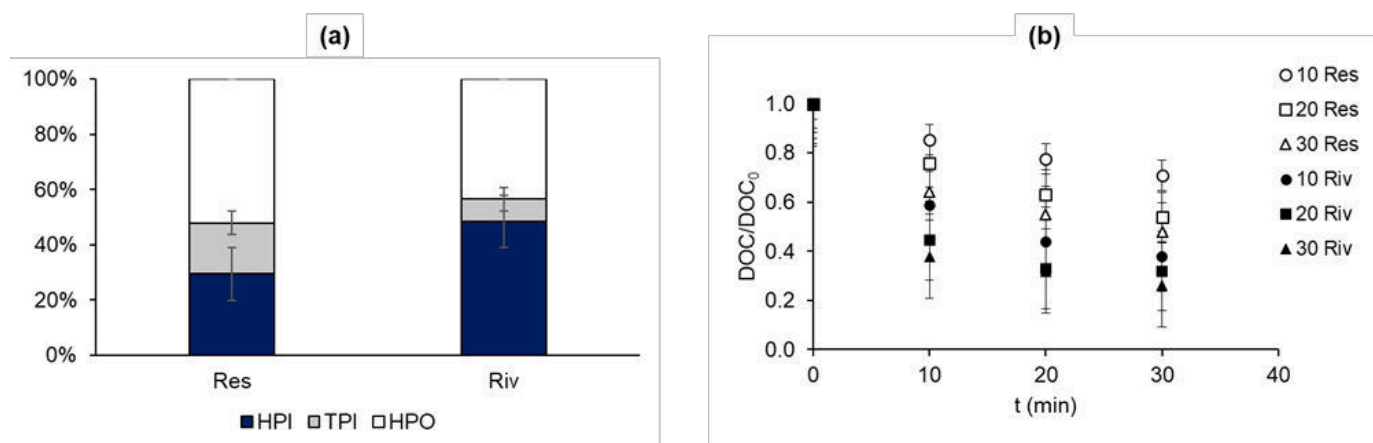
## **3. Results and discussion**

### **3.1. Water Chemistry**

Results of the hydrophobicity-based fractionation analysis (Fig. 1a) revealed a higher HPO content in the Res source (52%) compared with the Riv source (43%). Moreover, in the Riv

source the HPI fraction accounted for almost half of the organic content, compared with 30% for the Res sample. Results also showed more than twice the amount of TPI fraction in the Res than in the Riv source (18% vs 8%).

DOC removal from the raw water sources by SIX was explored at resin concentrations of 10-30 mL/L (Fig 1b) by way of characterising the organic matter chemistry. While the initial DOC content of the water sources was similar, SIX proved to be more efficient at removing Riv sample DOC, providing 60%-75% removal compared with 30%-50% for the Res source. The pseudo-first order kinetic constants (Table S1) supported this fact. The constant for 10 mL/L resin was almost four times higher in the Riv source ( $0.012$  vs  $0.44 \text{ min}^{-1}$ ), ca. three times higher for 20 mL/L ( $0.022$  vs  $0.61 \text{ min}^{-1}$ ), and more than twice for 30 mL/L ( $0.27$  vs  $0.65 \text{ min}^{-1}$ ) resin. This further indicates differing chemistries, the Riv water containing higher concentrations of charged organic material removable by ion exchange [17]. Based on these results, a dose of 30 mL/L was selected for subsequent trials and analysis as it provided the highest removal of DOC.



**Figure 1. Outcomes of DOC chemical analysis of Res and Riv sources (a) Organic fraction make-up, and (b) DOC removal transients at three SIX doses (in mL resin/L), jar testing. Error bars represent the standard error of the mean.**

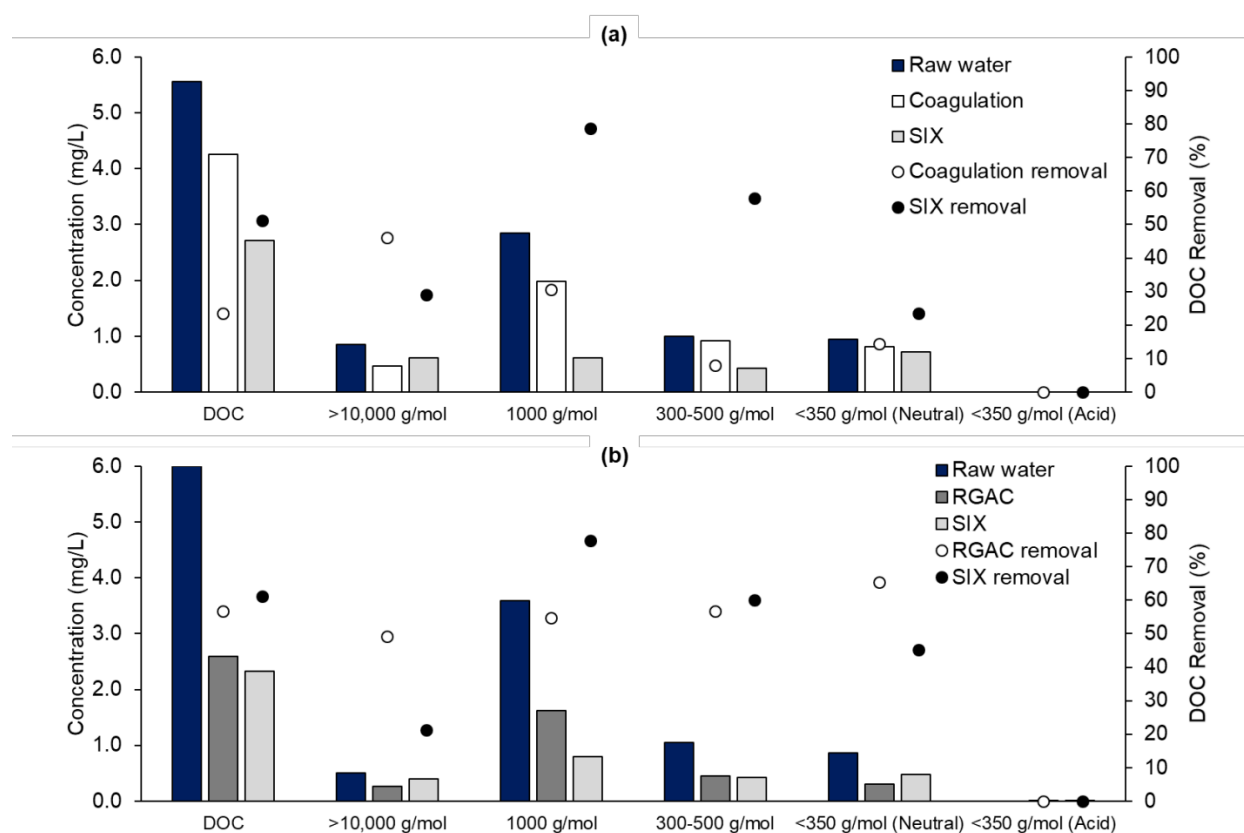
### 3.2 DOC molecular weight distribution trends

Recorded DOC molecular weight distributions within the bands of  $> 10,000$ ,  $\sim 1000$ ,  $300-500$  and  $< 350$  g/mol (Fig. 2) indicated that the size fraction at around  $1000$  g/mol dominated for all raw water and pre-SIX treated samples. The two raw water samples were similar in terms of total DOC concentration ( $5.6$  and  $6$  mg/L for the Res and Riv sources respectively) and the proportion of the dominant  $\sim 1000$  g/mol MW fraction ( $50\%$  and  $60\%$  for the Res and Riv sources, respectively). The main difference was in the percentage of the largest  $> 10,000$  g/mol fraction, which was  $16\%$  and  $8\%$  respectively for the Res and Riv sources. The molecular weight distribution was shifted towards higher values for the Res samples. No low-MW acid organics were detected for either source. The two water sources can thus be regarded as being comparable in quality with respect to MW distribution and DOC level, notwithstanding the substantially different sources and subsequent chemistries (Fig. 2).

Differences in removal across the four MW fractions were observed between the two processes. Whereas clarification of the Res source removed only  $25\%$  of the DOC, predominantly in the two largest size ranges ( $46\%$  and  $30\%$  for the  $> 10,000$  and  $\sim 1,000$  mg/L fractions respectively), GAC removed  $50-60\%$  of the DOC across all size fractions. In absolute terms the removal capability of the GAC was  $2.6$  times that of clarification, with  $3.4$  mg/L of DOC being removed compared with  $1.3$  mg/L for clarification. For the predominant  $\sim 1,000$  MW size fraction, removals were  $31\%$  ( $0.8$  mg/L) and  $55\%$  ( $2$  mg/L) for the Res and Riv waters, respectively.

The largest MW group ( $> 10,000$ ) has been reported to primarily contain biopolymers, such as polysaccharides, amino-sugars or proteins, but it might also contain a low proportion of aromatic moieties, with previous studies confirming that coagulation preferentially removes this fraction [14]. The second largest group ( $1,000$  mg/L) is typically constituted by humic-like substances [33], with complex chemical structures, charged and hydrophobic [34], also

justifying their removal by coagulation. However, organics with MW > 350 g/mol are known to contain building blocks of humic-like substances, more hydrophilic, and less efficiently removed by coagulation [14]. On the other hand, whilst MW fractions smaller than 1,000 g/mol have been shown to be efficiently removed by GAC, the larger size of organics with MW > 10,000 g/mol prevents them accessing adsorption sites [3,35]. This is in contrast with the present study, where the largest fraction was also efficiently removed, although this can be attributed to frequent regeneration of the GAC on site (bimonthly), making adsorption sites available.



**Figure 2.** Organic matter concentration and MW fractions of raw and treated waters for (a) Res and (b) Riv sources.

SIX removed 51-61% of the DOC from both raw water sources, with 78-79% removal of the predominant ~1000 g/mol fraction and 58-60% for the 300-500 g/mol fraction. These two groups contain similar acidic, negatively charged functional groups, which makes them amenable to SIX treatment [36]. Removals of the largest and smallest fractions revealed

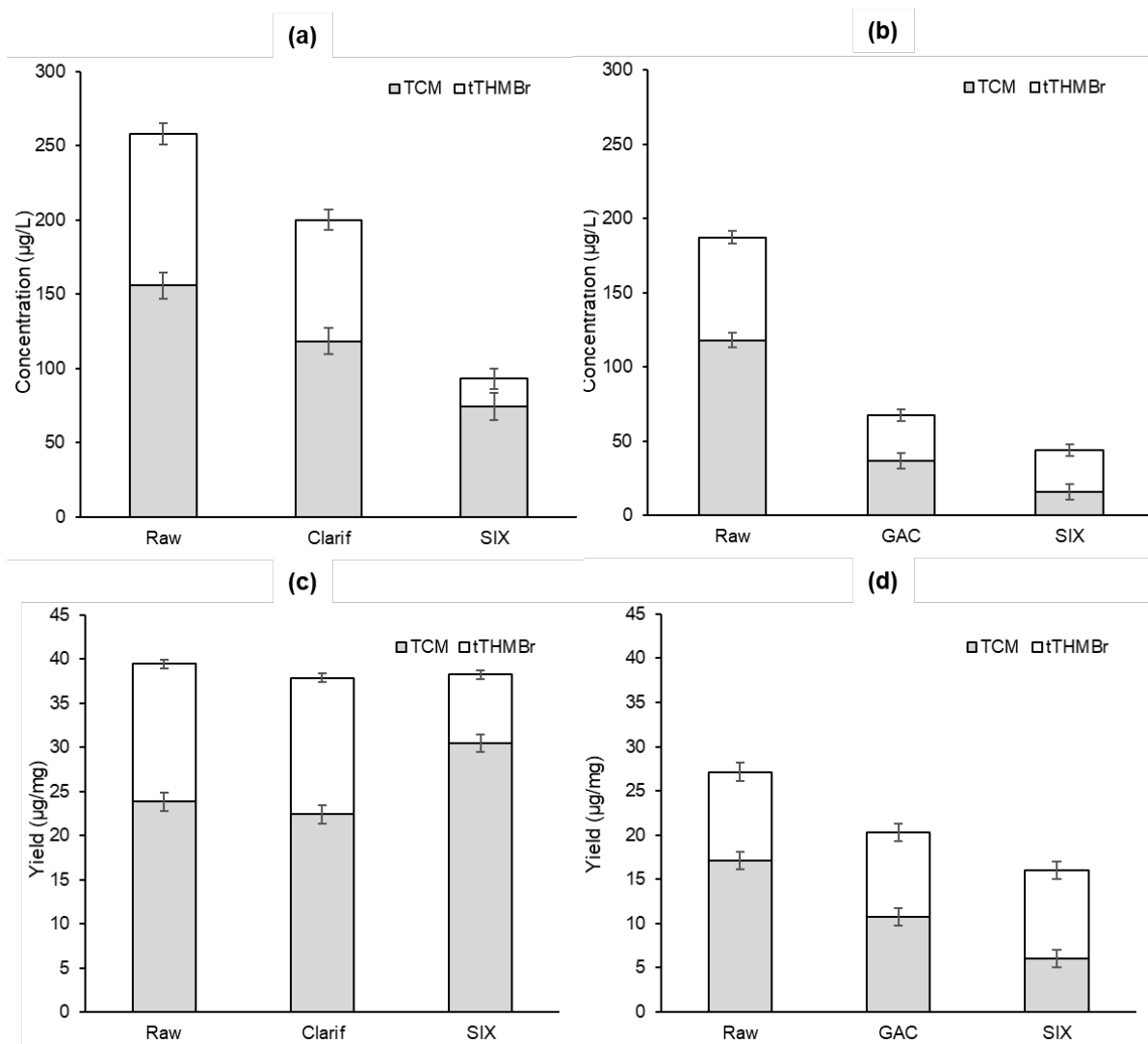
slightly differing propensities, with slightly greater removal of the > 10,000 g/mol fraction for the Res source (29% vs 21%) and the reverse trend (45% vs. 24%) for the < 350 g/mol neutral fraction. This can be attributed to the fact that the > 10,000 g/mol fraction blinds the adsorption sites for the < 350 g/mol MW compounds. This is consistent with that seen for SIX treatment of DOC from an upland source [37] and for GAC [3] such that these organic compounds are less readily removed compared to the same size fraction in the Riv source.

Recorded differences in bulk organic removal relate to differences in both the treatment technology and the organic matter chemistry such as compound hydrophobicity (Section 3.1), as well as the molecular functional chemistry of the DOC in each MW fraction.

### **3.3 DBP precursor removal trends**

#### **3.3.1 THMFP**

In keeping with the DOC removal trends (Fig. 2), twice the total THM (tTHM) precursors were removed by the GAC process for the Riv source (47%) than by the clarification process for the Res source (23%) (Fig. 3a and 3b). This is in line with reported DOC removal by non-enhanced coagulation and adsorption [3,38–41]. The tTHM precursor removals for the Res source (Fig. 3a) followed that of the DOC removal trends (Fig. 2a). The formation potential was reduced by 23% or 64% respectively, and such that the overall yield (tTHM/DOC) was constant throughout the process at 38-39 µg/mg (Fig. 3c). On the contrary, for the Riv source the overall DBP yield decreased (Fig. 3d) by 27% or 38% following GAC and SIX treatment, respectively, with an associated formation potential reduction of 47% and 69% (Fig 3b).



**Figure 3.** Distribution of THM concentration and yield, TCM and brominated species (tTHM<sub>Br</sub>), comprising BDCM, CDBM and TBM, for (a, c) Res and (b, d) Riv sources. Error bars represent the standard error of the mean.

Trends in the distribution of chlorinated and brominated species differed significantly between the two raw waters. For the lower-bromide concentration (Res source) the TCM yield was unchanged following clarification (22 µg/mg), showing that both primary ozonation and clarification had no impact on the yield, and increased following SIX treatment (31 µg/mg) (Fig. 3c). The yield for the total brominated species (tTHM<sub>Br</sub>), comprising BDCM, CDBM and TBM, remained constant after clarification (16 µg/mg), but decreased following

SIX treatment for this source (8  $\mu\text{g}/\text{mg}$ ). For the Riv source, with the higher  $\text{Br}^-$  level, the  $\text{tTHM}_{\text{Br}}$  yield remained unchanged after GAC or SIX treatment (9-10  $\mu\text{g}/\text{mg}$ ) (Fig. 3d). However, the TCM yield for this source decreased throughout the process from 17  $\mu\text{g}/\text{mg}$  in the raw water to 11  $\mu\text{g}/\text{mg}$  after GAC or to 6  $\mu\text{g}/\text{mg}$  after SIX treatment (Fig. 3d). The treated Riv water THMs thus had a significantly greater Br content – with an atomic mass more than double that of Cl. Yet it provided a lower mass concentration and yield of tTHMs than that of the Res source, which had a lower bromide concentration. It should also be pointed out that bromide was not removed by either coagulation (Res source) or GAC (Riv source), with < 11% removed by SIX (Res and Riv source).

Whilst this observation is counter-intuitive, in that higher tTHM levels would be expected from higher feed bromide concentrations [25–27], similar trends have been reported previously [14,28]. As with the current study, these two studies were based on real UK surface waters with bromide levels substantially lower than the DOC concentrations. The reported work of Szczuka et al. [25] and Cai et al. [27], on the other hand, were based either on groundwater with seawater intrusion with higher Br/DOC ratios or desalinated seawater blended with drinking water.

A possible explanation of the THM trends is provided from the dynamic molar yield trends  $Y_d = d[\text{THM}]/d[\text{DOC}]$  (Fig 4a), where the DOC was that of the raw water (Res or Riv) and the treated water (clarification, GAC or SIX).  $Y_d$  in  $\mu\text{M } \Delta\text{DBP}$  per  $\text{mM } \Delta\text{DOC}$  varied from 0.7 to 2.4  $\mu\text{M}/\text{mM}$ , with the highest values (1.9-2.4  $\mu\text{M}/\text{mM}$ ) obtained for TCM formation and the lowest for  $\text{tTHM}_{\text{Br}}$  (0.7-1.5  $\mu\text{M}/\text{mM}$ ). The  $Y_d$  for the brominated DBPs was shallower than the TCM slope, indicating that the  $\text{THM}_{\text{Br}}$  formation propensity from the halogenated intermediates was substantially lower than that for TCM formation.

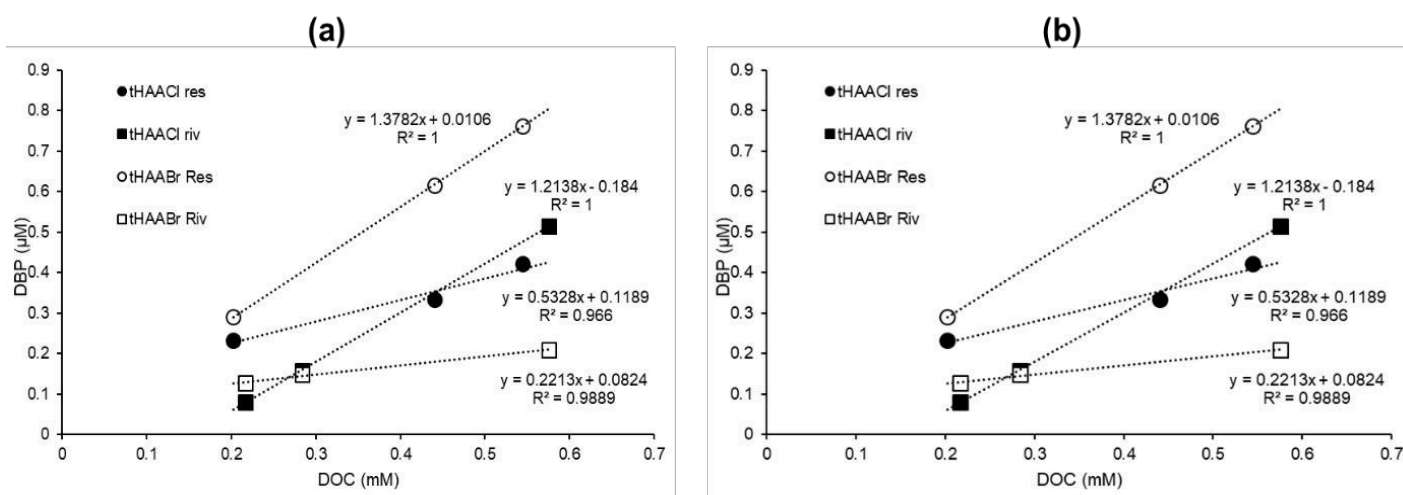
However, the effect of the higher  $\text{Br}^-$  levels in the Riv source appears to offset the TCM slope, i.e. the change in the y axis intercept, by  $\sim 0.27$   $\text{mM}$  DOC (3.2  $\text{mg}/\text{L}$ ). This offset

suggests that the organic matter preferentially reacts with HOBr (formed from HOCl and Br<sup>-</sup>) to produce intermediates, but that these intermediates are not converted to THM<sub>Br</sub> products as readily as the chlorinated intermediates are converted to TCM. This behaviour has been previously modelled by Mok et al. [42] who studied the reactions undertaken by an activated carbon atom and the steps required to produce chlorinated, brominated and mixed THMs. They demonstrated that the key to determining the species formed is the initial [HOBr<sup>-</sup>]:[HOCl] ratio, with a tipping point at [HOBr]/[HOCl] > 0.03, where brominated THMs dominate. The initial [HOBr]/[HOCl] ratios for this study were 0.004 and 0.006 for the Res and Riv, respectively, which explains the dominance of chloroform observed in this study.

The formation of intermediate DBPs has been suggested by Li et al. [43] who reported aromatic-based DBP intermediates, with the cytotoxicity of the brominated intermediates being higher than that of the chlorinated ones. Further to this, Jiang et al. [44] have proposed pathways for the formation of halogenated aliphatic DBPs (e.g. THMs and HAAs) which identified the formation of non-halogenated and halogenated aromatic DBPs prior to their degradation to halogenated aliphatic DBPs. The chlorine dose was a strong influencing factor on the formation of the intermediate DBPs governing the levels at which they formed. In terms of toxicity, recently, an approach has been taken to assess the toxicity of a water sample in terms of the relative cytotoxicity and genotoxicity of DBPs rather than the mass of the DBPs measured [45]. Although the present study looked solely at THMs and HAAs, there are a number of DBP groups (e.g. haloacetonitriles, haloacetamides, halonitromethanes, haloketones and iodinated compounds) that contribute towards the cytotoxicity and genotoxicity of a water sample and it is acknowledged that the values for THMs and HAAs are generally lower than the listed compounds. In terms of mass, the THMs and HAAs can dominate the DBPs formed but when assessed according to Li and Mitch [45], the other compounds found at lower concentrations can dominate the calculated toxicity of the water. This has been further explored by Cuthbertson et al. [46] who used similar calculations to determine whether GAC treatment produced water with lower cytotoxicity and



genotoxicity. Further research is needed to address the role of different treatment processes such as adsorption on these emerging DBP groups and their link with LC-OCD MW groups.

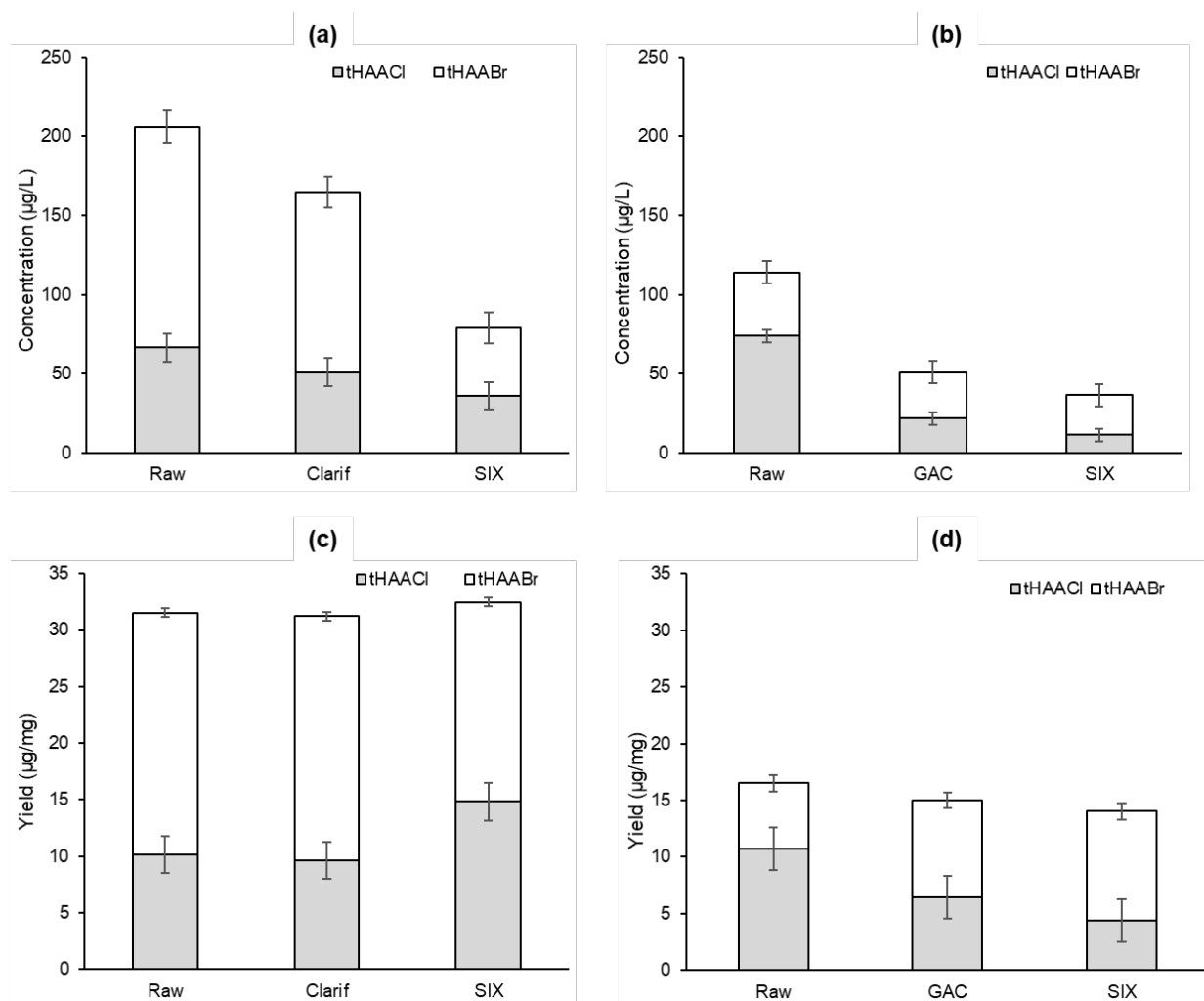


**Figure 4.** Dynamic molar yield trends: (a) molar THM concentration vs DOC concentration for TCM and brominated species (tTHM<sub>Br</sub>); and (b) molar HAA concentration vs DOC concentration for chlorinated (tHAACl) and brominated species (tHAABr) in the Res and Riv sources.

### 3.3.2 HAAFP

Trends in total HAA concentration and HAA speciation (Fig. 5) were similar to those of THMs. For the Res source the concentration of both the chlorinated and the halogenated species decreased from 206 μg/L to 165 μg/L following clarification or decreased further following SIX treatment (103 μg/L) (Fig. 5a), such that the overall yield was constant at around 33-34 μg tHAA/mg DOC (Fig. 5c), although the halogenated yield after SIX treatment was slightly lower than in the raw water or clarification (18 vs 22 μg/mg DOC). As with the THM yield trends the proportion of chlorinated byproducts increased following SIX treatment for the Res water from 10 μg/mg to 15 μg/mg (Fig. 5c). Also, for the Riv source both the tHAA concentration (Fig. 5b) and the yield (Fig. 5d) were significantly lower (by almost 50%)

than the corresponding values for the Res source and decreased with increasing brominated DBP content. However, in this case the yield increased after GAC (9  $\mu\text{g}/\text{mg}$ ) or SIX (10  $\mu\text{g}/\text{mg}$ ) in comparison to the raw water (6  $\mu\text{g}/\text{mg}$ ), a trend similar to that seen for the THMs (Fig. 3).



**Figure 5.** Distribution of HAA concentration and yield, tHAA<sub>Cl</sub> comprising MCAA, DCAA, TCAA, and tHAA<sub>Br</sub> comprising MBAA, BCAA, DBAA, BDCAA, DBCAA, and TBAA for (a, c) Res and (b, d) Riv sources.

On the other hand the dynamic molar yield trends  $\Delta[\text{HAA}]/\Delta[\text{DOC}]$ , whilst substantially linear ( $R^2 = 0.966-1.00$ ), did not follow the same trend as for the THMs (Fig. 4b). For the HAAs, the steepest slopes were recorded for the Res source brominated DBPs and the Riv source chlorinated products (Fig. 4b) due to the fact that the brominated yield (Fig. 5b) was greater

than the chlorinated yield in each source. For example, for the Res source brominated THM yield was between 20-40% of the total yield; while the brominated HAA yield was between 54-68%. A significant offset of 0.37 mM (4.5 mg/L DOC) between the Res and Riv samples for the chlorinated DBPs is evident, but this relates to the significant difference in slopes (1.21 vs 0.22  $\mu\text{M}/\text{mM}$  DOC) rather than the intercept alone as with the THM data.

### 3.4 DBP precursor removals and MW distribution

A statistical analysis comprising an Analysis of Variance (ANOVA) and a multiple linear regression was conducted to understand the statistical significance the possible relationship between the DBPFP concentrations and those of the individual MW fractions as determined by the LC-OCD analysis. To increase the statistical power and the ability of the analysis to find relationships between the variables, the sample size was expanded to include the data reported by Metcalfe et al. [14] and Finkbeiner et al. [17]. The larger dataset included data points from lowland river, upland river and reservoir source waters as well as the lowland river and reservoir sources pertaining to the current study. The ANOVA showed MW fractions > 350 g/mol to have a statistically significant impact on THM and HAA formation (P-Values below 0.05 for the 95% confidence interval) (Fig S2).

The adjusted coefficient of determination ( $R^2_{\text{adj}}$ ) values for the multiple linear regressions were very close to the predicted coefficients of determination ( $R^2_{\text{pred}}$ ) for the THMs and HAAs (92.5% vs 90.4% for THMs and 89.7% vs 86.4% for HAAs) (Table 2). The high  $R^2_{\text{adj}}$  value suggests that LC-OCD results can potentially be used to predict DBPFP if a validated method is developed, and that the high goodness of the fit was not due to the high number of predictors (three MW groups) [47]. Running the analysis with all the MW fractions did not improve the determination coefficient, verifying that the smallest fraction had no statistically significant impact on DBP formation. The fact that both coefficients of regression were similar also supported the fact that the analysis was not overfitted.

**Table 2.** Multiple linear regression analysis summary

Source data	Predictor	S	R <sup>2</sup> <sub>adj</sub>	R <sup>2</sup> <sub>pred</sub>	Regression equation
All studies*	THMs	137	92.5%	90.4%	THM = 153.6MW1 + 189.5MW2 - 270.9MW3
	HAAs	252	89.7%	86.4%	HAA = 301.8MW1 + 321.2MW2 - 683MW3

MW1: > 10,000 g/mol; MW2: 1,000 g/mol MW; MW3: 300-500 g/mol MW

S is the standard deviation of the data points around the fitted values

\*Data from this study and those extracted from Metcalfe et al. [14] and Finkbeiner et al. [17]

As a result of the ANOVA and multiple linear regression analysis, it is therefore reasonable to assume that there is a link between molecular weight fractions and chemical functionality within the fractions, since the latter is directly linked to DBPs. The most statistically-significant MW fractions must thus contain organic compounds with chemical functionality more conducive to DBP formation than other fractions. In particular, the regression coefficients for the two largest MW fractions were positive (Table 2), suggesting that as their concentrations increase, so does the formation potential for THMs, and more so for HAAs since the coefficients are greater (302 and 321 for THMFP vs 154 and 190 for HAAFP). Specifically, the > 10,000 g/mol fraction is associated with organic material such as proteins, peptides and polysaccharides, which has been previously linked to DBP formation [48–50], whilst humic-like substances (the ~1000 g/mol fraction) are known to have a high propensity to form DBPs [51]. On the contrary, the regression coefficient for the organic matter group with MW between 300-500 g/mol was negative for both THMs and HAAs, indicating that in this case, as the concentration of this fraction increased, the THMFP and HAAFP decreased instead. This could mean, and in line with the explanation suggested in Section 3.3, that building blocks of humic acids consume chlorine or hypobromous acid formed from HOCl and Br<sup>-</sup> to produce intermediates, but that these intermediates are not converted to either THMs or HAAs, but to other unmonitored DBPs. Further studies using high resolution mass spectrometry (HRMS) or Fourier Transform Infrared (FTIR) can provide additional information on the chemical functionality linking to DBP formation.

The outcomes of the LC-OCD analysis indicate that, notwithstanding the complexities of the halogenation chemistry affecting the comparative concentrations yields of the chlorinated and brominated DBPs (Section 3.3), the total DBPFP can be estimated from the MW fractions ( $MW > 350$  g/mol) as determined from LC-OCD analysis. This information can be useful to characterise water sources and identify potential DBP risks as well as target treatment technology to remove particular MW fractions.

A review of published correlations for DBPFP vs DOC (or, in one case [52], dissolved organic nitrogen, DON) concentration for raw waters reveals the  $R^2$  values to generally fall between 0.71 and 0.79 (Table 3); outliers of 0.65 and 0.85 for THMFP and HAAFP, respectively were determined for the correlation against DON for a highly polluted source [52]. These reported  $R^2$  values are substantially lower than the values of 0.90 or more produced from the regression analysis based on molecular weight fractions used in the current study. They are also higher than  $R^2$  values of 0.73-0.78 reported using fluorescence excitation/emission matrices for a similarly extensive dataset [53,54]. The  $R^2$  values for the THMFP and HAAFP correlations in this study are 0.93 and 0.90 respectively (Table 3), compared with 0.74 and 0.71 respectively for the classical correlation against DOC concentration.

**Table 3.** Summary of DBPFP ( $\mu\text{g/L}$ ) vs concentration (mg/L)

<i>Data source/reference</i>	<i>Source water</i>	<i>THMFP</i>		<i>HAAFP</i>	
		<i>Slope</i>	$R^2$	<i>Slope</i>	$R^2$
Xu et al. [52], DBPFP vs DON	Huangpu River	680	0.64	750	0.85
Pifer & Fairey [53], THMFP vs DOC	Various US, surface & ground	78	0.75	-	-
Golea et al. [55], DBPFP vs DOC	Scottish surface	149	0.79	216	0.74
<b>This study*, DBPFP vs DOC</b>	<b>UK surface</b>	<b>121</b>	<b>0.74</b>	<b>236</b>	<b>0.71</b>
<b>This study*, DBPFP vs LC-OCD data</b>	<b>UK surface</b>	<b>-</b>	<b>0.93</b>	<b>-</b>	<b>0.90</b>

\*Data from this study and those extracted from Metcalfe et al. [14] and Finkbeiner et al. [17]

#### 4. Conclusions

An analysis of DBPFP of a raw and treated UK surface waters has been conducted, employing both chemical (sorption-based) and physical (liquid chromatography organic carbon detection, LC-OCD) fractionation for organic matter characterisation. The selected raw waters were of similar MW distribution, but differed with respect to both their organic chemistry and bromide content. The impact of the higher bromide concentration was to increase the proportion of brominated DBP species whilst decreasing the total concentration, consistent with reported studies on UK surface waters but not with those for other water types. This effect has been attributed to the fact that organic matter reacted with HOBr<sup>-</sup> to produce intermediates, but that these intermediates were not converted to brominated THMs or HAAs as readily as the chlorinated intermediates. This highlights the importance of monitoring unknown DBP intermediates and further research on their potential risk.

An ANOVA of the MW fractions against THMFP and HAAFP showed that only MW > 350 g/mol were statistically significant in the formation of DBPs, and a multiple linear regression of DBP concentration against the concentration of individual MW fractions determined by LC-OCD provided a strong correlation ( $R^2 = 0.90-0.93$ ), indicating that LC-OCD analysis alone could be used to predict DBPFP with reasonable accuracy, if a validated model is developed. The LC-OCD analysis offers the potential for rapid assessment and optimisation of treatability of organics through quantifying the key MW fractions. The method represents a substantial improvement in precision of predicted DBPFP based on DOC, and is less laborious than chemical fractionation for quantifying the hydrophobic and hydrophilic organic content. It also appears to be unaffected by the vagaries of bromide-related DBPFP. However, the work would need to be extended to surface waters from multiple locations globally to provide a true assessment of its general efficacy.

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Contribution	Irene Carra	Javier Fernandez Lozano	Scott Johannesen	Max Godart-Brown	Emma H. Goslan	Peter Jarvis	Simon Judd
Conceptualization	x					x	
Methodology	x	x	x	x			
Validation	x				x	x	x
Formal analysis	x	x	x	x			
Investigation		x	x	x			
Resources	x						
Data Curation	x	x	x	x			
Writing - Original Draft	x						x
Writing - Review & Editing	x				x	x	x
Visualization	x						x
Supervision	x					x	
Project administration	x						
Funding acquisition	x						



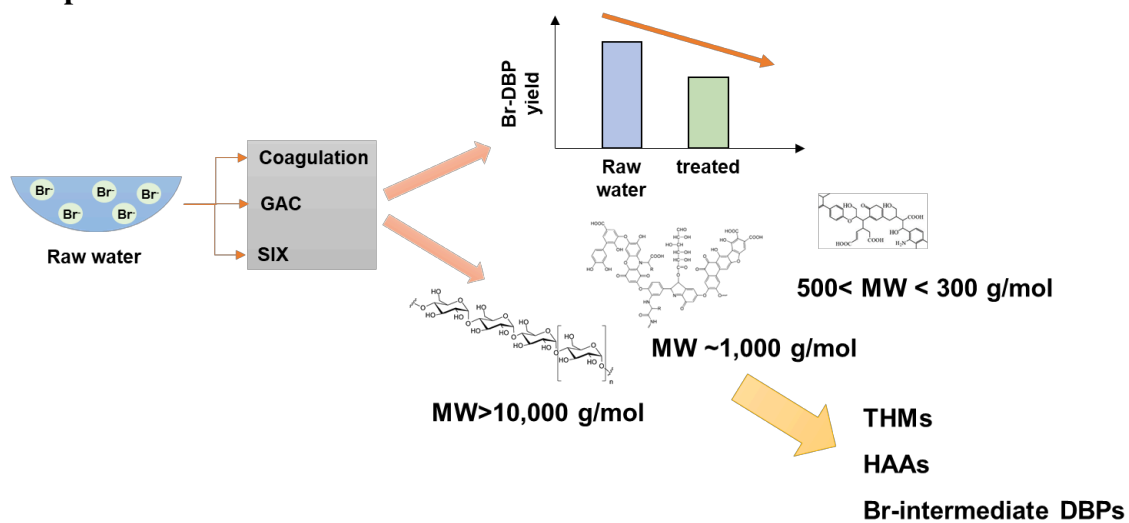
**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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## Graphical Abstract



**Highlights**

- Application of suspended ion exchange (SIX) to UK lowland waters
- Treatment efficacy assessed as minimisation of DBP concentration and yield
- Moderate/high bromide waters studied; efficacy compared with conventional processes
- Molecular weight >350 g/mol impacted THM and HAA formation
- Increased bromide level in feedwater led to decreased DBP concentration and yield

**Highlights Reviewed**

- Molecular weight >350 g/mol impacted THM and HAA formation
- Increased bromide level in feedwater led to decreased THM and HAA concentration
- LC-OCD was used to predict THM and HAA formation potential ( $R^2=0.90-0.93$ )
- Organics with 300-500 g/mol may form intermediates not transformed to THMs or HAAs

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# Sorptive removal of disinfection by-product precursors from UK lowland surface waters: impact of molecular weight and bromide

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2020-09-05

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