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The combined influence of hydrophobicity, charge and molecular weight on natural organic matter removal by ion exchange and coagulation

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Abstract

Three different source waters were investigated using virgin and pre-used anion exchange resins, coagulation, and ion exchange combined with coagulation (IEX&Coagulation). The hydrophobicity, size distribution and charge of natural organic matter (NOM) were used to evaluate its removal. Dissolved organic carbon (DOC) removal by pre-used IEX resin was 67-79%. A consistent ratio of different hydrophobicity fractions was found in the removed DOC, while the proportion and quantity of the molecular weight fraction around 1 kDa was important in understanding the treatability of water. For pre-used resin, organic compounds were hypothesised to be restricted to easily accessible exchange sites. Comparatively, virgin resin achieved higher DOC removals (86-89%) as resin fouling was absent. Charge density and the proportion of the hydrophobic fraction were found to be important indicators for the specific disinfection byproduct formation potential (DBP-FP). Treatment of raw water with pre-used resin decreased the specific DBP-FP by between 2-43%, while the use of virgin resin resulted in a reduction of between 31-63%. The highest water quality was achieved when the combination of IEX and coagulation was used, reducing DOC and the specific DBP-FP well below that seen for either process alone.

Keywords: ion exchange, charge density, natural organic matter, disinfection byproducts

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1. Introduction

Treatment of surface water to remove natural organic matter (NOM) is important for aesthetic reasons, the reduction of both disinfection byproduct precursors and the associated chlorine demand of the water, as well as minimisation of biofilm formation (Brezinski and Gorczyca, 2019; Fan et al., 2018; Ndiweni et al., 2019). NOM is derived from different sources and is distinguished between that of an allochthonous and autochthonous origin. The latter is produced in the aquatic environment as a result of microbial activity and is composed of aliphatic biomolecules that are usually of low colour (Pivokonsky et al., 2016). Allochthonous NOM originates from terrestrial sources and is mainly formed of breakdown products from plants and is a diverse mixture of organic compounds usually high in colour, due to aromatic moieties present in humic substances (Croué et al., 2000).

For removal of NOM from surface waters conventionally coagulation is used which involves the formation and separation of flocs. The addition of a coagulant (typically salts of aluminium or iron) leads to minimisation of repulsive forces between particles and molecules and hence results in agglomeration (Sillanpää et al., 2018). However, the variations and increase of NOM in surface waters has encouraged investigation of new technologies to improve overall NOM removal. This includes processes such as ion exchange (IEX), which has been successfully applied and proven to be particularly efficient when used in combination with coagulation (Finkbeiner et al., 2018; Kitis et al., 2007). The charge profile of the organic matter has been shown to be one of the dominant influences on its removal by IEX (Boyer and Singer, 2008). While IEX can remove organic compounds of all size ranges, a preference towards low molecular weight (LMW) compounds has been seen due to size exclusion of large molecules. Other researchers have evaluated the influence of aromaticity and found that IEX

favoured the removal of UV absorbing compounds (Grefte et al., 2013; Kitis et al., 2007). Preferential removal of hydrophobic compounds has been linked to physical attraction forces involving hydrophobic and van der Waals interactions between the lipophilic moieties and the resin, and hence an increase in entropy once removed (Li and SenGupta, 2004; Rahmani and Mohseni, 2017; Tan and Kilduff, 2007). However, as high charge density resides predominantly in the hydrophobic fraction of the NOM (Sharp et al., 2006a), this charge could have been a more important factor in the removal of NOM than its hydrophobicity.

Treatability with respect to how well NOM and its fraction are removed also needs to be linked to the state of the resin, where higher NOM removal has been seen with an increase in the hydrophobicity of the organic matter when using virgin resin (Mergen et al., 2008). Conversely, after resin had been used in multiple cycles, a decrease in water treatability was observed as the hydrophobicity of NOM increased. This was explained by blockage of the resin pores by the sorption of high molecular weight (HMW) organic matter that hindered other molecules from diffusing into the pores. This process was increased with consecutive use, inferring that the hydrophobic fraction was rich in HMW organics (Mergen et al., 2008). It has also been reported that in the presence of humic acid a loss of capacity was observed even after the resin had been regenerated as a result of resin fouling (Gönder et al., 2006). Resin fouling takes place when macromolecular organic compounds are irreversibly bound to the resin due to entrapment as well as hydrophobic and coulombic interactions. In addition, chemical and physical degradation of IEX resin leads to the reduction in the number of functional exchange groups (Harland, 1994).

To date, there has not been a comprehensive comparison of NOM removal by IEX that takes into account the combined effects of molecular size, the hydrophobicity and

charge of organic matter for a range of different source waters. Furthermore, the impact of using virgin and pre-used resin that has undergone multiple regeneration cycles has not been explored fully. Such resins are expected to deteriorate as a result of irreversible resin blinding by organic molecules. The aim of this work was therefore to determine the additional treatability information that can be obtained when these water and resin characteristics are considered together.

2. Materials and Methods

2.1. Ion exchange and coagulation tests

Three waters were collected from reservoirs fed by different catchment areas in Scotland. The different raw waters were collected and stored at 4°C until jar tests were performed. Water A was from a catchment composed of a mix of soils with more organic rich soils compared to mineral soils. Water B was from a reservoir fed by a small catchment that contained both mineral and organic rich soils. Water C was from a catchment of organic rich soils, composed equally of moorland and forestry (Zoe Frogbrook, Scottish Water, personal communication, 22/03/2018). All waters had relatively high dissolved organic carbon (DOC) concentrations and low nitrate, sulphate and alkalinity concentrations.

[Table 1 about here]

The water was treated in four different ways, using: i) virgin resin (fresh, unused resin); ii) pre-used resin from a full scale IEX plant that had been used in operation for more than 3 years and had undergone multiple loading and regeneration cycles, treating many thousands of bed volumes (BV) (the resin was regenerated with a sodium chloride solution after treating the equivalent of 67 BVs of water following a 30 minute contact time; iii) coagulation of the IEX treated water (pre-used resin) and iv) coagulation of the raw water. Each experiment was conducted in duplicate.

For all IEX experiments a strong base anion exchange resin (Lewatit S5128) was used. This resin has been successfully tested in pilot and full-scale operation (Koreman and Galjaard, 2016; Metcalfe et al., 2015). A resin dose of 25 mL with a 30 min contact time was selected as it was representative of the conditions used in the full scale process (Finkbeiner et al., 2018). Jar tests were carried out using both virgin and pre-used IEX resin. Virgin or pre-used resin was rinsed with DI (deionised) water (10-20x resin volume (RV)) and then stirred in 20 RV of DI water (150 rpm, 10 min). Subsequently the resin was converted fully to the chloride form by stirring (150 rpm, 30 min) in 20 RV sodium chloride solution (40 g L^{-1}). The supernatant was removed and the resin was rinsed with 20 RV DI water and cleaned by a washing step using 20 RV DI water, stirred for 30 min (150 rpm).

The regenerated resin was filled in a measuring cylinder and the volume was adjusted to 50 mL after the resin had settled. The resin was transferred into a beaker and excess water was removed by decanting or using a syringe. A raw water volume of 2 L was added to the resin and the suspension stirred for 15 min (150 rpm). The resin was then settled, and treated water was decanted and collected for subsequent

coagulation testing and analysis. This protocol was carried out in duplicate seven times to generate a total volume of 28 L of IEX treated water in order to produce sufficient volume for analysis and subsequent experiments (coagulation).

In coagulation jar tests (Phipps and Bird PB900, Virginia, USA), 1 L of raw or IEX treated water was used, following a similar protocol to Sharp et al (2006b). A predetermined volume of acid (HCl, 0.1 N) or base (NaOH 0.1 N) and polyaluminium chloride were added during the rapid mixing stage (250 rpm, 60 s). The slow mixing period was 20 min (40 rpm), and flocs were allowed to settle for 30 min. The optimum coagulant dose and pH (5.8) were determined by UV absorbance (UVA) and zeta potential measurements after the slow mixing stage from preliminary experiments, giving an aluminium concentration of 3.3 to 6.4 mg L^{-1} in raw and 0.4 to 1.3 mg L^{-1} in IEX treated water. The volume of three jar tests were combined for analysis.

2.2. Analysis

Samples were filtered (0.45 µm) and analysed for DOC, UVA_{254}, doc fractionation, liquid chromatography with organic carbon detection (LC-OCD) and a UV detector (LC-UVD), and THM-/HAA-FP. Charge measurements were carried out on unfiltered water to ensure that a zeta potential measurement could be made. A spectrophotometer (DR6000, Hach Lange, Germany) was utilised to measure UVA_{254} and a TOC analyser was used to determine DOC concentrations in duplicate (Shimadzu TOC-L). Tap water spiked with 8 mg L^{-1} potassium hydrogen phthalate and 5 mg L^{-1} calcium carbonate was used for quality control tests with a precision target of 5%.

To fractionate the DOC by their hydrophobicity, the samples were acidified and passed sequentially through XAD7 and XAD4 resin columns, which retain the hydrophobic

(HPO) and transphilic (TPI) fraction, respectively (Finkbeiner et al., 2018). The effluent from the second column was collected as the hydrophilic (HPI) fraction. Both columns were eluted with a sodium hydroxide solution (0.1 N) and analysed for DOC after acidification.

Charge measurement wes carried out in triplicate on a Zetasizer equipped with an autotitrator (Malvern Nano Series, Worcestershire, UK). A sample volume of 15 mL was adjusted to pH 7 and poly(diallyldimethylammonium chloride) (PDADMAC) (Sigma-Aldrich, Dorset, UK) was added incrementally to obtain concentrations between 0 and 30 mg L^{-1}. The sample was circulated to a connected folded capillary cell in the Zetasizer where the zeta potential was measured after each addition. The required concentration of PDADMAC to reach the point of zero charge was used to calculate the charge load of the sample based on the charge density of 6.2 meq/L for PDADMAC. Charge density (CD) of the sample was determined by normalising the charge load to the DOC concentration. The molecular weight profile of the organic compounds was established using LC-OCD and LC-UVD (Model 9, DOC Labor, Karlsruhe, Germany) using an enhanced method of the procedure described by Huber et al. (2011). See Supporting Information for full method description.

For analysis of haloacetic acids (HAA) and trihalomethanes (THM), samples were diluted to 1 mg L^{-1} DOC and chlorinated with NaOCl to five times the DOC concentration. The samples were incubated for 7 days at 25°C, before they were quenched with thiosulfate. HAAs were extracted with MTBE and methylated at 50°C with acidic methanol. The neutralised MTBE extract was reduced to 0.5 mL and the concentration of monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) were determined with gas chromatography mass spectrometer (GC-MS). A

headspace method was used to quantify the four THMs (chloroform, bromoform, bromodichloromethane and dibromochloromethane) on a GC-MS.

The total resin capacity was measured according to a modified procedure described by Harland (1994). Resin was converted to the chloride form using NaCl (100 g L^{-1}), following the regeneration steps for resin preparation. A volume of 10 mL resin was stirred in 500 mL of a sodium nitrate solution (1%) for 15 min (150 rpm). The displaced chloride was determined using argentometric titration with potassium chromate indicator to provide the total capacity of the resin.

3. Results and discussion

3.1. Source dependent DOC removal

The DOC of water A, B and C were 11.4±0.2, 7.6±0.1 and 8.4±0.0 mg L^{-1}, which were relatively high compared to the average concentration of 6.6±0.5 mg L^{-1} reported for raw waters across Scotland (Valdivia-Garcia et al., 2016). The high specific UVA (SUVA) values for all waters (between 4.3±0.0 and 5.6±0.4 L mg^{-1} m^{-1}) was indicative of the presence of aromatic compounds derived from humic substances of allochthonous origin, a reflection of the high proportion of organic rich soils present in the catchments.

DOC concentrations in the investigated waters were reduced by between 67 and 79%, equating to absolute removal ranging from 5.9±0.1 to 7.7±0.3 mg L^{-1}, using pre-used resin at a concentration of 25 mL L^{-1} (Supporting Information, Table S1). This removal of 0.24 to 0.31 mg_{DOC} mL_{resin}^{-1} was higher than the removal seen for other waters treated by the same IEX resin at comparable initial DOC concentrations. For example, from a low land river source 8 to 32% (up to 2.3 mg L^{-1}) was removed for raw water DOC concentrations of between 7 and 10 mg L^{-1} using 25 mL L^{-1} resin equating to 0.09 mg_{DOC} mL_{resin}^{-1} (Finkbeiner et al., 2018). Metcalfe et al. (2015) observed a DOC reduction of 38 and 65% (2.3 and 2.6 mg L^{-1}) from an upland and lowland river with initial DOC concentrations of 6 and 4 mg L^{-1}, respectively, at a resin concentration of 18 mL L^{-1} (0.13 – 0.14 mg_{DOC} mL_{resin}^{-1}). Overall, this indicates that the waters selected for this study were particularly amenable to IEX pre-treatment. The use of virgin resin increased the DOC removal to between 86 and 89%. For water A the removed DOC was 2.4±0.4 mg L^{-1} higher than for the pre-used IEX, while this was 0.6±0.1 mg L^{-1} for sources B and C.

Coagulation removed less DOC from raw water than IEX treatment with pre-used and virgin media for water B and C. For example, the residual DOC after treatment using pre-used resin, virgin resin and coagulation was 1.8±0.0, 1.1±0.1 and 2.3±0.1 mg L^{-1} in water C. Water A, however had a residual of 3.7±0.2 and 1.5±0.0 mg L^{-1} for IEX and coagulation treatment, respectively, whereas virgin resin achieved a higher removal resulting in a DOC concentration of 1.3±0.1mg L^{-1}. IEX combined with coagulation delivered the lowest DOC concentration for all waters with values between 0.6 and 0.7 mg L^{-1} equating to a total DOC removal of 91 to 94%. This was in agreement with previous studies in which the synergistic effect of the combination of the two treatments was demonstrated (Drikas et al., 2011; Humbert et al., 2007; Metcalfe et al., 2015). Additionally, IEX pre-treated water required a lower coagulant dose, with a reduction of 39, 42 and 24% Al^{3+} mg_{DOC}^{-1} for water A, B and C, respectively, consistent with other research (Grefte et al., 2013; Kitis et al., 2007).

3.2. The removal of fractions of differing hydrophobicity

XAD resin fractionation was used to distinguish hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) character of the organic compounds. In the raw water, the proportion of the HPO, TPI and HPI fraction were 62, 25 and 13% in water A, respectively (Fig. 1). Although the HPO was the dominant fraction, water B and C contained proportionally more transphilic and hydrophilic NOM, with 51, 28, 21% and 52, 30, 18% for HPO, TPI and HPI respectively. This is in agreement with previous studies which has shown the HPO to be the largest fraction in raw water (Golea et al., 2017; Sharp et al., 2006a).

[Figure 1 about here].

In each water, the concentration of all XAD fractions were reduced following treatment by pre-used IEX. The proportions of the XAD fractions after IEX in water A did not change substantially in comparison to the raw water, with values of 64, 20 and 16% for the HPO, TPI and HPI, respectively. This was in accordance with observations seen in previous research (Finkbeiner et al., 2018). However, for water B and C, IEX treatment changed the ratio considerably, with a shift towards more hydrophilic NOM; the proportion of the HPI fraction was 50 and 45% in treated water B and C, respectively. However, the proportion of each XAD fraction in the removed NOM by IEX was similar for all of the waters, regardless of the initial water composition: ranging from 57-61% for HPO; 27-31% for TPI; and 12-14% for HPI (Fig. S1).

When virgin resin was used, higher overall removal was observed for each XAD fraction in the three waters. The HPO, TPI and HPI fraction of water A were reduced by 93, 90 and 75% (Fig. 1) compared to 63, 71 and 59% for the pre-used resin. Similar trends were seen for water B and C, although the differences between virgin and pre-used resin were not as prominent as seen for water A. The lower relative removal of the DOC in water A was attributed to the high HPO fraction (6.28 mg L^{-1}), which was 1.5-1.7 times as high as in the other waters.

After coagulation alone the proportion of XAD fractions in the waters were 38-41% HPO, 24-28% TPI and 34-36% HPI, indicating a preferential removal of the HPO fraction. Evaluation of the removed DOC by coagulation of IEX pre-treated water A showed higher removal of the HPO fraction, while the HPI fraction was removed by only 35%. On the other hand, the relative reduction of the DOC in water B and C, was similar for all three XAD fractions (HPO 60-61%; TPI 63-66%; HPI 53-55%). In these cases, the HPI represented the highest proportion of the DOC in the removed organic matter. The high ratio of the HPI in the removed DOC was explained by the low

concentration of the HPO fraction after IEX treatment; 0.4 to 0.5 mg L^{-1} in water B and C, respectively. This enabled the coagulant to target other organic compounds that would normally be less well removed, a phenomena seen before in IEX treated water prior to coagulation (Metcalfe et al., 2015). These results align with that seen previously, where some researchers have seen improved removal of HPO (Sharp et al., 2006a; Matailanen et al., 2010), while others have seen no significant change in the removal of organic fractions of different hydrophobicity (Lefebvre and Croue, 1995).

3.3. Influence of the size of organic compounds on their removal

The LC-OCD traces of all three raw waters (Fig. 2) followed the same pattern with a dominant second peak (P2) at a retention time of 19 min, previously described as containing aromatic compounds in the region of 1 kDa (Huber et al., 2011). The proportion of chromatographed DOC (CDOC) in this peak increased with higher DOC values. For example, the peak was 77% of the CDOC for water A (total DOC = 11.4 mg L^{-1}), while for water B and C which had DOC concentrations of 7.6 and 8.4 mg L^{-1}, this peak was 68 and 69% of the CDOC. The first peak (P1) at 13 min, containing the largest MW compounds of a biopolymeric nature, had a low CDOC proportion (3.4%) for water A compared to proportions of 9.5% for water B and 8.6% for water C, with measured CDOC values of 0.29, 0.74 and 0.78 mg L^{-1}, respectively.

[Figure 2 about here]

The lowest reduction by IEX was seen for the high MW P1 compounds due to size exclusion of this fraction (Mergen et al., 2008). The removal for water A, B and C was 39, 34 and 9%, respectively. This fraction made up the majority of the residual CDOC in water B and C after IEX, which was 0.49 and 0.71 mg L^{-1} (equating to 36 and 38%

of the CDOC). On the other hand, the highest reduction of all size fractions by IEX was seen for P2. For example in water B, the CDOC of this fraction was reduced by 4.9 mg L^{-1} to a residual of 0.37 mg L^{-1}. The removal was dependent on the initial concentration of this peak and was greater for water B (93%) and C (91%), while in water A the reduction was 82%. However, when using virgin resin removal of P2 increased to 94-96% for all waters. These observations indicated that there was a limitation in the treatability of this size fraction. This can be linked to the type of organics found in this peak and how they occupy IEX exchange sites. P2 contains substances such as humic (HA) and fulvic acids (FA) (Huber et al., 2011). While such compounds are attracted to the exchange sites of the resin, the size of these molecules can be limiting. The hydrodynamic radii of these molecules have been determined to be >1.1 nm, with aggregated molecules having diameters in the micro meter range (Kawahigashi et al., 2011; Klučáková, 2018). Size exclusion phenomena can therefore occur as the microporous gel-type resins, with pore sizes typically < 2-4 nm can restrict compounds such as HA and FA to the exterior regions of the resin (Bhandari et al., 2016; Harland, 1994). Therefore, in the case of pre-used resin, where a degree of fouling has occurred, the more limited available exchange sites on the surface of the resin cannot satisfy the removal of these compounds, particularly for water sources that contain high loadings of NOM, such as in water A. Support for this hypothesis comes from the results observed for the virgin resin, where much higher removal was seen due to the absence of irreversibly bound NOM on easy to access exchange sites.

Within the polydisperse P2 fraction, generally a preference towards removal of smaller molecules was seen for IEX. This was demonstrated by an increase in the number-average molecular weight (M_n) of the P2 peak after IEX by up to 67% (Table S2). For

example, water A showed a M_n of 630 g mol^{-1} for raw water which increased to 903 and 837 g mol^{-1} for treated water by pre-used and virgin resin, respectively. This was consistent with previous reports showing greater removal of lower MW organics by IEX, due to increased diffusion (Bazri and Mohseni, 2016; Cornelissen et al., 2008).

For the three waters, the third (P3) peak eluting at 22 min had similar CDOC ranging from 0.83 to 0.94 mg L^{-1} equating to 9.7 to 10.9% of the CDOC. The fourth peak (P4) at 25 min was the least evident fraction, and was 1.9 to 3.2% of the CDOC. Compounds eluting after 29 min constituted the final fraction (P5), for which the proportions were between 8.2 and 8.9%. The lower MW compounds (P3-P5) were well removed by IEX (59-73%), however to a lesser extent than P2. Water A had the lowest removal of P3 and P4. This was attributed to the higher concentration of compounds in the larger P2 size fraction causing pore blockage, which hinders diffusion of LMW compounds into the pores (Gönder et al., 2006)

Coagulation proved to be efficient at removing size fraction P1 (83-88%) and P2 (86-94%) for all three waters. The lower MW fractions, P3 and P4, had a lower removal, especially for water C (Fig. 2c). These results were consistent with results showing the amenability of higher MW fractions, and limitations in the removal of LMW compounds, by coagulation (Drikas et al., 2003). As previously seen, IEX combined with coagulation was efficient in reducing DOC (Fig. 2 and Fig. S2). For example, the removal of P1 and P2 in water B was 94 and 98%, respectively, representing a slight improvement by IEX&Coagulation compared to coagulation alone. For the LMW fractions P3-P5, there was a generally higher increase in the removal than for P1 and P2 when the combination treatment was used.

3.4. The importance of charge load and density

In the IEX process, the charge of the organic compounds is the main driving force for their removal where exchange of anions has been seen to be enhanced for molecules with a higher charge density (Bazri and Mohseni, 2016; Boyer and Singer, 2008). The raw waters exhibited charge loads (CL) ranging from 53 μeq L^{-1} for water C, 73 μeq L^{-1} for water B, to 120 μeq L^{-1} for water A (Fig. 3). Water A and B had a high charge density (CD) of 10.5 and 9.7 meq g_{DOC}^{-1}, respectively. For these high CD waters, elevated absolute CL removal by IEX of 93 and 70 μeq L^{-1} was observed. This was 4.9 and 3.7 μeq meq_{resin}^{-1} based on a measured resin capacity for regenerated resin of 0.76 meq mL^{-1}. This is in the range that has been reported by Mergen (2008), who found values ranging from 0.3 to 5.0 μeq meq_{resin}^{-1} for different raw waters (CD 0.3 to 6.4 meq g_{DOC}^{-1}) treated by MIEX (capacity 0.52 meq mL^{-1}) resin. However, the residual CL was quite different in water A (26 μeq L^{-1}) compared to water B (3 μeq L^{-1}), equating to a CD of 7.1 and 1.9 meq g_{DOC}^{-1}, respectively. The high residual CD in water A supports the view that there was a limitation in the accessible exchange sites on the pre-used resin when treating this water type. Competition effects between NOM and inorganic anions (bicarbonate, sulphate and nitrate) were not thought to explain the high residual CD due to their relatively low concentration.

[Figure 3 about here]

The lowest CD was seen for the NOM in raw water C at 6.2 meq g_{DOC}^{-1}, which reduced to a CD of 3.3 meq g_{DOC}^{-1} after IEX treatment. This indicates either the presence of organics of overall lower valency or a higher proportion of un- or low charged molecules in water C. For this water the CL removal was 47 μeq L^{-1} with a residual of 6 μeq L^{-1}. It is important to note that in all cases the removal of charge was not

consistent with the relative DOC removal from the water, which was lowest for water A and similar for water B and C (Table S1).

When virgin resin was applied, a similar CL removal as for pre-used resin was observed for water B and C, for which CL was reduced by 71 and 49 μeq L^{-1}, resulting in CD of 2.1 and 2.9 meq g_{DOC}^{-1}, respectively. The CL in water B was very well removed by IEX. Both pre-used and virgin IEX reduced the CL by 96 and 97%, respectively. Water C, which had the lowest CD before treatment, experienced a CL removal of 94% by virgin resin compared to 89% by pre-used resin. A much larger difference, however, was observed for water A. The CL of this water was lowered by 117 μeq L^{-1} or 98%, giving a CD of 1.9 meq g_{DOC}^{-1} for the virgin resin, compared to a reduction of 93 μeq L^{-1} or 78% by pre-used IEX. The relative removal of CD and CL followed the order of A>B>C while the relative DOC removal by virgin resin was A>B≈C.

The ratio of the removed CL for pre-used and virgin resin was 0.80 in water A, compared to water B and C that had charge removal ratios close to unity (0.99 and 0.95, respectively). This implies some limitations in the removal of organic compounds from water A. However, in all cases the exchange capacity of the resin was not reached in the treated waters, with only a small proportion of the exchange capacity of the resin being utilised which has been found to be up to 1.5% of the total capacity (Finkbeiner et al., 2018; Mergen, 2008). The total capacity of the resin, estimated by titration of the resin against silver nitrate, was 0.76 meq mL^{-1} for regenerated resin, 0.27 meq mL^{-1} for unregenerated resin and 1.15 meq mL^{-1} for virgin resin, equating to 6.25 to 28.75 meq at the resin concentration of 25 mL L^{-1}. These results were consistent with the view that much of the removal of organic matter was limited to the surface (or near to) of the resin, on easily accessible exchange sites. For water with

lower NOM loads (such as water B and C), this was less important as the near-surface exchange sites could meet the demand of the water (hence the small or little differences in the removal between virgin and pre-used resin). For waters with high loads of charged NOM, reduction in removal was likely to occur as a result of reduction in available exchange sites.

3.5. Treatability evaluation of the different waters by IEX

Considering individual NOM properties provided only a partial answer to fully understand organic matter removal by IEX, as interactions with the resin was influenced by all parameters. As a result, evaluating the water treatability based on one of the characteristics can be misleading, and is illustrated below by considering all factors together.

The HPO was the fraction that was best removed, although the ratio of the XAD fractions removed was equal for the different waters. While this was as a result of selectivity that favoured exchange of HPO over HPI compounds, consideration of the charge provides more complete understanding. A positive correlation between CD and the proportion of the HPO fraction for raw and treated water supported the view that a high proportion of charged compounds reside in this XAD fraction (Table S3, $r = 0.39$, $p < 0.05$). This was supported by previous research that has identified high CD resides in the HPO fraction with minimum charge in the HPI fraction for a range of different waters (Sharp et al., 2006b).

Without the knowledge of the charge composition of the water, the large difference in removal of the HPO fraction from water A between the virgin and pre-used resin could be interpreted as a lack of resin capacity. However, as the measurements of the total capacity and the charge load of the water showed, this was not the case. The results

of the LC-OCD measurements provided further information, indicating that the high concentration of P2 led to blocking of pores by molecules that were too large to diffuse through the pores and blocking of surface sites by molecules which cover exchange sites. A high concentration of such compounds inhibits removal of large molecules, especially for pre-used resin where irreversible blinding is more likely to be seen. This limited the ability of the resin to remove NOM from high DOC waters. This was consistent with research showing a decline in removal efficiency when resins are used in multiple cycles (Bazri and Mohseni, 2016; Gönder et al., 2006; Harland, 1994; Mergen et al., 2008). The high SUVA and high proportion of the HPO fraction in the investigated waters, particularly water source A, indicates that the presence of this type of compound can lead to loss of capacity and removal efficiency.

If removal was explained solely by size exclusion of HMW compounds, a higher removal for molecules of decreasing MW would be expected. However, the results showed that P3 to P5 were removed to a lesser extent than P2 even though these had a lower MW and should be less affected by size exclusion. This was attributed to the higher CD of the organic compounds in the P2 size fraction as there was a positive correlation between water CD and the proportion of P2 present in the water (Table S3, $r = 0.43$, $p < 0.05$), a relationship not seen for other size fractions. Furthermore, the lowest relative removal and the highest residual in this size fraction (water A) coincided with the highest residual CD (water A).

Charge measurements considered in isolation showed an increased CL removal when the CD was higher and an improved CD reduction when virgin resin was used. However, the limited removal observed for a high CD water with used resin could not be explained through charge alone. When considering all three parameters the results show that the removal was limited due to surface and pore blockage by a fraction of

hydrophobic and medium molecular weight compounds (P2) of high charge. These results show that it is paramount to characterise the charge, hydrophobicity and molecular weight distribution simultaneously (Table S4).

3.6. Disinfection byproduct formation potential (DBP-FP)

For water A, which had a particularly high specific HAA-FP, no selective precursor removal by IEX was observed with specific HAA-FP of 230 and 221 mg g_{DOC}^{-1} for untreated and treated water, respectively (Fig. 4). Similar figures for the specific THM-FP were 139 mg g_{DOC}^{-1}, both before and after treatment. However, for water B and C, a reduction of 46 and 49 mg g_{DOC}^{-1} was seen for specific THM-FP for raw water values of 103 and 124 mg g_{DOC}^{-1}, respectively. A decrease in specific HAA-FP by IEX was only seen in water B, where a reduction of 54 mg g_{DOC}^{-1} was observed. These results were consistent with the literature, where some water sources have shown a decrease in DBP-FP by IEX, while others have seen no change (Finkbeiner et al., 2018; Metcalfe et al., 2015). Coagulation reduced the specific HAA- and specific THM-FP to values ranging from 63 to 75 mg g_{DOC}^{-1} and 76 to 80 mg g_{DOC}^{-1}, respectively. Treatment with IEX&Coagulation resulted in the largest reduction of the specific DBP-FP attributed to the removal of charged, LMW compounds by IEX and hence improved precursor removal by subsequent coagulation (Finkbeiner et al., 2018). Water A, B and C had specific HAA-FP of 44, 34 and 30 mg g_{DOC}^{-1} while the specific THM-FP was 52, 52 and 46 mg g_{DOC}^{-1}.

[Figure 4 about here]

DCAA and TCAA were responsible for 95-100% of the specific HAA-FP. The ratio of DCAA:TCAA was similar between the raw waters, ranging between 0.40 to 0.47 (Table S5). IEX treatment with pre-used and virgin resin changed the DCAA:TCAA ratio

slightly (0.41 to 0.75). After coagulation alone ratios between 0.82 and 0.95 were observed. The lower formation of TCAA compared to DCAA after coagulation has been seen previously and is linked to the removal of precursors with higher hydrophobicity (Bond et al., 2010). When IEX and coagulation was applied, ratios between 1.07 and 1.42 for the three water samples were observed. This was explained by the preferential removal of TCAA precursors by the combined treatment as well as the lower hydrophobicity in the treated water. Furthermore, a relationship between the DCAA:TCAA ratio and the proportion of the size fractions was found. Larger proportions of higher MW compounds (P1 and P2) were negatively correlated to the DCAA:TCAA ratio, while P3-P5 showed a positive correlation (Fig. S3). This shows that smaller MW organic compounds formed higher levels of DCAA. This is a result consistent with other research that has shown the lowest LMW fraction (<0.5 kDa) resulted in the highest DCAA (Hua and Reckhow, 2007).

The specific DBP-FP is related to the molecular structure of organic compounds, but readily measurable physicochemical properties can be used to correlate with the formation potential of important DBPs when comparing similar source waters (Fig. 5 and Fig. S4). The THMs and HAAs have been shown to represent approximately 50% of the total organic halide concentration in chlorinated water and up to 80% of the species that can be measured (Losty et al., 2018). In order to understand the relationship between the water quality, IEX treatment and DBPs of the investigated raw waters, the CD, P2 and HPO fraction of the different treatment steps were correlated with the sum of the specific THM- and specific HAA-FP (Fig. 5). Focus was placed on the P2 organic compounds due to their importance in controlling removal: relationships for P1, P3, P4 and P5 are presented in Fig S.4. The HPO fraction in water correlated positively with the specific DBP-FP in a linear manner when values

of all waters and treatment stages were considered (r^2 = 0.78, Fig. 5a). Water A showed the largest reduction of the HPO fraction from 62 to 25% and for the specific DBP-FP from 368 to 64 mg g_{DOC}^{-1} in raw water and after IEX&Coagulation treatment, respectively.

[Figure 5 about here]

Of note, the specific DBP-FP concentrations following coagulation were clustered together for water with and without IEX pre-treatment (δ and ε). To illustrate, after the treatment by coagulation alone the HPO fraction was between 37 and 40% with corresponding specific DBP-FPs ranging from 143 to 151 mg g_{DOC}^{-1}. In contrast, when water was treated by IEX using pre-used or virgin resin (β and γ) a larger variation was seen. For example, a HPO fraction of 28 and 30% for IEX treated water resulted in specific DBP-FPs of 131 and 247 meq g_{DOC}^{-1}, in water B and C, respectively. This implies that the molecules that were removed by IEX vary in terms of reactivity with chlorine for each water, while for treatment involving coagulation precursor removal was more consistent.

As the CD increased, there was an increase in the total specific DBP-FP, however, the relationship was not linear and was different for each water source (Fig. 5b). Even though raw waters generally had a higher specific DBP-FP before treatment, it is important to recognise that initially high CD waters did not necessarily correlate to high specific DBP-FP. For example, water A with a CD of 10.5 meq g_{DOC}^{-1} had a specific DBP-FP of 368 mg g_{DOC}^{-1}, whereas water B with a similar CD had a considerable lower specific DBP-FP of 230 mg g_{DOC}^{-1}. From different initial formation potentials, a reduction of the CD by IEX generally corresponded to a lower specific DBP-FP. The degree of the reduction was source water dependent and varied with the resin

condition. For example, water B was observed to show a reduction of 81% of the CD and 43% of the specific DBP-FP by IEX. On the other hand, CD and specific DBP-FP reduction by IEX were 32 and 2% for water A. Virgin resin increased the reduction of the CD and the specific DBP-FP to 82% and 63% for this water. Again a clustering was observed when coagulation was used alone or combined with IEX. In these cases, the CD was almost completely removed (< 0.3 meq g_{DOC}^{-1}) by coagulation and IEX&Coagulation with specific DBP-FP from 143 to 150 mg g_{DOC}^{-1} and 76 to 93 mg g_{DOC}^{-1}, respectively. The difference between the specific DBP-FP for coagulation with and without IEX pre-treatment was therefore linked to the removal of compounds of low charge, some of which are known to be high DBP formers (Bond et al., 2010).

As the proportion of the P2 size fraction increased, the DBP-FP increased (Fig. 5c). In water B, for example, the raw water showed a specific DBP-FP of 230 mg g_{DOC}^{-1} for a P2 proportion of 68%, which was reduced to 142 mg g_{DOC}^{-1} at 28% P2. A decline in the specific DBP-FP was seen when the CD, and HPO and P2 fraction were reduced, showing that the reactive precursors are predominantly of this character.

4. Conclusions

Three different source waters from catchment areas with organic rich soils were treated with IEX, coagulation and the combined treatment to compare their treatability. The following conclusions were drawn:

- Higher removal of the HPO was attributed to the resin having a higher affinity to hydrophobic compounds as well as there being a higher distribution of charged compounds in in the HPO fraction

- NOM in the size fraction P2 exerted the strongest influence on removal between the different waters and was associated with the charge of the organic compounds present in this fraction.
- A higher CD in raw water resulted in higher CL removal. However, CL reduction was not close to the available exchange capacity of the resin indicating that exchange was limited to the sites close to the surface of the resin.
- The raw water composition exhibited a greater influence on removal when pre-used resin was applied, compared to virgin resin, due to resin blinding. This in turn led to pore and surface blockage by molecules of the P2 fraction that influenced the removal.
- The combined treatment was able to reduce the DOC drastically and minimise the specific DBP-FP to values that were 42-53% and 32-42% below those obtained for coagulation for specific HAA-FP and specific THM-FP, respectively.

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Table 1: Water composition and catchment details

Water	Catchment area	Date	DOC (mg L^{-1})	SUVA (L mg^{-1} m^{-1})	pH	NO_3^-	SO_4^{2-}	HCO_3^-
A	Mix of soils (more organic than mineral soils)	01/05/18	11.4	5.0	8.0	3.6	<0.2	38.5
B	Mix of soils (from organic rich to mineral soils)	12/06/18	7.6	4.3	7.1	1.4	2.5	15.0
C	100% organic rich soils (50:50 mix of moorland and forestry)	03/07/18	8.4	5.6*	6.5	<0.5	3.4	10.0

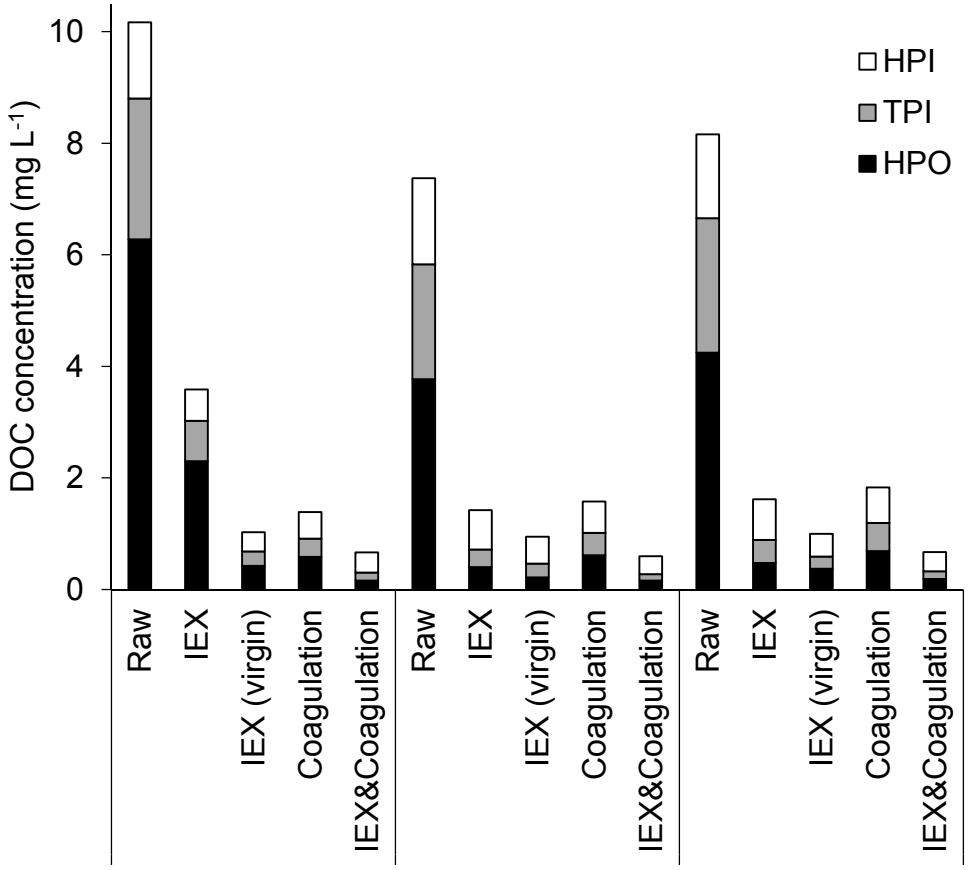

Fig. 1. Proportions of the different hydrophobicity fractions of the DOC for the different treatment steps; HPO = hydrophobic fraction, TPI = transphilic fraction, HPI = hydrophilic fraction, Raw = raw water, IEX = after ion exchange treatment using pre-used resin, IEX (virgin) = after ion exchange treatment using virgin resin, Coagulation = after treatment by coagulation, IEX&Coagulation = after treatment by IEX and subsequentially coagulation.

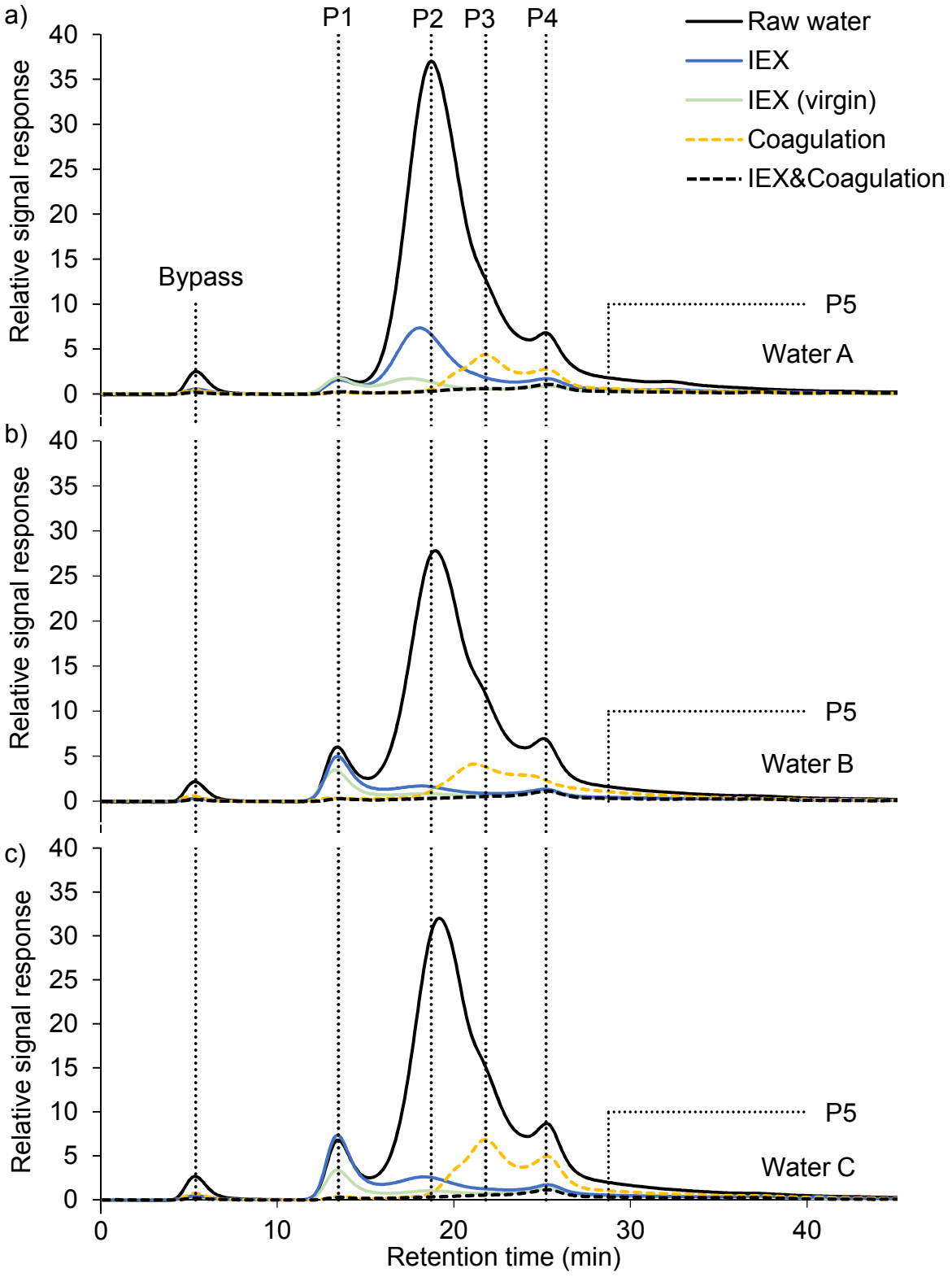

Fig. 2. LC-OCD traces for different waters and treatment stages; retention time of peak 1 (P1): 13 min, peak 2 (P2): 19 min, peak 3 (P3): 22 min, peak 4 (P4): 25 min, final fraction (P5): from 29 min; by-pass: detection of DOC from restricted flow that bypassed the column.

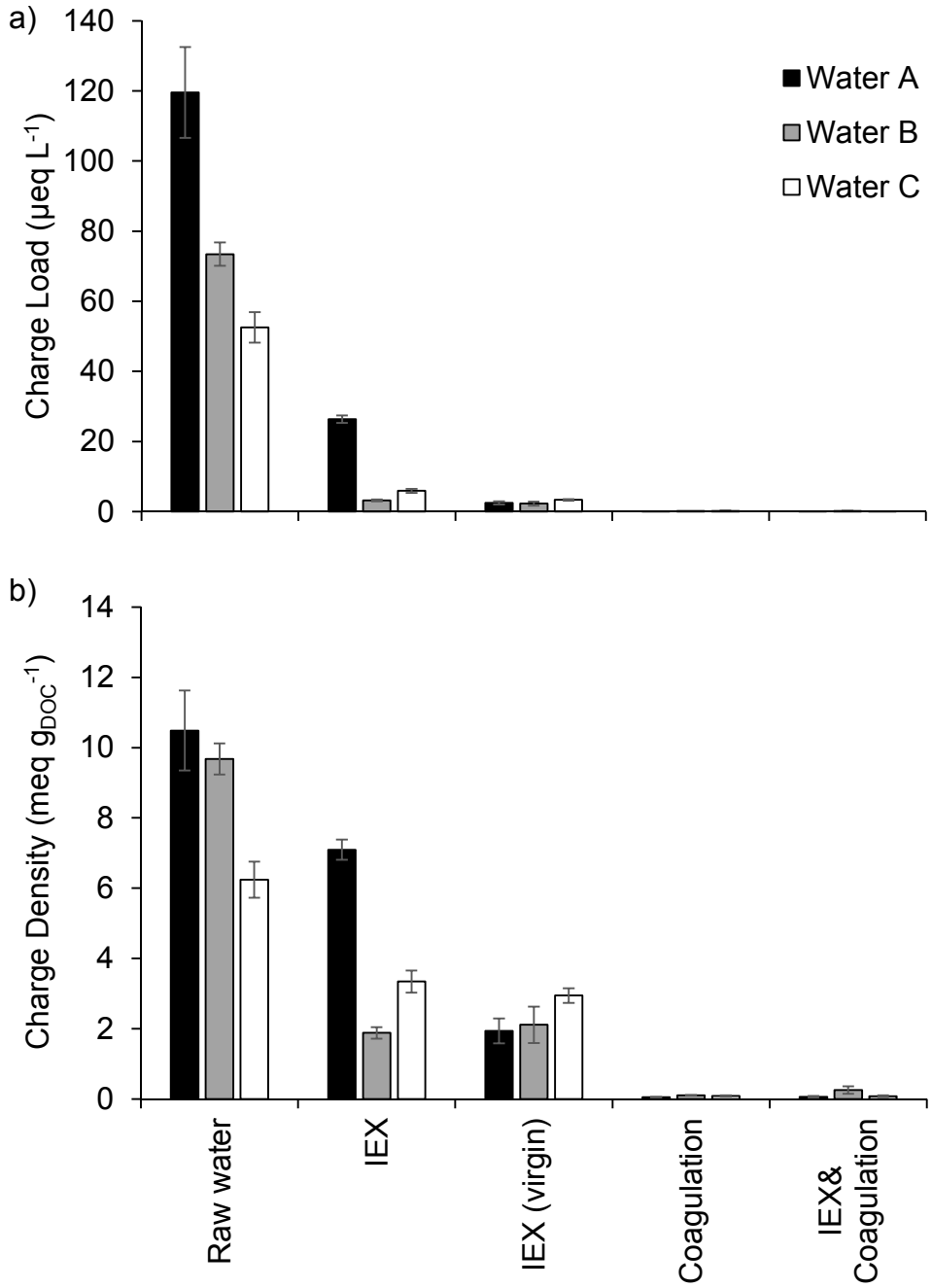

Fig. 3. Charge load (a) and density (b) of raw water and after the different treatment stages; Raw = raw water, IEX = after ion exchange treatment using pre-used resin, IEX (virgin) = after ion exchange treatment using virgin resin, Coagulation = after treatment by coagulation, IEX&Coagulation = after treatment by IEX and then coagulation.

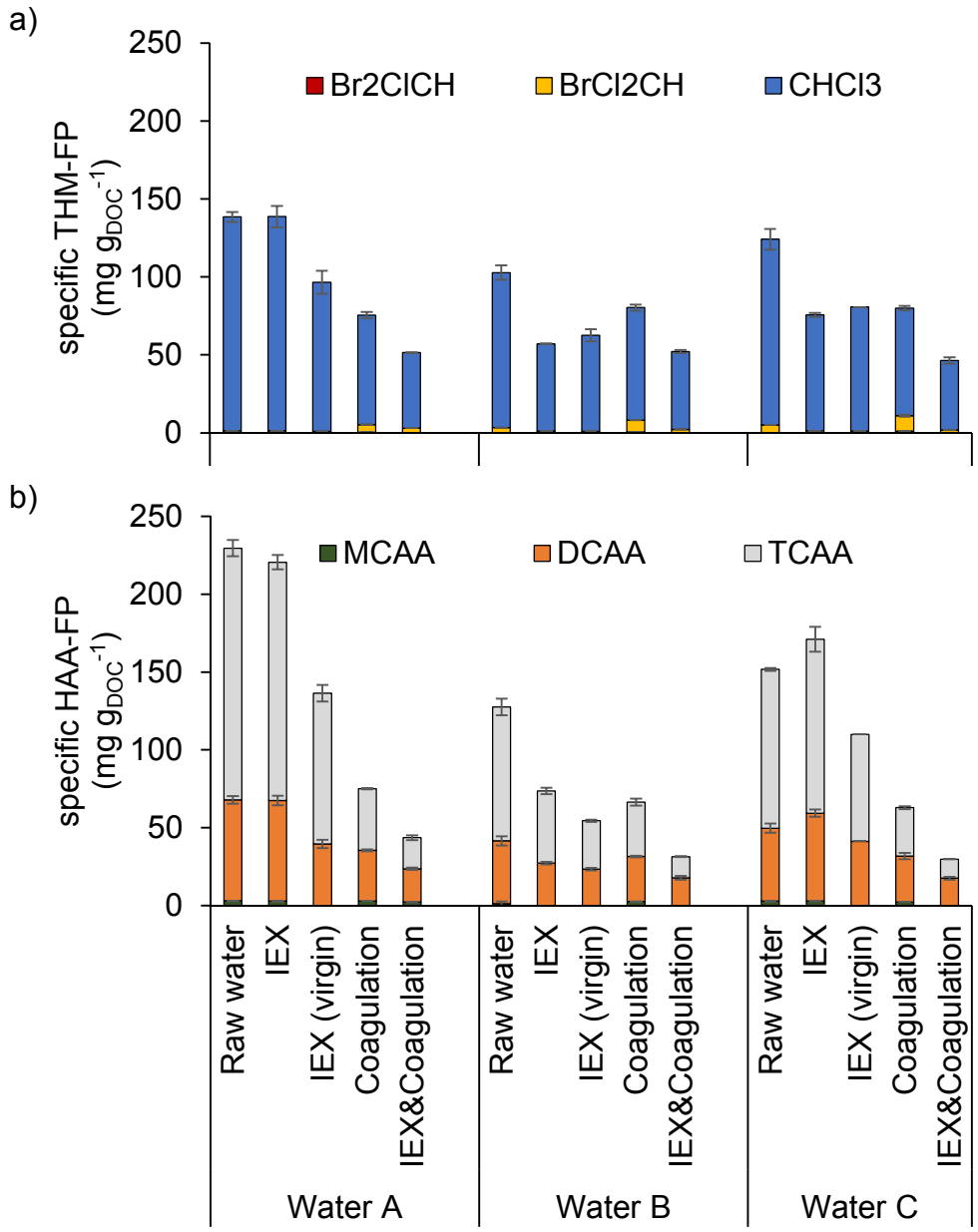

Fig. 4. Specific THM-FP (a) and specific HAA-FP (b) for raw waters and treatment methods of different source waters; CHCl3 = Chloroform, BrCl2CH = Bromodichloromethane, Br2ClCH = Chlorodibromomethane, MCAA = Monochloroaceticacid, DCAA = Dichloroaceticacid, TCAA = Trichloroaceticacid; Raw = raw water, IEX = after ion exchange treatment using pre-used resin, IEX (virgin) = after ion exchange treatment using virgin resin, Coagulation = after treatment by coagulation, IEX&Coagulation = after treatment by IEX and subsequentially coagulation.

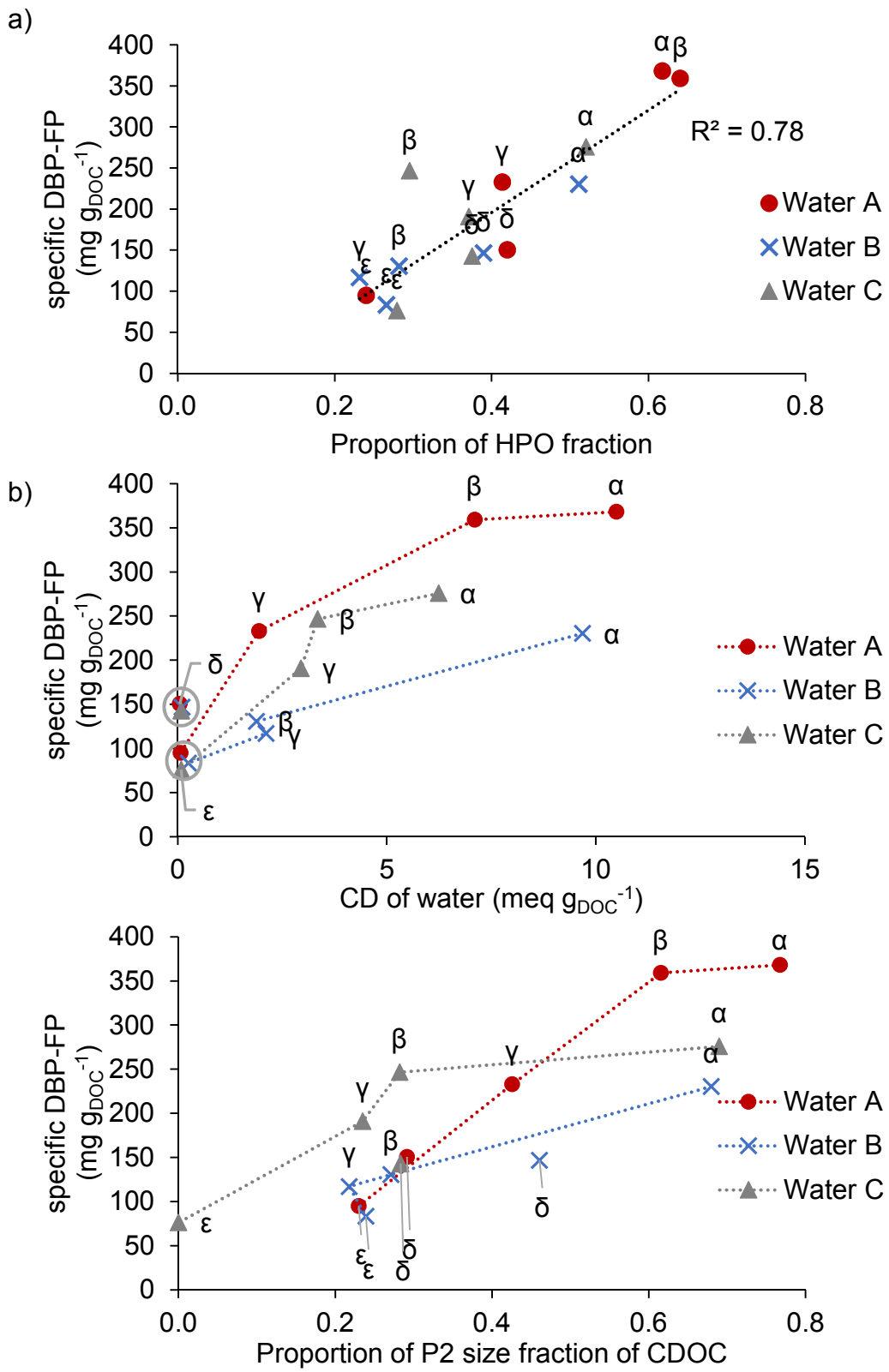

Fig. 5. Relationship between the specific DBP-FP and the water parameter a) HPO proportion, where r2 was calculated incorporating values of all waters, and b) CD, separated for the three waters; the different treatment stages are indicated by α = raw water, β = IEX, γ = IEX (virgin), δ = coagulation, ε = IEX&Coagulation.

Supporting Information

LC-OCD methodology

Samples for DOM fractions were filtered through 0.45 µm Polyethersulfone (PES) syringe filters and stored chilled (0-4 °C) in pre-combusted glass "TOC" vials until analysis, which occurred within 2 days of sample collection. LC-OCD-OND (organic nitrogen detection), allows ~1mL of whole water to be injected onto a size exclusion column (SEC; 2ml/min; HW50S, Tosoh, Japan) with a phosphate buffer (potassium dihydrogen phosphate 1.2 g/L plus 2g/L di-sodium hydrogen phosphate x 2 H_2O, pH 6.58) and separated into five "compound-group specific" NOM fractions: (i) biopolymers (P1; likely hydrophobic, high molecular weight, largely non-UV absorbing extracellular polymers); (ii) "humic substances" (P2; higher molecular weight, UV absorbing); (iii) "building blocks" (P3; lower molecular weight, UV absorbing humics); (iv) low molecular weight acids (P4); and (v) low molecular weight "neutrals" (P5; hydro- or amphi- philic, non-UV absorbing). The resulting fractions are identified using unique detectors for organic carbon, UV-amenable carbon and organic nitrogen (Huber et al., 2011). All peaks were identified and quantified with bespoke software (Labview, 2013) normalized to International Humic Substances Society humic and fulvic acid standards. The samples were analysed in duplicate. The reported peak area for each fraction and the LC-OCD profiles were obtained from average values of duplicates and replicates.

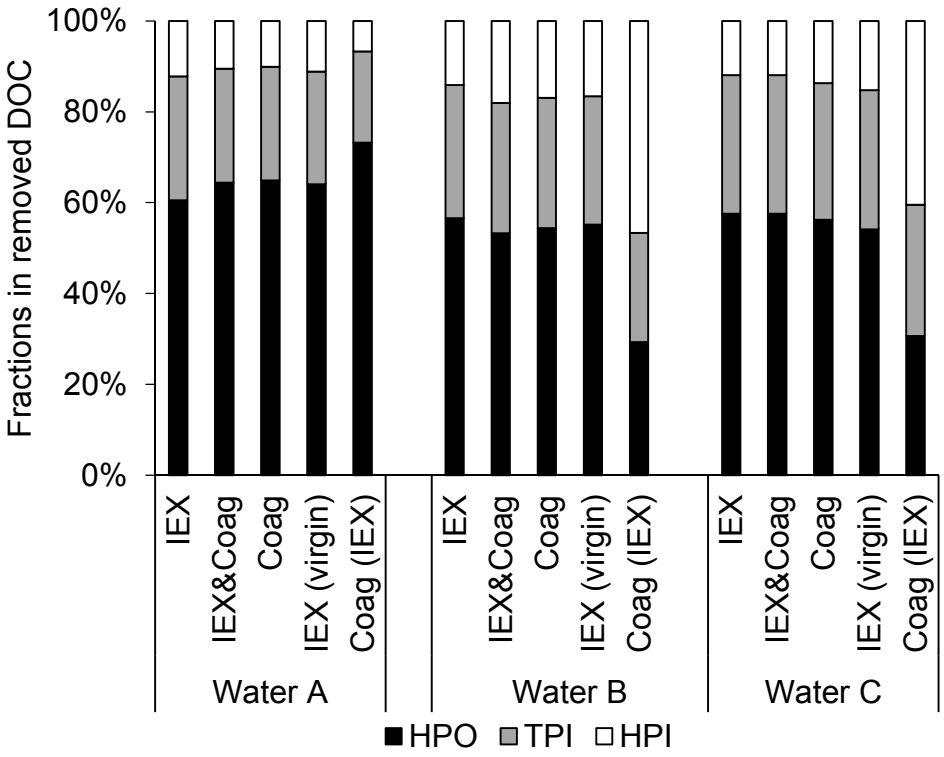

Fig S1: *Proportions of the different hydrophobicity fractions in the removed DOC for the different treatment steps.*

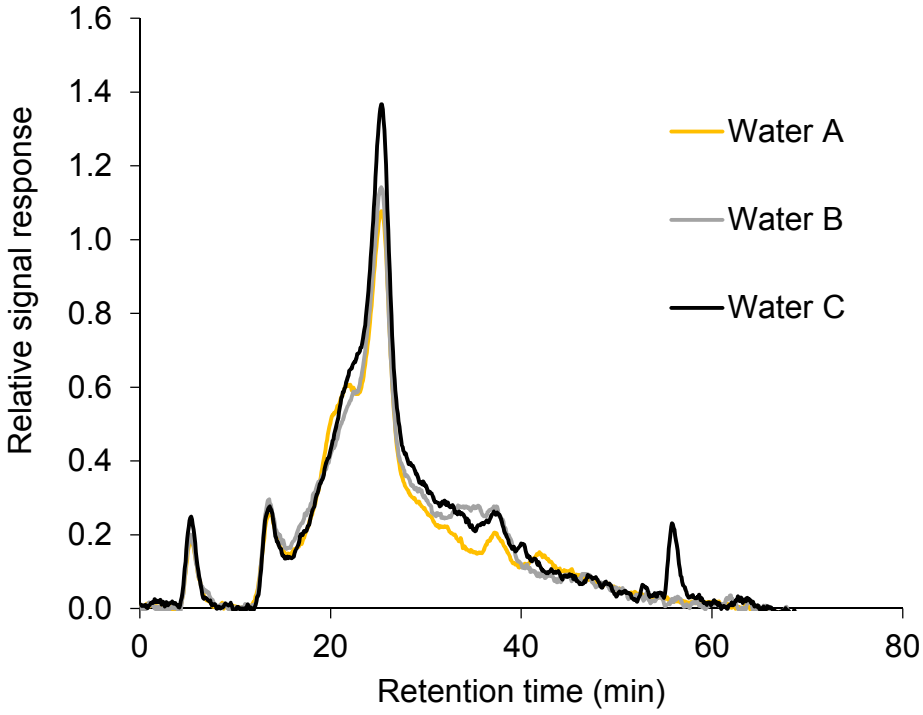

Fig S2: *LC-OCD traces for different waters after IEX&Coagulation treatment.*

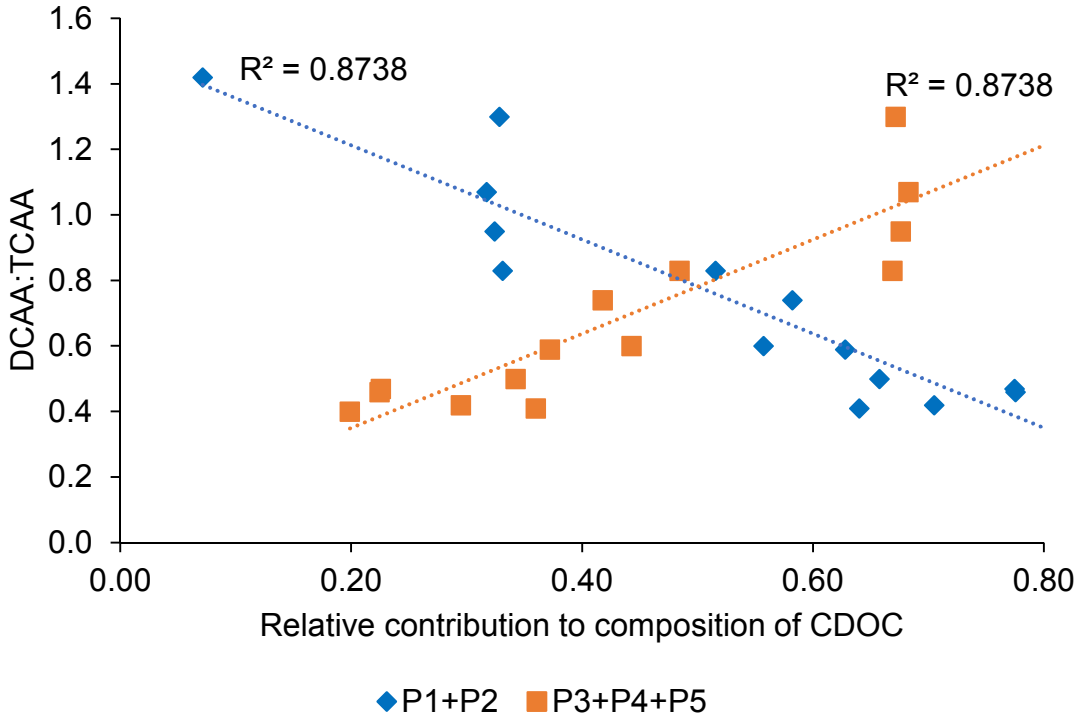

Fig. S3: *Relationship between DCAA:TCAA ratio and molecular size distribution. DCAA = Dichloroacetic acid, TCAA = Trichloroacetic acid.*

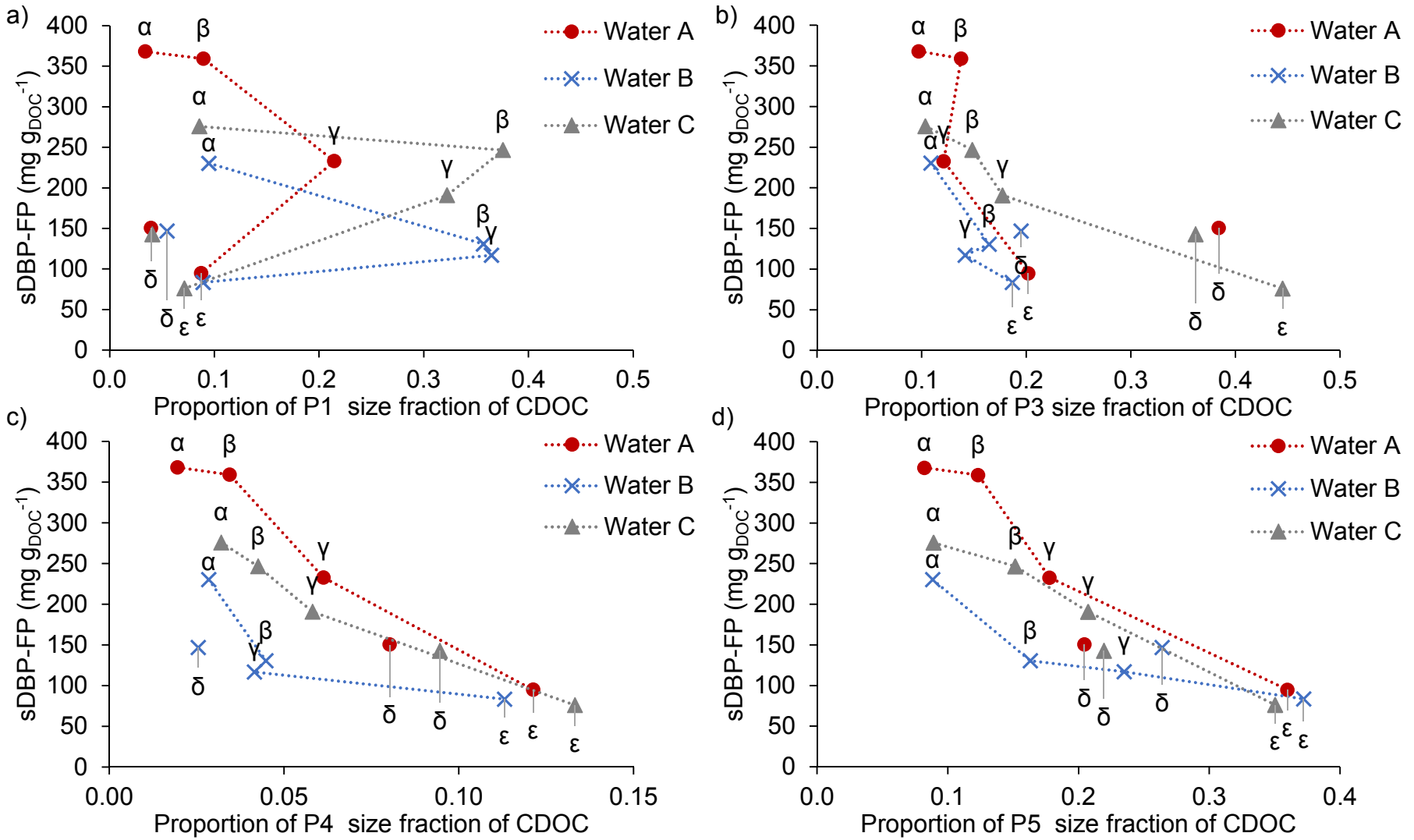

Fig. S4: *Relationship between the specific DBP-FP (sDBP-FP) and the proportion of the size fraction a) P1, b) P3, c) P4 and d) P5; the different treatment stages are indicated by α = raw water, β = IEX, γ = IEX (virgin), δ = coagulation, ε = IEX&Coagulation.*

Table S1: Concentrations of DOC after different treatment steps and SUVA values for raw water for the three water sources.

	Treatment step	Water A	Water B	Water C
DOC ($mg\ L^{-1}$)	**Raw**	11.4	7.6	8.4
	IEX	3.7	1.7	1.8
	IEX (virgin)	1.3	1.1	1.2
	Coag	1.5	1.8	2.3
	IEX+Coag	0.6	0.7	0.7
SUVA ($L\ mg^{-1}\ m^{-1}$)	**Raw**	5.0	4.3	5.6

Table S2: *Number-average molecular weight and aromaticity of NOM in P2 of waters at different treatment steps.*

	Number-average molecular weight M_n (g mol-1)		
	Water A	Water B	Water C
Raw	630	605	552
SIX	903	817	781
SIX (virgin)	837	1011	588
Coag	381	578	370
SIX+Coag	407	688	-
	Aromaticity of NOM in Peak 2		
	Water A	Water B	Water C
Raw	5.74	5.12	5.01
SIX	6.11	3.30	4.00
SIX (virgin)	1.15	0.49	0.00
Coag	3.06	2.96	2.17
SIX+Coag	5.79	2.09	2.51

Table S3: *Matrix showing Kendall's tau correlation coefficient (for non-parametric data) r, for hydrophobicity (HPO, TPI, HPI), size fraction proportions (P1 to P5) and charge density (CD) regarding raw, IEX treated (virgin and pre-used resin), coagulated and IEX&Coag treated water; ** Correlation is significant at the 0.01 level (1-tailed), *Correlation is significant at the 0.05 level (1-tailed).*

	HPO%	**TPI%**	**HPI%**	**P1%**	**P2%**	**P3%**	**P4%**	**P5%**	**CD**
HPO%	-								
TPI%	0.23	-							
HPI%	-0.90**	-0.35*	-						
P1%	-0.34*	0.00	0.32	-					
P2%	0.75**	0.33*	-0.75**	-0.26	-				
P3%	-0.33*	-0.32	0.39*	-0.23	-0.49**	-			
P4%	-0.50**	-0.33	0.56**	-0.01	-0.66**	0.63**	-		
P5%	-0.58**	-0.38*	0.68**	0.03	-0.62**	0.59**	0.65**	-	
CD	0.39*	0.25	-0.45**	0.19	0.43*	-0.75**	-0.65**	-0.63**	-

Table S4: Summary of results for the individually considered parameters and when they are considered together.

Parameter	Individual results		Combined results	
	IEX	Controlling factors	IEX	Controlling factors
Hydro-phobicity	Higher proportion of selective sites for hydrophobic compounds	Removal limited by the HPO fraction	Distribution of charge in different hydrophobicity fractions	Removal limited by high concentration of medium MW compounds
Size	Lower removal of high MW compounds due to size exclusion	Removal limited by organic matter in the P2 fraction	Lower removal of P3 to P5 due to lower CD of these compounds	Removal of different size fractions linked to limited reduction of CD and HPO fraction
Charge	Higher CL removal at higher CD Virgin: Larger CD reduction for higher initial CD	Removal limited by Increased CL	Removal of low/un-charged compounds reflected in LC-OCD measurement	Limit in removal due to surface blockage

IEX: Ion exchange, HPO: hydrophobic fraction, MW: molecular weight, CD: charge density, CL: charge load.

Table S5: *Speciation of sHAA- and sTHM-FP: MCAA = Monochloroacetic acid, DCAA = dichloroacetic acid, TCAA = trichloroacetic acid, $CHCl_3$ = Chloroform, $BrCl_2CH$ = Bromodichloromethane.*

		MCAA	**DCAA**	**TCAA**	**Total HAA**	**$CHCl_3$**	**$BrCl_2CH$**	**Br_2ClCH**	**Total THM**	**DCAA:TCAA**
		mg g_{DOC}^{-1}	mg g_{DOC}^{-1}	mg g_{DOC}^{-1}	mg g_{DOC}^{-1}	mg g_{DOC}^{-1}	mg g_{DOC}^{-1}	mg g_{DOC}^{-1}	mg g_{DOC}^{-1}	ratio
Water A	Raw water	3.0	64.9	161.8	229.7	137.2	1.3	0.0	138.5	0.40
	IEX	2.7	64.8	153.2	220.6	137.3	1.4	0.0	138.7	0.42
	IEX (virgin)	0.0	39.5	96.9	136.4	95.7	0.9	0.0	96.6	0.41
	Coag	2.8	32.7	39.5	75.0	70.2	5.0	0.3	75.5	0.83
	IEX&Coag	2.2	21.3	20.0	43.5	48.5	3.0	0.0	51.5	1.07
Water B	Raw water	1.1	40.4	86.1	127.6	99.5	3.4	0.0	102.8	0.47
	IEX	0.0	27.2	46.5	73.7	55.9	1.2	0.0	57.1	0.59
	IEX (virgin)	0.0	23.3	31.2	54.4	61.6	1.0	0.0	62.6	0.74
	Coag	2.5	29.0	35.0	66.5	72.1	7.7	0.5	80.3	0.83
	IEX&Coag	0.0	17.7	13.6	31.4	49.9	2.3	0.0	52.2	1.30
Water C	Raw water	2.7	46.9	102.1	151.7	119.1	5.1	0.0	124.2	0.46
	IEX	2.9	56.5	111.8	171.1	74.3	1.4	0.0	75.6	0.50
	IEX (virgin)	0.0	41.2	68.8	110.0	79.7	1.2	0.0	80.9	0.60
	Coag	2.2	29.6	31.2	62.9	69.0	10.0	1.1	80.0	0.95
	IEX&Coag	0.0	17.5	12.3	29.8	44.6	1.8	0.0	46.4	1.42

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The combined influence of hydrophobicity, charge and molecular weight on natural organic matter removal by ion exchange and coagulation

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