Natural organic matter – the relationship between character and treatability

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Abstract The characterisation and treatment of natural organic matter are becoming more important to the water utilities in the UK and around the world. This paper looks at the relationship between bulk and fractionated organic material and the performance of conventional water treatment processes.

Keywords Natural organic matter; characterisation; treatability

Introduction

Natural organic matter (NOM) is a 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 $\mu g\ L^{-1}$ (Lin *et al.*, 1999). A similar standard of 100 $\mu g\ L^{-1}$ is in force in the UK and the European Commission has proposed standards for chloroform (40 $\mu g\ L^{-1}$) and bromodichloromethane (15 $\mu g\ L^{-1}$), (Drinking Water Inspectorate UK, 1998).

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 for one water 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.

The treatment of water has traditionally focused on the removal of either colour or turbidity, however recently some water treatment facilities have started to optimise their works purely on the removal of natural organic matter (Chow *et al.*, 2000). To improve the performance of NOM removal it is key to firstly identify its character, as the type of organics will affect not only the choice of treatment process but also the performance of the selected

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process. This paper will look at the impact NOM character has on treatment process performance.

Materials and methods

Fractionation

Raw inlet water (75 L) and treated water collected after primary filtration (300 L) 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 (resin volume was 1,200 mL in each column). The effluent from both columns contained the non-acid hydrophilic fraction (HPI-NA). The XAD-8 column was back eluted with NaOH (0.1 M, 1,800 mL). The eluate was acidified to pH 2 and passed through a 60 mL XAD-8 column. This was the hydrophobic acid fraction (HPO-A). The XAD-4 column was back eluted with NaOH (0.1 M, 1,800 mL). The eluate was acidified to pH 2 and passed through a 60 mL XAD-4 column. This was the hydrophilic acid fraction (HPI-A). The pH of the HPO-A was adjusted to 1 by adding concentrated HCl, and left to settle for 24 hours and centrifuged. The supernatant (fulvic acid fraction – FAF) was decanted. The residual (humic acid fraction – HAF) was dissolved in the minimum required volume of NaOH (0.1 M, ~50 mL). The HAF was hydrogen saturated by passing it through a 5 mL column of Bio-Rad AG-MP-50 resin and rinsed with RO water (5 mL). The FAF was concentrated on a 20 mL column of XAD-8 and rinsed with RO water (20 mL) and desorbed with NaOH (0.1 M, 50 mL). The eluate was passed through a 5 mL column of Bio-Rad AG-MP-50 resin and rinsed with RO water (5 mL). The HPI-A was pumped through a 20 mL column of XAD-4 resin and rinsed with RO water (20 mL) and desorbed with NaOH (0.1 M, 50 mL). The eluate was pumped through a 5 mL column of Bio-Rad AG-MP-50 resin and rinsed with RO water (5 mL).

Analytical techniques

The samples were analysed for DOC and THMFP using the following methods. DOC (mg/L) was measured using a Shimadzu TOC-5000A, UV-Abs (1/m) was measured using a Jenway 6505 UV/Vis spectrophotometer, SUVA (L/mg.m) was calculated as a ratio of the UV-Abs to DOC and THM-FP was carried out using a method adapted from procedure 5710 in *Standard Methods for the Treatment and 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

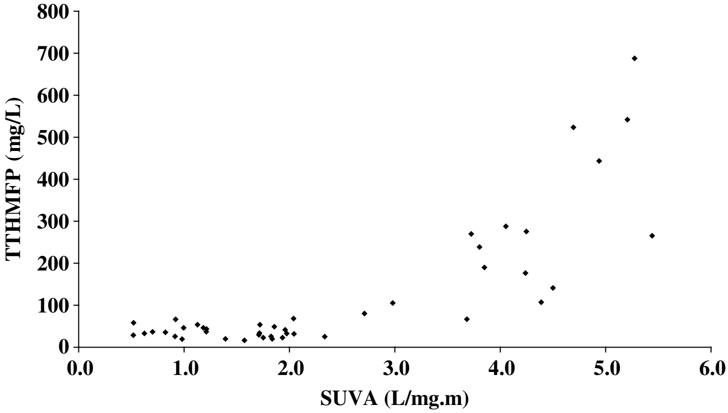

Figure 1 Relationship between SUVA and THMFP

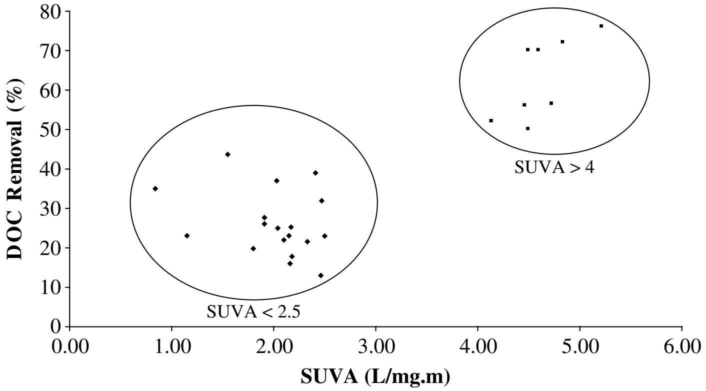

Figure 2 Relationship between SUVA and DOC focussing on hydrophobic and hydrophilic fractions. (Data taken from Croué *et al.*, 1993; Owen *et al.,* 1993; Edzwald, 1993; Crozes *et al.*, 1995; Chow *et al.*, 1999; Volk *et al.*, 2000; Bell-Ajy *et al.*, 2000)

the reaction to approach completion. The total THM (chloroform, dichlorobromoform, dibromochloroform and bromoform) concentration was measured using a SRI 9300A gas chromatograph.

Results and discussion

NOM can be characterised by bulk water parameters such as DOC, UV254, SUVA or can be fractionated into either charge or size fractions. Here we will look at what information on treatability we can gain from the analysis of bulk and fractionated organic material.

Bulk organic material

To investigate correlations between treatability, reactivity and organic character data from a number of raw and treated waters has been correlated. One parameter that has shown significant promise as an indicator of NOM character is SUVA. SUVA (specific UV absorbance), is defined as the UV absorbance of a given sample determined at 254 nm and divided by the DOC concentration of the solution, expressed in m^{-1} L/mg C and can be used to describe the composition of the water in terms of hydrophobicity and hydrophilicity,

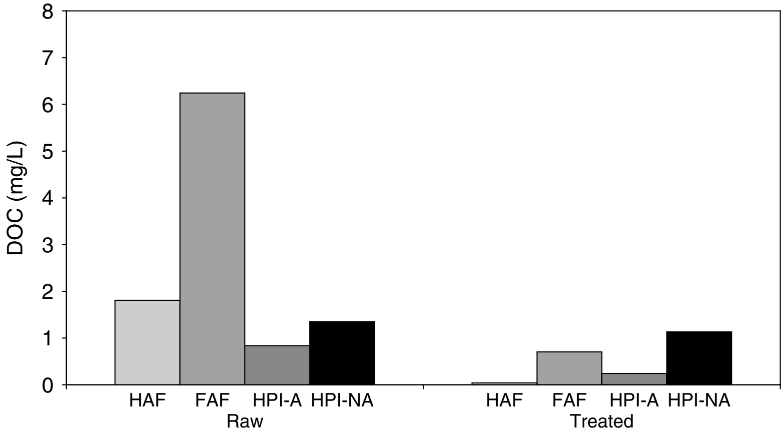

Figure 3 Isolated fraction DOC distribution of raw and treated water

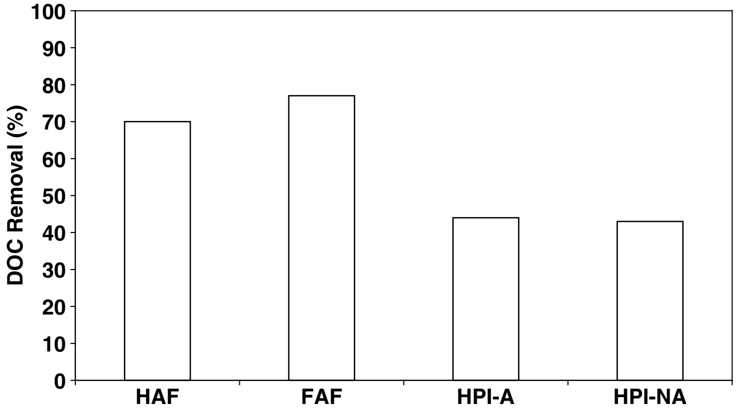

Figure 4 Optimum removal of individual NOM fractions with ferric sulphate coagulant (Fearing *et al.*, 2002)

where a SUVA > 4 indicates mainly hydrophobic and especially aromatic material whilst a SUVA < 3 mainly hydrophilic material (Edzwald and Tobiason, 1999).

Here a relationship was identified between SUVA and THMFP (Figure 1) where once SUVA is above 4 (i.e. mainly hydrophobic organics) there is a strong correlation between the two parameters – the higher the SUVA the higher the THMFP. For water with SUVA below 3 no relationship exists between SUVA and THMFP except to say that it is never higher than 100 μg/L. It is clear that the type of organic matter plays a major role in the effectiveness of process such as coagulation/flocculation. The impact of raw water SUVA on the performance of the coagulation process is shown in Figure 2 and whilst there is not a great correlation between SUVA and removal it is clear that the higher the SUVA the better the removal of DOC.

Fractionationed organic material

The fractionation of bulk organic matter (on XAD4 and XAD8 resins) in to hydrophilic and hydrophilic fractions is well known and widely used as a method to characterise NOM. The fractionation allows us to further understand the type of organic material found in a raw water source and hence gives us a better understanding of how well treatment processes deal with a

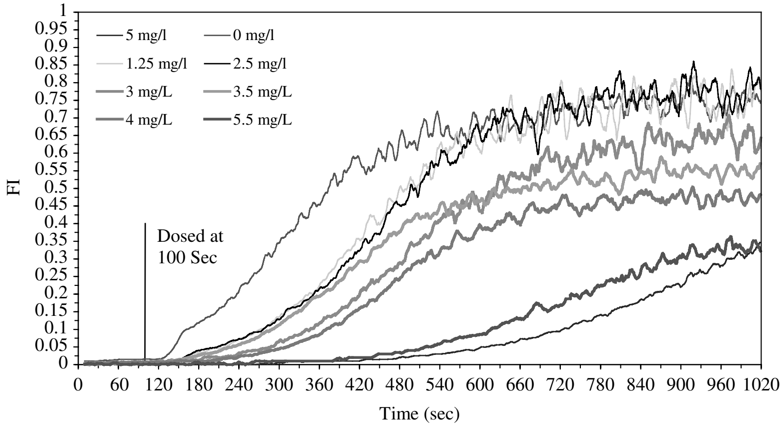

Figure 5 Effect of increasing concentrations of organic matter on the flocculation of kaolin with ferric chloride

variety of organics. Data from the fractionation of an upland water source is shown below (Figure 3). It can be seen that the principal raw water fraction in terms of DOC and reactivity is the fulvic acid fraction (FAF) (6.24 mg/L; THMFP 1164.2 μg/L respectively) followed by the humic acid fraction (HAF) (1.81 mg/L; THMFP 215.1 μg/L respectively). In addition the results shows the removals achieved by coagulation for the DOC for each of the individual organic fractions. The current treatment conditions employed at this WTW as able to achieve high removals of DOC for HAF, FAF and HPI-A (98, 89 and 71% respectively), whilst the THM-FP removal for those fractions is equally high (97, 94 and 93% respectively). However the treatment of the hydrophilic non-acids (HPI-NA) is poor with only 16% of the DOC and 31% of the THM-FP being removed by treatment.

To investigate the effect each fraction has on treatment each individual fraction was coagulated with ferric sulphate (Figure 4). HAF and FAF are fairly easily removed whilst even under optimised conditions the hydrophilic fractions are poorly removed. Further analysis of the results with high pressure size exclusion chromatography (HPSEC) showed that whilst large humic and fulvic molecules are easily removed the removal of small (>3,000 Daltons) is poor.

The organic material also effects the formation and strength of water treatment flocs. In the UK we have seasonal periods of elevated DOC (linked with rainfall) that lead to significant problems with treatment processes such as coagulation/flocculation, sedimentation, flotation and filtration. Reduced performance in any of these treatment stages leads to problems meeting quality standards and the remediation of these problems can be costly and often difficult to achieve with current process options. It is known that the efficacy of both coagulation and subsequent solid liquid separation processes for the removal of NOM is highly dependent upon the characteristics of the flocs formed and recent evidence has shown how certain organic fractions can significantly affect the growth and structure of flocs (Figure 5). Here it is clear that as the concentration of organic material increases then the rate of flocculation decreases as does the final floc size.

Conclusions

- Generally waters with a high SUVA will be more reactive with chlorine than those that have a low SUVA. It is also clear that generally these high SUVA waters are easier to treat by conventional treatment.
- The fractionation of bulk organic matter gives valuable information on the character and hence treatability of the water. It must be noted though that the fractionation is a snapshot of one period through the year and the type and reactivity of the fractions will change significantly from season to season.
- Conventional and membrane treatment processes are excellent at removing hydrophobic organic material whilst removal of hydrophilic material of small organic molecules is poor.
- Organic material also affects the nature of floc formed during treatment, often leading to weaker smaller flocs.
- The nature of organic plays a key role in the performance of treatment processes it is therefore important not only to consider bulk parameters such as DOC or colour when treating a water source.

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