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The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant

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Abstract

Dissolved organic matter (DOM) influences many aspects of water treatment, including the formation of potentially harmful disinfection by-products (DBPs) when disinfectants are applied. DOM from a conventional surface water treatment plant (WTP) in Northern New Jersey was isolated and fractionated using resin adsorption chromatography into six different fractions. These fractions are operationally categorized as hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base. The hydrophilic acid fraction was found to be the most abundant fraction in the source water. The hydrophilic acid fraction was found to be the most abundant fraction in the source water. The hydrophilic neutral, hydrophilic acid and hydrophobic acid fractions had the highest removal efficiency through the WTP (about 65%). The variation and removal effectiveness of each fraction along the WTP was studied. Seven-day chlorine DBP formation potential (FP) tests were performed on all DOM fractions through the WTP. For the source water studied, the hydrophilic acid fraction was found to be the most reactive precursor to the trihalomethane (THM) formation. The hydrophobic neutral fraction was found to be the fraction of concern with respect to the FP of haloacetic acids (HAAs) class of

Abbreviations: D/DBP, disinfectant/disinfection by-product; DBP, disinfection by-product; DOC, dissolved organic carbon; DOM, dissolved organic matter; ESWTR, enhanced surface water treatment rule; FP, formation potential; HAAs, haloacetic acids; ICR, information collection rule; LLE, liquid–liquid extraction; MCL, maximum contaminant level; MDL, minimum detection limit; MRDL, maximum residual disinfectant level; NOM, natural organic matter; PV, Passaic Valley Water Commission; THMs, trihalomethanes; TIC, total inorganic carbon; TOC, total organic carbon; WTP, water treatment plant

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DBPs. The FP of each fraction's class of DBPs was found to be amenable for reduction along the treatment train, specifically by coagulation/sedimentation. The fractionated approach concept showed to be very beneficial in the study of DBP precursors and their effective removal by physical and chemical treatment. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Disinfection by-products formation potential; DOM; Fractionation; Dissolved organic matter; Water treatment

1. Introduction

Dissolved organic matter (DOM) has been defined as having two main constituents — humic and non-humic substances. It consists of complex mixtures of organic compounds with relatively unknown structures and chemical composition. Humic substances have been known to make up a major portion of the DOM from surface waters, about 50–65% [1–3]. Aquatic humic substances are polar, straw-colored, organic acids that are derived from soil humus and terrestrial and aquatic plants as defined by Thurman and Malcolm [4] who also pioneered an isolation procedure by resin adsorption. Once isolated, humic substances can be subjected to further fractionation. At pH level of 1, the precipitate is called humic acid and the soluble fraction is called fulvic acid. However, there are more organic substances in DOM than just humic substances. To broaden the scope of DOM research, fractions of dissolved organic materials are usually defined operationally by the physical/chemical isolation procedure.

DOM was isolated from locations within a surface water treatment plant (WTP) on the Passaic River in New Jersey. Resin adsorption methods were used to isolate six fractions: hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral, and hydrophilic base, defined as follows:

1. Hydrophilic base — amphoteric proteinaceous materials containing amino acids, amino sugars, peptides and proteins [5];
2. Hydrophilic acid — an organic compound of the hydroxyl acid group [5];
3. Hydrophilic neutral — an organic compound made up of polysaccharides [6];
4. Hydrophobic base — the portion of the humic substance retained by DAX-8 resin at normal pH (~ 7) which can be eluted by hydrochloric acid [5]
5. Hydrophobic acid — a soil fulvic [7];
6. Hydrophobic neutral — a mix of hydrocarbon and carbonyl compounds [5].

DOM has been the subject of recent regulatory activities and agenda. Among them are the disinfectants/disinfection by-product (D/DBP) rule [8] and the interim enhanced surface water treatment rule (ESWTR) [9]. Both have provisions to limit the formation of disinfection by-products (DBPs) by controlling reactivity and/or removal of DOM [10].

Due to the complexity of the issues, the D/DBP regulations were proposed in two stages. Stage 1 of the D/DBPs rule was promulgated in December 1998 [8]. It lowered the total trihalomethane (THM) maximum contaminant level (MCL) from 0.100 to 0.080

mg/l and provided MCLs for three other classes of DBPs: the sum of the five haloacetic acids (HAA₅, mono-, di-, trichloroacetic acids, monobromo- and dibromoacetic acid) at 0.060 mg/l, bromate ion at 0.010 mg/l, and chlorite ion at 1.0 mg/l. Stage 1 of the rule also sets maximum residual disinfectant levels (MRDL) for three disinfectants: chlorine at 4 mg/l, chloramines at 4 mg/l, and chlorine dioxide at 0.8 mg/l. Stage 2 regulations are anticipated to be even more stringent (e.g., anticipated total THM MCL to be 0.040 mg/l and HAA₅ MCL to be 0.030 mg/l).

The formation of the products in the above reaction is a function of chlorine dosage, reaction time, pH, temperature, bromide concentration and other factors, and the concentration and type of DOM. The general reaction of DOM with chlorine, which produces DBPs, is as follows [10,11]:



The U.S. Environmental Protection Agency [8,9] proposed the total organic carbon (TOC) parameter as a measure of DBP precursors. TOC is an aggregate parameter and therefore, cannot represent or target reactive precursory material that forms DBPs. This paper examines the reactivities of DOM fractions throughout a conventional chlorination WTP. The effectiveness of treatment on the fractions removal and their chlorine DBP formation potential (FP) is presented.

2. Methods

Several sampling locations through the Passaic Valley surface WTP of Passaic Valley Water Commission (PV; Little Falls, NJ) were used in this study. The WTP draws from the Passaic River located in northern New Jersey and has an average process flow of about 210,000 m³/day. The WTP utilizes pre-chlorination, coagulation, sedimentation, post-chlorination, and anthracite over-sand filtration. Fig. 1 shows a schematic, general water quality and chemical feed data, and sampling locations; intake (following bar screens), sedimentation basin effluent, filter effluent, and post-treatment.

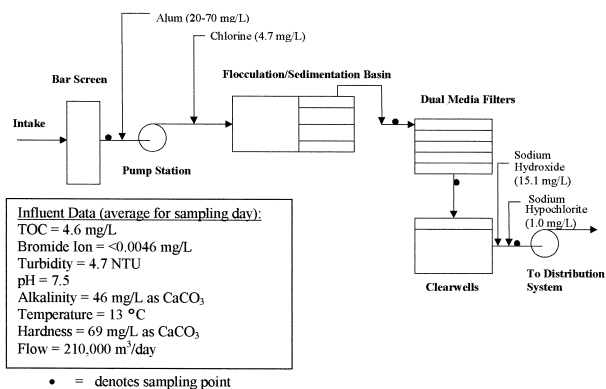


Fig. 1. Passaic Valley WTP.

Samples were directly collected, thermally stabilized and properly transported to ensure consistent quality control. Samples were refrigerated in the laboratory at 4°C throughout the 14-day holding time. Milli-Q water (Millipore, Bedford, MA) was used for all dilutions, solution preparation and final glassware washing.

2.1. Isolation and fractionation

A modified resin isolation and fractionation procedure to the one originated by Leenheer [5] was used in this research. The modified procedure was described by Marhaba et al. [12]. All samples were filtered through a 0.45- μm cellulose filter to obtain the DOM. Amberlite resin DAX-8, a macroporous methylmethacrylate copolymer (Supelco, Bellefonte, PA), AG-MP-50, a strong acid, sulfonated, polystyrene macroporous resin (BioRad, Hercules, CA) and Duolite A7, a weak base, phenol–formaldehyde condensation macroporous resin (Supelco) were all purified by soxhlet extraction prior to being used in the process. As a result of the fractionation technique, six fractions of the DOM were isolated based on chemical characteristics. They were termed operationally as hydrophobic base, hydrophobic acid, hydrophobic neutral, hydrophilic base, hydrophilic acid and hydrophilic neutral. All fractions were preserved in the applicable eluting HCl or NaOH and refrigerated at 4°C. Modification to the Leenheer [5] procedure involved using NaOH instead of NH_4OH when eluting the hydrophilic base and acid fractions to address the concern of possible formation of chloramine in subsequent THM FP studies. All elutions in this procedure were done in a forward direction or gravity flow (not backflush). This was done to facilitate the recovery procedure. Forward elution was conducted by Day et al. [13] and is the preferred flow configuration for the column. All chromatography columns were of borosilicate glass (Kontes, Vineland, NJ) with 20- μm polyethylene bed support disc.

The fractionation approach, such as the one that is being used in this work, is not valid without criticisms. Leenheer [5] and Crum et al. [14] expressed concerns that since DOM materials must be exposed to extreme pH conditions during the process (i.e., less than 2 and greater than 10), potential alterations in DOM structure and in natural chlorinated reactivities of the materials may be the consequences. General consensus is that fractionation approach via resin adsorption is very tedious and time-consuming. Despite the drawbacks, Thurman [1] acknowledged that the approach has advanced our fundamental understanding of the nature and behavior of natural organic material in water. Although sample fractionation provided the opportunities to study the mechanism about which DOM interacts with chlorine, it is important to note that the collective behavior of the individual fractions may not be the same as the behavior of the unadulterated water sample in an actual WTP.

2.2. DBPs

THMs and HAAs analyses were conducted using a Varian 3400 Gas Chromatograph (Palo Alto, CA) that was equipped with two fused silica capillary columns (0.25 mm \times 30 m), a linearized electron capture detector (ECD), and a Leap Technologies (Carrboro, NC) CTC A200S autosampler. THMs were analyzed in accordance with EPA

method 551.1, whereas HAAs by EPA method 552.2. The THMs that were analyzed were chloroform (0.055 $\mu\text{g}/\text{l}$ being the minimum detection limit; MDL), bromodichloromethane (0.003 $\mu\text{g}/\text{l}$ MDL), dibromochloromethane (0.001 $\mu\text{g}/\text{l}$ MDL) and bromoform (0.004 $\mu\text{g}/\text{l}$ MDL). HAAs were analyzed, consisting of six analytes — monochloroacetic acid (0.273 $\mu\text{g}/\text{l}$ MDL), dichloroacetic acid (0.242 $\mu\text{g}/\text{l}$ MDL), trichloroacetic acid (0.079 $\mu\text{g}/\text{l}$ MDL), monobromoacetic acid (0.204 $\mu\text{g}/\text{l}$ MDL), dibromoacetic acid (0.066 $\mu\text{g}/\text{l}$ MDL), and tribromoacetic acid (0.820 $\mu\text{g}/\text{l}$ MDL). Methyl-*tert*-butyl-ether was used as the only extraction solvent in this method. Bromofluorobenzene (Ultra Scientific) and decafluorobiphenyl (Ultra Scientific) were used as internal and surrogate standard, respectively, for THM analysis. For HAA analysis, the internal standard used was 1,2,3-trichloropropane (Supelco) and the surrogate standard was 2,3-dibromopropionic acid (Supelco). All extracts were analyzed within 24 h of the completion of the liquid–liquid extraction (LLE) procedure. After the analyses, the sample bottles were secured with new caps and stored in freezer at -10°C . Data were collected and processed by the MiniChrome v. 1.60 software package (VG Data Systems, Cheshire, UK).

2.3. Organic carbon analysis

Dissolved organic carbon (DOC) was used to measure the original non-fractionated and fractions' organic content. DOC was analyzed by an OI Analytical 700 system (OI, College Station, TX) TOC analyzer using the method of sodium persulfate oxidation (Standard Methods 5310-D) [15]. Original source samples were filtered through a 0.45- μm cellulose filter prior to analysis and fractionation to remove suspended particles. Five percent phosphoric acid was used to first acidify the sample which was then purged with total inorganic carbon (TIC) by nitrogen. Sodium persulfate was subsequently introduced as an oxidant in the process for the oxidation of the organic compounds at 100°C . As CO_2 is purged and trapped at the end of the oxidation process, an infrared photometric beam was used for the analysis of carbon mass. The analyzer was regularly calibrated with 1000 ppm potassium hydrogen phthalate (KHP) standard in either the TIC or TOC calibration mode, as recommended by the manufacturer. Each sample was prepared and diluted differently depending on whether the solvent was 0.1 N HCl, 1 N NaOH or 2 N NaOH. The analyzer was programmed accordingly with the proper amount of acid, oxidant and reaction time as recommended by the manufacturer. At least three blanks were analyzed prior to the analysis of each sample to establish and verify the appropriate background for quality assurance and control. Duplicates were run randomly.

2.4. DBP FP

A 7-day chlorine DBP FP test was carried out in accordance with Standard Methods 5710B [15] at a chlorine dosage of 100 mg/l. Chlorine solution was prepared from calcium hypochlorite in powder form of 69.7% available chlorine. The chlorine dosage of 100 mg/l was selected to ensure maximum oxidation of the organic carbon in the sample. This condition of satisfying the maximum demand of the materials involved in

the FP test was verified at the end by measuring the residual chlorine in each sample. When no or low residual chlorine was detected (< 2 ppm), the test was repeated. Post-FP test data showed that a range of 4–6 ppm of residual chlorine was attained. All samples were adjusted to a pH of 7 ± 0.2 using 1 N HCl and 1 N NaOH. The neutralized solution was then buffered with a phosphate solution prior to being incubated at $25 \pm 2^\circ\text{C}$ in amber bottles for 7 days. All bottles were capped head-space free. All sample solutions were prepared using Milli-Q (Millipore) water system. At the end of 7-day chlorine contact time, samples were dechlorinated using ammonium chloride (NH_4Cl) as the sole dechlorinating agent. This was a deviation from the above Standard Methods 5710B [15] to be in compliance with the applicable EPA methods (551.1 and 552.2).

3. Results and discussion

3.1. DOM recovery and fraction mass

Mass balance, using DOC measurement of the sum of fractions' mass compared to the original unfractionated samples along the four WTP locations, confirms the effectiveness of the fractionation procedure, giving a -14 to 10% tolerance (filter -14% , finished -8% , intake 2% , basin 10%) of DOM recovery. Day et al. [13] reported similar tolerance, which was due to loss of the hydrophilic acid fraction from the strong anionic nature of the AG-MP-1 resin. Variations from 8% to 12% were also reported by Croue et al. [16]. Surplus recovery in this study was probably due to the contribution of inorganics, such as HCl and NaOH, that were introduced in the process for acidity adjustment as well as elution. It should be noted that because natural organic matter (NOM), and for that matter DOM, varied significantly on such parameters as temperature, seasons of the year and geographical locations of the watersheds, any such comparison should take those variations into account. Non-volatile enrichment by rotary vacuum evaporation of the fractions was not conducted because concentrated forms of the isolated fractions were not of interest to the study and certainly not at the expense of "considerable" losses of the volatile organic compounds [17]. Although the fractionation process is time-consuming, it provided the opportunity to isolate the components of the DOM and ascertain their respective reactivity with chlorine for DBP FP tests. The fractionation procedure was repeated several times for different sampling points in the WTP prior to actually implementing the experimental strategy to statistically confirm the precision of the results.

3.2. Mass and DBP FP of fractions in the source water

Humic and non-humic substances in DOM greatly vary from one source water to the next. This is due to the complex nature of DOM which is a function of geography, geology, industrial and municipal discharges, natural landscape and water resources. Humic and non-humic substances are considered hydrophobic and hydrophilic substances, respectively, based on the operational definition [5,13,16]. Fig. 2 shows the

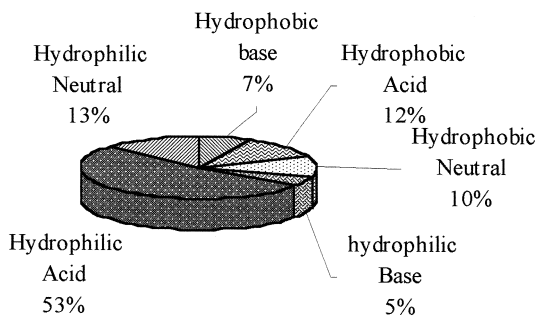


Fig. 2. Fraction mass distribution of the intake water on the Passaic River, NJ (DOC = 41.6 mg).

breakdown of the mass of fractions in the source water (i.e., intake). Hydrophilic acid accounted for 53% of the total DOC. Depending on the watersheds, other researchers have reported the contribution of hydrophilic acid in the range from 8% to 50% [13,18–20].

Chlorinated relative reactivity of DOM fractions is defined as a measurement of the FP of the DBPs (THMs or HAAs) per unit mass DOC of the original unfractionated water sample when the organic materials in the various fractions are exposed to the FP tests. The THM FP was found to be most dominating followed by HAAs. These results are in agreement with those reported by others for similar source waters [21–23]. A discussion of the chlorinated reactivity of the different DOM fractions in the influent and through the PV WTP follows.

The DBP FP of the humic (hydrophobic) and non-humic (hydrophilic) fractions was examined and compared to the sum. The contributions of humic and non-humic substances toward the formation of THMs were 28% and 72%, respectively. As for HAA, the contributions were 87% and 13%, respectively. The raw water in this study indicated a characteristic dominance of non-humic substances in the overall DOM (Fig. 2) although the fraction precursors to THMs were shown to be about equally distributed.

The 7-day FP test of each fraction provides insight into the chlorinated reactivity of each contributing precursor. As shown in Fig. 3a, the hydrophilic acid fraction was the most reactive precursor fraction for the formation of total THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform). The reason for the high degree of chlorine affinity of this fraction can be explained by the fact that chlorine species are electrophiles, and as such, have the tendency to react with electron-rich sites in organic structures [24–26]. Data from Fig. 3a indicated that the hydrophilic acid fraction of DOM appeared to present such reactive sites.

The hydrophilic acid fraction played the dominating role in the THM FP, but all six fractions of DOM were found to contain precursors to lesser levels. The abundance of the hydrophilic acid fraction mass in the original samples may be conducive to the competitive reaction with chlorine. The same competitive phenomenon was observed by Owen et al. [27] when chlorinating humic and non-humic substances separately. The removal of the hydrophilic acid fraction, as shown in the figure, may effectively remove a major portion (~70%) of THM precursors. Removal of this fraction alone, therefore,

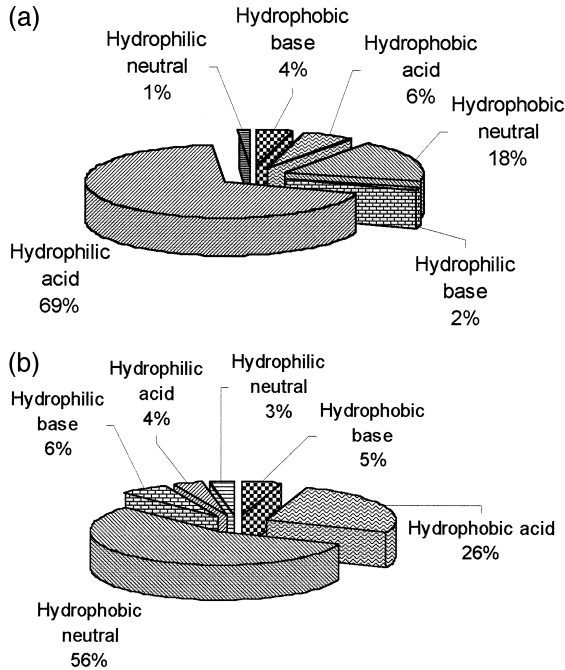


Fig. 3. (a) THM FP of fractions (intake water at Passaic River, NJ). (b) HAA FP of fractions (intake water at Passaic River, NJ).

may be sufficient to be in compliance with either the existing or proposed total THMs MCL. Knowing the fraction precursor that is responsible for most THM formations is the key factor in optimizing the removal of THM precursors.

The hydrophobic neutral fraction in this source water, on the other hand, had the highest reactivity to the formation of HAAs (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid, and tribromoacetic acid) as shown in Fig. 3b. This suggests that the hydrophilic acid and hydrophobic neutral fractions have different contributing precursors toward the formation of THMs and HAAs, respectively. This notion of “contributing precursor” would not be revealed or clearly perceived with the use of TOC as a measurement tool. Because of the proposed MCL on HAAs, it is vital to focus on the removal of the problematic DOM fraction(s) from the raw water for the purpose of controlling DBP formation. Results from Fig. 3b show that removing hydrophobic neutral alone would remove about 56% of the overall relative HAA reactivity formed, which may be adequate to be in compliance with the proposed MCL at many drinking water facilities. As for the individual halogenated species of the HAAs, di- and trihaloacetic acids are known to have different precursors, and since they are greatly affected by the pH [28], the formation of each individual HAA in each fraction of DOM will be covered in a different study which will include the pH and temperature sensitivity on chlorinated DBP reactivities.

In the analyses of DBPs such as THMs and HAAs, the effect of bromide ion could be significant [27,29,30]. The concentration of bromide ion in this source water as shown

was quite low in the nationwide range of $< 5\text{--}429 \mu\text{g/l}$ [31]. Although the primary objective of the study was to examine the sum of the DBPs such as those of four THMs, it is interesting to note the contribution of brominated THMs such as dichlorobromomethane, dibromochloromethane and bromoform to the total THMs. On average, brominated THMs accounted for about 20% of total THM value. With regard to the individual fractions, brominated THMs accounted for about 30% in the hydrophobic base, 34% in the hydrophobic acid, 20% in the hydrophobic neutral, 30% in the hydrophilic base, 49% in the hydrophilic acid, and 19% in the hydrophilic neutral fractions when examining their THM FP.

3.3. Variation of fraction mass and DBP FP through treatment

Fig. 4 shows the fractions' removals through the treatment train. While the figure shows the expected general behavior in that the total DOC would gradually be reduced going through the treatment train, it is interesting to note that at the fractions' level, this behavior also holds true, taking into account the 15% tolerance of the TOC analyzer. Having known the variation of the fractions, Section 3.3.1 presents the data and the discussion of the resultant DPBs of each fraction as subjected to the different unit operations in the plant.

3.3.1. Hydrophobic base fraction

As shown in Fig. 5, the fraction's THM FP can be reduced by conventional coagulation/sedimentation although less so with regard to the HAA DBP precursor. The effectiveness of the dual-media filter on this fraction was not apparent. The hydrophobic base fraction, being a humic substance as it is widely referred to in the literature [5,13,16], fits well in the criteria for being suitable to oxidation by chlorination as described by Marhaba et al. [20] who studied the similar source water. The fraction

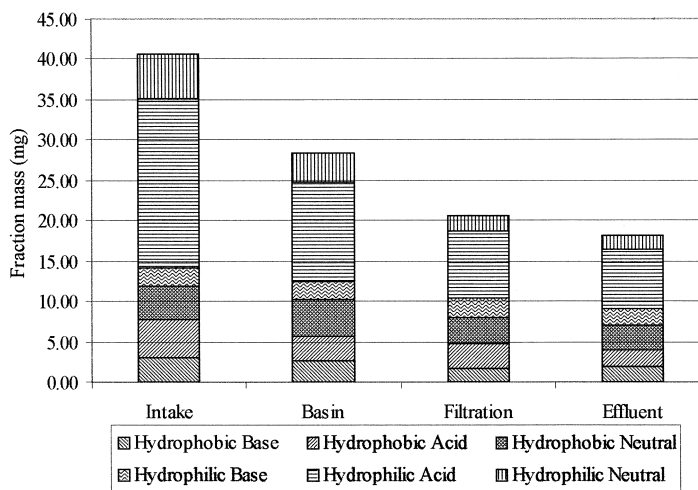


Fig. 4. Fraction mass along the treatment train.

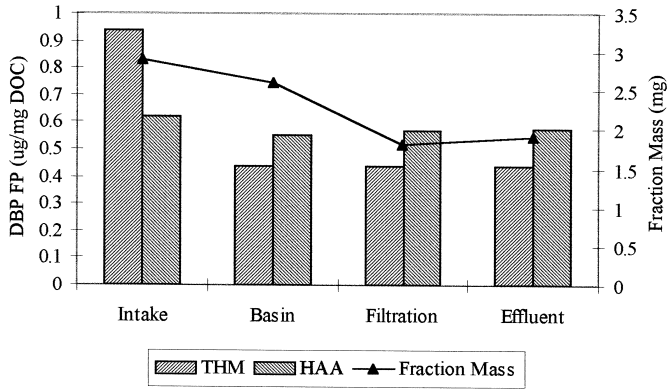


Fig. 5. DBP FP and mass variation of the hydrophobic base fraction along the treatment train.

contains amino acids, proteic materials, sugars and polysaccharides [32], and, except for polysaccharides, is prone to react with chlorine to produce THM and HAA DBPs [33]. Because the magnitude of these DBPs is directly proportional to the availability of this fraction precursor, as will be shown later, reduction of DBP FP as shown in the figure was expected. The overall reductions in the FP of the chlorinated DBPs of this fraction were 55% (THMs) and 8% (HAAs). This behavior is consistent with the overall reduction (34%) of the mass of the fraction’s organic material.

3.3.2. Hydrophobic acid fraction

Coagulation/sedimentation played a more pronounced role here in the reduction of HAA FP than for THM FP, as shown in Fig. 6. Overall, the reduction of THM FP from this fraction was ~ 30% (compared to ~ 55% for hydrophobic base fraction) and of HAA FP, 52%. Either the filter banks were not very effective at removing this fraction or it was removed by coagulation/sedimenta-

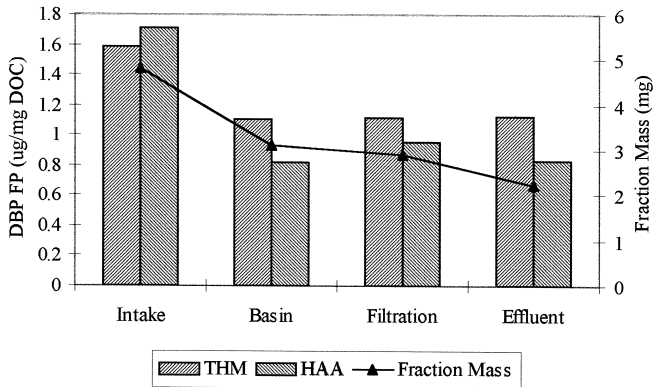


Fig. 6. DBP FP and mass variation of the hydrophobic acid fraction along the treatment train.

tion as a possible method of removal of this fraction's precursory material. As a verification for consistency, the mass of the fraction itself also experienced an overall reduction of about 55%, of which 36% was in the sedimentation basin.

3.3.3. Hydrophobic neutral fraction

As shown in Fig. 7, each unit operation played its role in the overall FP removal of this fraction (47% and 63% for THM and HAA, respectively). Coagulation/sedimentation as a unit operation, however, showed to be more efficient for the task with regard to the HAA class of the DBP precursors. Filtration was found to be effective for the removal of THM precursors while coagulation/sedimentation was effective for HAA precursors. The hydrophobic neutral fraction did not appear to be a problematic fraction for THMs; however, it was problematic for the formation of HAAs as shown in Fig. 3a and b.

The hydrophobic neutral fraction was the most abundant fraction of the hydrophobic substances from the water being studied, ranging from 10% to 18% (includes all sampling locations). Others reported this fraction to be between 0% and 25% [13,18,19]. The hydrophobic neutral fraction is of humic character in nature, which contains a mixture of hydrocarbon and carbonyl compounds [5]. The mass of the fraction shows the expected parallel reduction going through the treatment train. While Fig. 7 shows an overall reduction of about 27%, it had an unexpected increase in mass across the sedimentation basin. Since the deviation reflecting a slight increase in the mass of this fraction is small and within the instrument's known tolerance of accuracy, it can be concluded that the mass of this fraction also follows the expected trend of being reduced throughout the treatment train.

3.3.4. Hydrophilic base fraction

The concentration of this fraction decreased in the overall treatment. Fig. 8 shows, however, that the conventional unit operations were not very conducive to removing the

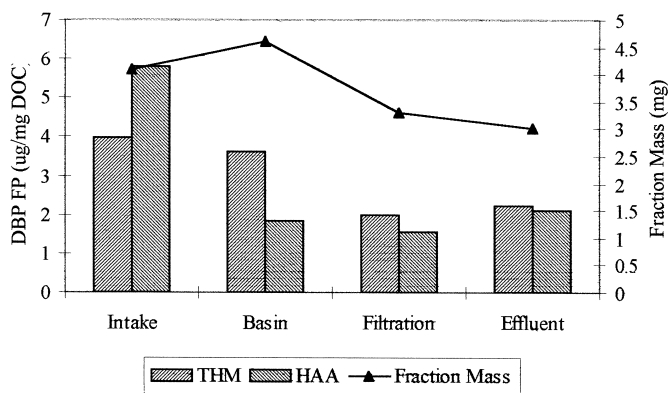


Fig. 7. DBP FP and mass variation of the hydrophobic neutral fraction along the treatment train.

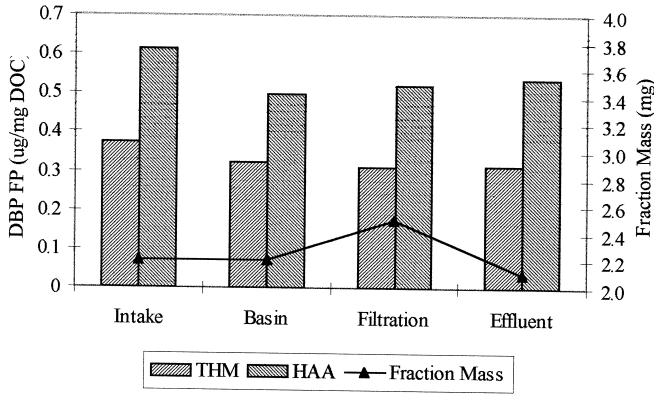


Fig. 8. DBP FP and mass variation of the hydrophilic base fraction along the treatment train.

DBP FP of this fraction. Overall reduction of THM FP following coagulation/sedimentation of this fraction was about 15% and that for HAAs was about 13%. Compared to the removal of hydrophobic substances (i.e., hydrophobic base, acid and neutral fractions) as discussed above, the removal of the hydrophilic base fraction either by coagulation/sedimentation or filtration was not very effective. Fortunately, results showed that the hydrophilic base fraction was not found to be a problematic precursor to THMs and HAAs under the conditions examined. In fact, the hydrophilic base fraction was the least reactive in forming THMs (2%) and HAAs (6%) (Fig. 3a–b). When the reduction of fraction mass is used to confirm the result, it is noted that the data show a slight increase in the mass of the hydrophilic base fraction across the anthracite–sand filtration units. The increase in mass of this fraction, however, is smaller than the deviation in the case of the hydrophobic neutral fraction as discussed earlier. We can conclude that the conventional treatment train cannot be used to remove this class of DBP precursor, both in the sense of mass reduction and FP.

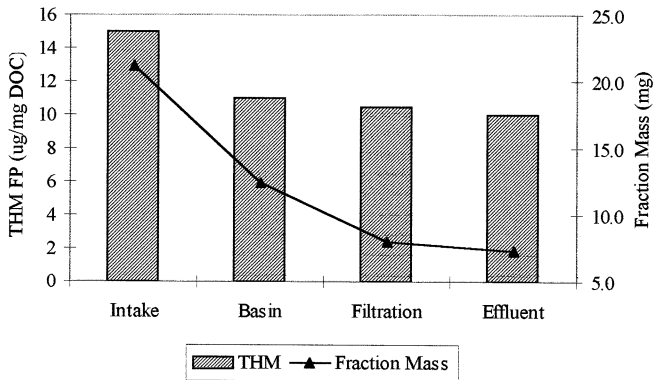


Fig. 9. THM FP and mass variation of the hydrophilic acid fraction along the treatment train.

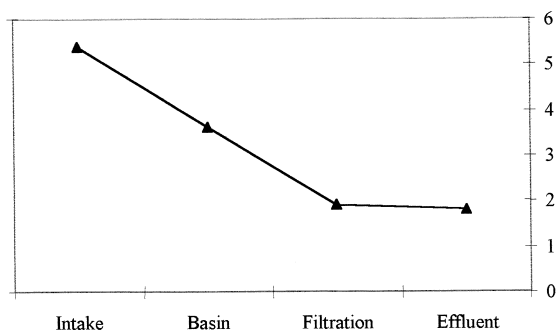


Fig. 10. Mass variation (mg) of the hydrophilic neutral fraction along the treatment train.

3.3.5. Hydrophilic acid fraction

The hydrophilic acid fraction was the most reactive fraction when exposed to chlorine as well as the most problematic precursor to the formation of THMs. The overall reduction of THM FP was about 30% after going through the treatment train (Fig. 9). This was relatively low as compared to other fractions in the humic or hydrophobic category that was discussed previously. This is an engineering problem since the hydrophilic acid fraction was shown to be the targeted problematic fraction as far as the formation of THMs is concerned. Data shown in Fig. 9 suggest that this fraction should receive focused attention in the treatment strategy for the control and removal of chlorinated THM DBP precursors. Due to very low FP of HAAs (close to MDLs), the HAA results were inconclusive.

3.3.6. Hydrophilic neutral fraction

Coagulation/sedimentation and filtration were very effective in reducing the mass of the hydrophilic neutral fraction, as shown in Fig. 10. The FP of THMs and HAAs was close to the MDLs and hence, was not conclusive. This finding is confirmatory because the hydrophilic neutral fraction is primarily made up of polysaccharides [6] and as such, it does not react very well during the chlorination disinfection process [33] (Fig. 3a and b). Hence, fraction is not likely to be a significant precursor to the formation of THMs [34] based on our current knowledge on this class of DBPs.

4. Conclusions

The results reported herein were based on a single sampling event along a conventional surface WTP in northern New Jersey.

The hydrophilic acid fraction was found to be the most abundant (53%) of all fractions in the source water, followed by hydrophilic neutral (13%), hydrophobic acid (12%), hydrophobic neutral (10%), hydrophobic base (7%), and hydrophilic base (5%). The hydrophilic neutral, hydrophilic acid, and hydrophobic acid fractions had the highest removals through the WTP (67%, 65% and 64%, respectively), followed by hydrophobic base, hydrophobic neutral, and hydrophilic base (34%, 27% and 5%, respectively).

THMs and HAAs were formed by all six DOM fractions, but with different proportions. The hydrophilic acid fraction was found to contain most reactive precursors with regard to the FP of THMs. This fraction must be the primarily removed to minimize the FP of THMs. The same can be concluded about the hydrophobic neutral fraction with regard to the FP of HAAs.

In general, the mass of the various DOM fractions is amenable for reduction along the treatment train, which engenders reduction of DBP FP of the fractions at different levels. The reduction of DBP FP along the treatment train varies and may range from being effective to non-effective, depending on the type of DOM fraction under consideration.

Selective removal studies of the most reactive fractions to THMs and HAAs (hydrophilic acid and hydrophobic neutral) are needed. Furthermore, it is not known whether other fractions will be more reactive to chlorine once these two fractions are removed.

Unlike DOC, the aggregate measurement, isolation and fractionation of DOM provide some insight into the study of the reactivity of organic matter species and their optimized removal in water treatment.

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