

## Relationships between trihalomethanes, haloacetic acids, and haloacetonitriles formed by the chlorination of raw, treated, and fractionated surface waters

Paolo Roccaro, Federico G. A. Vagliasindi and Gregory V. Korshin

### ABSTRACT

This study examined effects of coagulation and fractionation of natural organic matter on the distribution of trihalomethanes (THM), haloacetic acids (HAA), and haloacetonitriles (HAN) formed in chlorinated water. The precursors of HAA and THM were determined to be associated primarily with the hydrophobic fraction although the hydrophilic fraction is important as well. On the other hand, the precursors of HAN are overwhelmingly hydrophilic with only a negligible contribution of the hydrophobic and transphilic fractions. Higher percentages of HAN were found in the treated waters compared with raw waters, collected from three different full scale water treatment plants. Very strong correlations were found between THM, HAA, and HAN concentrations. Two main correlations between THM and HAN were observed. One was applicable to all raw waters regardless of their fractionation and provenance, while the other was formed by the treated waters, again regardless of their source and fractionation. This result emphasizes that a significant removal of THM and HAA precursors can be achieved via coagulation but it results in a negligible removal of HAN precursors. As a consequence, some changes in treatment trains or operating conditions may need to be considered to minimize the formation of HAN.

**Key words** | coagulation, disinfection by-products, drinking water, fractionation, hydrophilic natural organic matter

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### INTRODUCTION

Chlorination of drinking water in public facilities was one of the most important public health measures during the twentieth century because it reduced the transmission of deadly waterborne diseases such as typhoid and cholera. Apart from the limited disinfection efficiency against some chlorine-resistant pathogens, the main drawback of chlorination is the formation of harmful disinfection by-products (DBP) that result from reactions between chlorine and both natural organic matter (NOM) present in all source water or effluent organic matter (EfOM) occurring in wastewater impacted water bodies (Krasner *et al.* 2009; Sedlak & von Gunten 2011).

The content and reactivity of NOM and EfOM plays a major role in the formation of DBP (Leenheer & Croue

2003; Krasner *et al.* 2009), but other water quality parameters (e.g., pH, temperature, bromide, and iodide) can impact the concentration and speciation of DBP (Obolensky & Singer 2008). Trihalomethanes (THM) and haloacetic acids (HAA) are generally present at the highest levels (from a few to hundred ppb) in chlorinated drinking water. Among known but unregulated DBP, several species have been found in drinking waters at much lower concentrations than those of THM and HAA but their potential toxicity is higher (Roccaro *et al.* 2005; Richardson *et al.* 2007). Recent studies (Muellner *et al.* 2007; Richardson *et al.* 2007; Plewa *et al.* 2008) have determined that the nitrogenous DBP (N-DBP) are much more toxic than carbonaceous DBP (C-DBP). Haloacetonitriles (HAN) are a class of

nitrogen-containing DBP which are ubiquitous in chlorinated waters (Richardson *et al.* 2007) and due to their high cytotoxicity and genotoxicity require more consideration (Muellner *et al.* 2007).

Although several studies have been carried out to examine the relationships and relative distributions between DBP species (Liang & Singer 2003; Serodes *et al.* 2003; Malliarou *et al.* 2005), these relationships have not been fully investigated for nitrogenous DBP such as HAN. Accordingly, the objective of this study was to examine the yields and speciation of regulated DBP (THM and HAA) and emerging DBP (HAN) in chlorinated raw, treated, and fractionated surface waters at varying reaction conditions.

## MATERIALS AND METHODS

### Water sources and materials

Experiments were conducted using water samples from the inlet and outlet of a water treatment plant (WTP) that treats the water from Ancipa reservoir (Sicily, Italy) and water samples from the Potomac River (Washington, DC) and from two WTPs (McMillan and Dalecarlia) that utilize its water.

The dissolved organic carbon (DOC) concentration of the Ancipa Inlet (influent of the WTP) sample was 2.9 mg/L, SUVA<sub>254</sub> was 2.8 L mg<sup>-1</sup> m<sup>-1</sup> (SUVA: specific ultraviolet absorption). On the other hand, the DOC in Ancipa Outlet (effluent of the WTP) sample was 2.0 mg/L, SUVA<sub>254</sub> was 1.8 L mg<sup>-1</sup> m<sup>-1</sup>. Both Ancipa Inlet and Outlet were also fractionated and the effluents from the XAD-8 (namely 'Ancipa Inlet XAD-8 effluent' and 'Ancipa Outlet XAD-8 effluent') and XAD-4 (namely 'Ancipa Inlet XAD-4 effluent' and 'Ancipa Outlet XAD-4 effluent') bench scale columns were used for chlorination as well as the unfractionated samples. The DOC of the Potomac water sample (Potomac Inlet) was 2.7 mg/L and SUVA<sub>254</sub> was 2.4 L mg<sup>-1</sup> m<sup>-1</sup>. At the Potomac WTPs, samples of effluents from the sedimentation tanks (denoted as 'Potomac MS' and 'Potomac DS' for McMillan and Dalecarlia, respectively) and from filters (denoted as 'Potomac MF' and 'Potomac DF' for McMillan and Dalecarlia plants) were taken. DOC values were 1.6, 1.7, 2.0, and 2.0 mg/L for MS, MF, DS, and DF samples, respectively. SUVA<sub>254</sub> values were 1.7, 1.3, 1.8, and 1.5 L

mg<sup>-1</sup> m<sup>-1</sup> for MS, MF, DS, and DF samples, respectively. The bromide level in Ancipa and Potomac water was about 0.05 mg/L.

All samples were filtered through a 0.45 mm nylon membrane filter (Polycap AS Capsule Filter) and stored at 4 °C. All chemicals were ACS reagent grade or better. Solvents used in extractions were high-purity grade. Reagent water was obtained from a Millipore Super-Q Plus water system. Chlorine stock solution was prepared by dilution of a reagent-grade sodium hypochlorite solution (5% available chlorine) with Milli-Q water. Amberlite XAD-8 (now called Supelite DAX-8, Supelco #20278) and Amberlite XAD-4 (Supelco #20276) resins were used for all fractionation procedures.

### Experimental methods

NOM fractionation was carried out using the simplified NOM fractionation scheme that utilized small (8 mL) resin volumes packed into a 30 cm × 1.0 cm (24 mL) glass column. XAD-8 and XAD-4 resins were used for all fractionation procedures, in order to separate NOM into hydrophobic (HPO), transphilic (THP), and hydrophilic (HPI) fractions, following published methods (Leenheer & Croue 2003; Roccaro & Vagliasindi 2009).

Chlorination experiments were conducted in the dark at 20 °C at chlorine doses between 1.5 and 2.0 mg of chlorine per mg of DOC and varying reaction time (10 min to 3 days). The water samples were chlorinated with sodium hypochlorite at pH 7.0 in the presence of 0.03 mol L<sup>-1</sup> of phosphate buffer. In each case the chlorinated samples collected were analyzed only if chlorine residual was found. Sodium sulfite or ammonium chloride was used to quench the residual chlorine. Chlorinated samples were refrigerated at 4 °C for no more than 10 days before being analyzed for DBP concentrations.

### Analytical methods

DOC was analyzed using an O.I. Analytical 1010 or a Shimadzu VCSH organic carbon analyzer. UV absorbance was analyzed using a 5 cm quartz cell on a Perkin-Elmer Lambda 18 UV/Vis Spectrophotometer at  $\lambda = 200\text{--}600$  nm. All spectra were normalized to a 1 cm cell length.

Concentrations of THM, other volatile and semi-volatile DBP (including HAN) and HAA were determined using standard analytical procedures (EPA methods 551.1 and 552.2) and a Perkin-Elmer AutoSystem gas chromatograph equipped with an electron capture detector. Other aspects of these analyses are described in previous publications (Korshin *et al.* 2002; Roccaro *et al.* 2011).

## RESULTS AND DISCUSSION

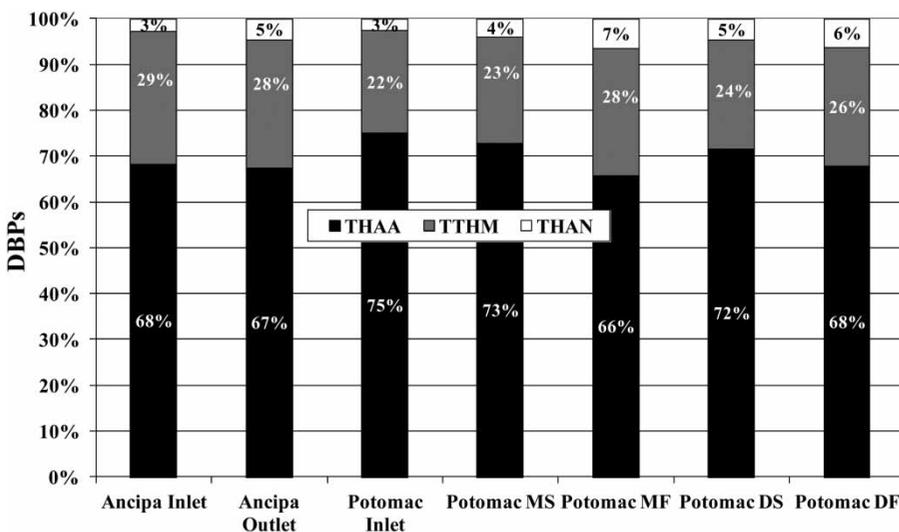
### Impact of coagulation on the removal of organic precursors in the formation THM, HAA, and HAN

Coagulation followed by clarification and/or filtration is the standard process used to remove turbidity and NOM from surface waters. However, the removal of NOM by coagulation is usually limited to about 30–50%, except for water with a high content of humic material which can result in removal higher than 70% (Edzwald 1993). Coagulation is more efficient for the removal of the most hydrophobic and high molecular weight fraction of NOM (Chow *et al.* 2004, 2005; Kim & Yu 2005; Matilainen *et al.* 2005). In this study, the removal of NOM at the Ancipa WTP was 30% as DOC and 56% as  $A_{254}$ . The DOC removal for Potomac MS and MF was 39 and 35% as DOC, respectively, and 24% for both Potomac DS and DF. The removal of  $A_{254}$

was 57, 65, 45 and 52% at Potomac MS, MF, DS, and DF, respectively.

Coagulation also resulted in consistent changes of relative contributions of the three different classes of DBP investigated, namely total HAA (THAA, sum of the nine chloro- and bromo-substituted HAAs), total THM (TTHM, sum of the four chloro- and bromo-substituted THM), and total HAN (THAN, sum of dichloroacetonitrile, bromochloroacetonitrile, dibromoacetonitrile and trichloroacetonitrile) as shown in Figure 1. Indeed, the contribution of THAA decreased after the treatment of Potomac water, while TTHM increased (Figure 1). The changes in the contributions of THAA and TTHM after the treatment at Ancipa WTP were almost negligible. On the other hand, a significant increase in the contribution of THAN was observed for all the coagulated waters, as shown in Figure 1.

These results agree with the data of previous studies which showed that the aromatic and high molecular weight fraction NOM removed by coagulation contains the main precursors for HAA and some precursors for THM (Liang & Singer 2003). However, other research suggested that low-MW, non-humic NOM contributes more prominently in HAA formation (Siddiqui *et al.* 2000; Kim & Yu 2005). The higher relative contribution of THAN in the coagulated waters observed in this study is likely to be associated with the higher hydrophilic content in coagulated NOM. This finding corroborates some recent studies which



**Figure 1** | Speciation of THAA, TTHM, and THAN in chlorinated raw and treated Ancipa and Potomac waters at reaction time of 24 hours. Chlorine doses from 1.5 to 2.0 mg  $Cl_2$  per mg DOC.

reported moderate removal of nitrogenous DBP (N-DBP) precursors by coagulation and higher N-DBP formation in chlorinated hydrophilic fractions which are rich in nitrogen (Dotson *et al.* 2009; Bond *et al.* 2011; Shah & Mitch 2012).

It is noteworthy that the treated water contains a higher bromide to DOC ratio because of the negligible removal of bromide by coagulation. Therefore, the higher contribution of a specific class of DBP in the treated water (Figure 1) may be ascribed to the higher bromide to DOC ratio. For instance, Table 1 shows the percentage distribution of THM species for the chlorinated Ancipa and Potomac water at 24 hours of reaction time. The speciation of THM, HAA, and HAN is also affected by the reaction time, but as reported in prior research carried out on the Ancipa water (Roccaro *et al.* 2008, 2009), there is a small decrease of the bromine substitution in THM, HAA, and HAN with the extent of the reaction. Overall, considering the moderate level of bromide in Ancipa and Potomac water, the chlorine dose and the resulting change in the speciation of THM (Table 1), the impact of bromide in total THM, HAA and HAN formation is limited according to prior research (Cowman & Singer 1996; Chang *et al.* 2001) and the removal of the more aromatic and hydrophobic

NOM by coagulation plays a major role in the speciation of the investigated DBP.

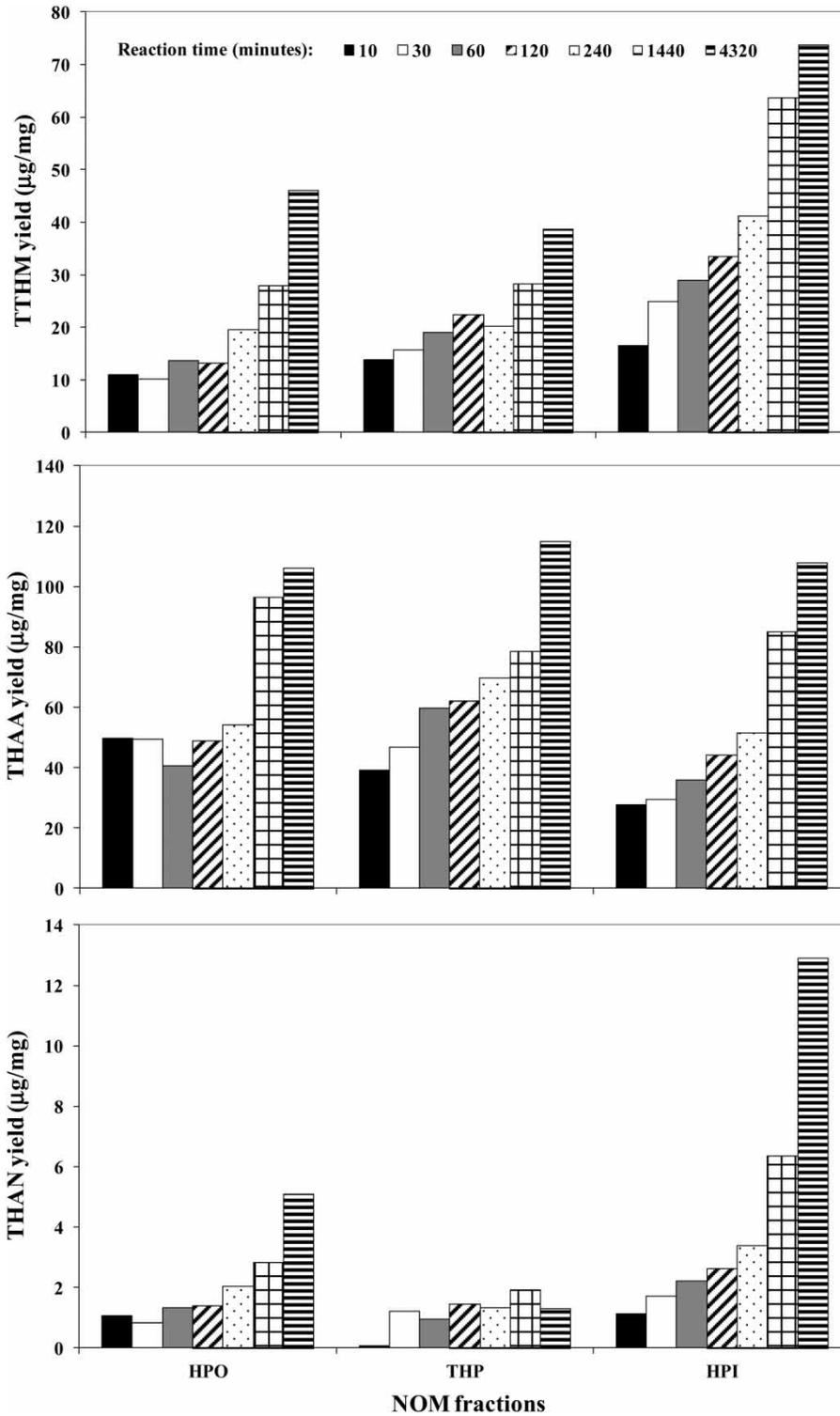
### Contribution of hydrophobic, transphilic, and hydrophilic fractions of NOM to the formation of THM, HAA, and HAN by chlorination

In order to assess the relative contributions of NOM fractions with different polarities in DBP formation and speciation, four rounds of NOM fractionation of Ancipa Inlet and Outlet water were carried out. These contributions were calculated by differences of values obtained by the chlorination of unfractionated and fractionated (XAD-8 effluent or XAD-4 effluent) samples. In accord with prior studies (Liang & Singer 2003; Hua & Reckhow 2007), both hydrophobic and hydrophilic fractions of Ancipa NOM were found to play an important role in the production of DBP. The contributions of NOM fractions to TTHM, THAA, and THAN yields in Ancipa Inlet and Outlet waters varied with the reaction time, as shown in Figures 2 and 3 for experiments carried out with 1.5 mg of chlorine per mg of DOC. As expected, higher reaction times were associated with higher DBP yields, except for the formation of THAN by the chlorination of the THP fraction of Ancipa Inlet water (Figure 2) and for THAN formed by the chlorination of HPO and TPI fractions of Ancipa Outlet water (Figure 3). The latter result is probably due to a low reactivity of THP and HPO fractions in HAN formation.

The contributions of the HPI fraction to TTHM yields for chlorinated Ancipa Inlet waters was somewhat higher than those of the HPO and THP fractions, as shown in Figure 2. In particular, the contribution of the HPI fraction increases with increasing reaction time possibly because the HPO and THP fractions react faster with chlorine (Liang & Singer 2003), generating a large amount of TTHM and of THAA, as shown in Figure 2. A negligible contribution of the HPO fraction to TTHM yields was observed for chlorinated Ancipa Outlet water (Figure 3). This was apparently caused by a significant removal of the HPO fraction at Ancipa WTP. This point is confirmed by the fractionation data showing that the removal of the HPO, THP, and HPI fractions (quantified by their  $A_{254}$  values) at Ancipa WTP was 63, 48 and 49%, respectively. At reaction times higher than 4 hours, the NOM fraction contribution to TTHM

**Table 1** | Speciation of THM in chlorinated raw and treated Ancipa and Potomac waters at reaction time of 24 hours. Chlorine doses from 1.5 to 2.0 mg Cl<sub>2</sub> per mg DOC

Water	CHCl <sub>3</sub> , %	CHCl <sub>2</sub> Br, %	CHClBr <sub>2</sub> , %	CHBr <sub>3</sub> , %
Ancipa Inlet	83	16	1	0
Ancipa Inlet XAD-8 effluent	75	23	2	0
Ancipa Inlet XAD-4 effluent	63	31	6	0
Ancipa Outlet	71	26	4	0
Ancipa Outlet XAD-8 effluent	67	27	6	0
Ancipa Outlet XAD-4 effluent	59	31	10	1
Potomac Inlet	74	22	3	1
Potomac MS	68	26	6	0
Potomac MF	68	25	6	1
Potomac DS	74	22	3	1
Potomac DF	74	21	3	2



**Figure 2** | Yields of THAA, TTHM, and THAN in chlorinated fractions of Ancipa raw water at varying reaction times. Chlorine dose of 1.5 mg  $\text{Cl}_2$  per mg DOC.

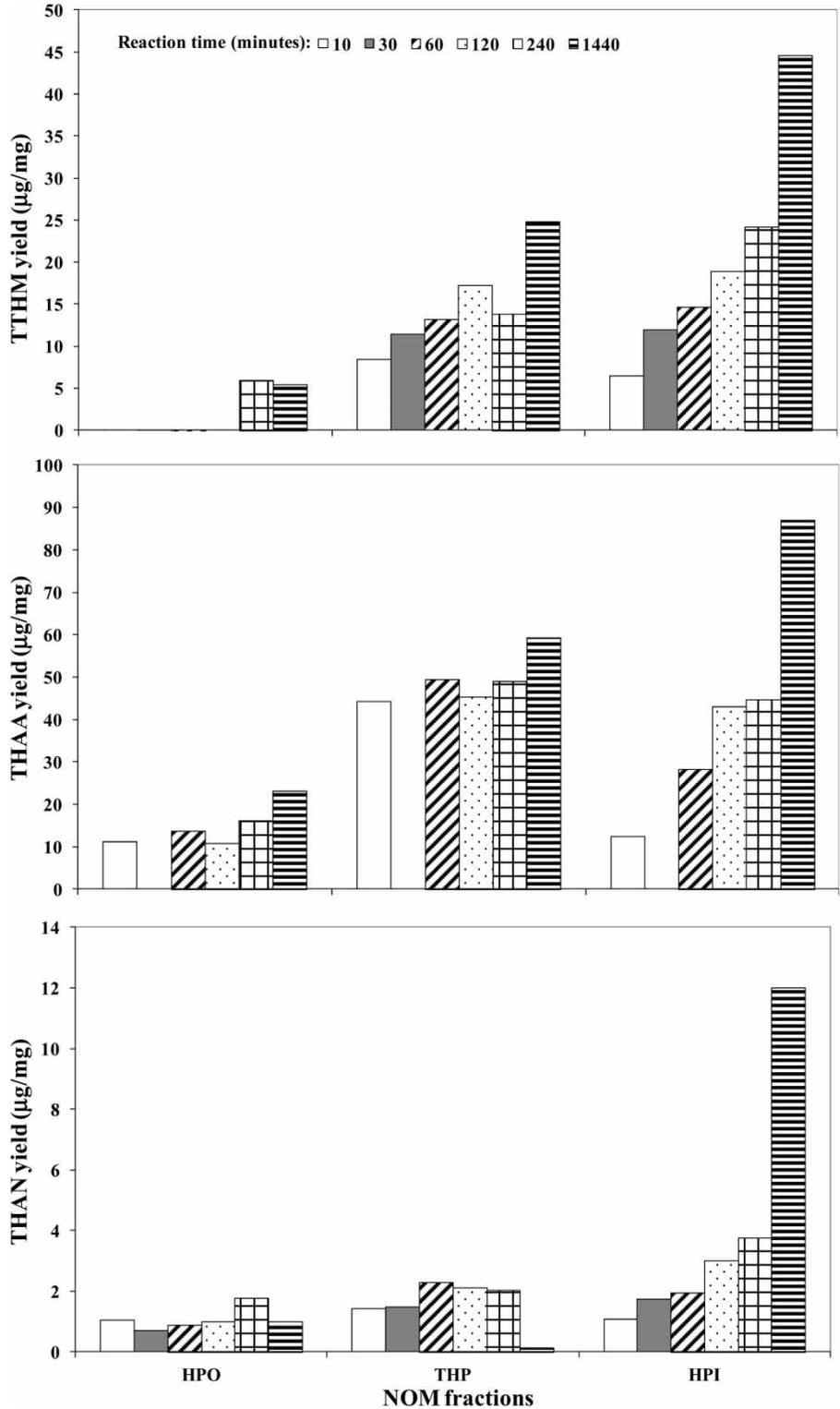


Figure 3 | Yields of THAA, TTHM, and THAN in chlorinated fractions of Ancipa treated water at varying reaction times and chlorine dose of 1.5 mg Cl<sub>2</sub> per mg DOC.

yields was in the order  $HPI \gg THP = HPO$  for Ancipa Inlet water and  $HPI > THP \gg HPO$  for Ancipa Outlet water.

On the other hand, all the NOM fractions contributed extensively to THAA yields (Figure 2), with especially prominent contributions of both THP and HPI fractions in Ancipa Outlet water. These results further support the point that the HPO fraction plays an important role in TTHM and THAA formation but the HPI fraction also contains important precursors for TTHM (Liang & Singer 2003; Zhao *et al.* 2009) and for THAA formation (Kim & Yu 2005).

Contributions of the examined NOM fractions in THAN yields were different, with the HPI fraction being the dominant part of NOM contributing to THAN (Figures 2 and 3). In fact, relative THAN yields increased after coagulation confirming that the HPI fraction contains the major precursors for THAN and that coagulation does not remove this fraction.

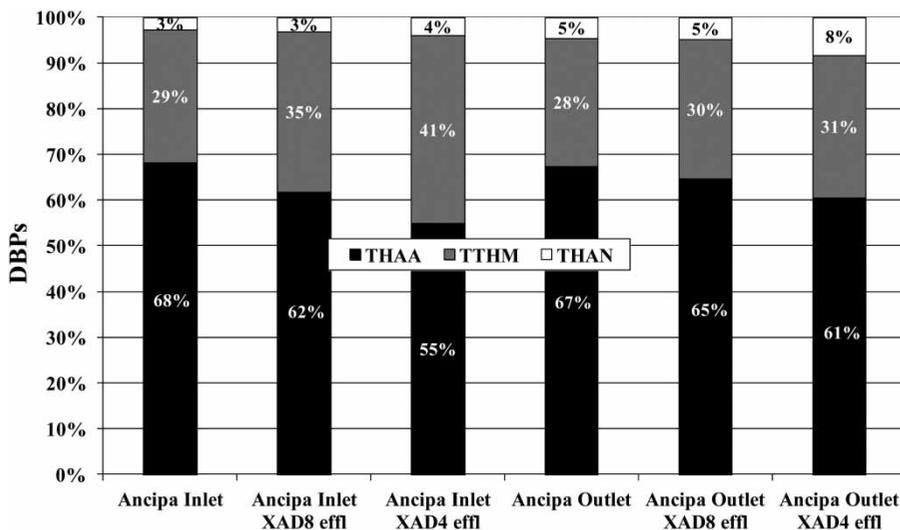
Similarly to the effect of coagulation on the bromide to DOC ratio, also the fractionation of NOM used in this study increases the bromide to DOC ratio of the resulting solutions and therefore the speciation of THM, HAA, and THAN, as shown in Table 1 for THM, but the impact of bromide in total THM, HAA, and HAN formation is limited according to prior research (Cowman & Singer 1996; Chang *et al.* 2001).

Overall, the data show that coagulation removes mostly the more aromatic and hydrophobic fractions of NOM. This

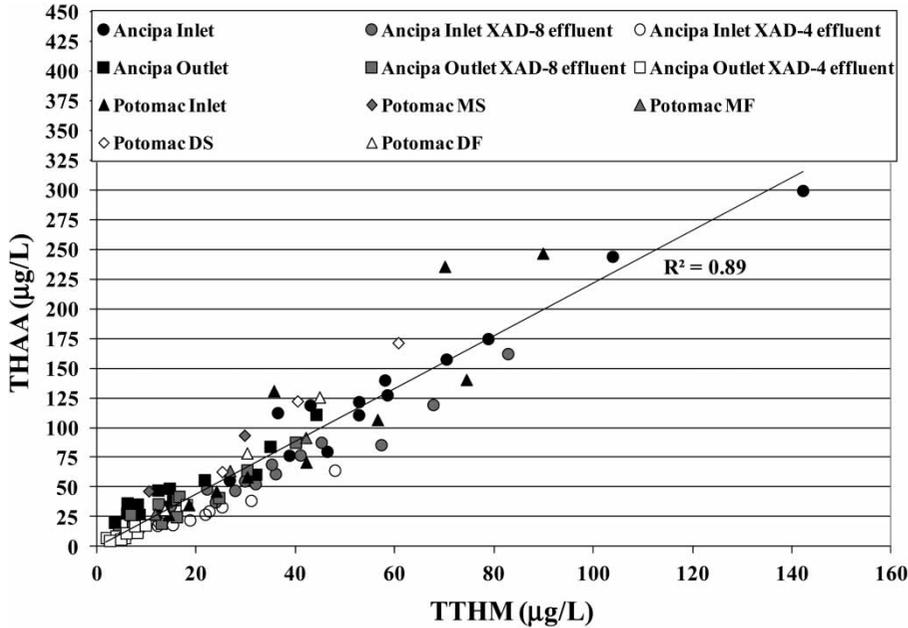
results in the preferential removal of HAA and some THM precursors (Figure 1), in accord with Liang & Singer (2003). In contrast with this result, the hydrophilic HAN precursors escape the coagulation process resulting in higher relative yields (in  $\mu\text{g}$  per mg DOC) of THAN in coagulated waters, as shown in Figure 1. Furthermore, as shown in Figure 4, the more hydrophilic NOM fractions of both Ancipa Inlet and Outlet waters produced relatively lower percentages of THAA and higher percentages of TTHM and THAN.

### Relationships between trihalomethanes, HAA, and haloacetonitriles

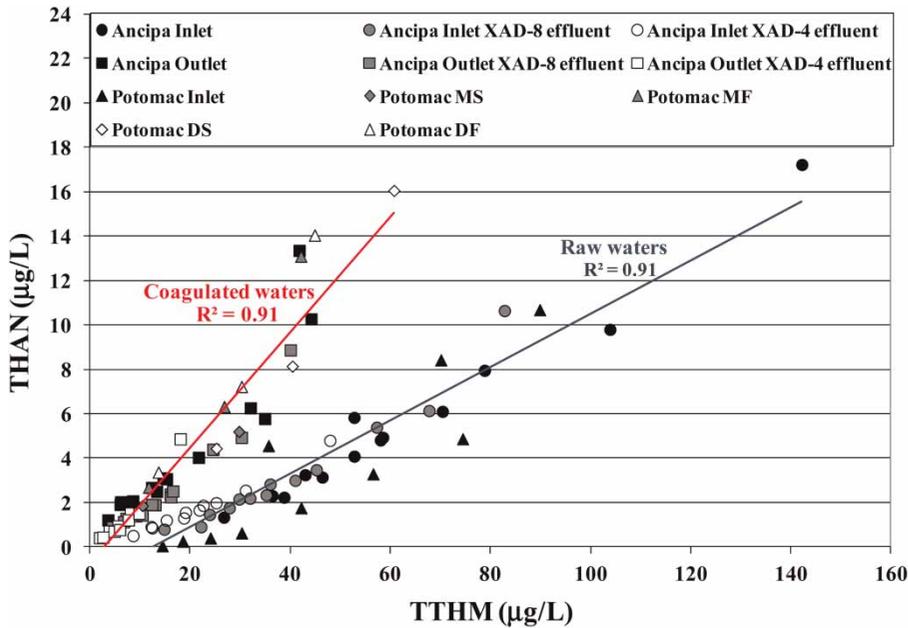
Very strong correlations were found to exist between TTHM, THAA, and THAN (Figures 5 and 6). However, while correlations between TTHM and THAA were not significantly affected by the alterations of NOM properties caused by the treatment and/or fractionation, different patterns were observed in the relationship between TTHM and THAN for raw and treated samples. Two main types of the observed correlations could be distinguished. One of them was applicable to dataset generated for the raw waters regardless of their fractionation and provenance while the other corresponded to the combined treated water data, irrespective of the type of water source and fractionation (Figure 6). The negligible impact of fractionation



**Figure 4** | Speciation of THAA, TTHM, and THAN in chlorinated raw, treated, and fractionated Ancipa water at reaction time of 24 hours and chlorine doses from 1.5 to 2.0 mg  $\text{Cl}_2$  per mg DOC.



**Figure 5** | Correlations between concentrations of THAA and TTHM in Ancipa (raw, treated, and fractionated) and Potomac (raw and treated) waters at varying chlorination conditions (reaction time from 10 min to 3 days and chlorine doses from 0.75 to 2.0 mg Cl<sub>2</sub> per mg DOC).



**Figure 6** | Correlations between concentrations of THAN and TTHM for Ancipa (raw, treated, and fractionated) and Potomac (raw and treated) waters at varying chlorination conditions (reaction time from 10 min to 3 days and chlorine doses from 0.75 to 2.0 mg Cl<sub>2</sub> per mg DOC).

on these correlations emphasizes that some of the THAA and TTHM precursors are hydrophilic while almost all HAN precursors are hydrophilic and therefore their removal is limited.

It should be recognized that the observed correlations may not be uniformly applicable to all distribution systems because some DBP, for instance selected HAA species, may undergo decay in them (Tung & Xie 2009;

Zhang et al. 2009), but this issue was not examined in this study.

## CONCLUSIONS

Results obtained in this study indicate that TTHM measurements could be used as a DBP surrogate to estimate the concentrations of the unregulated THAN whose presence in drinking water may prove to be of public health concern. The main precursors for HAA and THM were found to be associated with the hydrophobic and transphilic NOM fractions with the hydrophilic fraction playing a smaller but important role. In contrast, HAN precursors were determined to be strongly associated with the hydrophilic NOM fraction, with negligible contribution of the HPO and THP fractions. The data show that because conventional full scale coagulation processes tend to preferentially remove THM and HAA precursors but not those of HAN, this results in higher relative contributions of HAN in the sum of THM, HAA, and HAN species formed in treated water. The toxicity of nitrogenous DBP, including HANs, and the relative persistence of their precursors in conventionally treated water may require that alternative advanced water treatment processes and/or operating conditions be considered to control the levels of these N-DBP in drinking water.

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