Halogen-Specific Total Organic Halogen Analysis: Assessment by Recovery of Total Bromine

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Abstract: Determination of halogen-specific total organic halogen (TOX) is vital for studies of disinfection of waters containing bromide, since total organic bromine (TOBr) is likely to be more problematic than total organic chlorine. Here, we present further halogen-specific TOX method optimisation and validation, focusing on measurement of TOBr. The optimised halogen-specific TOX method was validated based on the recovery of model compounds covering different classes of disinfection by-products (haloacetic acids, haloacetonitriles, halophenols and halogenated benzenes) and the recovery of total bromine (mass balance of TOBr and bromide concentrations) during disinfection of waters containing dissolved organic matter and bromide. The validation of a halogen-specific TOX method based on the mass balance of total bromine has not previously been reported. Very good recoveries of organic halogen from all model compounds were obtained, indicating high or complete conversion of all organic halogen in the model compound solution through to halide in the absorber solution for ion chromatography analysis. The method was also successfully applied to monitor conversion of bromide to TOBr in a groundwater treatment plant. An excellent recovery (101%) of total bromine was observed from the raw water to the post-chlorination stage. Excellent recoveries of total bromine (92-95%) were also obtained from chlorination of a synthetic water containing dissolved organic matter and bromide, demonstrating the validity of the halogen-specific TOX method for TOBr measurement. The halogen-specific TOX method is an important tool to monitor and better understand the formation of halogenated organic compounds, in particular brominated organic compounds, in drinking water systems.

Keywords: total organic bromine, dissolved organic matter, bromide, chlorination, drinking water, health effects

1. Introduction

Natural processes, such as salt water intrusion, high evaporation conditions in arid watersheds and natural salt deposits from ancient seas, as well as pollution from industrial activities, can result in elevated bromide and iodide concentrations in natural waters (Agus et al., 2009; von Gunten, 2003). Bromide is usually detected in natural waters in the range of ~10 to >1000 µg L^{-1} (Heeb et al., 2014), while iodide is found at much lower concentrations (~50 µg L^{-1}) (Agus et al., 2009). We have found that many source waters in Western Australia (WA) contain moderate to extremely high concentrations of bromide (up to 8.5 mg L^{-1}) (Gruchlik et al., 2014), likely demonstrating all three natural processes of salt water intrusion, arid climate and ancient sea deposits, and leading to our focus on studies of the impact of bromide in drinking water treatment (e.g. Allard et al. 2013a; Allard et al. 2013b; Allard et al. 2015; Criquet et al. 2012; Criquet et al. 2015; Tan et al. 2016; Langsa et al. 2017). Conventional coagulation/flocculation drinking water treatment processes do not effectively remove bromide (Kristiana et al., 2015; Tan et al., 2016), leading to bromide being present during the disinfection process. Bromide is rapidly oxidised by oxidants such as chlorine to produce hypobromous acid (HOBr), which can then react with natural organic matter (NOM) in the water to form brominated disinfection by-products (DBPs), in a similar way to chlorine (hypochlorous acid, HOCl) forming chlorinated DBPs. These DBPs may lead to potential adverse health effects (Hua and Reckhow, 2006). In fact, brominated DBPs have been reported to be hundreds of times more toxic than their chlorinated analogues in cell bioassays (Richardson and Kimura, 2016; Richardson et al., 2007; Yang et al., 2014).

Total organic halogen (TOX) represents all the chlorinated, brominated and iodinated organic compounds in a water sample. In drinking water treatment, TOX is generally used as a measure of the total halogenated DBP formation in disinfected water. In chlorinated waters, the measured individual DBPs have been reported to account for only 16-70% of TOX (Pressman et al., 2010; Richardson and Ternes, 2011; Tan et al., 2016), while in chloraminated waters, less than 20% of TOX can reportedly be assigned to individually measured species of DBPs (Hua and Reckhow, 2007; Li et al., 2002). Therefore, the measurement of TOX includes both known DBPs and the significant fraction of TOX which remains unidentified and uncharacterised. Analysis of TOX offers the water industry and regulators a method to quantify all halogen incorporation into DBPs to better protect the public against the potential adverse health risks (e.g. bladder cancer (Richardson et al., 2007) from chlorinated or chloraminated drinking water. This is in contrast to the existing focus on two sets of individual DBPs (the trihalomethanes (THMs) and haloacetic acids (HAAs)) which are not believed to be causative for the health risks (Bull et al., 2011). Moreover, recent studies have found that TOX not only represents the total concentration of all halogenated DBPs but is also an indicator of the overall toxicity of these halogenated DBPs (e.g. Yang et al., 2014).

Analytical methods used to identify and measure TOX in water systems involve: adsorption of dissolved organic matter (DOM), including halogenated organic compounds, onto activated carbon; combustion of the activated carbon; collection of resultant hydrogen halide gases in an absorber solution; determination of the concentration of halide ions in the absorber solution; and calculation of the concentrations of halogen originally incorporated into DOM in the water sample. While a method for the analysis of bulk TOX has long been standardised (APHA et al., 1995), more recently, it has become apparent that determination of the three specific TOX species, total organic chlorine (TOCl), total organic bromine (TOBr) and total organic iodine (TOI), is vital for studies of disinfection of waters containing bromide and iodide. This is because TOI is likely to be of greater health concern than TOBr, which itself is likely to be more problematic than TOCl (Plewa et al., 2004). Ion chromatography (IC) is the preferred detection method due to instrumentation costs and availability (Brandt and Kettrup, 1987; Hua and Reckhow, 2006; Li et al., 2011; Oleksy-Frenzel et al., 2000), and it enables the quantification of TOCl, TOBr and TOI in the original water sample by separation of chloride, bromide and iodide ions present in the absorber solution.

Brandt and Kettrup (1987) first reported the use of IC to separate between TOCl, TOBr and sulphur compounds in water samples. In their method, the combustion was conducted at 1050°C in the presence of oxygen at a flow rate of 300 mL min^{-1}. Hydrogen peroxide solution was chosen to collect the resultant gases in the absorber, followed by off-line IC detection of halides in the absorber solution. Recoveries of model compounds containing chlorine and bromine varied from 3 to 109%. Chloramin-T, a biocide chemical, exhibited the lowest recovery, while the highest recovery was obtained for trichloroacetic acid (Brandt and Kettrup, 1987). The poor recovery of Chloramin-T is likely due to its decomposition in water to form hypochlorite, which would not be absorbed onto the activated carbon but rather oxidise the carbon surface (Potwora, 2009), forming chloride which would remain in the water phase and not be recovered in the TOX method. Oleksy-Frenzel et al. (2000) then developed a method of differential TOX analysis with IC detection which optimised the combustion conditions and the gas absorption system. The combustion temperature chosen was also 1050°C but the oxygen flow rate was 150 mL min^{-1}. A sulphuric acid solution was used prior to the absorber for drying of the combustion gases, followed by collection of the gases in a sodium sulfide absorber solution. Recoveries of model compounds containing chlorine, bromine and iodine were reported to range from 14 to 103% (Oleksy-Frenzel et al., 2000). While the selection of model compounds by Brand and Kettrup (1987) focussed on halogenated non-phenolic based compounds, Oleksy-Frenzel et al. (2000) covered a wider range of halogenated compounds including iodinated X-ray contrast media. The lowest recoveries were found for chloro- and iodo-acetamide (14% and 37%, respectively), while the highest recovery corresponded to iodoacetic acid (103%) (Oleksy-Frenzel et al., 2000). Echigo *et al.* (2000) used a similar combustion system to the system described by Brandt and Kettrup (1987), except that ultrapure water was used as the absorber solution. Recoveries of chlorinated and brominated model compounds ranged from 76 to 84%.

Hua and Reckhow (2006) developed a method for the analysis of halogen-specific TOX using a conventional Euroglass TOX analyser (similar to the combustion system reported by Oleksy-Frenzel et al. (2000)) and an off-line IC, and reported high recoveries (92-104%) of model compounds containing chlorine, bromine and iodine. Finally, in a more recent study, we established a halogen-specific TOX method using a state-of-the-art on-line TOX-IC system (Kristiana et al., 2015). In this study, a broad assessment of key analytical parameters for accurate measurement of halogen-specific TOX in waters was performed, including the use of different types of granular activated carbon, two different absorber solutions, and selected model compounds covering different classes of DBPs. The recoveries of the model compounds were all reported to be greater than 85% (Kristiana et al., 2015).

The accuracy of the halogen-specific TOX measurement depends on the performance of each step of the process, which includes several analytical challenges, such as the activated carbon adsorption process. Previous studies applied different types of activated carbon for the enrichment of organic halogen compounds. Brandt and Kettrup (1987) used sugar activated carbon (ZAK, Merck, FRG), Oleksy-Frenzel et al. (2000) chose Mitsubishi's activated carbon (Japan), and Hua and Reckhow (2006) selected CPI and Calgon activated carbon.

Kristiana et al. (2015) tested different commercially available activated carbons, including Acticarb GC1200N, Filtrasorb®, Carbon 437, Carboxen™572, CPI International, Darco®, Ecologix, and Mitsubishi, for release of inorganic contaminants before and after the nitrate wash. It was found that CPI International and Darco® were the two types of activated carbon which released the minimum amount of inorganic contaminants (Kristiana et al., 2015). Using Mitsubishi activated carbon columns, (Li et al., 2010; Li et al., 2011) found that the activated carbon can also act as a reductant, reducing up to 20% of TOCl and 10% of TOBr to their respective halides. Li et al. (2011) also reported that 3-10% of polar brominated DBPs formed from chlorinated reference NOM standards penetrated through the Mitsubishi activated carbon column, although ozonation of the activated carbon minimised this loss of TOBr. Kristiana et al. (2015) investigated the CPI International activated carbon in terms of acting as a reducing agent and potential breakthrough of TOX. With careful examination of the effluent collected after adsorption of a halophenol mixture (2,4,6-trichlorophenol, 2,4,6-tribromophenol, and 2-iodophenol; up to 1000 µg L^{-1} each) with two activated carbon columns in series, it was found that there was no breakthrough of analytes. In addition, each halophenol standard, measured as TOCl, TOBr and TOI, respectively, was fully recovered (104±4%, 102±4% and 96±4%, respectively) (Kristiana et al., 2015). This indicates that two activated carbon columns in series effectively adsorbed all of the halophenol standards, without reduction to the halides, thus suggesting minimal errors in the adsorption process using CPI International activated carbon.

Our on-line TOX-IC system was also applied to study the mechanisms of TOBr formation (Langsa et al., 2017) and for measurement of halogen-specific TOX concentrations in a WA drinking water treatment plant. This plant treated source water containing a moderate bromide concentration (346 µg L^{-1}) and a very low DOC concentration (0.3 mg L^{-1}) by a water softening/filtration process followed by chlorination (Kristiana et al., 2015). In this system, a total bromine recovery (concentrations of TOBr and bromide (after quenching of the oxidant residual)) of 89% was measured in the disinfected water compared to the raw water bromide concentration (Kristiana et al., 2015). The same halogen-specific TOX method was used in a subsequent study of two WA water treatment plants treating raw waters with moderate (400 µg L^{-1}) to high (754 µg L^{-1}) bromide concentrations and corresponding DOC concentrations of 3.5 and 1.2 mg L^{-1} by chlorine disinfection only (Tan et al., 2016). Full bromine recoveries (109 and 103%, respectively) were observed in the distribution system samples (Tan et al., 2016). The recovery of total bromine in the distribution system of a WA treatment plant treating raw water of again moderate bromide concentration (415 µg L^{-1}) and DOC concentration of 3.7 mg L^{-1} by a conventional coagulation/flocculation process followed by chlorine disinfection was 82% (Tan et al., 2016). Thus, very good recoveries of total bromine have been observed in water treatment systems containing moderate to high bromide in the raw water, using the TOBr method.

Since brominated DBPs are generally accepted to be of greater health concern than their chlorinated analogues (Plewa et al., 2004; Richardson and Kimura, 2016), it is likely that TOBr will be of greater health concern than TOCl, however, there are only limited studies of the relationship between TOBr and toxicity. Echigo et al. (2004) separately treated standard humic acid with HOBr and HOCl and found that the activity inducing chromosomal aberrations (mutagenicity) per unit of TOX was two to six times higher in the case of TOBr than TOCl, concluding that TOBr was more mutagenic than TOCl. The TOX (and TOBr) concentration was found to increase throughout the treatment train in an Eastern Australian conventional drinking water treatment plant, correlating with the trend in nonspecific toxicity measured in a laboratory bioassay up until the final chloramination stage (Neale et al., 2012). Neale et al. (2012) suggested that the high TOBr/TOCl ratio may have contributed to the high nonspecific toxicity observed. Yang et al. (2014) disinfected a source water (treated to the pre-disinfection stage) with added bromide (500 µg L^{-1}) and iodide (100 µg L^{-1}) by chlorination and chloramination in the laboratory. In these experiments, both cytotoxicity and genotoxicity were found to be highly correlated with TOBr and TOI. Pan et al. (2014) found that TOX and TOBr concentrations and mammalian cell cytotoxicity all decreased after boiling simulated chlorinated tap water (with no chlorine residual) for 5 minutes. These studies highlight the application and growing importance of TOBr as an indicator of potential toxicity in chlorinated drinking waters.

The objectives of our study were to expand the optimisation and validation of the halogen-specific TOX method previously developed in our laboratory (Kristiana et al., 2015), with a focus on analysis of the potentially problematic TOBr fraction. This was first achieved through optimisation of the absorber solution and the gas line washing process, and expansion of the study of the recoveries of model compounds to include 8 haloacetic acids, 6 haloacetonitriles and a total of 6 new halogenated compounds (4 brominated compounds). Then, the method was applied to measurement of halogen-specific TOX concentrations in a drinking water treatment plant treating source water containing a very high bromide concentration (1350 µg L^{-1}) and a high DOC concentration (9.4 mg L^{-1}), with the focus on understanding the fate and recovery of total bromine. Finally, laboratory chlorination of a standard NOM sample in the presence of a moderate (500 µg L^{-1}) concentration of bromide allowed study of the fate and recovery of the initial bromide through analysis of the TOBr formed. This is the first report of the use of such a mass balance approach for halogen-specific TOBr method validation.

2. Materials and Methods

2.1 Chemicals and Standard Solutions

All inorganic reagents, organic solvents and organic compounds were of analytical grade purity or higher, and were used without further purification. Specific details on chemicals and preparation of solutions are provided in the Supporting Information (Text SI1 and SI2, **Table S1**).

2.2 Halogen-Specific TOX Analysis using an On-Line TOX-IC System

Standard solutions and water samples (50 mL) were analysed using an on-line TOX-IC system according to the method of Kristiana et al. (2015) (**Figure S1**). Additional details are that the activated carbon columns were washed with aqueous nitrate solution (5 mL, 5 g L^{-1}) to remove inorganic halides, the combustion of the activated carbon was conducted at 1000ºC and a small amount of water was passed through the gas lines leading into the gas absorption tube to ensure all halide gases were collected, before an aliquot of the absorption solution was automatically injected into the IC system with the injection volume loop being 100 µL. In a separate experiment, an alternative aqueous absorbing solution containing approximately 0.5 g L^{-1} Na_2S was also trialled in order to compare the effectiveness of the collection of halide gases. The effect of different parameter settings for washing of the gas line (number of washes and duration of washes) on the concentration factor was also studied. The concentration factor of TOX in the initial solution to halide in the absorber solution allows calculation of the TOX concentrations in samples. The total volume of the absorber solution (ultrapure water) was measured by weight (five replicates).

The concentrations of halogen-specific TOX (i.e. TOCl, TOBr and TOI) in the absorber solution were measured as chloride, bromide and iodide, respectively, and the concentrations of halogen-specific TOX in the initial standard solution or water sample were calculated by dividing the concentrations measured in the absorber solution by the concentration factor (6.16; based on TOX in 50 mL of sample being concentrated into 8.12

mL of the final absorber solution; **Table S2**). The quantification limit was 3 µg L^{-1} for chloride, 2 µg L^{-1} for bromide, and 1 µg L^{-1} for iodide.

2.3 Measurement of Halogen-Specific TOX in Drinking Water Treatment Plant Samples

Water samples from sampling points in a WA drinking water groundwater treatment plant (GWTP1) were collected for application of the halogen-specific TOX measurement to a drinking water system. GWTP1 raw water contained a very high bromide concentration (0.42-1.35 mg L^{-1}; **Table S3**). The water treatment process at GWTP1 is comprised of pre-chlorination, alum coagulation/flocculation, filtration, fluoridation, pH adjustment and chlorination for disinfection. Free chlorine equivalent concentrations of the water samples were measured at the sampling locations using a portable pocket colorimeter (HACH, Loveland, CO, USA; *N*,*N*-diethyl-phenylene-1,4-diamine (DPD)). For water samples to be analysed for TOX, any chlorine equivalent residual remaining in the water samples was quenched immediately with aqueous sodium sulphite solution (10x excess based on chlorine equivalent concentration). In the laboratory, the samples were filtered through a 0.45 µm membrane filter and stored at 4°C prior to analysis for bromide, dissolved organic carbon and halogen-specific TOX. Dissolved organic carbon concentrations were measured using a Shimadzu TOC-V_{ws} Total Organic Carbon Analyser according to the Standard Method 5310C (APHA et al., 1995). Bromide concentrations were analysed according to the method of Salhi and von Gunten (1999) using a Dionex ICS 3000 IC system (UV detector). The quantification limit was 2.8 (±0.9) µg L^{-1}.

2.4 Measurement of Halogen-Specific TOX from a Chlorinated Synthetic Water containing Bromide and DOM

An aqueous solution (2 L, pH 8) containing Nordic Reservoir DOM (NR-DOM) (4 mgC L^{-1}) and bromide (500 µg L^{-1}, 6.26 µM) was treated with chlorine (75 µM, ~5.3 $mgCl_2$ L^{-1}) for contact times of 5, 10, 15, 30, 45 and 60 minutes. The residual oxidant (sum of HOCl and HOBr, expressed as a free chlorine equivalent concentration in mg L^{-1}) in each sample was quenched with sodium sulphite solution (750 µM or 10x excess based on initial chlorine concentration) prior to analysis of halogen-specific TOX and bromide ion.

3. Results and Discussion

3.1 Further Optimisation of the Halogen-Specific TOX Method

The first objective of our study was to optimise the absorber solution and the gas line washing process. The gas absorber (GA-100) unit is a part of the AQF-IC system that receives the reaction gas containing hydrogen halides (HX) from the combustion unit. The hydrogen halide gases dissolve in the ultrapure water in the absorber and the halide ions (X^-) are separated and detected by IC. A mixed halogenated organic compound standard solution (2,4,6-trichlorophenol, 2,4,6-tribromophenol, 2-iodophenol, bromobenzene, 1,4-dibromobenzene; each halogenated organic compound at 100 µg L^{-1}, unless otherwise stated) was used in these optimisation studies. Halophenol standards were chosen due to their frequent previous use for this purpose (e.g. APHA et al., 1995; Oleksy-Frenzel et al., 2000; Kristiana et al., 2015), while mono- and dibromobenzenes representing brominated benzene compounds were used in addition to the halophenol standards. The concentration of each halogenated organic compound was 100 µg L^{-1}, a mid-range concentration that can be easily detected.

3.1.1 Optimisation of Absorber Solution

The use of an aqueous sodium sulphide solution as an absorber solution was recommended by Oleksy-Frenzel et al. (2000) since they proposed that oxyhalogen species may be formed along with hydrogen halides during the combustion step and sodium sulphide can reduce these oxyhalogen species to halide ions. However, since Oleksy-Frenzel et al. (2000) only used aqueous sodium sulphide solution as an absorber solution and did not compare this to the simpler option of ultrapure water, it was important to compare the use of both of these absorber solutions in the current halogen-specific TOX method using the AQF-IC instrumentation. The recoveries of the mixed halogenated organic compound standards when ultrapure water and aqueous sodium sulphide solution (0.5 g L^{-1}) were separately used as the absorber solutions are presented in **Figure 1**.

Use of ultrapure water, rather than aqueous sodium sulfide solution, resulted in higher recoveries for all of the selected halogenated organic compounds (**Figure 1**), possibly due to the effect of ionic strength. The higher concentration of ionic species in the sodium sulphide solution compared to the ultrapure water may have resulted in lower absorption of hydrogen halide gases. The recoveries of the three individual halophenol standards with the use of ultrapure water were 87-107%, while only 68-93% of these compounds were found to be recovered with the use of aqueous sodium sulfide solution. For the bromobenzenes, the recoveries were again higher with the use of ultrapure water. Calibration studies (using halides calculated as Cl^-, Br^-, I^-) showed negligible difference between the use of ultrapure water and sodium sulphide solution as the solvent for analysis (results not shown). The higher recoveries from the use of ultrapure water in the absorber indicate that formation of oxyhalogen species in the combustion process was not significant and that sodium sulphide solution in the absorber was not necessary, in contrast to the hypothesis of Oleksy-Frenzel et al. (2000). Oleksy-Frenzel et al. (2000) used a different set of model compounds (4-chloro-, 4-bromo-, and 4-iodo-phenol), which were essentially fully recovered, to verify their method using sodium sulfide solution in the absorber. However, their recoveries of a wider range of halogenated organic compounds were very variable (14-103%) and their recovery of the only compound present in both studies, 1,4-dibromobenzene, was 49% (Oleksy-Frenzel et al. (2000)) compared to 77% using sodium sulphide as the absorber solution and 94% using ultrapure water as the absorber solution in the current study. Thus, ultrapure water has been found to be superior to sodium sulphide as the absorber solution and therefore ultrapure water was chosen as the solvent for the absorber solution in this analytical method.

3.1.2 Effect of Gas Line Washing Time

In our previous study, a key to understanding the halogen-specific TOX method was the realisation that the plug of water used to rinse the gas line from the combustion unit to the absorber unit just prior to injection of the absorber solution into the IC added 3.34 mL of water to the volume of absorber solution (5 mL) (Kristiana et al., 2015). The purpose of washing the gas line is to ensure that there is no carryover between the samples. This 67% increase in volume of the absorber solution (total 8.34 mL) affects the concentration factor in the calculation of the measured halogen-specific TOX concentration, and therefore the recovery of model compounds. Taking this increased volume of absorber solution into account resulted in recoveries of studied model compounds ranging from 85 (±0.4) to 126 (±20)% (Kristiana et al., 2015).

Following on from the work of Kristiana et al. (2015), the influence of different gas line washing parameters to the total volume of the absorber solution, and thus the impact on the recoveries of the halophenol standard compounds, was assessed. The volume of absorber solution dispensed from the GA-100 unit to the gas absorber tube was set constant at 5 mL. The AQF-100 system program has a setting range for the number of gas line washes from 0 to 99, with the duration of washing time being varied from 0.1 to 2.0 s. In these experiments, the number of washes and the time for each wash was varied. One or two washes, for 0.1, 0.5

or 1.0 s, were selected, as the maximum capacity of the gas absorber tube is only 10 mL (flow rate was 1 mL min^{-1}). The results are presented in **Table S2**.

Increasing the number of washes and the time of washing consistently increased the measured total absorber volume, as expected. The minimum washing volume (0.37 mL) was added with one wash for 0.1 s. The maximum washing volume (3.12 mL) was added with two washes of 1.0 s each.

There was little difference in the recoveries of the halophenol standard compounds with the exception of the smallest volume increase experiment (one wash for 0.5 s) where slightly lower recoveries were observed (**Figure S2**). Most likely, under these conditions, not all of the halides remaining in the gas line were washed into the absorber solution, resulting in incomplete recoveries. A statistical analysis using a Kruskal-Wallis rank sum test (α=0.05, $H_{stat} > X^2_{crit}$) showed that there were significant differences between the recoveries of halophenol standard compounds and the number of washes and the time of washing. The setting of two washes at 1.0 s was found to produce the optimum recoveries of the halophenol standards, therefore, these gas line setting parameters were selected for this halogen-specific TOX method.

3.2 Further Validation of the Halogen-Specific TOX Method

3.2.1 Recoveries of Organic Halogen in Model Compounds

Recoveries of organic halogen in model compounds have been previously reported as TOX method validation approaches (e.g. Brandt and Kettrup (1987); Oleksy-Frenzel et al. (2000), Hua and Reckhow (2006); Kristiana et al. (2015)), where several halogenated organic compounds have been selected for validation of the optimised method. Brandt and Kettrup (1987) selected one or two organic chlorine, bromine and sulphur compounds, representing different organic functional groups, for their method validation. Oleksy-Frenzel et al. (2000) focused on chloro- and bromo-benzenes and included several X-ray contrast media as model compounds. Hua and Reckhow (2006) and Kristiana et al. (2015) chose HAAs and THMs, respectively, as their main model compounds. In the current study, the recoveries of organic halogen from a wide range of halogenated organic compounds, representing major classes of DBPs (i.e. HAAs, haloacetonitriles (HANs), halophenols and halogenated benzenes) were investigated. The list of model compounds included 6 model compounds not previous studied (**Table S4**). The THMs were not studied as the recoveries from this class of DBPs have been previously reported (e.g. ten THMs studied by Kristiana et. al., (2015)).

The recoveries of organic halogen from 26 model compounds, along with their pK_a, molecular weight, and octanol/water partition coefficient (log K_{ow}), are presented in **Table S4**. Very good recoveries of organic halogen from all model compounds were obtained, indicating high or complete conversion of all organic halogen in the model compound solution through to halide in the absorber solution for IC analysis. The recoveries ranged from 78 to 135% for organochlorine compounds, with only monochloroacetic acid found to be recovered less than 80% (78%). The TOX-IC method performed particularly well for the organobromine compounds, where the range of recoveries was slightly better than the organochlorine compounds, being 83 to 118%, with most of the organobromine model compounds exhibiting recoveries around 100%. 2-Iodophenol represented the only organoiodine compound studied and its recovery was 85%.

Since the recoveries were consistently high across all chemical classes studied, functional groups did not appear to affect the recoveries achievable in the halogen-specific TOX method. The recoveries were also consistently high across different molecular weight, pK_a, and log K_{ow} values. Likewise in several previous studies, there has been no observable significant trend between molecular weight or octanol-water partition coefficient and recovery of TOX from model compounds (e.g. Brandt and Kettrup (1987); Hua and Reckhow (2006); Kristiana et al (2015); Oleksy-Frenzel et al. (2000).

In the current study, the recoveries of 1,2-dichlorobenzene and 1,4-dibromobenzene were 94 and 98%, respectively, while Brandt and Kettrup (1987) and Oleksy-Frenzel et al. (2000) both reported low recoveries (< 49%) for these benzenes. The excellent recovery observed currently for 1,4-dibromobenzene was consistent with the recovery (93%) for this compound reported by Kristiana et al. (2015). The recoveries of the dihalobenzenes obtained from the current study were > 94%, indicating that the CPI activated carbon may offer superior adsorption of the dihalobenzenes compared to the Mitsubishi activated carbon and "Sugar Activated Carbon" used by Oleksy-Frenzel et al. (2000) and Brandt and Kettrup (1987), respectively.

In terms of the recoveries of the HAAs, Oleksy-Frenzel et al. (2000) reported a low recovery of 2-chloroacetic acid (35%) and proposed that this compound did not fully adsorb onto the Mitsubishi activated carbon. They suggested that molecular weight could affect the recoveries of the HAAs, since HAAs with increasing molecular weight had increasing recoveries (83% recovery for trichloroacetic acid). The excellent recoveries of all of the HAAs in the current study (> 80%, **Table S4**) are in contrast to the findings of Oleksy-Frenzel et al. (2000) and suggest superior adsorption of these model compounds onto the CPI activated carbon. In our study, CPI activated carbon was chosen due to its minimal or low release of TOX contamination compared to the Mitsubishi activated carbon used by Oleksy-Frenzel et al. (2000) as reported by Kristiana et al. (2015). The very good recoveries of model compounds achieved in our study indicate that the CPI activated carbon appears to offer the added benefit of an improved enrichment process of TOX from waters containing organic halogen compounds.

In conclusion, this model compound study across a wide range of functional groups and molecular weights, including the three types of organohalogen compounds (organochlorine, organobromine and organoiodine), demonstrates very good method performance in terms of recovery of organic halogen in the halogen-specific TOX method.

3.2.2 Validation of Improved Halogen-Specific TOX Method in Drinking Water Treatment Plant Samples

The optimised halogen-specific TOX method was applied to study the formation of halogen-specific TOX and the fate and recovery of total bromine in a WA groundwater treatment plant treating water containing a very high bromide concentration (1350 µg L^{-1}) and a high DOM concentration (9.4 mg L^{-1} as DOC) (GWTP1). **Figure 2** shows a schematic of the GWTP1 conventional treatment process and the concentrations of various water quality parameters at the two sampling points: raw water inlet and after final chlorination. Some historical concentrations of bromide and DOM in the raw water for GWTP1, as well as the concentrations measured in the current study (28 May 2012), are presented in **Table S3** (WCWA, 2009). The DOM concentration of the raw water sample collected for the current study was similar to the historical average concentration, while the bromide concentration was almost twice the historical average concentration. This is likely due to the input, from December 2009, to GWTP1 of a new bore into a deep artesian aquifer, where the water typically contains lower concentrations of DOM (~ 1 mg L^{-1}) but much higher concentrations of bromide ($[Br^-] > 2$ mg L^{-1}) than the shallow aquifer (Gruchlik et al., 2014).

In the post-chlorination sample, final disinfection with chlorine (3 mgCl_2 L^{-1}) resulted in high TOBr formation, with 79% of initial bromide (1350 µg L^{-1}, 16.9 µM) being converted to TOBr (1072 µg L^{-1}, 13.4 µM), while about 22% of the initial bromide was detected as bromide after quenching (**Figures 2 and 3a**). The TOBr formed in 2 steps. First, chlorine (from pre- and final-chlorination additions) oxidised bromide in the raw water to bromine, then bromine reacted with reactive functional groups in the DOM through electrophilic addition or substitution to form TOBr. The total bromine, calculated as a sum of TOBr and bromide (after quenching), was fully recovered in the post-chlorination sample (1372 µg L^{-1}; 17.1 µM) when compared to the initial bromide concentration in the raw water inlet. In contrast to TOBr, TOCl was detected at a low concentration (100 µg L^{-1}, 2.8 µM) in the post-chlorination sample (**Figures 2 and 3b**), indicating that only 12% of the added chlorine (3 mgCl_2 L^{-1}) was incorporated into the DOM moieties to form chlorinated organic compounds (measured as TOCl). The DOM concentration was also observed to decrease for a total of 48% reduction across the treatment plant (**Figure 2**).

The lower chlorine incorporation into DOM compared to high bromine incorporation, from raw water to post-chlorination water, despite the lower concentration of bromine than chlorine, is consistent with many previous reports that bromine is more reactive and faster to react than chlorine towards DOM reactive sites for electrophilic addition and substitution (Acero et al., 2005; Criquet et al., 2015; Westerhoff et al., 2004). Therefore, bromine is a better substitution/addition agent for halogenation compared to chlorine. A chlorine equivalent residual was still detected (2.2 mg Cl_2 L^{-1}) in the post-chlorination sample and residual bromide (300 µg L^{-1}, 3.8 µM) was measured after quenching the chlorine equivalent residual. Our previous studies of bromine recoveries in drinking water treatment plants receiving moderate to high bromide concentrations demonstrated similarly good to excellent recoveries of bromine from raw water to disinfected water (82-109% for moderate bromide concentrations; 103% for high bromide concentration) (Kristiana et al., 2015; Tan et al., 2016). By comparing the formation of TOBr in the post-chlorination sample with the initial bromide concentration in the raw water inlet, there was about 79% bromide conversion into TOBr, along with the excellent mass balance of total bromine across the plant (101%). These good to excellent mass balances of bromine following the fate and transformation of bromide from the raw water through the treatment process support the validity of the halogen-specific TOX method as an important tool to monitor and better understand the formation of halogenated organic compounds, in particular the potentially more problematic brominated organic compounds, in drinking water systems.

3.2.3 Measurement of Halogen-Specific TOX during Halogenation of DOM Extract Solutions: Accuracy of TOBr Method

The halogen-specific TOX method was finally used to study the fate and recovery of bromide after chlorination of a DOM sample in the presence of a moderate concentration of bromide, through analysis of the TOBr formed. An aqueous solution of NR-DOM (4 mgC

L^{-1}) was treated with chlorine (75 µM, ~ 5 mg Cl_2 L^{-1}) in the presence of bromide ion (6.26 µM, 500 µg L^{-1}) at pH 8, and the formation of halogen-specific TOX and the total amount of bromine and bromide (measured as bromide after quenching the oxidant residual) was measured over 1 h.

TOCl and TOBr, as well as the reduced bromine (measured as bromide after quenching) and the total bromine (calculated as the sum of TOBr and bromide), are shown in **Figure 4**. Only 6% of the added chlorine (75 µM) was incorporated into NR-DOM and measured as TOCl (4.1 µM) in the first 5 min. Thereafter, TOCl continuously increased, albeit more slowly, for the rest of the experimental period (9% Cl-incorporation, 7 µM, after 1 h). In contrast, 44% of the initial bromide was incorporated into NR-DOM to form TOBr (2.6 µM) in the first 5 min and bromide incorporation appeared to plateau after 30 min (57%, 3.3 µM). The higher percentage of bromide incorporation (≥44%) after only 5 min of reaction confirms the fast reaction of bromine with DOM reactive sites (Criquet et al., 2015; Westerhoff et al., 2004).

To evaluate the recovery of the initial bromide, as TOBr or bromine/bromide, the total bromine represented by these three species was calculated (**Figure 4**). The recovery of the initial bromide was excellent at all times over the 1 hour period (≥ 95%), giving an excellent mass balance of bromine in the system. This result indicates that the halogen-specific TOBr method provides an accurate measure of the TOBr formed in the system. This is the first report of the use of such a mass balance approach for halogen-specific TOBr method validation. The high recovery of the initial bromide in this approach is also consistent with the very good recoveries of model compounds demonstrated above for the halogen-specific TOX method.

4. Conclusions

Optimisation of the instrumental conditions of the gas absorber module of the AQF-IC system was conducted. Very good recoveries (78-135%) of a wide range of halogenated organic model compounds (as TOCl, TOBr and TOI) were achieved, indicating very good method performance in converting organic halogen in the model compound solution through to halide in the IC detector.

Studies of the flow and transformation of bromide in a groundwater treatment plant with a very high concentration of bromide and DOM in the inlet water showed good bromine recovery (mass balance of TOBr and bromide concentrations compared to initial bromide concentration). This supports the validity of the halogen-specific TOX method, especially for TOBr measurement, in drinking water systems. The application of this analytical method to study the formation of TOBr upon chlorination of an aqueous solution of a standard DOM extract and bromide was successful in monitoring the conversion of bromide to TOBr through electrophilic substitution and addition reactions. The recovery of the initial bromide as the total measured bromine (sum of TOBr and bromide) was excellent (92-95%) over the 1 hour reaction period, indicating that the halogen-specific TOBr method provided an accurate measure of the TOBr formed in the solution.

Due to the potential health impacts of brominated organic compounds (TOBr) in drinking waters, minimisation of TOBr in drinking water treatment plants and distribution systems is essential. The halogen-specific TOX method provides an important tool to monitor and better understand the formation and fate of halogenated organic compounds, in particular the potentially more problematic TOBr, in drinking water systems. The halogen-specific TOX method provides comprehensive information about the overall incorporation of halogen into organic compounds, rather than the incorporation of halogen into a few small individual DBP molecules (e.g. THMs and HAAs), as are currently monitored and regulated. It is recommended that drinking water utilities consider inclusion of halogen-specific TOX analysis in their monitoring regimes. Further studies of halogen-specific TOX formation in drinking water systems as related to health impacts (e.g. epidemiological studies) would allow governments and health regulators to consider developing new guideline values for TOX concentrations in drinking waters.

Acknowledgements

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List of Figures

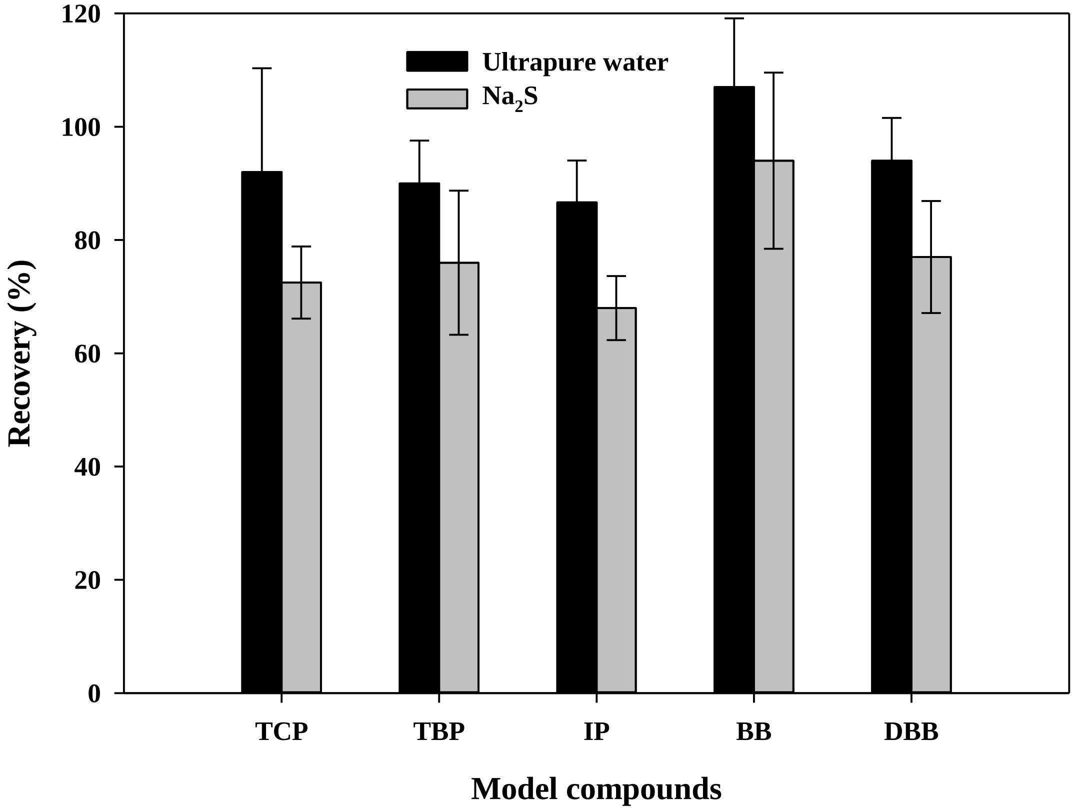

Figure 1 The effect of different absorber solutions (ultrapure water and aqueous sodium sulphide solution) on the recovery of selected standard compounds. TCP: 2,4,6-trichlorophenol; TBP: 2,4,6-tribromophenol; IP: 2-iodophenol; BB: bromobenzene; DBB: 1,4-dibromobenzene (concentration of each halogenated organic compound in the sample was 100 µg L^{-1}).

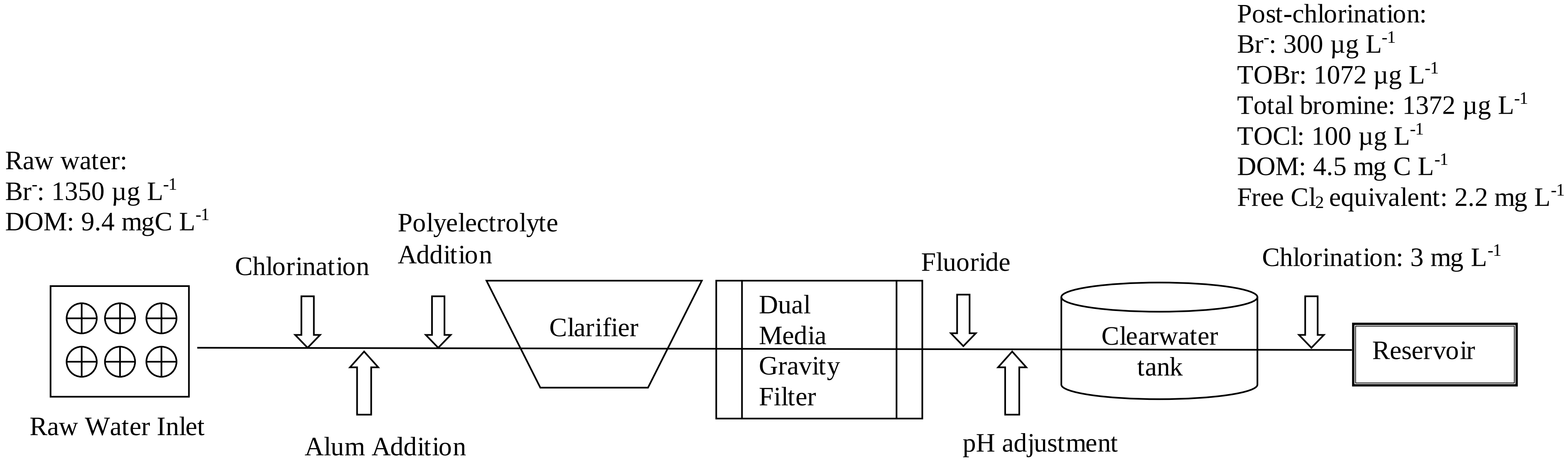

Figure 2 Schematic of the treatment process at GWTP1. Concentrations of bromide, dissolved organic matter, halogen-specific TOX, total bromine (calculated as the sum of bromide and TOBr concentrations) and free chlorine equivalents at the two sampling points are shown.

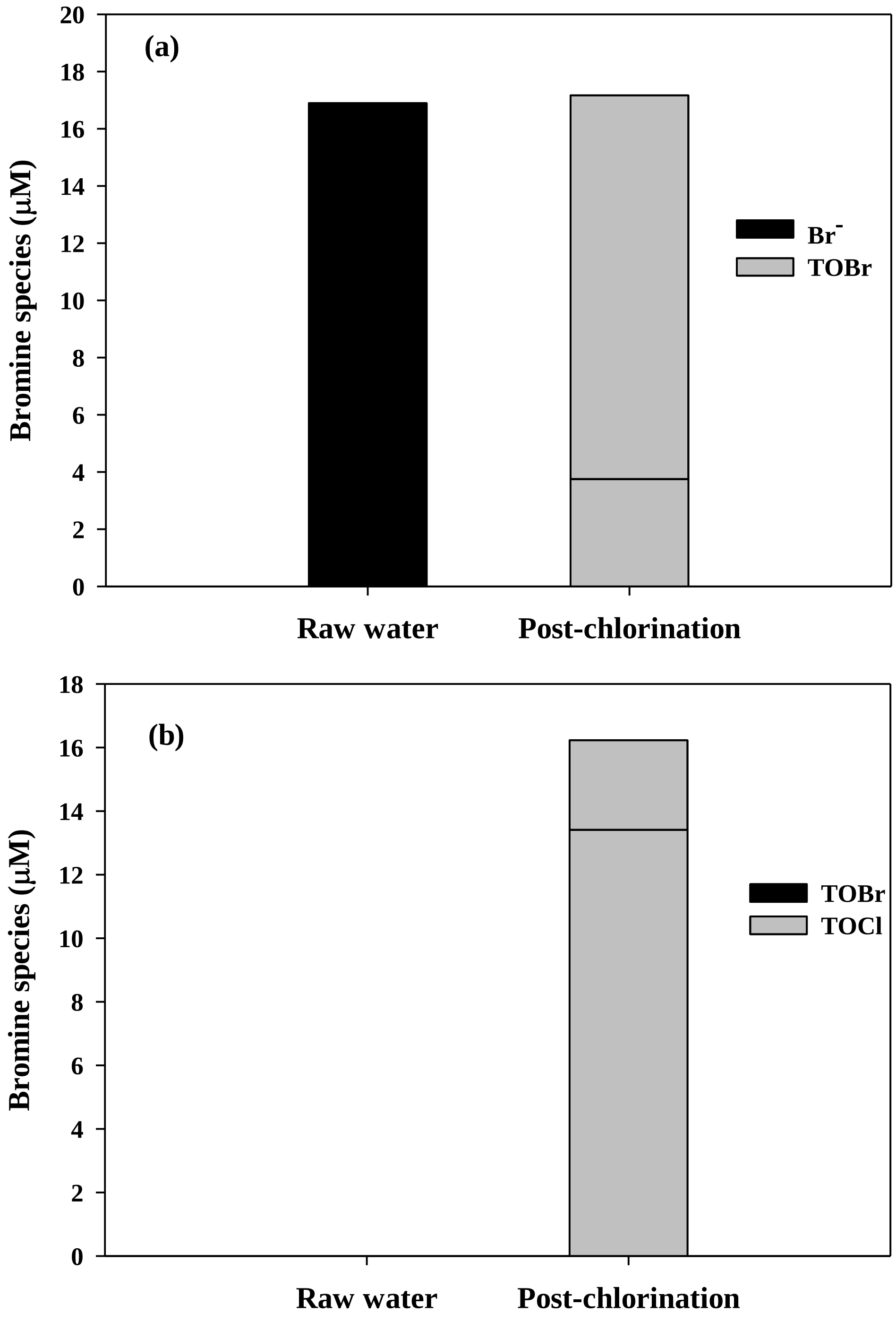

Figure 3 Halogen-specific TOX formation showing (a) conversion of Br^- to TOBr and (b) TOCl vs TOBr through the water treatment train at GWTP1.

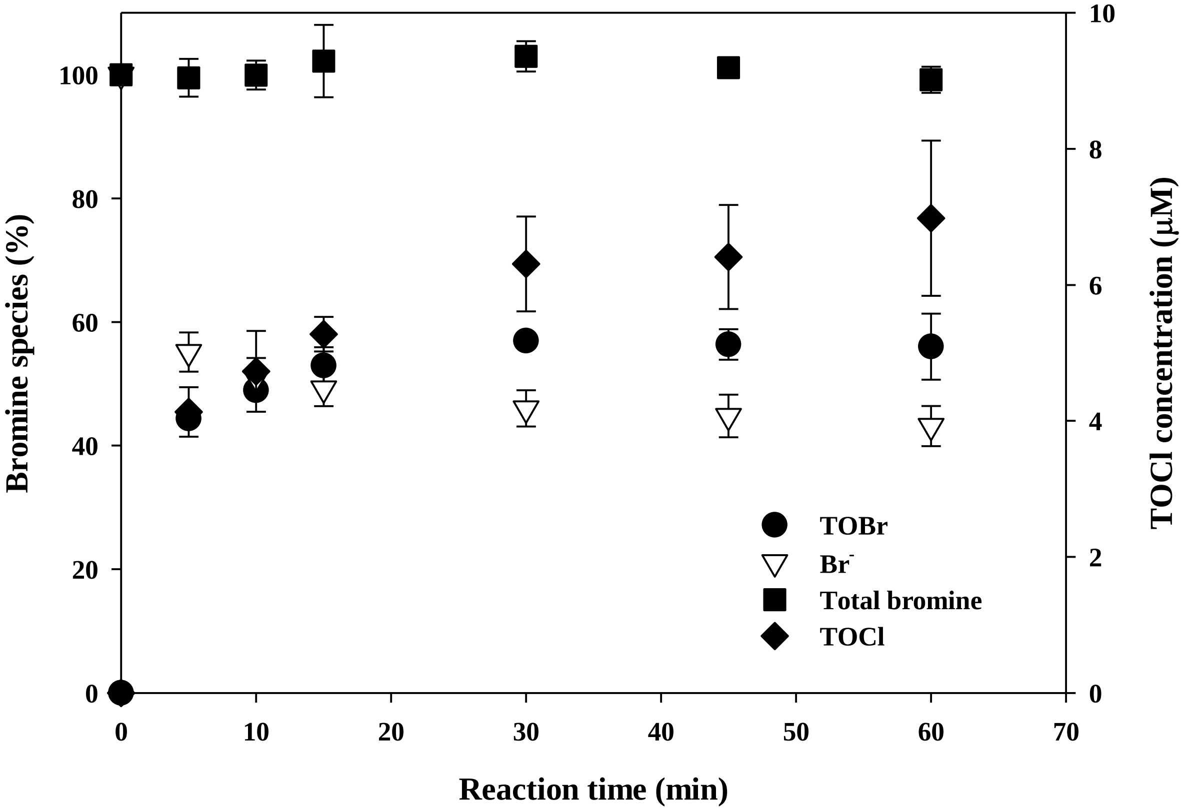

Figure 4 Concentrations of halogen-specific TOX (TOCl and TOBr with TOBr concentrations expressed as Br-incorporation (%)) and the inorganic bromine species (measured as Br^- after quenching the oxidant residual) over time. Experimental conditions: NR-DOM (4 mgC L^{-1}), bromide (500 µg L^{-1}, 6.26 µM), phosphate buffer (1.0 mM), pH = 8, chlorine (75 µM, ~ 5 mg Cl_2 L^{-1}), Na_2SO_3 (750 µM) for quenching. The "black squares" represent the total bromine measured in the system at the sampling times, being the sum of measured TOBr and bromide. Lines are shown as a guide.

Supporting Information

Halogen-Specific Total Organic Halogen Analysis: Assessment by Recovery of Total Bromine

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This section includes 2 texts, 4 tables and 2 figures.

Text SI1: Chemicals and solutions

A list of all of the chemicals used in this study is given in Table S1 below.

Table S1 Chemicals and standards used for validation of the halogen-specific TOX method

Chemicals*	**Purity (%)**	**Number of halogen atoms**		
		Chlorine	**Bromine**	**Iodine**
Model compound				
Chloroacetic acid	99	1		
Dichloroacetic acid	99.9	2		
Chlorodibromoacetic acid	94.6	1	2	
Trichloroacetic acid	99	3		
Bromoacetic acid	99		1	
Bromochloroacetic acid	99.9	1	1	
Bromodichloroacetic acid	99.9	2	1	
Dibromoacetic acid	98.7		2	
Bromoacetonitrile	97		1	
Dibromoacetonitrile	>90		2	
Chloroacetonitrile	99	1		
Dichloroacetonitrile	98	2		
Bromochloroacetonitrile	NA	1	1	
Trichloroacetonitrile	98	3		
2-Chlorophenol	>99	1		
4-Chlorophenol	>99	1		
2,6-Dichlorophenol	99	2		
Pentachlorophenol	97	5		
4-Bromophenol	99		1	
2,4-Dibromophenol	95		2	
Bromobenzene	>99.5		1	
1,2-Dichlorobenzene	99	2		
1,4-Dibromobenzene	98		2	
Halophenol standards				
2,4,6-Trichlorophenol	98	3		
2,4,6-Tribromophenol	99		3	
2-Iodophenol	98			1
Halide standards				
Potassium chloride	>99.5			
Potassium bromide	>99.5			
Potassium iodide	>99			
Buffer				
Dipotassium phosphate	>98			
Potassium di-hydrogen phosphate	>99			
Quenching agent				
Sodium sulphite	>98			

* Purchased from Sigma-Aldrich (Castle Hill, NSW, Australia), except for dibromoacetonitrile (Supelco) and bromochloroacetonitrile (Accustandard Inc. New Haven, CT, USA).

Test SI2: Preparation of Solutions

Ultrapurified water (ultrapure water) (resistivity of 18.2 mΩ), produced with a Purelab Ultra Analytic purification system (Elga, UK), was used for all experiments.

A mixed halophenol standard solution, as used in the Standard Method (APHA et al., 1995) and in the AQF-100 Mitsubishi combustion module manual for the measurement of halogen-specific TOX concentration in water samples, was prepared. This solution contained 2,4,6-trichlorophenol, 2,4,6-tribromophenol and 2-iodophenol. A stock solution (50 mL; 2 g L^{-1} of the respective halogen) was prepared in methanol. A working solution of halophenols (100 mg L^{-1}) was prepared by dilution of the stock solution in methanol. Aliquots of the working solution were further diluted into ultrapure water to achieve working standard solutions ranging in concentration from 0 – 1000 µg L^{-1}.

A series of halogenated organic compounds were selected as model compounds for the evaluation of the use of different absorber solutions on the recoveries of the model compounds. These halogenated organic compounds included a mixed of halophenol compounds (2,4,6-trichlorophenol, 2,4,6-tribromophenol and 2-iodophenol) and 2 other brominated benzenes (bromobenzene and 1,4-dibromobenzene). Each halogenated organic compound was used at 100 µg L^{-1}.

For calibration of the IC system, aqueous individual stock solutions (1000 mg L^{-1}) of the three anions (chloride, bromide and iodide) were prepared from reagent grade potassium salts. These stock solutions were then diluted with water to make working standard solutions with concentrations varying from 10 to 1000 µg L^{-1}.

Model organic compounds (26) containing chlorine, bromine and/or iodine, representing some major classes of DBPs, were selected to validate the optimised halogen-specific TOX method. The model compounds included haloacetic acids (HAAs), haloacetonitriles (HANs), chlorophenols, bromophenols and halogenated benzenes (Table S1). A stock solution of each organic halogen compound was prepared at a concentration of 100 mg L^{-1} in methanol. Final working solutions (100 µg L^{-1} in water; 250 mL) were then prepared. All stock solutions were kept at -15 °C to avoid degradation. A commercial dissolved organic matter (DOM) extract from the International Humic Substances Society (IHSS) was used in this study (Nordic Reservoir DOM, NR-DOM, catalogue number: 1R108N). The aromatic rich NR-DOM extract was selected for the halogenation of a DOM extract experiments. A NR-DOM stock solution (100 mg C L^{-1}) was prepared by dissolving the NR extract powder in water and filtration through a 0.45 µm membrane filter. A series of

NR-DOM working solutions (approximately 1 to 8 mgC L^{-1}) were prepared and their DOC concentrations determined by the UV/persulfate oxidation method using a Shimadzu TOC-V_{ws} Total Organic Carbon Analyser. A stock aqueous bromide solution was 1 g L^{-1} (12.5 mM). A stock aqueous sulphite solution for quenching of oxidant residuals was 1.3 g L^{-1} (10 mM).

Table S2 The impact of the number and repetitions of gas line washing on recoveries of selected model compounds.

Gas Line Washing		**Final Absorber Volume (mL)**	**Concentration Factor**$^{*)}$	**Recovery (%)**		
Number of Washes	**Time (s)**			**TCP**	**TBP**	**IP**
1x	0.1	5.37 ± 0.15	9.31	78 ± 2	80 ± 3	84 ± 4
1x	0.5	5.96 ± 0.08	8.39	89 ± 1	92 ± 4	86 ± 2
1x	1.0	6.71 ± 0.18	7.45	89 ± 4	91 ± 1	87 ± 4
2x	0.1	5.60 ± 0.00	8.93	88 ± 6	90 ± 3	86 ± 4
2x	0.5	6.82 ± 0.15	7.33	88 ± 1	89 ± 1	84 ± 2
2x	1.0	8.12 ± 0.13	6.16	91 ± 6	91 ± 4	85 ± 1

$^{*)}$ Volume of sample (50 mL) divided by final absorber volume; TCP: 2,4,6-trichlorophenol; TBP: 2,4,6-tribromophenol; IP: 2-iodophenol (concentration of each halophenol in the sample was 100 μg L^{-1}).

Table S3 Averages and ranges of some water quality characteristics of the raw groundwater blends at GWTP1 over a time period of approximately 3 years (2006-2009) (WCWA, 2009), and the concentrations of these water quality parameters on 28 May 2012.

Water sample	**Raw water**			
	Min	**Max**	**Average**	**28 May 2012**
DOM concentration (mgC L^{-1})	5.6	25.1	9.6	9.4
Bromide concentration (μg L^{-1})	420	1020	760	1350

Table S4 Physical and chemical properties of selected model compounds, as well as their recoveries through the optimised halogen-specific TOX method.

No.	**Compound**	**MW (g mol^{-1})**	**log K_{ow}**	**pK_a**	**Recovery (%)**)**		
					TOCl	**TOBr**	**TOI**
	Haloacetic Acids						
1	Chloroacetic acid	94.5	0.34	2.86	78 ± 6 (96 ± 2)[a] (92 ± 4)[b] (56)[c] (35)[d]		
2	Dichloroacetic acid	128.9	0.52	1.35	110 ± 12 (101 ± 5)[b]		
3	Chlorodibromoacetic acid	252.3	1.62		80 ± 10	97 ± 2	
4	Trichloroacetic acid	163.4	1.44	0.66	85 ± 4 (97 ± 4)[b] (109)[c] (83)[d]		
5	Bromoacetic acid	138.9	0.43	2.86		95 ± 4	
6	Bromochloroacetic acid	173.4	0.61		94 ± 4 (109 ± 2)[a] (100 ± 5)[b]	111 ± 4 (110 ± 0.6)[a] (100 ± 5)[b]	
7	Bromodichloroacetic acid	207.8	1.53		87 ± 6	92 ± 8	
8	Dibromoacetic acid	217.9	0.70			95 ± 6 (101 ± 4)[b]	
	Haloacetonitriles						
9	Bromoacetonitrile	120.0	0.20			108 ± 2 (127 ± 2)[a]	
10	Dibromoacetonitrile	198.8				107 ± 6	
11	Chloroacetonitrile	75.0	0.11		80 ± 8 (85 ± 10)[a]		
12	Dichloroacetonitrile	109.9			105 ± 4		
13	Bromochloroacetonitrile	154.4			135 ± 15 (126 ± 20)[a]	118 ± 10 (113 ± 0.3)[a]	
14	Trichloroacetonitrile	144.4			115 ± 10 (124 ± 2)[a]		
	Chlorophenols						
15	2-Chlorophenol	128.6	2.16	8.3	101 ± 6		
16	4-Chlorophenol	128.6	2.16	9.2	89 ± 4 (90.7)[c] (99)[d]		
17	2,6-Dichlorophenol	163.0	2.80	7.7	93 ± 8		
18	2,4,6-Trichlorophenol*)	197.5	3.58	6.25	91 ± 5 (104 ± 4)[a] (84)[d]		
19	Pentachlorophenol	266.3	4.74		82 ± 12		
	Bromophenols						

20	4-Bromophenol	173.0	3.40			99 ± 2 (99.2)[c] (96)[d]	
21	2,4-Dibromophenol	251.9	3.29	7.71		83 ± 6 (108 ± 0.9)[a]	
22	2,4,6-Tribromophenol*)	330.8	4.18	5.97		91 ± 2 (102 ± 4)[a]	
	Iodophenol						
23	2-iodophenol*)	220.0	2.68	8.41			85 ± 1 (96 ± 4)[a] (98)[d]
	Halogenated benzenes						
23	Bromobenzene	157.0	2.88			109 ± 6 (113 ± 6)[a] (79.8)[c]	
24	1,2-Dichlorobenzene	147.0	3.28		94 ± 4 (40.6)[c]		
25	1,4-Dibromobenzene	235.9	3.77			98 ± 2 (93 ± 3)[a] (46.1)[c] (49)[d]	

*) Halophenol standards

**) numbers in brackets refer to recovery values reported in references: [a] (Kristiana et al., 2015), [b] (Hua and Reckhow, 2006), [c] (Brandt and Kettrup, 1987), [d] (Oleksy-Frenzel et al., 2000).

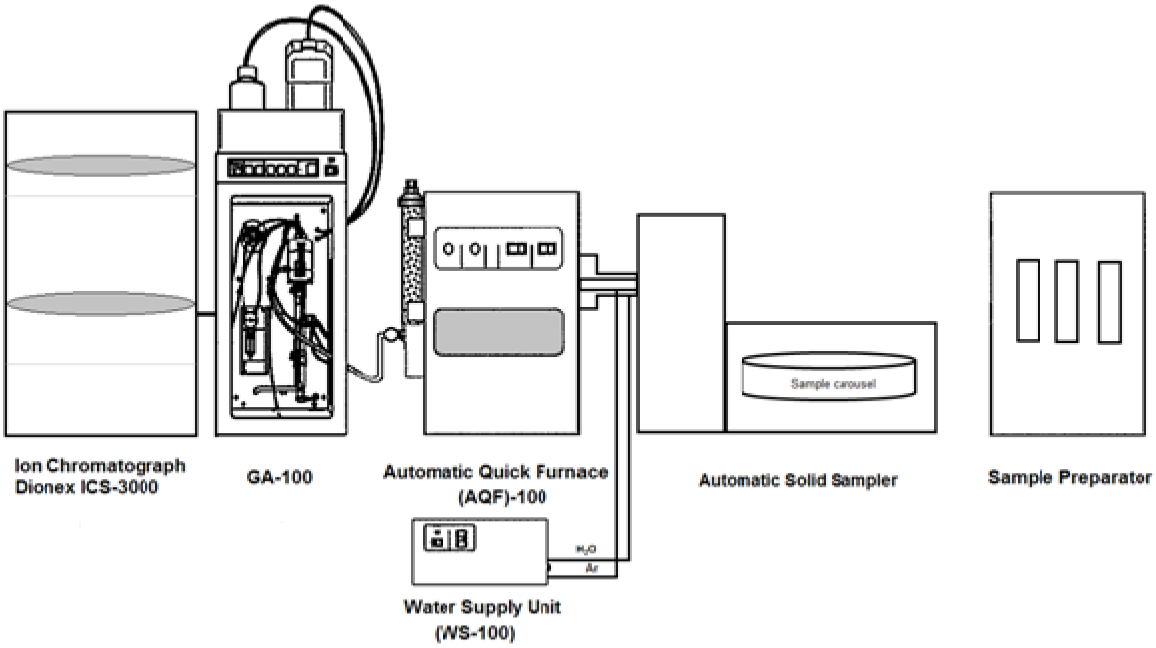

Figure S1 Schematic Diagram of Automatic Quick Furnace (AQF-100) with online Ion Chromatography and off-line Sample Preparator (after Kristiana et al. (2015)).

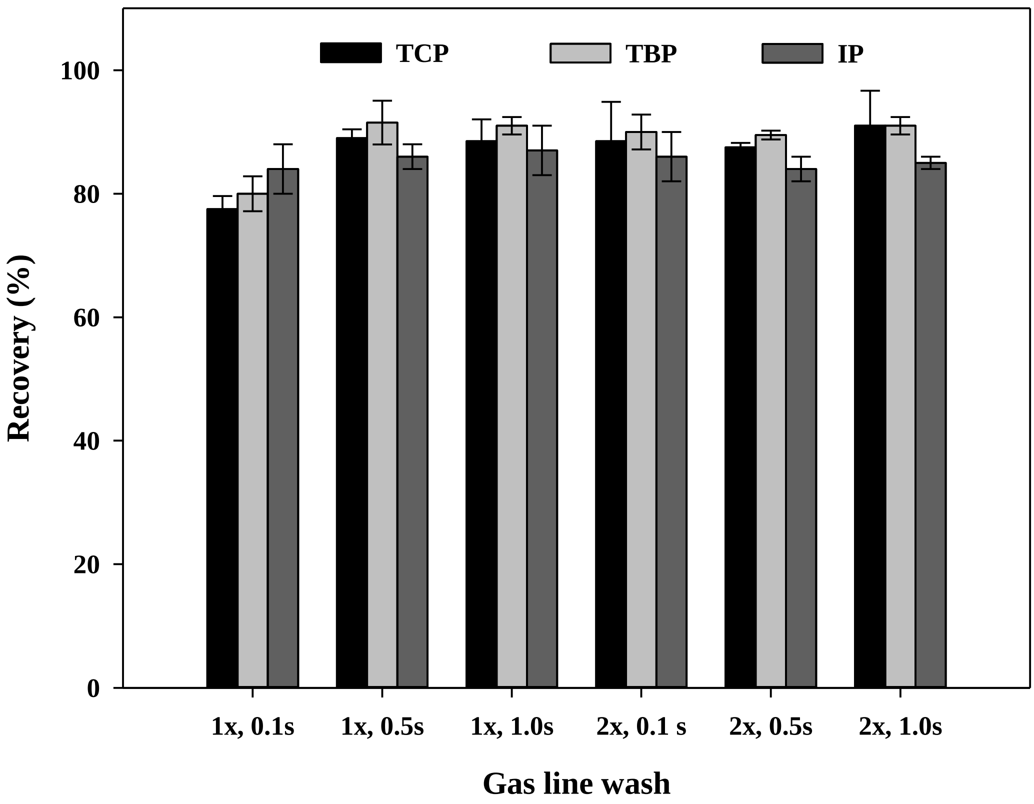

Figure S2 Recoveries of model compounds when different numbers of washes for different lengths of time in the gas line between the combustion unit and the absorber unit were used. TCP: 2,4,6-trichlorophenol, TBP: 2,4,6-tribromophenol, IP: 2-iodophenol (concentration of each halophenol in the sample was 100 µg L^{-1}).

Supporting Information References

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