Molecular changes among non-volatile disinfection by-products between drinking water treatment and consumer taps†

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The formation of disinfection by-products (DBPs) during drinking water treatment has been associated with various health concerns but the total DBP exposure is still unknown. In this study, molecular level non-target analysis by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to study non-volatile DBPs, and how their composition changes during water distribution in four drinking water treatment plants (DWTPs) in Sweden using different types of raw water and disinfection processes. The largest portion of tap water DBP compositions were detected also at the DWTPs, highlighting that these DBP formulae were rather stable and contribute to human DBP exposure. Yet the number of detected DBPs decreased 14–48% between drinking water treatment and consumer taps in the three plants in which no mixing of water from other DWTPs in the distribution system occurred showing active DBP processing in the water distribution network. While considerable amounts of bromine-containing DBPs were detected upon chemical disinfection in some DWTPs, few of them were detected in the tap water samples, likely due to debromination by hydrolytic reactions. The overall fewer non-volatile DBPs detected in tap waters, along with changed distribution among chlorine and bromine DBPs, demonstrate that DBP mixtures are highly dynamic and that DBP measurements at DWTPs do not adequately reflect exposure at the point-of-use. Clearly, more knowledge about changes of DBP mixtures through the distribution system is needed to improve DBP exposure assessments.

1. Introduction

The production of drinking water of high quality is of great societal importance. Chemical disinfection, where, e.g., chlorine, chloramine, chlorine dioxide or ozone is added, leads to reactions with natural organic matter (NOM) and the formation of potentially toxic disinfection by-products (DBPs).1

The formation of DBPs has been related to various health risks, such as bladder cancer and effects on adverse birth outcomes.2 A recent study based on ~500,000 births in Sweden found indications of a dose-dependent association between total trihalomethanes (THM) and adverse reproductive health effects (decreased fetal growth) in populations exposed to chlorinated drinking water, while no association was found in populations exposed to water treated with chloramine.3 Instead, human exposure to THM

Water impact

To mitigate health concerns from disinfection by-products (DBPs), potential changes to DBPs during distribution are important to account for. Non-target analysis demonstrates that the DBP mixture changes during distribution and that fewer bromine-containing DBPs were detected at consumer taps.
from chloraminated water was dose-dependently associated to other health risks connected to prenatal development, including malformations of the nervous system, urinary system, genitals and limbs. The differences in health risk associations between chlorinated and chloraminated water, while mutually based on TTHM exposure, shows that THMs are likely not the agents of these health concerns. In fact, which specific DBPs that cause the observed health risks are still not known. Recent findings indicate that nitrogen-containing DBPs, such as haloacetonitriles, constitute important components of toxicity in treated drinking water.

To date, most efforts have been directed towards analyzing DBPs using gas chromatography (GC) and a range of different detectors, which is important due to the regulatory status of DBPs determined with GC, e.g., THMs and haloacetic acids (HAAs). However, bioassay assessments based on fractionation experiments show that the non-volatile fraction contribute higher to total toxicity from DBPs compared to the volatile fraction. Logically, attempts to reduce health risks from DBPs are directed at new treatments or adaptations of routines, however, potential shifts in DBP composition during water distribution is important to account for as such changes may affect DBP exposure and associated health effects.

A promising way to study complex DBP mixtures and to investigate specific changes of the molecular compositions of these mixtures is non-target analyses using ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). FT-ICR MS enables the detection of thousands of distinct molecular formulae and has successfully been used to characterize individual elemental compositions in complex mixtures in, e.g., marine environments and boreal lakes. A multitude of DBPs have already been detected at drinking water treatment plants (DWTPs) through such non-targeted screening approaches. But the fate of these compounds in the distribution system remains uncertain, as well as if samples taken at the DWTP reflect exposure and risks to consumers at the point-of-use.

This study was undertaken to investigate potential changes to DBP composition between the DWTP effluent and the point-of-use (at consumer taps). By adopting a non-targeted approach using FT-ICR MS, DBPs of higher molecular weight, compared to commonly monitored DBPs, could be detected, offering a focus on a part of the DBP pool that is less known. This study comprises a multi-seasonal one-year sampling campaign at four Swedish DWTPs.

2. Methods

2.1 Description of water sources and treatment processes

The four Swedish DWTPs investigated were Berggården in Linköping (LIN), Borg in Norrköping (NOR), Görväln in Stockholm (STO) and Bulltofta in Malmö (MAL). Together, these plants supply approximately 800,000 consumers with drinking water. These DWTPs were chosen to cover some of the diversity in Swedish drinking water production. For MAL, there were no points in the distribution system featuring drinking water from the studied DWTP only, i.e., the MAL tap water point represented mixed drinking water from three DWTPs, one of which is MAL. The resulting dilution of MAL water in the distribution system should be considered throughout this study. MAL was included as some comparisons still are relevant.

The water sources used by each DWTP, named raw water in tables and figures, differ. At LIN, surface water from the river Motala Ström is used. This water originates from Vättern, a deep clear-water lake. NOR also takes water from Motala Ström, but at a point about 50 km further downstream, after the water has passed two large lakes surrounded by agricultural areas and forests, adding particles and dissolved organic matter. STO uses water from lake Mälaren, a water source with rather high levels of organic material, utilized by multiple DWTPs in the Stockholm area making Mälaren one of the most important raw water sources in Sweden. Finally, MAL uses a groundwater source, which has been utilized for drinking water production since the DWTP was built in 1879.

These raw waters were treated in different ways (Table 1). LIN was operated with rapid and slow sand filtration, followed by UV-disinfection and chlorination. At NOR, aluminum sulphate (Al₃(SO₄)₃) coagulation was followed by granular activated carbon filtration (GAC), slow sand filtration, and dosing of hypochlorite and ammonia to the water stream with hypochlorite added slightly in excess, forming monochloramine in the water stream. The GAC filter reduces taste and odor and is regenerated every four years, hence, it mostly operates as a biological filter (BAC). At STO, Al₃(SO₄)₃ coagulation was followed by rapid sand filtration to remove remaining particulates from the water, GAC, UV-disinfection and dosing of preformed monochloramine. In MAL (groundwater), aeration and softening removed dissolved iron and hardness, i.e., calcium and magnesium ions, followed by rapid sand filtration, UV-disinfection, and dosing of chloramine. At MAL, hypochlorite and ammonia were added to the water stream in theoretically equivalent proportions to form monochloramine, i.e., hypochlorite was not added in excess.

2.2 Sample collection

Water samples were collected repeatedly at the four DWTPs, during five sampling campaigns throughout a one year cycle, in March, May, August, and November 2016 and in January 2017. On each occasion, the following samples were collected: raw water, water after each treatment step (described in 2.1 and Table 1), finished water (drinking water leaving the DWTP) and water from a tap water point connected to the DWTP. This study focuses on the sampling points chemical disinfection, finished water, and tap water; some background information from the other sampling points, such as temperature, pH and various bulk DOM.
characteristics is presented in the supplement (Fig. S1–S8†). In NOR, the available sampling point after chemical disinfection did not represent well-mixed water and, thus, this sampling point was excluded at NOR. Samples were collected in duplicates in pre-washed amber 5 L glass bottles.

### 2.3 Water characteristics

Temperature was measured during sample collection. pH and conductivity were measured at room temperature within six hours after sample collection using a HACH HQ 40 (Hach, Stockholm). Total nitrogen (TN) was measured for duplicate samples of filtered water (Whatman GF/F, 0.7 μm porosity) using a Shimadzu TOC-V CSH TOC analyzer. The level of TN represents the sum of nitrate, nitrite, organic nitrogen, and ammonia. Total chlorine was measured on-line at the DWTPs and for tap water samples, an eXact idip photometer (Scantec Nordic, Jonsered) was used.

Dissolved organic carbon (DOC) and absorbance at 254 nm (UVA254) were determined in filtered water (Whatman GF/F, 0.7 μm porosity). DOC was measured at the accredited lab of each DWTP using the nPOC method. UVA254 was analyzed with an Ultrospec 2100 pro (Biochrom, Cambridge) using a 5 cm quartz cuvette and was reported as the absorbance per centimeter (cm⁻¹). Based on UVA254 and DOC, SUVA was computed by dividing the absorbance at 254 nm (cm⁻¹) by the DOC (mg C L⁻¹) and was reported in the unit L mg⁻¹ m⁻¹. UVA254 provides information on the abundance of organic molecules absorbing light at this wavelength, which depend on the overall organic content and the number of π-bonds and delocalized electrons in the organic molecules. SUVA is a proxy for DOC-normalized aromatic content based on correlations between % aromatic content and SUVA values for reference dissolved organic matter (DOM) samples.²²

### 2.4 Sample preparation for FT-ICR MS

For detailed DOM characterization, the organic material was isolated from the water by solid phase extraction (SPE).²³ The water samples were filtered through pre-combusted (5 hours at 450 °C) glass fiber filters (Whatman GF/F, pore size 0.7 μm, Whatman) into a second set of glass bottles and pH was adjusted to ∼2.5 using 3 M HCl (prepared by 32% HCl, p.a. and ultrapure water, spectrophotometric grade). At this lower pH, residual chlorine was not detected, and quenching agents were avoided to prevent potential interferences upon FT-ICR MS analysis. DOM was extracted using Bond Elut PPL cartridges (1 g, 6 mL, Agilent Technologies), a modified styrene and divinylbenzene copolymer adsorbent, providing ∼60% DOC extraction efficiency. The cartridges were conditioned with methanol (10 mL, LC-MS ultra CHROMASOLV®) and acidified ultrapure water (10 mL, pH 2.5, spectrophotometric grade, acidified with 32% HCl, p.a.). Filtered water (2 L for NOR and STO raw waters due to high DOC content, 4 L for the other sampling points) was passed through the SPE cartridges (flow rate kept below 20 mL min⁻¹) using Teflon tubing that connected each water sample bottle and cartridge. The cartridges were positioned on a vacuum manifold (Standard 24-port, 57 250-U, Sigma-Aldrich) and the extraction was driven by a peristaltic pump (Vantage 3000 C S10, Svenska pump AB). After the whole sample had
passed through, cartridges were washed with 0.1% formic acid water (10 mL, LC-MS ultra CHROMASOLV®) to remove ions that might interfere during FT-ICR MS analysis. A previous analysis of extracted DOM samples from multiple boreal lakes and streams that were washed with pH adjusted water using HCl instead of formic acid, showed the consistent formation of chloride adducts in FT-ICR MS (Fig. S9†), which would bias the interpretation of DBP formation. Parallel sample preparation and the usage of formic acid water for washing avoided this effect. Finally, the cartridges were dried for ~15 seconds using nitrogen gas (except for STO where air with a hydrocarbon trap was used, because nitrogen gas was not available) and DOM was eluted with methanol (10 mL). In previous work by the authors, a lower volume of 6 mL of methanol has been shown to not quantitatively desorb DOM from the cartridge and hence the volume of 10 mL was chosen to quantitatively elute DOM adsorbed to the PPL resin. Extractions were performed <4 hours after sample collection and for every extraction, a blank using 100 mL 0.1% formic acid water (LC-MS ultra CHROMASOLV®) was run. The extracts were stored at ~20 °C until analysis.

2.5 FT-ICR MS analysis
Analysis was performed using a Bruker Solarix 12 T FT-ICR MS operating with electrospray ionization in negative mode, ESI(−). Negative mode was chosen to allow largest possible diversity of compositions detected. FT-ICR MS measurements and data processing including formula assignments, filtration and verification (for halogenated DOM compositions) were conducted using protocols described previously.16 The elements included in formula assignment were: 12C0−100, 1H0−x, 18O0−80, 14N0−3, 32S0−2, 35Cl0−3 and 79Br0−3. The assigned formulae were filtered based on peak amplitude (total ion count >3 000 000), mass error (error <0.2 ppm between the experimental and theoretical mass) and the so-called nitrogen rule. A subsequent filtration procedure removed chemically unrealistic formulae, keeping formulae with C, O and H > 0, O/C ratio ≤ 1, H/C ratio ≤ 2.5, and double bond equivalences (DBE) ≥ 0. Furthermore, the number of nitrogen and sulfur atoms were limited to one during data analysis. A specific verification procedure was adopted as a quality control in the assignment of halogenated compounds. In short, a Matlab script was developed to identify halogenated compositions (assigned based on the presence of 35Cl or 79Br), for which a mass peak for the second stable isotope (37Cl or 81Br) was computed and searched for in the mass lists. Halogenated formulae determined in this study were limited to those that comprised both 35/37Cl or 79/81Br variants, using this procedure. Therefore, compounds for which the least abundant halogen isotope was below the detection limit were not included. From the molecular formulae, elemental ratios and various indices were computed. The indices used were double bond equivalences (DBE), DBE/C ratios, a modified aromaticity index (AImod), the average carbon oxidation state (COS) and modified Kendrick mass defects (−KMD/_adapter^e).16,24–26 Average weighted values were obtained by computing the ratio of individual mass peak amplitudes by the consolidated intensities of all mass peaks in a spectrum.

2.6 Approach for data analysis
Two replicate samples were analyzed and in general, the coherence between them were high. However, for a few samples the spectral intensities of one replicate were significantly lower and to enable homogenized treatment of data, the replicate with the highest overall abundance, representing the highest level of molecular information, was chosen for data analysis. Data analysis focused on compositional changes among DBPs between DWTPs and taps at an aggregated level, i.e., a qualitative, rather than a quantitative analytical approach was adopted.

3. Results and discussion
3.1 Differences in raw water characteristics
Water characteristics that were clearly different between the groundwater source (MAL) and the surface water sources (LIN, NOR, STO) regarded conductivity and TN. The higher conductivity in MAL (Table S1†) was explained primarily by the presence of chloride, sulphate, calcium, magnesium and sodium. The higher TN concentration in MAL (Table S1†), was primarily explained by ammonium ions. Water temperatures were most stable in the groundwater (MAL) and varied most in LIN (from 1.2 °C in January to 23.2 °C in August). Variations of pH were rather small (7.2–8.0).

The raw water of STO had the highest DOC concentrations (7.0–7.9 mg L−1), followed by the raw water of NOR (5.6–7.0 mg L−1) (Table S1†). The DOC in LIN and MAL raw waters ranged between 2.2–3.0 mg L−1. STO and NOR had similar UVA254, indicating a similarity in optical bulk DOM characteristics. In LIN, UVA254 and SUVA were low, demonstrating a low abundance of aromatic DOM.

FT-ICR MS compositional data of raw water DOM formulae consolidated for all five sampling months, are shown in Table S2.† Molecules containing carbon, hydrogen, and oxygen (CHO) dominated (69–75%), followed by molecules with an additional nitrogen (CHNO) (16–22%), sulfur (CHOS) (8–11%), and a few molecules containing both nitrogen and sulfur (CHNOS) (<1%).* LIN CHO formulae were more saturated (higher H/C ratio, lower double bond equivalences (DBE) and modified aromaticity index (AImod), compared to the other water sources, which is in accordance with the low absorbance observed (Table S1†). Nitrogen-containing DOM had higher DBE, compared to the CHO compositions, suggesting a higher abundance of unsaturated compounds among the nitrogen-containing DOM. The sulfur-containing DOM instead had lower weighted average of DBE and relatively elevated H/C ratio, suggesting higher relative proportions of near saturated aliphatic compounds. Few halogenated formulae were detected in the raw water (n = 16, 14, 10, 2) at LIN, NOR, STO and MAL, respectively, when summarizing formulae from the five
sampling occasions, including both chlorine- and/or bromine-containing compounds.

3.2 Overall treatment-induced changes

Temperature did not change significantly during treatments while conductivity increased slightly from source to tap, except in MAL, where softening reduced conductivity by ~50% (Fig. S1–S4†). pH was adjusted to optimize certain treatments, such as coagulation (pH 6.4–6.9) in NOR and STO (Fig. S2 and S3†) and softening (pH ~9) in MAL (Fig. S4†). pH was also adjusted before distribution to avoid corrosion in the distribution network. TN was slightly affected by coagulation (NOR and STO) and chloramine addition (STO) (Fig. S2 and S3†) and showed great variation at the consumer tap in MAL (Fig. S4†). Of the treatments (Table 1), coagulation, used in NOR and STO, showed the largest effect on DOM properties, including decreases in both DOC concentration (2.8–3.7 mg L\(^{-1}\) in NOR and 2.9–3.5 mg L\(^{-1}\) in STO), UVA\(_{254}\) (0.11–0.19 cm\(^{-1}\) in NOR and 0.11–0.15 cm\(^{-1}\) in STO) and SUVA (0.9–1.8 L mg\(^{-1}\) m\(^{-1}\) in NOR and 0.8–1.2 L mg\(^{-1}\) m\(^{-1}\) in STO). Tables S3- and S4† summarize relevant water characteristics at the point right before chemical disinfection.

3.3 Halogenated DOM from source to tap

Some halogenated organic molecules, which were mostly brominated were detected and verified in all raw waters, but a major change was observed after chemical disinfection (Fig. 1), explained by the formation of DBPs. CHO-type molecules were the most significant precursors to halogenated DBPs but verified CHNO- and CHOS-based DBPs were also detected (Fig. S10 and S11†). The DBPs were mostly

Fig. 1 Bar plot showing the number of halogenated (Cl/Br) molecular formulae (CHO-, CHNO- or CHOS-type) present from source to tap at the four DWTPs, including formulae combined for all five sampling months. Note the different y-scales.
chlorinated, but at STO and especially at MAL, significant numbers of brominated compounds were detected, likely due to the relatively high concentration of bromide (\(\sim 0.28 \text{ mg L}^{-1}\)), analyzed at Eurofins accredited laboratory in the source water of MAL. When including all variants of CHO-, CHNO- and CHOS-based brominated DBPs (Br-DBPs) detected at MAL, 18% had Al_{mod} > 0.50, which has been used as a threshold for aromatic structures, while 11% of the chlorinated DBPs (Cl-DBPs) were above that threshold. At STO, aromatic DBPs were found in similar proportions among Cl-DBPs (9%) and Br-DBPs (8%).

3.4 Changes in the distribution system

From the point of disinfection to consumer taps, the abundance of halogenated compounds detected by FT-ICR MS decreased in LIN (33%), NOR (14%) and STO (48%), representing the DWTPs for which outgoing water is directly comparable with the tap water sample (Fig. 1). The observed molecular formula changes indicate a dynamic DBP pool that changes in the distribution system and the observed trend might be explained by (1) transformation to DBPs not detectable with FT-ICR MS, e.g., volatile DBPs, such as THMs or (2) decomposition reactions, e.g., biodegradation leading to release of chloride or bromide ions and compounds lacking organically bound halogens, or (3) transformation to DBPs detected both at the DWTP and at the tap.

In previous work, an overall decrease among phenolic DBPs during distribution of chlorinated and chloraminated water was observed and the pattern might be explained by hydrolytic reactions of these larger DBP molecules forming low molecular mass volatile compounds, such as THMs, which usually increase in number with increased contact times. In particular, this is likely for water treated with chlorine. However, for the DWTPs using chloramine in this study, such volatile DBPs were rarely detected. Through model-based experiments, aimed to explain changes in total organic halogen balances, the pathway that was suggested to lead to significant decay during chloramination (i.e., \(\sim 15\%\) of Cl-DBPs and \(\sim 33\%\) of Br-DBPs), was hydrolytic reactions leading to decomposition, i.e., resulting in an altogether decrease in halogenated organic compounds. Such reactions can be catalyzed by dehalogenase enzymes during biodegradation, the rates of which increase with higher total organic carbon levels and availability of nutrients, such as phosphate, as observed for haloacetic acids.

Changes to overall DOM composition during distribution was small (Fig. S5–S8 and Tables S5 and S6) and most of the individual DOM formulae were detected both at the DWTPs and in the tap waters (Fig. S12†). Thus, changes among detected CHO-, CHNO- and CHOS-molecular formulae could not explain the DBP shifts observed. Contact times in the system may be indicated by differences in total chlorine between DWTPs and consumer taps (Table 2). For example, total chlorine levels at NOR were rather unchanged between finished water and the tap (Table 2), which can be linked to a shorter contact time between DWTP and the tap point, compared to the other locations, possibly also explaining the smaller changes of halogenated compounds at NOR (Fig. 1). The exact contact times in the distribution system are difficult to estimate and vary with water use but were expected to be relatively similar for LIN and NOR (<24 hours), while being longer in STO (up to 4 days). In MAL, a higher number of DBPs was detected at the tap than at the DWTP (Fig. 1), likely due to the contribution of DBPs from other DWTPs in the distribution system. However, from the point of chloramine addition to the tap water point, the number of detected DBP formulae decreased by 51%.

3.5 The fate of Br-DBPs

The fate and contribution of Br-DBPs in consumer drinking water are particularly relevant, since they are generally 10–100 times more cytotoxic than their chlorine-containing analogues. The number of detected bromine-containing formulae decreased from the point of chloramine addition to tap (STO) and from the point of chloramine addition to finished water (MAL, comparison to tap not included for MAL because of the mixing of water from other DWTPs in the distribution system). This indicates changes in the balance between Cl-DBPs and Br-DBPs during distribution to consumers, potentially explained by the different stabilities of Cl-DBPs and Br-DBPs, where Br-DBPs are less stable.

Debromination by hydrolytic reaction is faster than dechlorination as the Br–C bond is longer and its dissociation energy lower, i.e., the C–Br bond is weaker. The degradation rate increases under alkaline conditions (Fig. S1–S4†).

Br in a phenolic Br-DBP can be substituted by Cl to form its Cl-DBP analogue and during chlorination, up to 30% of the organically bound bromine was estimated to be transformed to organically bound chlorine. However, such replacement reactions involving chlorine have not been considered likely, due to the lower reactivity of chloramine, compared to chlorine. The potential influence on DBP speciation of the biofilm inside the pipes in the distribution system may be indicated by differences in total chlorine between DWTPs and consumer taps (Table 2). For example, total chlorine levels at NOR were rather unchanged between finished water and the tap (Table 2), which can be linked to a shorter contact time between DWTP and the tap point, compared to the other locations, possibly also explaining the smaller changes of halogenated compounds at NOR (Fig. 1). The exact contact times in the distribution system are difficult to estimate and vary with water use but were expected to be relatively similar for LIN and NOR (<24 hours), while being longer in STO (up to 4 days). In MAL, a higher number of DBPs was detected at the tap than at the DWTP (Fig. 1), likely due to the contribution of DBPs from other DWTPs in the distribution system. However, from the point of chloramine addition to the tap water point, the number of detected DBP formulae decreased by 51%.
system, which can be considered an additional source of DOM, has been investigated, both for chlorine and chloramine residuals, however, for the low residual levels of disinfectant reported in this study (Table 2), such reactions are not expected to contribute significantly to the shift in the Br- and Cl-DPB balance. Altogether, the more likely reasons for the Br-DBP decrease in the distribution system is attributed to their faster hydrolysis reactions.

### 3.6 Characterization of tap water DBPs

The higher weighted average oxidation state of carbon (COS) among tap water DBPs (except in STO) compared to DBPs detected at the point of disinfection (Table 3) are likely linked to the continuous oxidation reactions with the residual disinfectant in the distribution system. The opposite trend observed in STO was linked to an overall lower oxygen and higher hydrogen content among tap water DBPs (except in STO) compared to DBPs detected after disinfection only are substantially different from those detected at the DWTP (Fig. 2 and S13†) and not a single Br-DBP of those formed after chloramine addition were detected in the tap water (Fig. 1 and 2 and S13†). This was probably a result both of mixing in of water from other DWTPs in the system and potential transformations of MAL DBPs and highlights the challenges of addressing end-user DBP exposure via water from multiple DWTPs. DBPs detected after disinfection only are summarized in Table S10.†

| DBP characteristics | LIN | NOR | STO | MAL |
|---------------------|-----|-----|-----|-----|
| Number of DBP formulae | 276 | 264 | 471 | 222 |
| Mass weighted average [Da] | 382.5 | 373.6 | 372.7 | 375.1 |
| Average DBE | 7.6 | 7.8 | 7.7 | 7.8 |
| Average A_lamod | 0.35 | 0.38 | 0.38 | 0.38 |
| Average carbon oxidation state (COS) | 0.070 | 0.130 | 0.036 | 0.063 |
| Average DBE/C | 0.48 | 0.51 | 0.49 | 0.50 |
| Average H [%] | 40.5 | 39.2 | 40.3 | 39.9 |
| Average C [%] | 37.1 | 37.7 | 37.8 | 37.8 |
| Average O [%] | 19.7 | 20.2 | 19.1 | 19.5 |
| Average N [%] | 0.00 | 0.03 | 0.00 | 0.00 |
| Average S [%] | 0.01 | 0.01 | 0.01 | 0.01 |
| Average CI [%] | 2.7 | 2.8 | 2.7 | 2.8 |
| Average Br [%] | 0.0 | 0.0 | 0.1 | 0.0 |
| Computed average H/C ratio | 1.09 | 1.04 | 1.07 | 1.05 |
| Computed average O/C ratio | 0.53 | 0.54 | 0.51 | 0.52 |

DBPs solely detected in tap waters probably formed after longer contact times and were characterized by lower average O/C ratios (LIN and STO) and higher average mass (all DWTPs) (Table S7†) and are listed in Table S9†. At MAL, the DBPs detected at the tap were substantially different from those detected at the DWTP (Fig. 2 and S13†) and not a single Br-DBP of those formed after chloramine addition were detected in the tap water (Fig. 1 and 2 and S13†). This was probably a result both of mixing in of water from other DWTPs in the system and potential transformations of MAL DBPs and highlights the challenges of addressing end-user DBP exposure via water from multiple DWTPs. DBPs detected after disinfection only are summarized in Table S10.†

### 3.7 Dynamic DBP mixtures

The patterns observed through non-target DBP analysis at the different stages, i.e., directly after chemical disinfection, finished water leaving the DWTP and tap water, demonstrate that the mixture of DBPs in drinking water leaving a DWTP is not the same as the DBP mixture consumers are exposed to. A perspective of dynamic transformations of DBPs, where the contribution of different DBP classes to the total DBP pool decrease or increase during drinking water distribution is in contrast to the commonly adopted static perspective, assuming that each DBP class contributes equally over time. The dynamic perspective suggests that high molecular weight...
DBPs decrease in contribution to the DBP pool with increased chlorine/chloramine residual contact time, while the typically monitored DBPs, including THMs and haloacetic acids (HAAs), and other volatile DBPs increase in contribution with increased contact time. This is likely a consequence of the continuous halogenation which finally results in ring opening (in case of aromatic precursors) and release of THMs.
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Because brominated DBPs are often more toxic than chlorinated analogues,\textsuperscript{43} the lower counts of Br-DBPs detected by FT-ICR MS in tap waters seem favorable in terms of toxicity considering this group of DBPs only, but effects on overall toxicity is unclear as potential shifts to non-detected DBPs is not assessed.

The fate of different DBP groups vary; at specific conditions some will accumulate, while others degrade.\textsuperscript{35,46} If original DBP mixtures are transformed to less toxic mixtures over time it might have implications for the operation of drinking water distribution systems, \textit{e.g.}, optimizing water age of distributed drinking water as means to reduce health effects caused by DBPs. It seems logical to follow up this work using, \textit{e.g.}, TIC-TOX approaches,\textsuperscript{6} or effect-based methods\textsuperscript{47–49} to further investigate how the combined toxic effects from DBP mixtures change in distribution systems.

While the non-target FT-ICR-MS approach used here offers broadest coverage of molecular compositions and highest sensitivity among currently available chemical screening methods, it is still subject to ionization selectivity, which makes considerable parts of the DBP pool undetectable; the used extraction procedure was also selective.\textsuperscript{50} Moreover, the verification process was highly conservative and likely missed many DBP formulae. To improve FT-ICR-MS-based DBP detection including isotope verification, a database with verified DBP formulae, to which actual mass spectra could be matched, would be a useful asset. Halogenated DBPs, for which the $^{37}\text{Cl}^{81}\text{Br}$ isotope is not detected but has been previously verified, could then be indirectly confirmed.

4. Conclusions

Despite an expected dehalogenation or transformation of DBPs to smaller, volatile compounds during distribution, FT-ICR MS detected DBPs were found in various tap water samples, showing that these oxygen-rich aromatic compounds, are relevant for human exposure. The dynamic changes of DBP mixtures between DWTPs and consumer taps highlight that DBP exposure cannot be accurately assessed by measurements at the DWTP alone but require DBP monitoring at points-of-use. Better understanding of the variability and changes (from DWTP to tap) of DBP mixtures is needed. Given that specific characteristics, unique for each distribution system, seem important for the local spatial variability and dynamics of DBPs, collaborations between researchers and engineers specialized on the water distribution systems will be beneficial to better assess and manage future DBP exposures.

Conflicts of interest

There are no conflicts of interest to declare.

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