

Selective Chlorination of Natural Organic Matter: Identification of Previously Unknown Disinfection Byproducts

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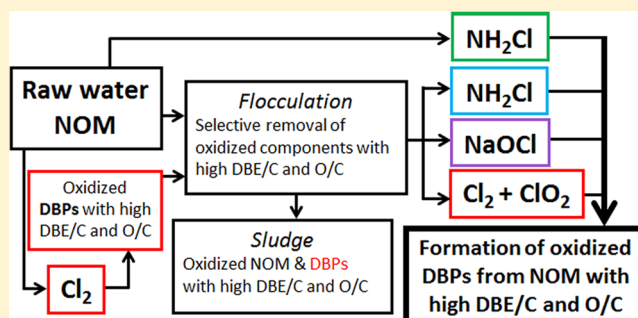
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Supporting Information

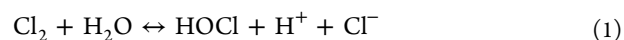
ABSTRACT: Natural organic matter (NOM) serve as precursors for disinfection byproducts (DBPs) in drinking water production making NOM removal essential in pre-disinfection treatment processes. We identified molecular formulas of chlorinated DBPs after chlorination and chloramination in four Swedish surface water treatment plants (WTPs) using ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Chlorine-containing formulas were detected before and after disinfection and were therefore classified to identify DBPs. In total, 499 DBPs were detected, of which 230 have not been reported earlier. The byproducts had, as a group, significantly lower ratio of hydrogen to carbon (H/C) and significantly higher average carbon oxidation state ($\overline{C_{OS}}$), double bond equivalents per carbon (DBE/C) and ratio of oxygen to carbon (O/C) compared to Cl-containing components present before disinfection and CHO formulas in samples taken both before and after disinfection. Electrophilic substitution, the proposed most significant reaction pathway for chlorination of NOM, results in carbon oxidation and decreased H/C while O/C and DBE/C is left unchanged. Because the identified DBPs had significantly higher DBE/C and O/C than the CHO formulas we concluded that chlorination of NOM during disinfection is selective toward components with relatively high double bond equivalency and number of oxygen atoms per carbon. Furthermore, choice of disinfectant, dose, and pre-disinfection treatment at the different WTPs resulted in distinct patterns in the occurrence of DBP formulas.



1. INTRODUCTION

Identification of previously unknown byproducts formed during disinfection of drinking water is of great importance because many known disinfection byproducts (DBPs) have been shown to cause severe health effects.^{1–3} Natural organic matter (NOM) constituents serve as precursors for DBPs and its presence may also lead to problems with (i) taste, color, and odor, (ii) cotransportation of organic pollutants⁴ and heavy metals,⁵ (iii) fouling of membranes⁶ and active carbon,⁷ (iv) biological regrowth in the distribution system,^{8,9} and (v) increased coagulant demand.¹⁰ The increasing levels of NOM that have been recorded in many lakes in northern and central Europe as well as North America during the last decades^{10–15} may therefore have a large impact on drinking water quality. This paper addresses the formation of chlorinated organic byproducts during chlorination and chloramination in drinking water disinfection processes. Although as many as 600 different DBPs formed during disinfection have been identified,²

research on halogenated DBPs has been mainly focused on trihalomethanes (THMs), haloacetic acids (HAAs), or total organic halides (TOX).^{16–20} Accordingly, more than 50% of the TOX produced when chlorinating drinking water³ and as much as 80% formed when using chloramine and chlorine dioxide²¹ are unknown and remain to be identified on a molecular level. Chlorine (Cl₂), chloramine (NH₂Cl), and chlorine dioxide (ClO₂) are widely used as disinfectants in drinking water production. In water, Cl₂ hydrolyses to form hypochlorous acid:



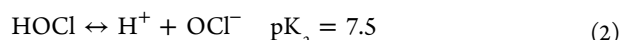
which further dissociates to hydrogen and hypochlorite ions:

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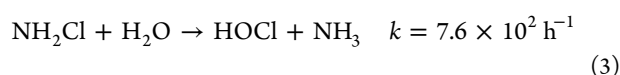
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Possible reactions between chlorine and NOM include (i) oxidation, (ii) addition to unsaturated bonds, and (iii) electrophilic substitution where the two latter lead to the production of organochlorine compounds.²² Humic substances show high reactivity toward chlorine.^{23–25} Thus, in order to minimize DBP formation removal of these compounds is essential in pre-disinfection treatment processes. Chlorine dioxide, unlike chlorine, does not hydrolyze in water²⁶ and is generally considered mainly to oxidize NOM producing nonchlorinated byproducts and, hence, fewer chlorinated DBPs arise than when using chlorine.²³ The formation of DBPs from monochloramine is generally thought to be limited compared to chlorine due to its lower reactivity,²⁷ but byproducts can still be produced because NH_2Cl slowly hydrolyzes to free chlorine in aqueous solution:²⁶



The limited number of identified chlorinated organic DBPs is not surprising when considering the molecular complexity of the precursor material; NOM. Ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) is an emerging technique to determine the molecular composition of NOM. The formation of chlorinated organic byproducts identified with FT-ICR-MS has been previously studied in both laboratory scale experiments and in samples from full scale water treatments.^{28,29} However, no attempt has been made to differentiate DBPs from chlorinated components that are present before disinfection. In this study FT-ICR-MS was used to identify chlorinated components formed during chlorination and chloramination in four Swedish water treatment plants (WTPs) and a classification, based on the presence of Cl-containing formulas in samples taken before disinfection, was designed to determine their probable origin. We believe it is important to discriminate DBPs from CHCl formulas present before disinfection in order to provide target components to be further studied for determination of precursor components and reaction pathways. The investigated WTPs supply ~15% of all drinking water in Sweden. The raw water sources of these WTPs are used to produce approximately one-third of all Swedish drinking water which represents ~70% of the total national drinking water production from surface waters. We investigated characteristics of chlorinated DBPs through elemental ratios, double bond equivalency, and the average oxidation state of carbon, patterns in the presence of DBPs arising from differences in choice of disinfectant and pre-disinfection treatment, as well as changes in NOM composition during disinfection. A detailed description of chlorinated DBPs is essential in order to minimize byproduct formation for WTPs facing the need of adapted treatment processes due to increasing NOM levels in surface waters.

2. MATERIALS AND METHODS

2.1. Sampling. Water samples (1–4 L) were collected in pre-rinsed polyethylene bottles on 17–18th of October, 2011, from four Swedish WTPs; Lovö, Kvarnagården, Ringsjö and Lackarebäck (Supporting Information (SI) Figure S1), employing different treatment processes (Figure 1). Lovö WTP was investigated most thoroughly with duplicate samples taken after each treatment step. In the three other WTPs only raw and treated waters were considered. No chemical was added to

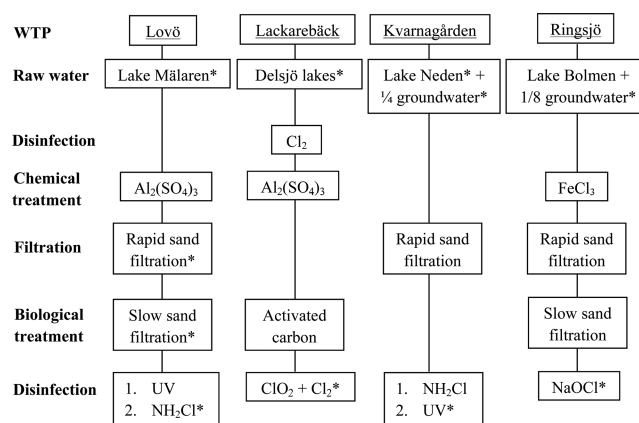


Figure 1. Lake water sources, treatment processes and sampling points (*processes after which samples were taken).

quench free chlorine as all samples were extracted within 24 h from sample collection (i.e., within the residence time the drinking water typically spends in the distribution system before reaching consumers). All samples were analyzed for dissolved organic carbon (DOC), absorbance (254 nm) and pH while disinfectant dose and residual were measured or calculated at the WTPs. Samples were further extracted and analyzed with FT-ICR-MS. Basic characteristics, extraction efficiency and disinfectant dose are given in Table 1.

2.2. Organic Carbon and Absorbance Analysis. All samples were filtered through 0.45 μm cellulose acetate filters (Minisart, Sartorius) within 24 h. Filters were rinsed with ultrapure water (Milli-Q, 18.2 Ω) prior to sample filtration. The samples were analyzed for DOC with a Shimadzu TOC-V_{CPH} carbon analyzer. Prior to analysis all samples were acidified to pH 2 with 2 M HCl and purged with CO_2 -free air for 10 min to remove inorganic carbon. Samples were injected in triplicate with a resulting coefficient of variation below 2%. Results were calibrated against potassium phthalate standards (2.0–20 mg C L⁻¹) and instrument performance was controlled by an EDTA standard (10 mg C L⁻¹) or the certified reference material Big Moose-02 (3.9 mg C L⁻¹) (Environment Canada). Absorbance was measured at 254 nm (Perkin-Elmer Lambda 40) in a 5 cm cuvette and used to calculate DOC-normalized absorbance (specific UV absorbance - SUVA). Milli-Q was used as blank for the absorbance measurements.

2.3. FT-ICR-MS Analysis. **2.3.1. Extraction.** Samples for FT-ICR-MS analysis were filtered through Whatman GF/F glass fiber filters (approximately 0.7 μm effective pore size). Earlier measurements of the same waters (data not shown) demonstrated no difference in DOC concentration between dissolved fractions filtered with 0.7 and 0.45 μm . Concentrated HCl (32%, p.a. grade, Merck) was added to the filtered samples in order to achieve pH 2. The samples were then gravity fed through activated Agilent Bond Elut PPL solid-phase extraction (SPE) cartridges filled with 1 g of the polar functionalized polystyrene divinylbenzene (PPL) for extraction of organic compounds following the procedure described by Dittmar et al.³⁰ High molecular weight organic compounds including their chlorinated byproducts are expected to be extracted with high yields due to their hydrophobicity and the optimization of the SPE resin toward polar compounds. Generally, small highly polar organic acids and compounds of similar polarity will partly escape the used SPE resin and are likely to be mainly responsible for losses of DOC during extraction. The

Table 1. Basic Characteristics of the Water Samples Taken for FT-ICR-MS Analysis^a

WTP	sample	DOC (mg L ⁻¹)	DOC _{ex} (%)	SUVA	pH	Cl-dose (mg Cl ₂ L ⁻¹)	total (free) Cl residual (mg Cl ₂ L ⁻¹)
Lovö	raw	9.0	74–84 ^b	2.5	7.5		
	RSF	5.6	75–82 ^b	1.7	7.1		
	SSF	4.9	75–77 ^b	1.7	7.6		
	drink	4.8	69–70 ^b	1.7	7.9	0.27 ^c	0.28
Lackarebäck	raw	5.0	76	3.0	7.2	0.39	
	drink	2.3	66	1.4	7.5	0.86 ^d	0.28 (0.19)
Ringsjö	raw/mix	10.5	86	3.9	6.7		
	drink	2.9	70	1.5	8.0	0.88 ^c	0.29 (0.20)
Kvarnagården	surf	3.4	69	2.7	7.1		
	raw/mix	3.2	60	2.4	7.2		
	drink	3.2	74	2.2	8.0	0.30	0.17

^aDOC_{ex} = DOC fraction recovered in the SPE. Raw = surface water used as raw water, raw/mix = surface water mixed with groundwater (used as raw water), surf = surface water, RSF = rapid sand filtrate, SSF = slow sand filtrate, drink = drinking water. ^bRange of values for double samples. ^cCalculated value. ^dDivided approximately 50/50 between Cl₂ and ClO₂.

traditional DBPs are possible to extract even though they either have a very high polarity (e.g., halogenated acetic acids) or volatility (e.g., dichloromethane) but are too small to be analyzed with FT-ICR-MS. The extraction efficiency, calculated from DOC concentration before and after SPE, was $74 \pm 7\%$ (Table 1), which is about 10% higher than reported values by Dittmar et al.³⁰ for freshwater organic matter.

2.3.2. Analysis. Analysis of extracted samples was performed at the Helmholtz Center for Environmental Science in Munich, Germany using a Bruker Solarix QE 12 T FT-ICR mass spectrometer. Electrospray ionization (ESI) in negative ion mode, a soft ionization technique operating at atmospheric pressure, was used to generate ions (Apollo II). This ionization technique is known to mainly produce unfragmented, singly charged molecular ions.³¹ Multiple-charged mass peaks are easily distinguished due to the ultrahigh resolution of the exact mass peaks. These peaks occur at very low abundances and can only be detected if several thousands of scans are averaged or if the concentration of the sample is far too high causing oversaturation in the ICR cell. External calibration of all mass spectra was obtained using arginine and its specific mass peaks. Internal calibration was also performed to further enhance the precision and to achieve an error <0.2 ppm using known exact mass peaks between 200 and 600 Da that are always present in NOM samples.

2.3.3. Data Processing. Formulas were assigned from the *m/z* peaks based on ¹²C_{0–100}, ¹⁶O_{0–80}, ¹H_{0–∞}, ³²S_{0–1}, ¹⁴N_{0–2}, ³⁵Cl_{0–3}, and ¹³C_{0–1}. The nitrogen rule was applied and a conservative approach used where only peaks that could be validated with their ¹³C isotopomer were allowed. Because the focus in this paper is on formation of high molecular weight DBPs only molecular formulas containing C, H, O, or Cl were further investigated. The ³⁷Cl isotopomer of chlorine (natural abundance ≈ 24%) was also found and sporadically used to cross-validate the parent molecular formulas. If residual chloride ions are present, reactions with NOM are unavoidable, especially for carbohydrates, leading to the formation of chloride ion adducts in the electrospray source.^{32,33} SPE was systematically used to desalt the samples before analysis. Thus, formulas could be assigned covalently bound Cl comparable to previous studies.^{28,29,34} Ion accumulation time was set to 0.2s and 1000 scans were averaged for each mass spectrum to

increase peak intensities and mass resolution in order to further evaluate small peaks initially found using 500 scans. Molecular formulas containing chlorine generally show very low abundances before disinfection and could only be conclusively detected after averaging 1000 scans.

2.3.4. Limitations. To interpret the ESI-FT-ICR-MS data it needs to be considered that (i) only extractable NOM is analyzed, (ii) acidification to pH 2 before extraction may alter the compounds, and (iii) electrospray ionization is a competitive process where compounds that are more easily ionized will suppress less ionizable compounds. FT-ICR-MS should, therefore, be considered as a qualitative method that at best can be used semiquantitatively when comparing similar matrices. It is possible to look at differences in relative abundance of mass peaks and their assigned molecular formulas in similar samples, for example, along a gradient or from a treatment process, but not compare actual abundances in two different samples since the same compound may be suppressed due to matrix effects and the presence of highly efficient ionizing compounds (e.g., sulfonic and carboxylic acids). Furthermore, the FT-ICR-MS used in this study has a mass cutoff at 147 Da. Therefore, and with the selective extraction in mind, the detected chlorinated components do not represent the entire pool of chlorinated organic compounds present in the raw and treated waters.

2.3.5. Calculations and Statistics. Ratios of O/C and H/C for single formulas were used to construct van Krevelen diagrams^{35,36} as bubble plots where bubble size represents the relative abundance of the mass peaks within a sample. Double bond equivalents per carbon (DBE/C) and average carbon oxidation state (\overline{C}_{OS})³⁷ were calculated according to eqs 4 and 5.

$$DBE/C = 1 + 0.5 \times \frac{(nC \times 2) - nH - nCl}{nC} \quad (4)$$

$$\overline{C}_{OS} = -\frac{(nH \times 1) + (nO \times -2) + (nCl \times -1)}{nC} \quad (5)$$

Weighted mean values (against the relative abundance of the mass peaks) of O/C, H/C, DBE/C and \overline{C}_{OS} were calculated and are hereafter referred to as O/C_w, H/C_w, DBE/C_w and $\overline{C}_{OS,w}$. The weighted mean values were tested statistically for

differences between samples and different groups of formulas with ANOVA in JMP (SAS Institute Inc.). Hierarchical cluster analysis was performed in PAST³⁸ using Ward's method of similarity. Ward's method, also called the minimum variance method, merges pairs of clusters based on the Euclidean distance between centroids in order to minimize the increase in the total within-group error sum of squares. Details regarding Ward's method can be found elsewhere.³⁹

3. RESULTS AND DISCUSSION

3.1. Classification of Chlorinated Components. The presence of chloroorganic components in samples taken before disinfection complicated the identification of DBPs and all assigned formulas in the drinking water samples needed to be classified according to their probable origin. The classification of specific formulas was done systematically in several steps (Table 2). At first all WTPs were examined individually and all

Table 2. Classification Terms for Origin of Formulas Containing C, H, O, and Cl

first classification				
●all WTPs investigated separately				
●DBPs = only found in drinking water samples for the individual WTPs				
WTP	present before disinfection (nr of formulas)	unique for drinking water, 1Cl (nr of formulas)	unique for drinking water, 2Cl (3Cl) (nr of formulas)	
Lovö	448	164	11	
Lackarebäck	265	56	50	
Ringsjö	347	433	227 (2)	
Kvarnagården	404	248	24	
↓				
second classification				
●cross-check between WTPs				
●DBPs = only found in drinking water samples				
●already present = found prior to disinfection in ≥66% of the WTPs where the formula was identified				
●unclassified = detected prior to disinfection in 50% of the samples or less				
WTP	already present (nr of formulas)	DBPs, 1Cl (nr of formulas)	DBPs, 2Cl (3Cl) (nr of formulas)	unclassified (nr of formulas)
Lovö	471	60	11	75
Lackarebäck	369	13	50	39
Ringsjö	524	142	227 (2)	114
Kvarnagården	364	210	24	77
In total	538	266	230 (2)	118

CHOC1 formulas that were unique for the drinking water samples were considered as DBPs. However, after cross-checking the formulas between the plants it was discovered that some formulas that were unique for drinking water in one WTP were found prior to disinfection in another plant. Because a large fraction of organic carbon was removed from the raw waters at Lackarebäck and Ringsjö WTPs (where only raw and fully treated waters were available) we hypothesize that some of the new Cl-containing formulas in the drinking water appeared as an effect of decreased ion suppression and had actually been present before chlorination, but could not be detected. Also, even if the reproducibility of the instrument on average results in less than 5% difference in the relative abundance, the relative abundance of some mass peaks with low signals in two spectra of the same sample may vary as much as 10% in any given duplicate sampling. Therefore, a new (second) classification

was designed which resulted in a combined list of unique formulas from the four drinking water samples where, in total, 1154 Cl-containing formulas were included. 43% of the formulas, including all with 2Cl and 3Cl, were classified as DBPs, 47% as being present prior to disinfection while 10% remained unclassified. Note that for all differences between weighted mean values described ahead in the paper the unclassified formulas could be included as either DBPs or already present CHOC1 formulas without changing the results significantly. Cl-containing formulas detected before disinfection may be (i) naturally chlorinated compounds,^{40–42} (ii) reaction products from Cl⁻ in the HCl used when acidifying the samples prior to SPE, (iii) originating from an, for us, unknown source or a combination of the alternatives. For the two plants, where several samples were taken before disinfection the newly appearing chlorinated components in each step before chloramination occurred randomly in the van Krevelen diagram among the ones common with the samples taken closest before in the treatment trains (SI Figure S2). The formulas classified as DBPs, on the other hand, cluster in a separate area of relatively high O/C and low H/C (see Section 3.2) which supports our classification. Some of the DBP formulas may, however, still have appeared due to removal of other NOM components leading to decreased ion suppression and the possibility that some of the components that we classified as being already present were still formed during disinfection cannot be excluded. Therefore, both groups of components need to be studied further to fully confirm their origin.

3.2. DBP Characteristics. All chlorinated formulas detected before disinfection contained 1Cl while the DBPs were a mixture with one, two, or three chlorine atoms. It is noteworthy that already present CHOC1 formulas have higher relative abundance than the DBPs in many cases. This can be an effect of higher actual abundance or differences in their ionizability. Because the origin of the already present formulas is unknown and the focus in this paper is on DBPs we have not addressed this further. The DBPs had, in all drinking water samples, significantly higher O/C_w and lower H/C_w ($p < 0.0001$, Table 3) than the CHOC1 formulas already present. This is demonstrated with van Krevelen diagrams (Figure 2), and indicates that the newly formed chlorinated components, as a group, are more oxidized than the ones already present. Accordingly, $\overline{C}_{OS,w}$ was higher for the DBPs compared to the already present CHOC1 formulas ($p < 0.0001$) in each drinking water sample. Furthermore, the chlorinated DBPs were significantly more oxidized ($p < 0.0001$) and had, in a majority of the drinking water samples, significantly higher O/C ($p < 0.03$) as well as lower H/C ($p < 0.03$) and DBE/C ($p < 0.0001$) than CHO formulas in drinking water and for the treatment plants where samples taken both close before and right after disinfection were available also compared to the precursor CHO formulas (Table 3). It is not surprising that the DBPs are oxidized compared to the other NOM components because chlorination of organic compounds both through addition to unsaturated bonds and electrophilic substitution always leads to an increase in the average carbon oxidation state. Addition of $\delta^+Cl-OH^{\delta-}$ to double bonds increases H/C and O/C and decreases DBE/C²² while electrophilic substitution where, usually, a hydrogen atom is displaced by chlorine⁴³ leads to a decreased H/C but leaves O/C and DBE/C unaffected. Because addition reactions have been proposed to be insignificant under water treatment conditions due to low chlorination rate constants²² electrophilic substitution is the

Table 3. Mean Values Weighted against Relative Abundance for Ratios of Oxygen to Carbon (O/C_w) and Hydrogen to Carbon (H/C_w) as Well As Averaged Carbon Oxidation State ($\overline{C_{OS,w}}$)^a

WTP	sample	formulas	O/C_w	H/C_w	$\overline{C_{OS,w}}$	DBE/C_w
Lovö	raw	CHO	0.58	1.11	0.053	0.51
	RSF	CHO	0.55*	1.16*	-0.057*	0.48*
	SSF	CHO	0.54**	1.18**	-0.095**	0.47**
	drink	CHO	0.55**	1.18	-0.073	0.47
	drink	CHOCl-AP	0.47	1.20	-0.20	0.43
	drink	CHOCl-DBP	0.59*	0.86*(*)	0.40*(*)	0.60*(*)
Lackarebäck	raw	CHO	0.56	1.10	0.024	0.51
	drink	CHO	0.54*	1.21*	-0.13*	0.46*
	drink	CHOCl-AP	0.45	1.28	-0.32	0.39
	drink	CHOCl-DBP	0.61*(**)	1.01*(**)	0.36*(*)	0.51*
Ringsjö	raw/mix	CHO	0.61	1.05	0.20	0.55
	drink	CHO	0.52*	1.18*	-0.14*	0.47*
	drink	CHOCl-AP	0.45	1.26	-0.29	0.40
	drink	CHOCl-DBP	0.59*(*)	0.94*(*)	0.37*(*)	0.54*(*)
Kvarnagården	surf	CHO	0.55	1.09	0.017	0.52
	raw/mix	CHO	0.56	1.11	0.0050	0.51
	drink	CHO	0.58*	1.03*	0.13*	0.54*
	drink	CHOCl-AP	0.49	1.05	-0.016	0.51
	drink	CHOCl-DBP	0.62*(**)	0.72*(*)	0.59*(*)	0.67*(*)

^aAsterisks denote significant changes in a parameter from, for CHO formulae, the sample taken closest before in the treatment train and for DBPs compared to already present (AP) CHOCl formulae. Asterisks given in parentheses for CHOCl-DBP show significance in differences between DBPs and CHO formulae in drinking water where the same significance levels are valid for differences between DBPs and CHO formulae in the sample taken closest before disinfection for Lovö and Kvarnagården WTPs (slow sand filtrate and raw/mix water respectively). * $p < 0.0001$. ** $p < 0.03$.

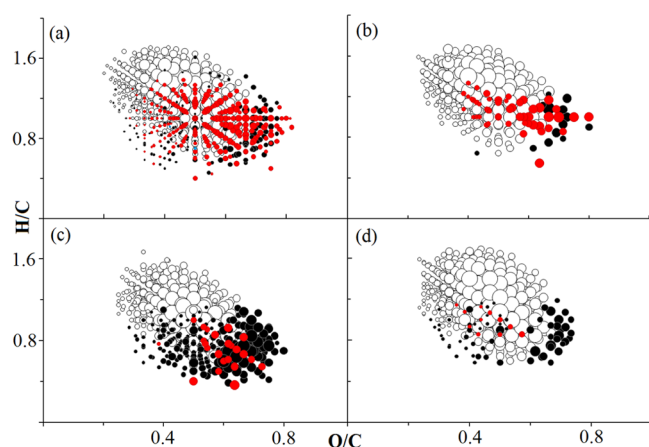


Figure 2. van Krevelen diagrams of chlorinated organic compounds found in drinking water from the water treatment plants (a) Ringsjö, (b) Lackarebäck, (c) Kvarnagården, and (d) Lovö. White bubbles = formulas present before chlorination, black bubbles = DBPs with 1 Cl, red bubbles = DBPs with 2 Cl. Two small blue bubbles in (a) illustrate DBPs with 3 Cl. Bubble size represents the relative abundance of a formula. Unclassified formulas are not included.

most plausible reaction pathway for chlorination of NOM molecules. The DBPs identified in this study have relatively high O/C_w and DBE/C_w (Table 3) indicating that the chlorination of NOM is selective toward components that have high values of these parameters. These components likely correspond to compounds with a relatively high content of aromatic carbon substituted with oxygen-containing functional groups. This is consistent with earlier studies, for example, by Rook,⁴³ where it was concluded that dihydroxylated benzene

moieties were the most reactive sites for haloform reaction and Croué et al.²⁴ who found that the TOX formation potential increased for samples with high aromatic carbon and aromatic phenol content.

3.3. Patterns in CHOCl Formulas Occurrence. The CHOCl formulas classified as being already present were very similar in the different drinking water samples with 89% of the formulas found in at least two of the four WTPs (SI Figure S3). For the DBPs, however, 65% of all formulas were found in one WTP only (SI Figure S3). The contrast between the ubiquitous CHOCl formulas and the site-specificity of the DBPs demonstrates that the byproduct formation is very sensitive to conditions in the water treatment plant, and supports our classification system. Thus, differences in DBP formula presence at the four WTPs (Figure 3) may have occurred due to variations in choice of disinfectant and dose, or precursor NOM character. Precursor NOM character may, in turn, vary due to differences in raw water NOM composition or pre-disinfectant treatment processes selectively removing certain compounds. A corresponding overview of already present CHOCl formulas is given in SI Figure S4. Chlorination of raw water, without removal of DBP precursors, might be expected to produce a greater number of chlorinated compounds in drinking water. Conversely, Lackarebäck, as the only WTP in this study that applies raw water chlorination, had the lowest amount of DBP formulas in the finished product. At least a part of the byproducts formed in the raw water may have precipitated in the following flocculation treatment, in particular because this process selectively removed relatively oxidized components with low H/C_w as well as high DBE/C_w and O/C_w at Lovö WTP where the same coagulant is used (Table 3). This implies that chlorinating raw water with

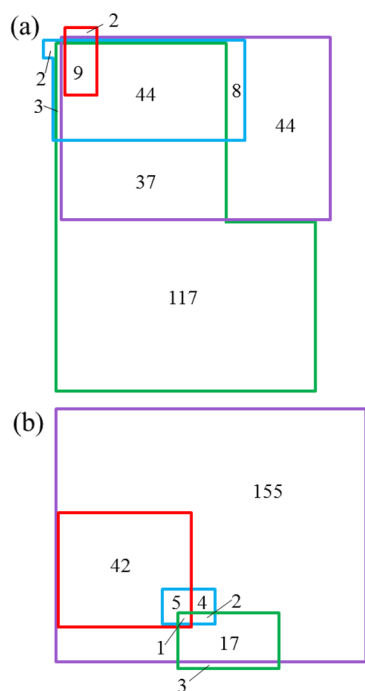


Figure 3. Distribution of DBP formulas with (a) 1 Cl (266 formulas) and (b) 2 Cl (230 formulas) in drinking water samples from the four WTPs. Areas within squares are relative estimates of the number of formulas. Overlapping areas demonstrate the number of formulas that are common for two or more samples. Purple = Ringsjö, red = Lackarebäck, blue = Lovö, green = Kvarnagården. Formulas with three Cl were excluded since they were only two in number and only found at Ringsjö WTP.

subsequent flocculation could actually be favorable because NOM that is reactive toward chlorine can be removed before chlorination is applied again in the end of the treatment train. This is supported by the smaller differences in DBE/C_w between DBPs and CHO formulas in drinking water at Lackarebäck compared to the other WTPs. On the other hand, chlorination followed by flocculation may then result in chloroorganic compounds in the floc sludge constraining its further use or disposal. Also, we cannot conclude whether prechlorination affects the concentration of DBPs since we used an analytical method that is only semiquantitative. An earlier study found only small improvements or increases in the formation potential of five haloacetic acids after prechlorination and flocculation with polyaluminum chloride.⁴⁴ Clearly, further studies are needed to determine the impact of prechlorination on both concentration and diversity of DBPs in drinking water. Lackarebäck is also the only WTP in this study that uses ClO₂ (in combination with Cl₂) to disinfect the drinking water. 85% of the DBPs with 1Cl and all with 2Cl detected at Lackarebäck WTP were also found at Ringsjö. Because chlorine forms hypochlorite, the disinfectant used at Ringsjö, in aqueous solution, the chlorinated components detected in Lackarebäck drinking water are likely to be products from reactions including hypochlorite formed from Cl₂ hydrolysis. The almost complete lack of unique DBPs at Lackarebäck (Figure 3) suggests that ClO₂ does not produce a unique set of chloroorganic byproducts that can be identified with FT-ICR-MS. More than 90% of the detected DBPs at Lovö WTP were recovered at Ringsjö and there was also a great overlap between Kvarnagården and Ringsjö WTPs even if both sites had many

unique formulas (Figure 3). Vikesland et al.⁴⁵ suggested that DBPs formed from chloramination which are the same as those produced during chlorination are results of reactions between HOCl formed from monochloramine hydrolysis and NOM, corresponding to our finding. The potential formation of other DBPs that contain nitrogen when using chloramine cannot be ruled out, because nitrogen-containing compounds are in general suppressed in negative mode ESI. Kvarnagården and Lovö WTPs had almost 60 common DBPs, however, at Kvarnagården 120 unique ones were identified (Figure 3). At Kvarnagården almost half of the added chloramine was consumed (0.12 mg Cl₂ L⁻¹) (Table 1) while at Lovö the dosed amount usually only decreases by approximately 5% (0.01–0.02 mg Cl₂ L⁻¹) before the drinking water enters the distribution system (personal communication⁴⁶). The greater chloramine consumption at Kvarnagården may reflect the production of a larger variety of DBP formulas which, in turn, could be a function of differences in the predisinfection treatment at the two WTPs. Flocculation, the main process at Lovö, selectively removed formulas with relatively high O/C and DBE/C while, at Kvarnagården, no chemical treatment is performed. This is reflected in the significantly higher O/C ($p = 0.001$) and DBE/C_w ($p < 0.0001$) of Kvarnagården raw water compared to slow sand filtrate at Lovö (Table 3). We analyzed this further by a cluster analysis of all samples using presence/absence of molecular formulas containing C, H and O. There are two major clusters in the resulting dendrogram (SI Figure S5) where one contains all samples not subjected to flocculation, including all samples from Kvarnagården, and the other includes samples taken after flocculation. Hence, the character of the extractable NOM in the samples taken closest prior to disinfection is deviating for Kvarnagården WTP where flocculation is not applied. Accordingly, SUVA, an indicator of DOC aromaticity,⁴⁷ was higher in Kvarnagården raw water compared to Lovö slow sand filtrate (Table 1). Higher SUVA has been shown to result in a larger production of organic halides.²⁴ It is therefore likely that the variety of byproduct precursors was higher at Kvarnagården due to the lack of flocculation treatment, leading to a larger diversity of DBP components formed during chloramination. The fact that Kvarnagården WTP had precursor material with higher O/C_w and DBE/C_w than at Lovö WTP and a higher amount of DBPs implies that flocculation treatment reduces the DBP diversity though removal of precursor compounds.

3.4. Effects on CHO Formulas. At Lovö and Kvarnagården WTPs samples were taken both close before and after disinfection, allowing us to investigate the processes effect on CHO formulas. Lovö water was subjected to both UV treatment and chloramination between the two samples (slow sand filtrate and drinking water), whereas at Kvarnagården rapid sand filtration and disinfection with chloramination and UV was applied in stated order (between sampling of raw and drinking water) (Figure 1). For both WTPs ΔDOC between the two samples was negligible and ΔSUVA nonexistent or small (Table 1). We expected the disinfection process to have affected CHO components to a greater extent at Kvarnagården WTP due to the significantly higher monochloramine consumption compared to Lovö WTP. For chlorine it has been estimated that only 10% of added dose lead to the production of chlorinated organic compounds leaving 90% to potentially react in other ways.²⁶ Thus, it is likely that a significant amount of the added chloramine at Kvarnagården has reacted to form nonchlorinated oxidized byproducts. In line

with our hypothesis, our results show that, at Kvarnagården, CHO formulas have significantly higher $\overline{C_{OS,w}}$ ($p < 0.0001$) after disinfection which was not the case at Lovö (Table 3). The UV radiation dose used for disinfection purposes was low (20 and 25 mWs cm^{-2} for Lovö and Kvarnagården, respectively). Effects on DOC composition from this treatment should therefore be small which is supported by the modest changes for CHO formulas at Lovö during disinfection (Table 3). Due to the probably dominating effect of other reactions over chlorination of NOM molecules the specific precursors of chlorinated DBPs cannot be determined. Nonetheless, it can be concluded that on top of the production of chlorinated components, chloramination can significantly oxidize CHO components, even at the low doses used by the WTPs in this study.

3.5. Comparison with DBPs Detected Previously. All 1154 CHOCI formulas identified in this study were compared to a list of 107 single and double chlorinated compounds with at least 1 oxygen atom and no other heteroatoms than chlorine and oxygen derived from Richardson.³ The selected compounds listed by Richardson³ were, in most cases, analyzed with gas chromatography/mass spectrometry (GC/MS) or derivatization-GC/MS. The 1154 formulas were also compared to 1007 formulas (659 with 1Cl and 348 with 2Cl) from a laboratory scale chlorination study using ESI-FT-ICR-MS by Zhang et al.²⁸ Zhang and colleagues have also identified 556 formulas (357 with 1Cl and 199 with 2Cl) in full scale drinking water disinfection,²⁹ most of which (96%) overlap with their laboratory scale study. There was no match between DBPs identified in this study and the ones listed by Richardson³ which is a result of different capabilities of the employed analytical methods. The high molecular weight chlorinated byproducts found in this study are likely to be part of the TOX formed during chlorination and chloramination that so far has been unknown on a molecular level.^{3,21} Our data overlap considerably (710 common formulas, SI Figure S6) with the chlorination study by Zhang et al.²⁸ The greatest overlap (403 formulas) occurred among the formulas that were present before disinfection followed by 262 DBPs (of which 72 with 1Cl and 190 with 2Cl) and 45 that were unclassified. Zhang et al.²⁸ assumed that all their CHOCI formulas were DBPs, but as many of those were found prior to disinfection in this study a comparison was difficult. However, when comparing only the formulas we classified as DBPs it was found that 99% of the formulas with 2Cl and 89% with 1Cl found by Zhang et al.²⁸ were also detected at Ringsjö. This is an interesting result because Zhang et al.²⁸ used NaOCl to chlorinate their samples which is also applied at Ringsjö WTP. The similar CHOCI profiles of these two studies, despite of the geographically different sources, suggests that choice of disinfectant has a large impact on DBP formation. A high number (121) of the formulas with 2Cl matched with DBPs at Ringsjö WTP but were absent in the other treatment plants where other disinfectants are used, indicating that there might be a specific group of earlier unidentified compounds formed solely during chlorination. The pattern was similar for the full scale chlorination byproducts identified by Zhang et al.²⁹ where we found half of the Cl-containing formulas reported by Zhang et al.²⁹ in samples before disinfection and almost all formulas classified as DBPs in Ringsjö drinking water. It is worth noting that in both studies by Zhang and colleagues^{28,29} the fraction of DBP formulas (according to our classification) with 2Cl was considerably larger than in this study. The use of higher chlorine doses (20 and 1.8 mg $\text{Cl}_2 \text{L}^{-1}$ in the laboratory and full

scale respectively) compared to the WTPs in this study (0.27–0.86 mg $\text{Cl}_2 \text{L}^{-1}$) is likely to have influenced this. Our results demonstrate that ESI-FT-ICR-MS is a powerful tool for identification of chlorinated organic components. In total, 499 chlorinated formulas detected in four major Swedish WTPs were identified as DBPs of which 230 have never been reported before. The results reported here may guide WTPs to minimize the occurrence of chlorinated organic byproducts in drinking water.

■ ASSOCIATED CONTENT

📄 Supporting Information

Formulas for all detected chlorinated components as well as figures and tables referenced in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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