

Electronic supplementary information

Selective removal of natural organic matter during drinking water production changes the composition of disinfection by-products

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Method discussion

Sample preparation

Most analytical methods including Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) have potential issues. One part of the method preparation is the acidification of the sample prior to the solid-phase extraction. Solely acidifying the sample is not expected to degrade DOM constituents, but potential hydrolysis of DOM compounds that are stable at higher pH cannot be ruled out. A more likely effect is the protonation of the carboxylic acid groups leading to more efficient adsorption in the solid phase extraction. Another potential effect would be precipitation of some humic acids in line with the classic soil humus fractionation (although the humic acid precipitation step is done at pH 1). Any precipitation would presumably also favor retention of organic molecules in the PPT columns (no particles were observed visually in the outflow). The effects of the acidification on retention efficiency is general for similar solid-phase extractions, and we used the approach being among the most effective ones in previous tests^{1,2}. Another possible pathway of transforming specific DOM components in the sample processing is the possibility of methylation (i.e. transformation of -OH into -OCH₃ groups by methanol), and this effect would render DOM molecules being ionized with less efficiency and hence would either not be visible in direct infusion FT-ICR MS or with only very weak intensities.

FT-ICR MS analysis

Care must be taken to not falsely assign molecular formulae to adducts. To minimize the formation of chlorine adducts we used 10 mL formic acid water to wash out any possible chloride ions. Ionization efficiency remains a concern and dilution of samples is essential in not overloading the ICR cell as well as allowing a more efficient ionization of weaker ionizing components. The ionization influence detection limits and low intensity compounds can easily be lost by dilution in some sample compositions, rendering the current FT-ICR MS approach being conservative. Ionization could also potentially fragment organic molecules. While we do not expect fragmentation during electrospray ionization, i.e. cleavage of covalent bonds, there is likely breakage of weaker (but non-covalent) bonds, such as hydrophobic interactions, binding units of fulvic or humic acids together. Correct assignment of the molecular formulae can also be a challenge, which we addressed by the stable isotopic matching for halogenated peaks, considered to be robust and conservative. Altogether, FT-ICR MS, as all methods has both pros and cons, but at present it still represents one of the best available methods for non-target analyses of complex organic matter mixtures.

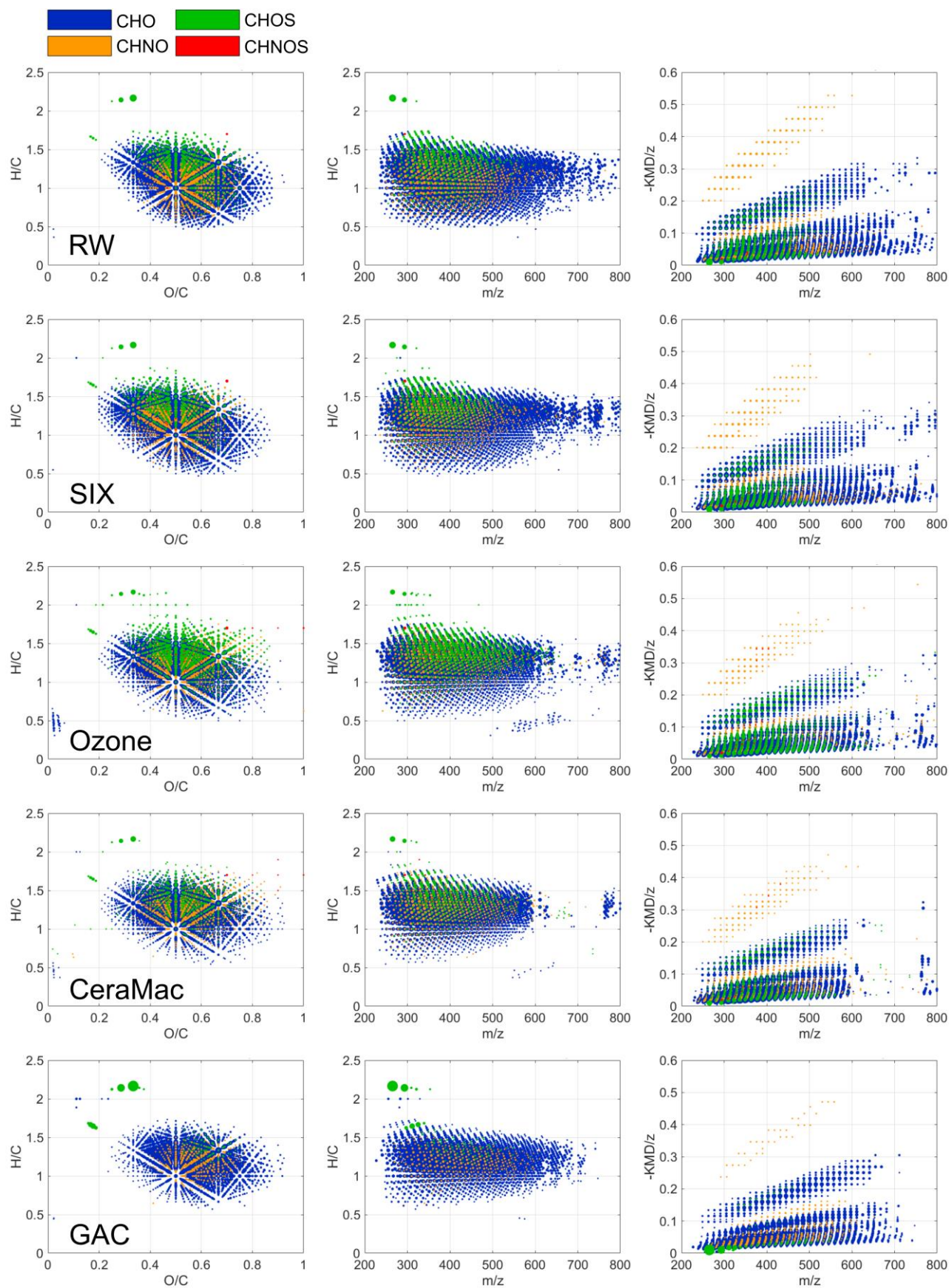


Fig. S1 Molecular formulae detected throughout the pilot treatment presented with van Krevelen (left panel), mass-edited H/C ratios (middle panel) and modified Kendrick mass plots (right panel). Formulae presented were detected in all three replicates.

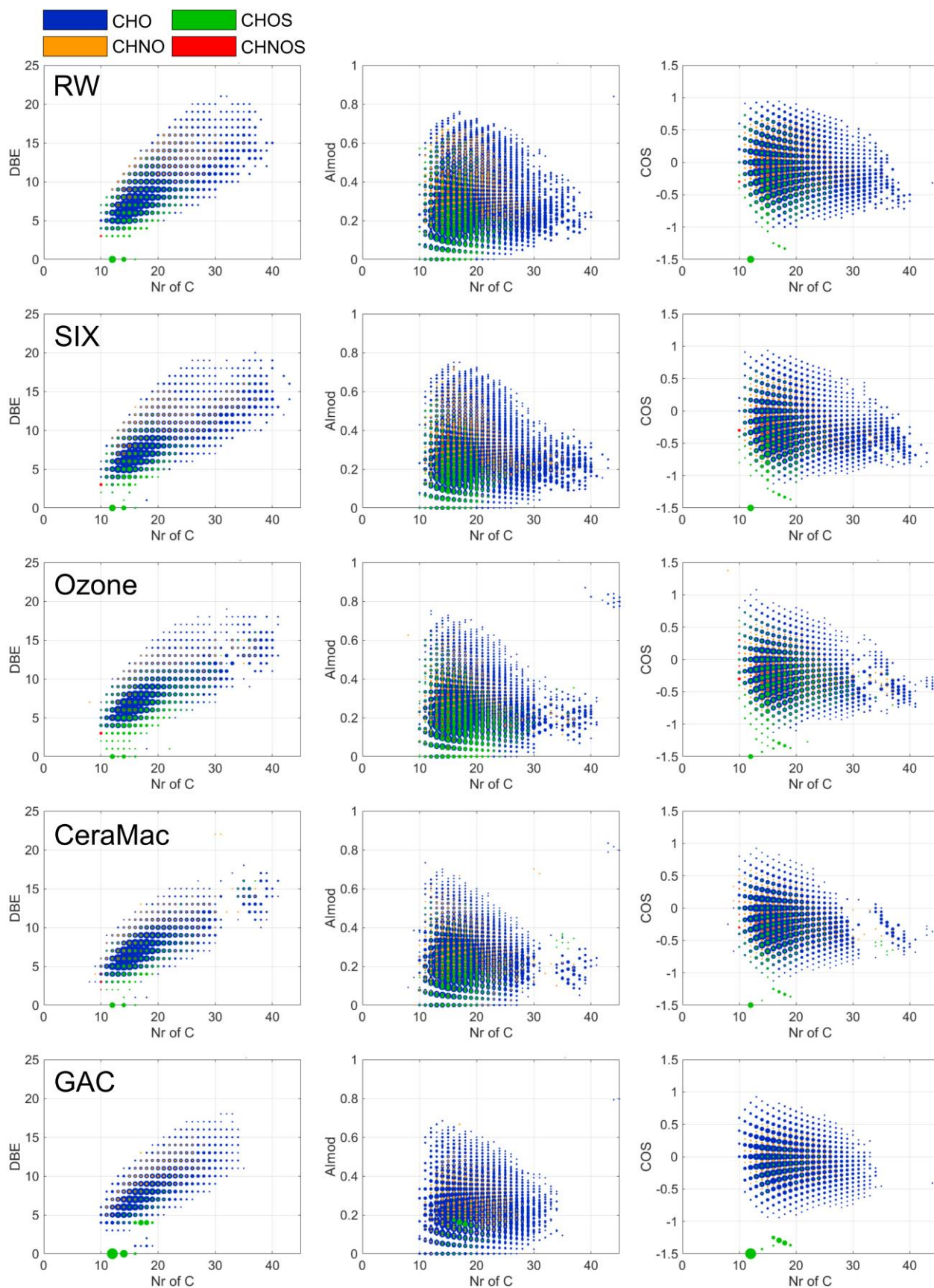


Fig. S2 Molecular formulae detected throughout the pilot treatment presented with double bond equivalences, DBE (left panel), a modified aromaticity index, AI_{mod} (middle panel) and the average oxidation state of carbon, COS (right panel). Formulae presented were detected in all three replicates.

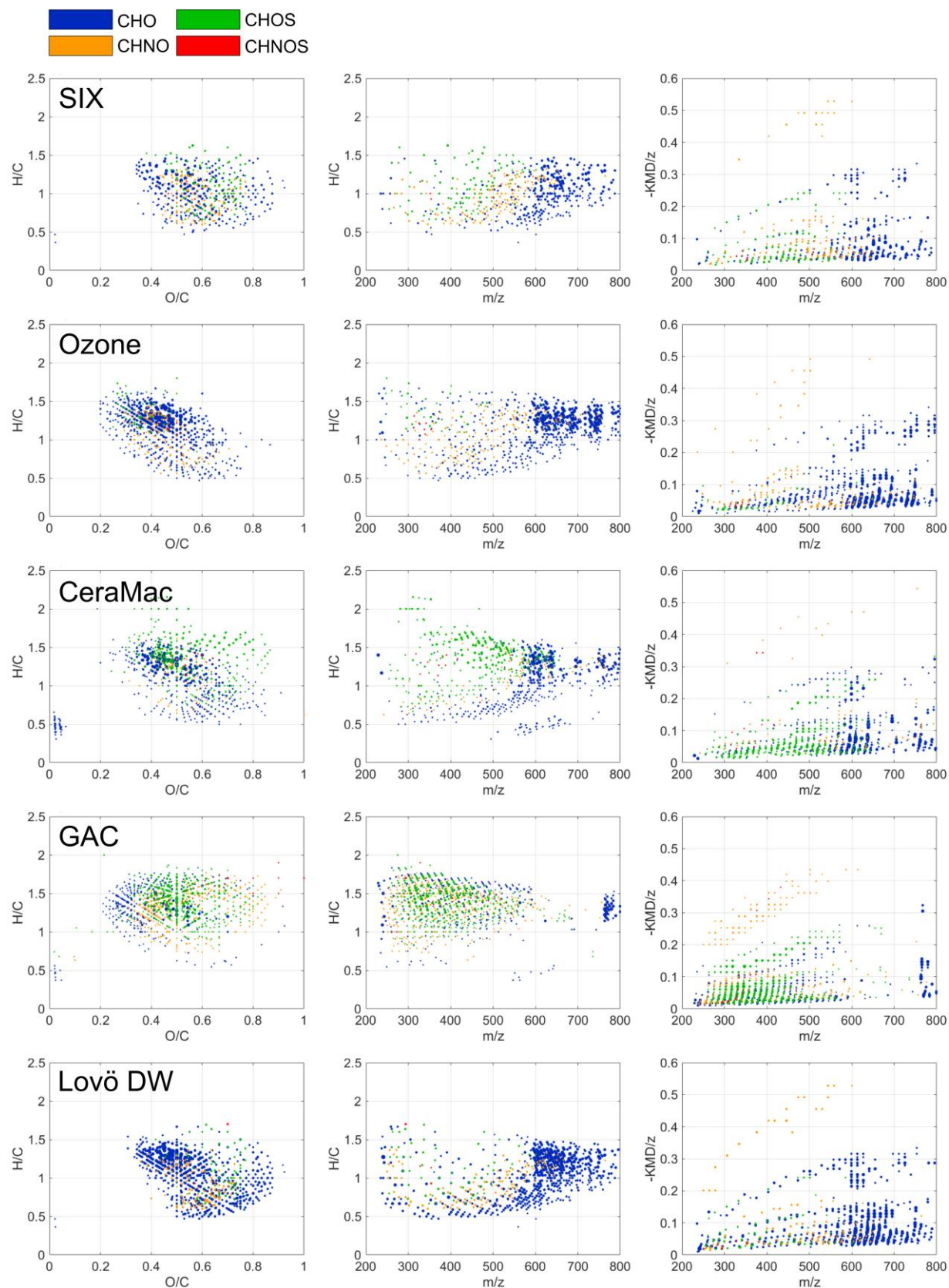


Fig. S3 Analysis of compositions that were removed by individual pilot treatment processes, i.e., not detected after respective treatment, presented with van Krevelen (left panel), mass-edited H/C ratios (middle panel) and modified Kendrick mass plots (right panel). Comparisons were made for compositions detected in three replicates and the conventional treatment at Lovö was used as a reference.

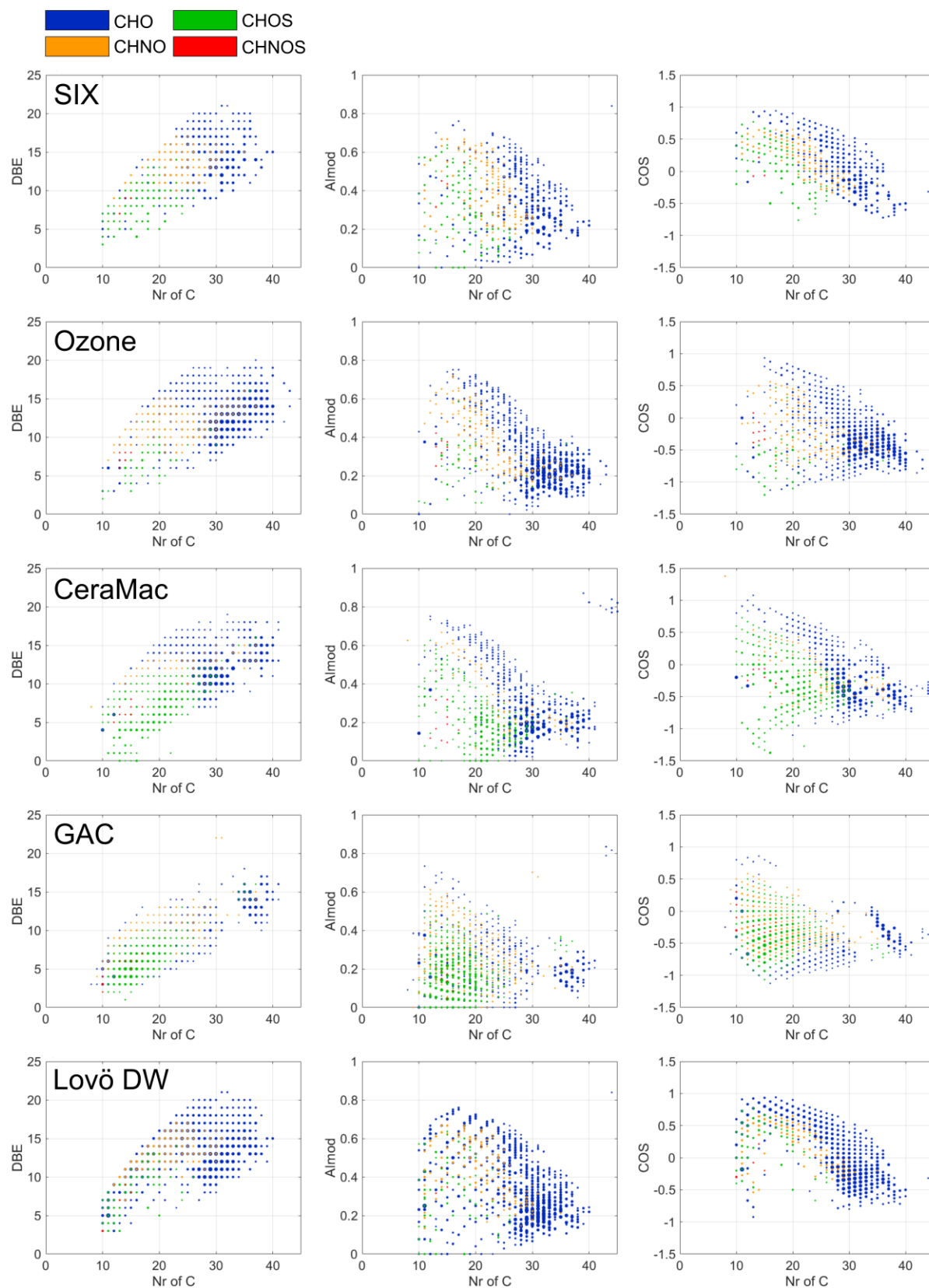


Fig. S4 Analysis of compositions that were removed by individual pilot treatment processes, i.e., not detected after respective treatment, presented with double bond equivalences, DBE (left panel), a modified aromaticity index, Al_{mod} (middle panel) and the average oxidation state of carbon, COS (right panel). Comparisons were made for compositions detected in three replicates and the conventional treatment at Lovö was used as a reference.

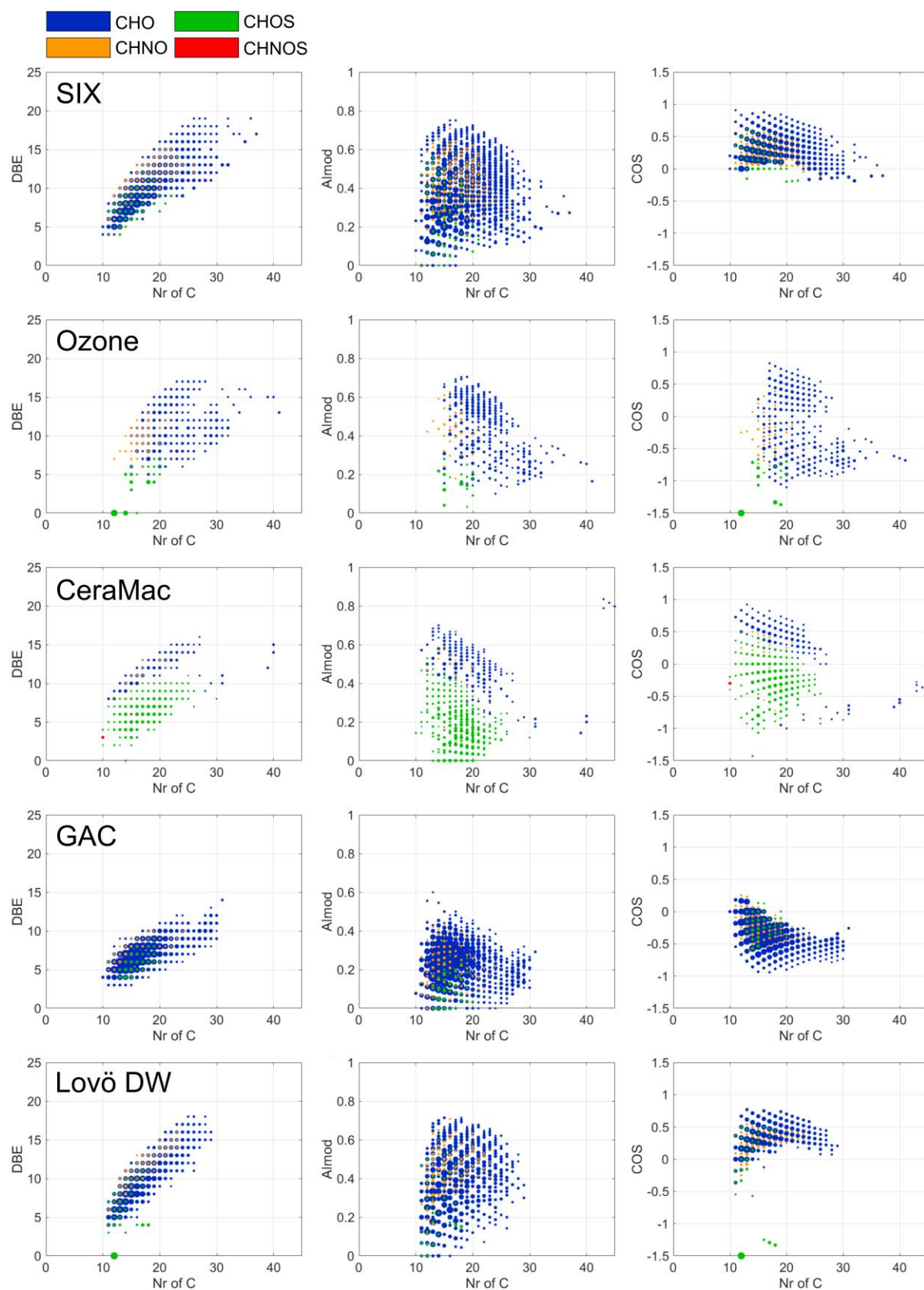


Fig. S5 Analysis of molecular compositions that decreased in relative abundance by more than 50% after each pilot treatment process, presented with double bond equivalences, DBE (left panel), a modified aromaticity index, AI_{mod} (middle panel) and the average oxidation state of carbon, COS (right panel). Comparisons were made for compositions detected in three replicates and the conventional treatment at Lovö was used as a reference.

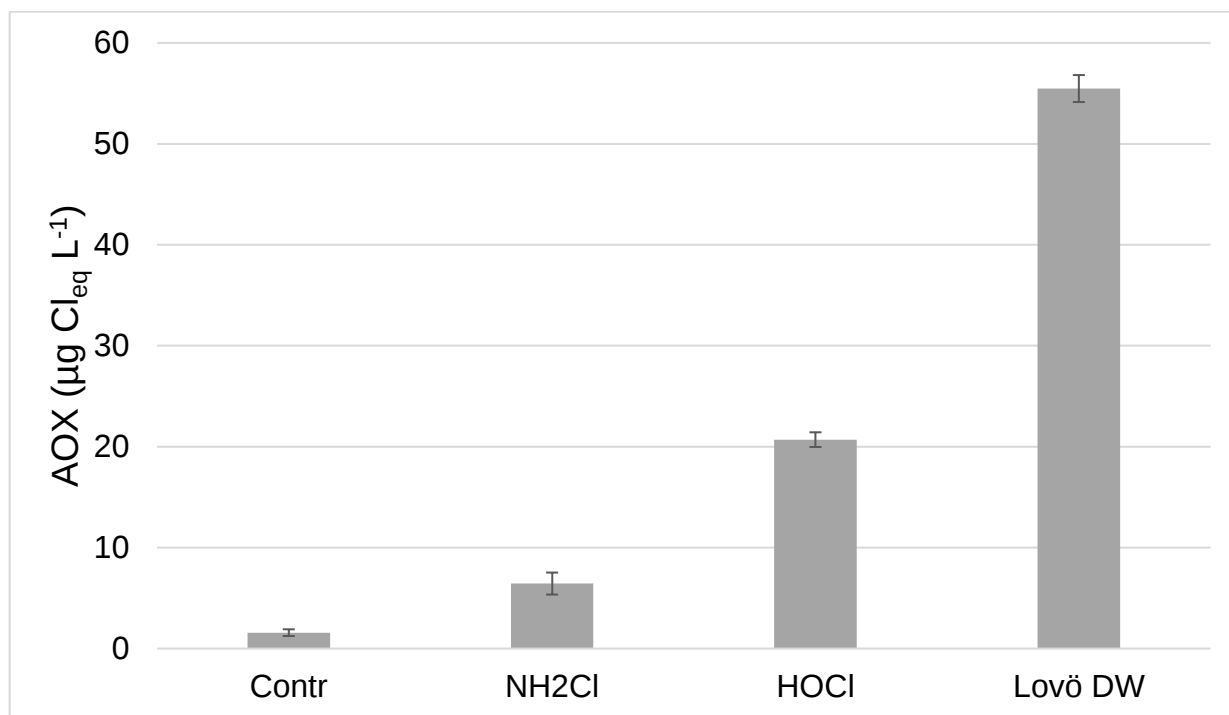


Fig. S6 AOX after normal-dose chlorination (HOCl) and chloramination (NH₂Cl) of finished water (GAC_{out}) from the pilot process (Experiment 2). Finished water from the conventional treatment at Lovö, dosing monochloramine, was used as a reference.

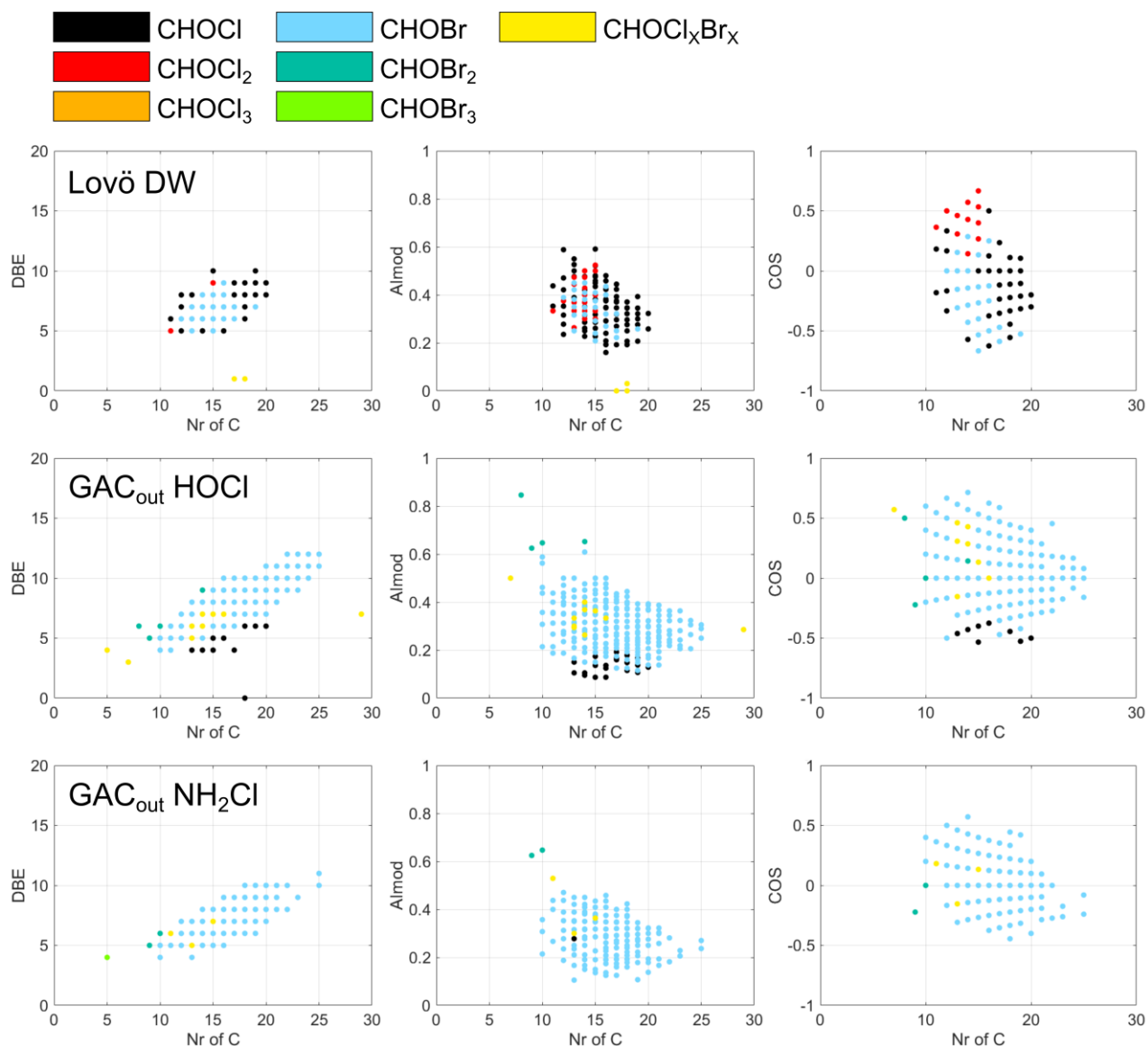


Fig. S7 DBE, Al_{mod} and C_{OS} plotted against the number of carbon atoms of verified chlorine and bromine containing molecular formulas (neutral form) present after the normal-dose chlorination (HOCl) and chloramination (NH₂Cl) of finished water (GAC_{out}) from the pilot process (Experiment 2). Finished water from the conventional treatment at Lovö, dosing monochloramine, was used as a reference. Data were acquired from FT-ICR MS analysis operated in negative ionization mode and DBPs shown are limited to the formulae present in three replicates.

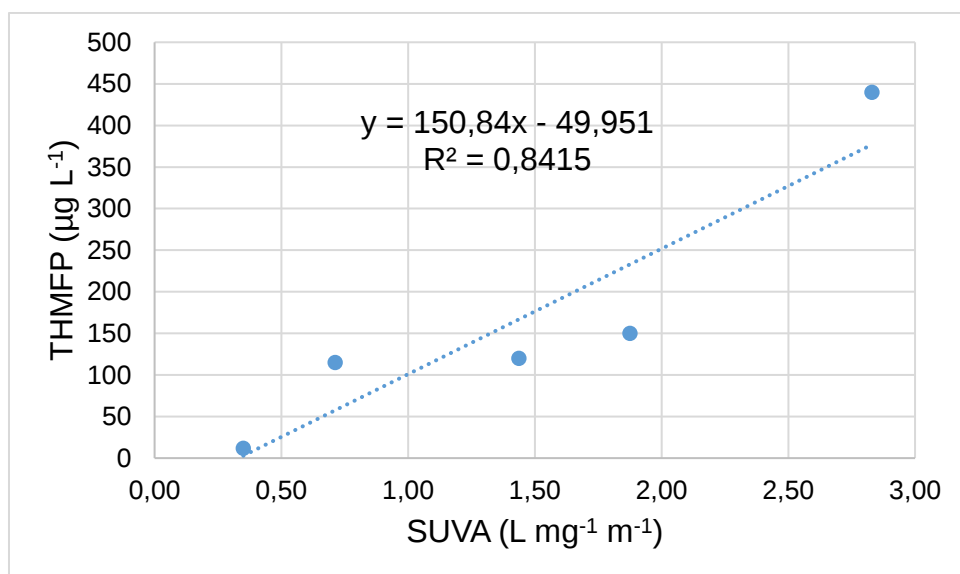
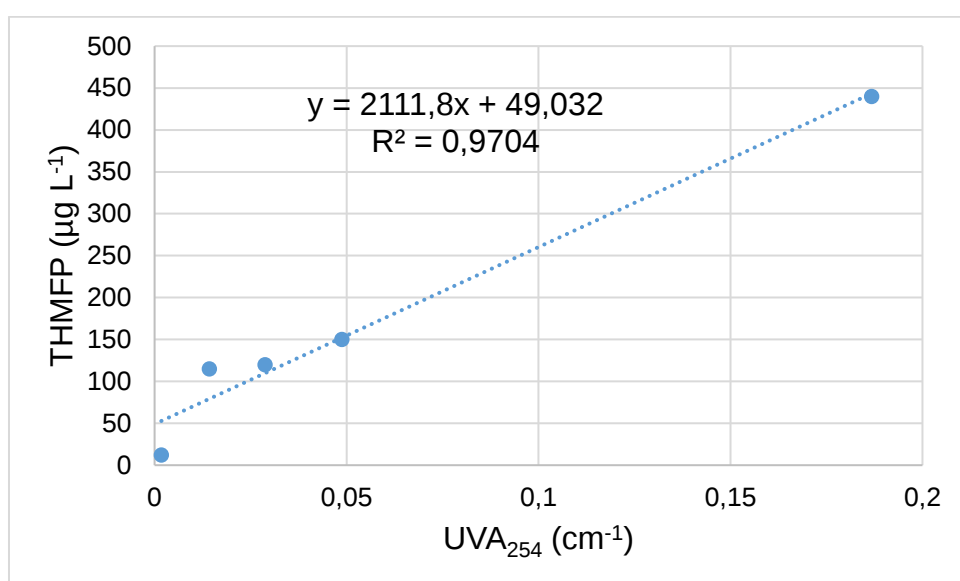
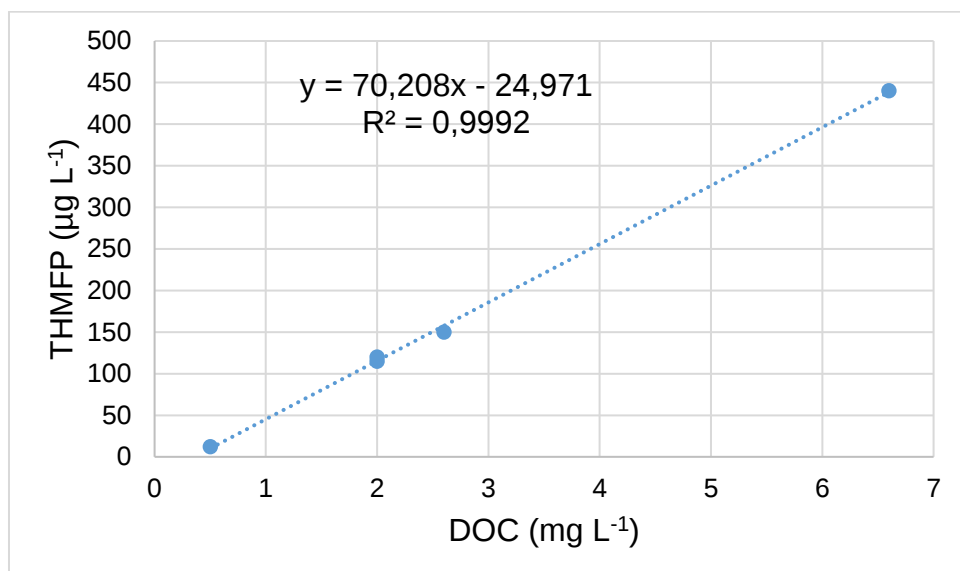


Fig. S8 THM formation potential plotted against DOC (upper panel), UVA_{254} (middle panel) and SUVA (lower panel) for the high-dose chlorination experiment (Experiment 3).

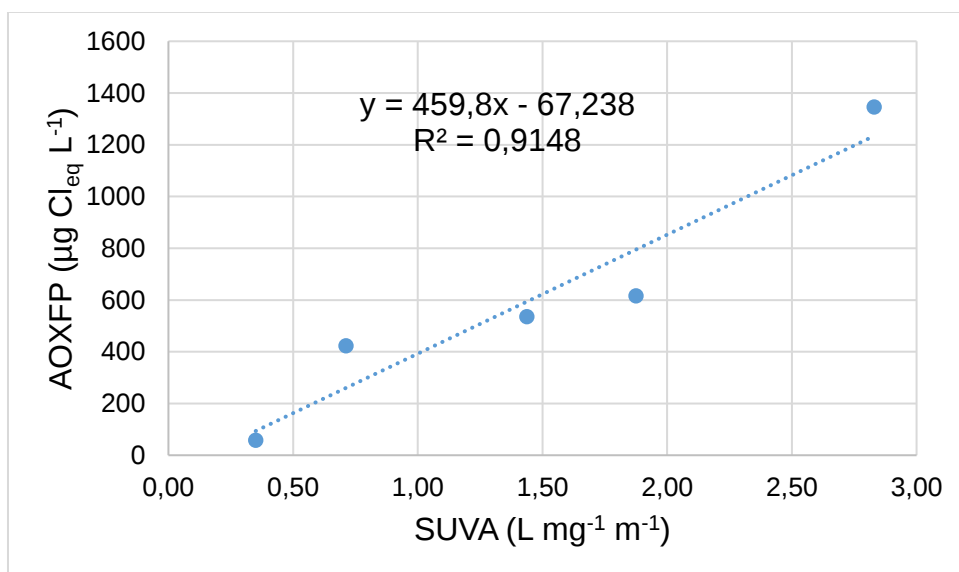
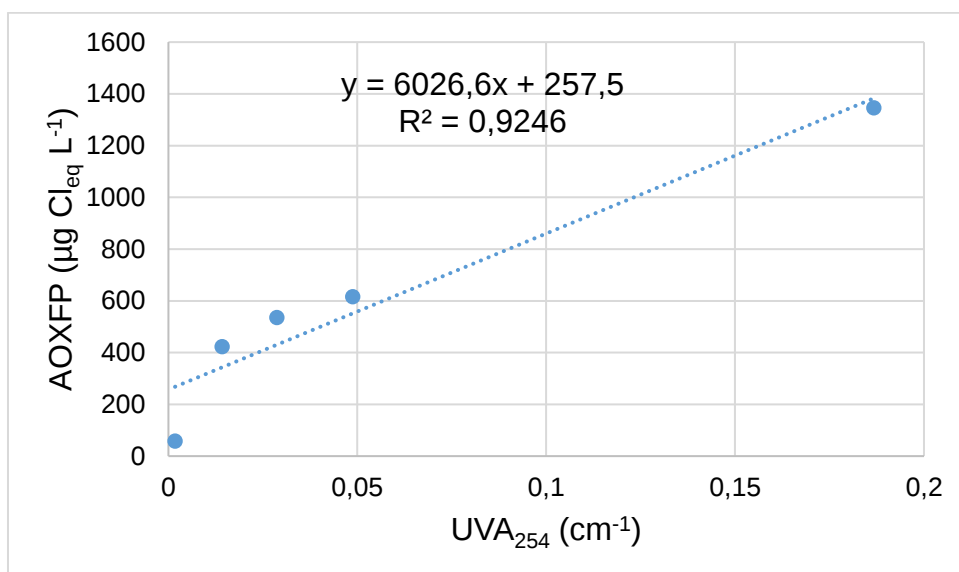
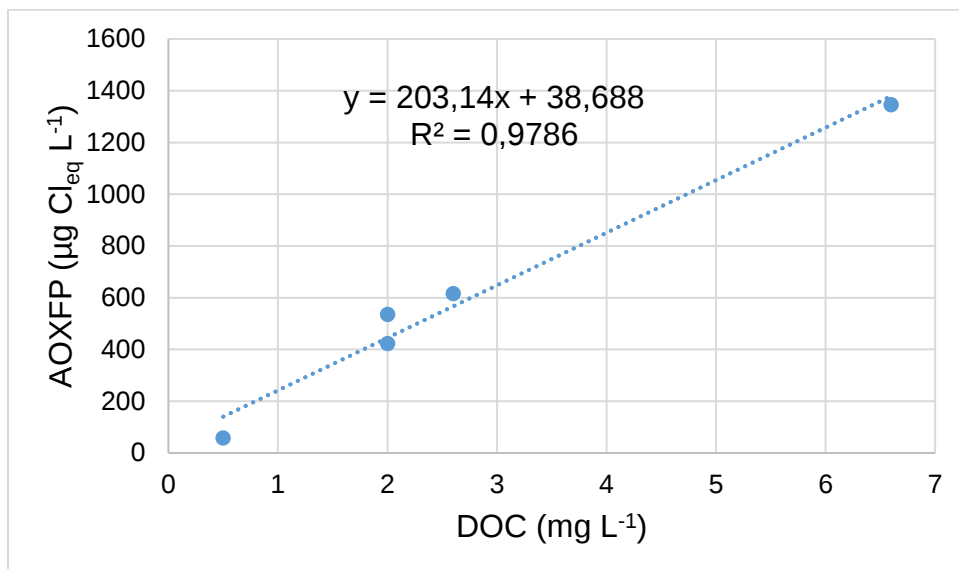


Fig. S9 AOX formation potential plotted against DOC (upper panel), UVA_{254} (middle panel) and SUVA (lower panel) for the high-dose chlorination experiment (Experiment 3).

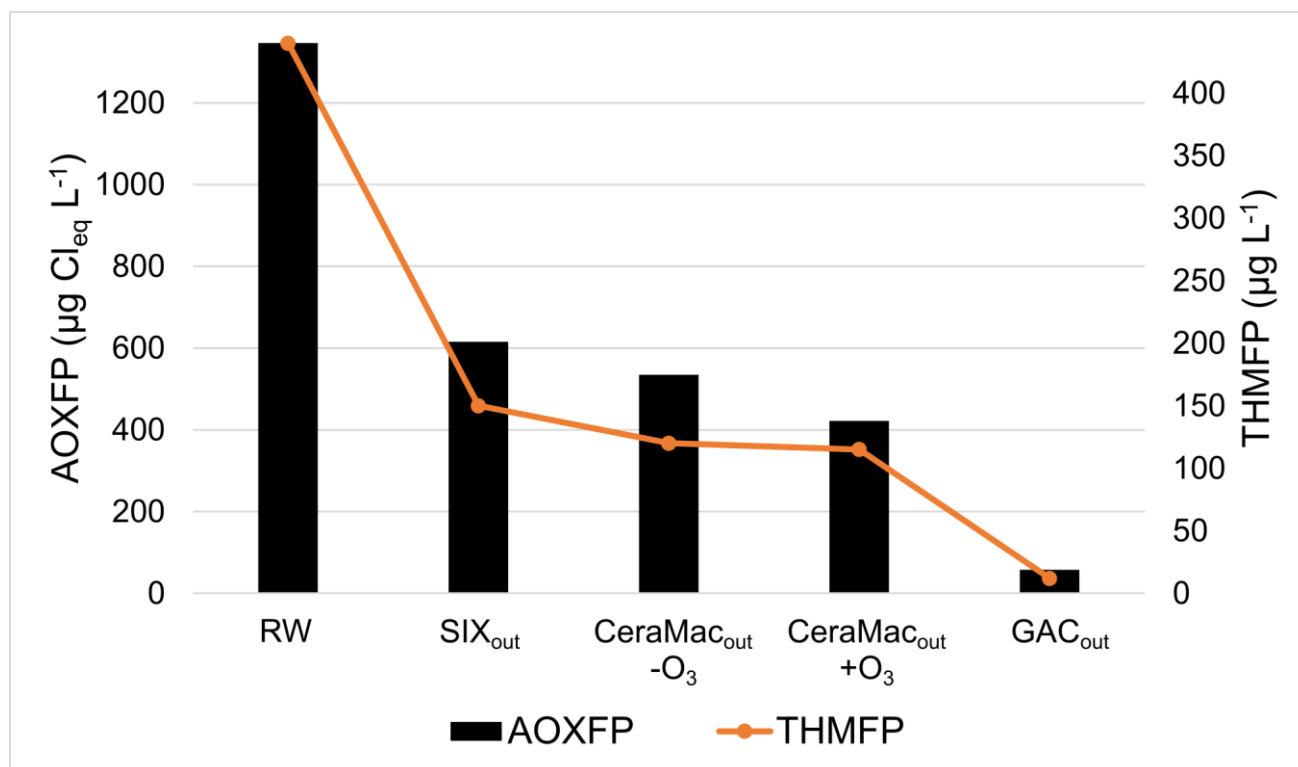


Fig. S10 Combined diagram simultaneously showing AOX and total THM formation potential at different stages of the pilot process (RW, SIX_{out}, CeraMac_{out} - O₃, CeraMac_{out} + O₃, GAC_{out}) when high dose chlorination was used with $\sim 10 \text{ mg L}^{-1}$ chlorine residual (Experiment 3).

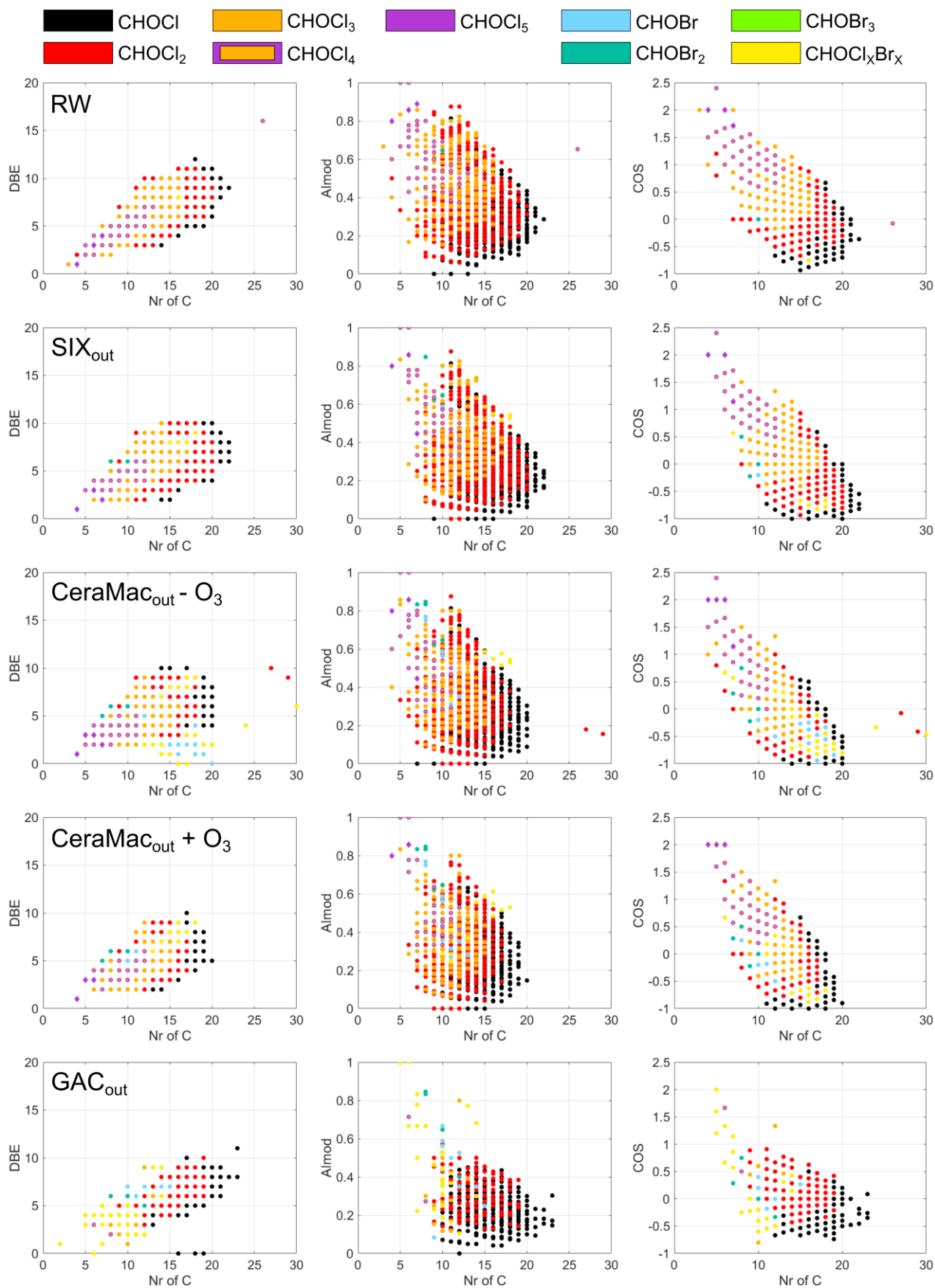


Fig. S11 DBE, Al_{mod} and COS plotted against the number of carbon atoms of verified chlorine and bromine containing molecular formulas (neutral form) present after high-dose chlorination at different stages of the pilot treatment (RW, SIX_{out}, CeraMac_{out} - O₃, CeraMac_{out} + O₃, GAC_{out}, Experiment 3).

Table S1 Average values weighted against relative abundance, of CHO, CHNO, CHOS and CHONS compositions in neutral form (the mass of a proton added) computed from negative electrospray (ESI) 12 T FT-ICR mass spectra. Data represent compositions that were common to three technical replicates and the relative abundance was calculated based on the average intensity of the three replicates. NA = not available.

CHO compositions	RW	SIX _{out}	Ozone _{out}	CeraMaC _{out}	GAC _{out}	Lovö DW
average H [%]	42.8	45.3	45.2	45.4	43.7	44.5
average C [%]	37.3	37.0	36.5	36.0	36.0	37.0
average O [%]	19.9	17.7	18.3	18.6	20.3	18.5
computed average H/C ratio	1.15	1.22	1.24	1.26	1.21	1.20
computed average O/C ratio	0.53	0.48	0.50	0.52	0.56	0.50
average carbon oxidation state (C _{OS})	-0.07	-0.25	-0.22	-0.21	-0.07	-0.20
average DBE	9.30	8.77	8.25	7.76	8.77	8.67
average DBE/C	0.48	0.44	0.43	0.42	0.45	0.45
average AI _{mod}	0.29	0.26	0.24	0.22	0.23	0.27
mass weighted average [Da]	422.1	419.0	406.1	394.4	438.3	407.6
CHNO compositions						
average H [%]	39.9	43.1	43.7	43.9	41.8	41.8
average C [%]	37.5	36.7	35.5	35.0	35.7	37.0
average O [%]	20.4	18.2	18.8	19.1	20.5	19.2
average N [%]	2.1	2.0	2.0	2.0	1.9	2.0
computed average H/C ratio	1.06	1.17	1.23	1.25	1.17	1.13
computed average O/C ratio	0.54	0.50	0.53	0.54	0.57	0.52
computed average N/C ratio	0.06	0.06	0.06	0.06	0.05	0.05
average carbon oxidation state (C _{OS})	0.03	-0.17	-0.16	-0.15	-0.02	-0.08
average DBE	9.87	8.90	8.29	7.97	9.19	9.48
average DBE/C	0.55	0.50	0.47	0.46	0.50	0.52
average AI _{mod}	0.34	0.29	0.24	0.21	0.25	0.31
mass weighted average [Da]	403.3	392.6	396.7	394.0	428.8	408.5
CHOS compositions						
average H [%]	45.7	48.3	46.9	47.8	55.5	46.3
average C [%]	34.0	33.8	33.3	33.1	30.5	34.3
average O [%]	18.1	15.9	17.8	17.0	11.9	17.4
average S [%]	2.1	2.1	2.0	2.0	2.1	2.0
computed average H/C ratio	1.34	1.43	1.41	1.44	1.82	1.35
computed average O/C ratio	0.53	0.47	0.54	0.51	0.39	0.51
computed average S/C ratio	0.06	0.06	0.06	0.06	0.07	0.06
average carbon oxidation state (C _{OS})	-0.28	-0.49	-0.33	-0.43	-1.11	-0.34
average DBE	6.29	5.58	6.06	5.50	2.33	6.62
average DBE/C	0.39	0.35	0.36	0.34	0.16	0.38
average AI _{mod}	0.17	0.14	0.11	0.10	-0.06	0.17
mass weighted average [Da]	385.2	368.1	406.9	382.9	325.4	402.2
CHNOS compositions						
average H [%]	41.4	44.2	44.8	45.3	NA	40.8
average C [%]	34.1	32.9	31.2	29.2	NA	36.4
average O [%]	19.2	17.7	19.2	20.5	NA	18.2
average N [%]	2.7	2.6	2.4	2.5	NA	2.3

average S [%]	2.7	2.6	2.4	2.5	NA	2.3
computed average H/C ratio	1.22	1.34	1.44	1.55	NA	1.12
computed average O/C ratio	0.56	0.54	0.62	0.70	NA	0.50
computed average N/C ratio	0.08	0.08	0.08	0.09	NA	0.06
computed average S/C ratio	0.08	0.08	0.08	0.09	NA	0.06
average carbon oxidation state (C _{OS})	-0.11	-0.27	-0.20	-0.12	NA	-0.12
average DBE	6.51	5.60	5.12	4.14	NA	8.54
average DBE/C	0.51	0.45	0.40	0.35	NA	0.53
average AI _{mod}	0.21	0.14	0.02	-0.13	NA	0.34
mass weighted average [Da]	330.2	320.3	346.6	335.9	NA	384.3

Table S2 Average values weighted against relative abundance, of verified DBP formed in the normal-dose experiment, including both chlorinated and brominated CHO compositions in neutral form (the mass of a proton added) computed from negative electrospray (ESI) 12 T FT-ICR mass spectra. Data represent compositions that were common to three technical replicates and the relative abundance was calculated based on the average intensity of the three replicates.

Number of filtered formulas found	GAC _{out} (HOCl)	GAC _{out} (NH ₂ Cl)	Lovö DW
n of total Cl- and Br- CHO formulas	720	543	535
n of verified Cl- and Br- CHO formulas	278	140	144
Characteristics of verified DBPs			
average H [%]	41.9	41.7	42.7
average C [%]	36.1	36.0	37.1
average O [%]	19.6	19.9	17.5
average Cl [%]	0.8	0.1	2.3
average Br [%]	1.6	2.3	0.3
computed average H/C ratio	1.16	1.16	1.15
computed average O/C ratio	0.54	0.55	0.47
computed average C/Cl ratio	45.2	258	15.8
computed average C/Br ratio	22.2	15.9	115
average carbon oxidation state (C _{OS})	0.014	0.031	-0.115
average DBE	7.35	7.18	6.96
average DBE/C	0.45	0.45	0.45
average AI _{mod}	0.29	0.29	0.34
mass weighted average [Da]	431.0	433.6	362.4

Table S3 Average values, weighted against relative abundance, of verified DBPs formed in the high-dose Experiment 3, including both chlorinated and brominated CHO compositions in neutral form (the mass of a proton added) computed from negative electrospray (ESI) 12 T FT-ICR mass spectra. Data represent compositions that were common to three technical replicates (RW, SIX_{out}, GAC_{out}) and two technical replicates (CeraMac_{out} - O₃, CeraMac_{out} + O₃) respectively. The relative abundance was calculated based on the average intensity of the replicates.

Experiment 3					
Number of filtered DBP formulae found	RW	SIX _{out}	CeraMac _{out} -O ₃	CeraMac _{out} +O ₃	GAC _{out}
n of total Cl- and Br- CHO formulae	1392	1257	1536	1031	774
n of verified Cl- and Br- CHO formulae	847	892	827	696	357
Characteristics of verified DBPs					
average H [%]	38.9	43.4	44.3	43.2	42.5
average C [%]	36.1	35.4	35.0	34.9	35.3
average O [%]	20.6	17.5	17.0	18.0	18.0
average Cl [%]	4.3	3.6	3.6	3.8	3.1
average Br [%]	0.0	0.0	0.1	0.1	1.0
computed average H/C ratio	1.08	1.23	1.27	1.24	1.20
computed average O/C ratio	0.57	0.49	0.49	0.52	0.51
computed average C/Cl ratio	8.3	9.8	9.7	9.3	11.4
computed average C/Br ratio	8288	1738	362	595	34.1
average carbon oxidation state (Cos)	0.256	-0.074	-0.126	-0.046	0.022
average DBE	6.42	5.87	5.30	5.35	5.71
average DBE/C	0.48	0.41	0.39	0.40	0.41
average AI _{mod}	0.37	0.29	0.27	0.28	0.32
mass weighted average [Da]	357.1	358.3	339.7	337.3	370.6

References

1. T. Dittmar, B. Koch, N. Hertkorn and G. Kattner, A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater, *Limnology and Oceanography: Methods*, 2008, **6**, 230-235.
2. Y. Li, M. Harir, J. Uhl, B. Kanawati, M. Lucio, K. S. Smirnov, B. P. Koch, P. Schmitt-Kopplin and N. Hertkorn, How representative are dissolved organic matter (DOM) extracts? A comprehensive study of sorbent selectivity for DOM isolation, *Water Research*, 2017, **116**, 316-323.