## Supplementary Information

# Comparison of the impact of ozone, chlorine dioxide, ferrate and permanganate pre-oxidation on organic disinfection byproduct formation during post-chlorination

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**Text S1** Analytical method for THMs and HANs

The THMs and HANs were analyzed by headspace GC-MS with a method adapted from previously published methods.[1, 2] 3.60 g of sodium sulfate and 0.13 g of a quenching mixture (24 mg ascorbic acid, 1.2 g $Na_2HPO_4$, 19.8 g $KH_2PO_4$) were added to 10 mL of a sample previously spiked with an internal standard (5 µg $L^{-1}$ of 1,2-dibromopropane) in a 20 mL screw top amber vial. Within 24 h, samples were shaken in an agitator for 15 min at 50°C, extracted on a DVB-CAR-PDMS fiber for 15 min at 50°C, and desorbed for 5 min in the GC-MS inlet at 220°C. The oven programming was as follows: 40°C hold for 5 min, 3°C $min^{-1}$ to 54°C, 5°C $min^{-1}$ to 150°C and 25°C $min^{-1}$ to 300°C for a total analysis time of 39.9 min. SIM mode was used and the m/z ions used for quantification were similar to the published methods.[1, 2] THMs and HANs were measured up to 5 µM and 0.2 µM, respectively. The limits of quantification ranged between 2 and 10 nM, except for bromoacetonitrile which had a limit of quantification of 20 nM. The analytical repeatability (based on duplicate analyses) ranged from 3% to 10% for THMs and from 8% to 16% for HANs.

**Table S1** Abbreviation of the haloacetonitriles (HANs) and trihalomethanes (THMs).

| **Haloacetonitriles** | | **Trihalomethanes** | |
|---|---|---|---|
| BCAN | Bromochloroacetonitrile | DBCM | Dibromochloromethane |
| CAN | Chloroacetonitrile | DCBM | Dichlorobromomethane |
| DBAN | Dibromoacetonitrile | TBM | Tribromomethane |
| DCAN | Dichloroacetonitrile | TCM | Trichloromethane |
| TCAN | Trichloroacetonitrile | | |

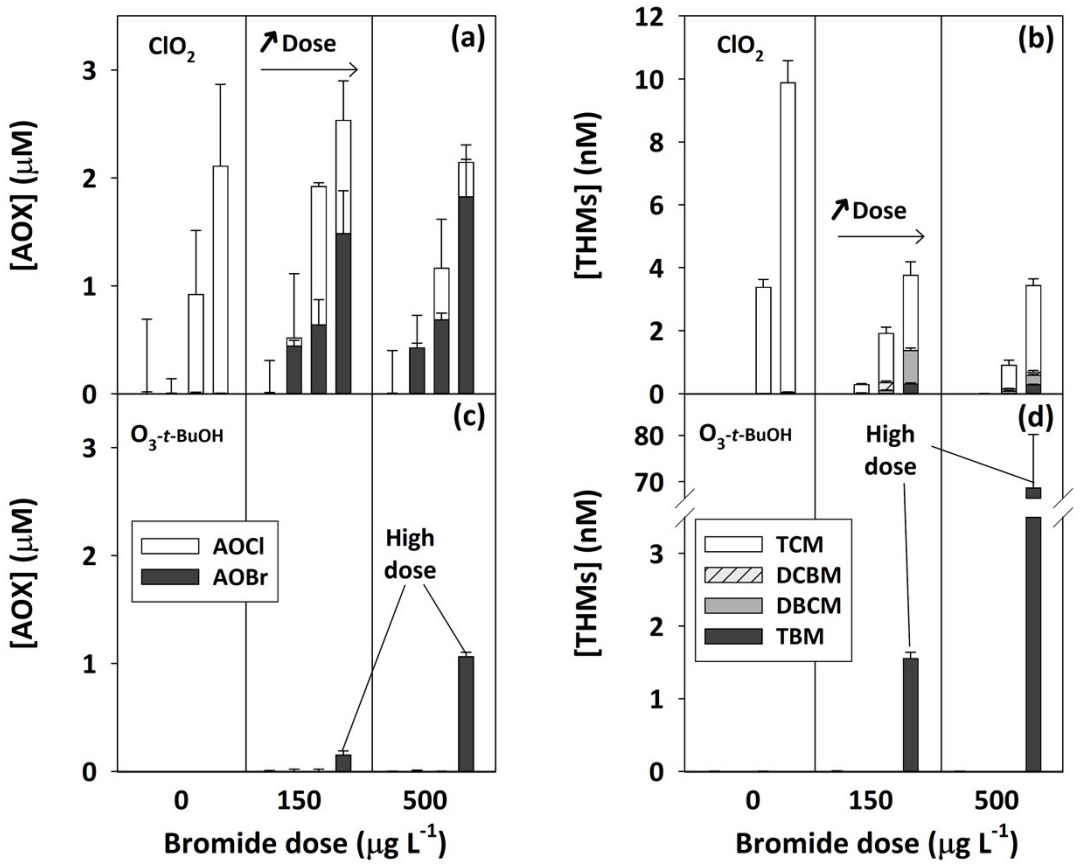


**Figure S1** Formation of (a,c) AOX and (b,d) THMs after $ClO_2$ and $O_3$-*t*-BuOH oxidation. Oxidant doses: [$ClO_2$] = 3.5–39.3 μM, [$O_3$-*t*-BuOH] = 2.0–94.3 μM, [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), [$Br^-$] = 0–500 μg $L^{-1}$. Error bars represent the range of duplicate analysis for one experiment.

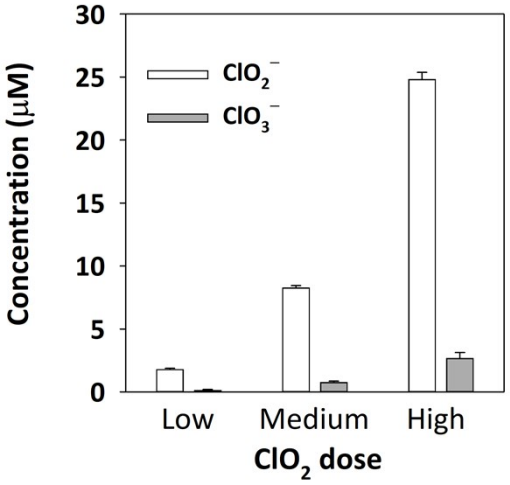


**Figure S2** Formation of chlorite ($ClO_2^-$) and chlorate ($ClO_3^-$) after $ClO_2$ pre-oxidation. $ClO_2$ dose= 3.5–39.3 μM, [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), no $Br^-$. Error bars represent the range of analytical results for duplicate experiments.

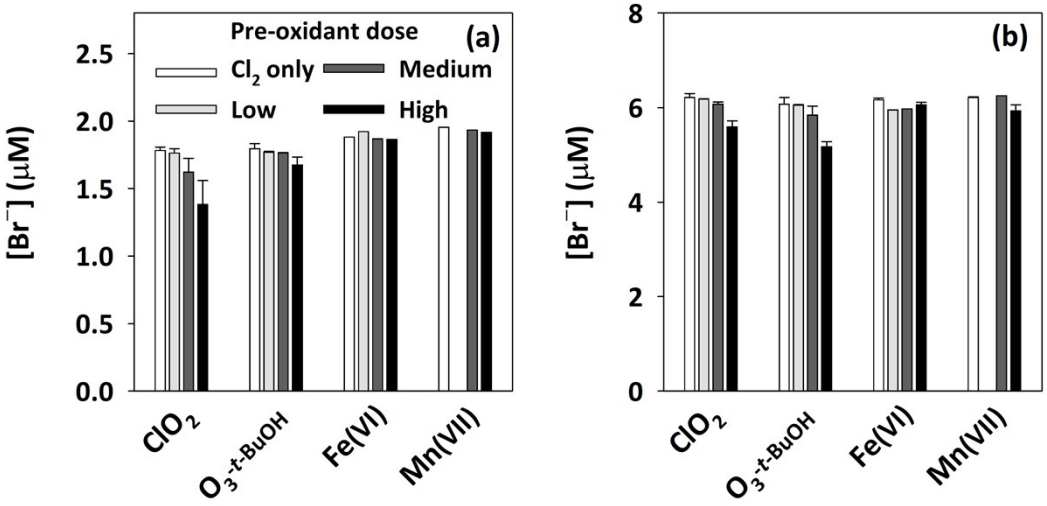


**Figure S3** Chlorination of SRNOM: Bromide concentrations chlorination or after pre-oxidation followed by chlorination at pH 8. Pre-oxidant doses: [$ClO_2$] = 3.5–39.3 μM, [$O_3$-*t*-BuOH] = 2.0–94.3 μM, [Fe(VI)] = 2.5–50 μM, [Mn(VII)] = 1–8.6 μM, [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), [$Br^-$] = (a) 1.9 μM (150 μg $L^{-1}$) and (b) 6.3 μM (500 μg $L^{-1}$). Error bars represent the range of analytical results for duplicate experiments.

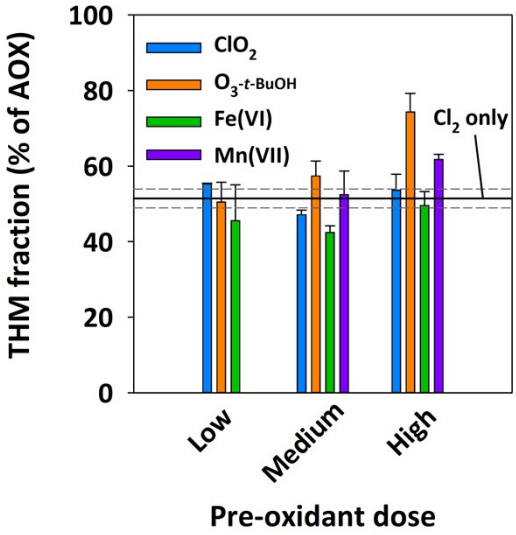


**Figure S4** Chlorination of SRNOM: Impact of pre-oxidation on THM fraction (% AOX in moles of halogen). The dashed lines represent the upper and lower limits of the THM fraction in the replicates without pre-oxidation. Pre-oxidant doses: [$ClO_2$] = 3.5–39.3 μM, [$O_3$-*t*-BuOH] = 2.0–94.3 μM, [Fe(VI)] = 2.5–50 μM, [Mn(VII)] = 1–8.6 μM. Chlorine dose = 85 μM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), no bromide, 72 h. Error bars represent the range of analytical results for duplicate experiments (except the high dose of Fe(VI) and Mn(VII) for which error bars represent duplicated analysis).

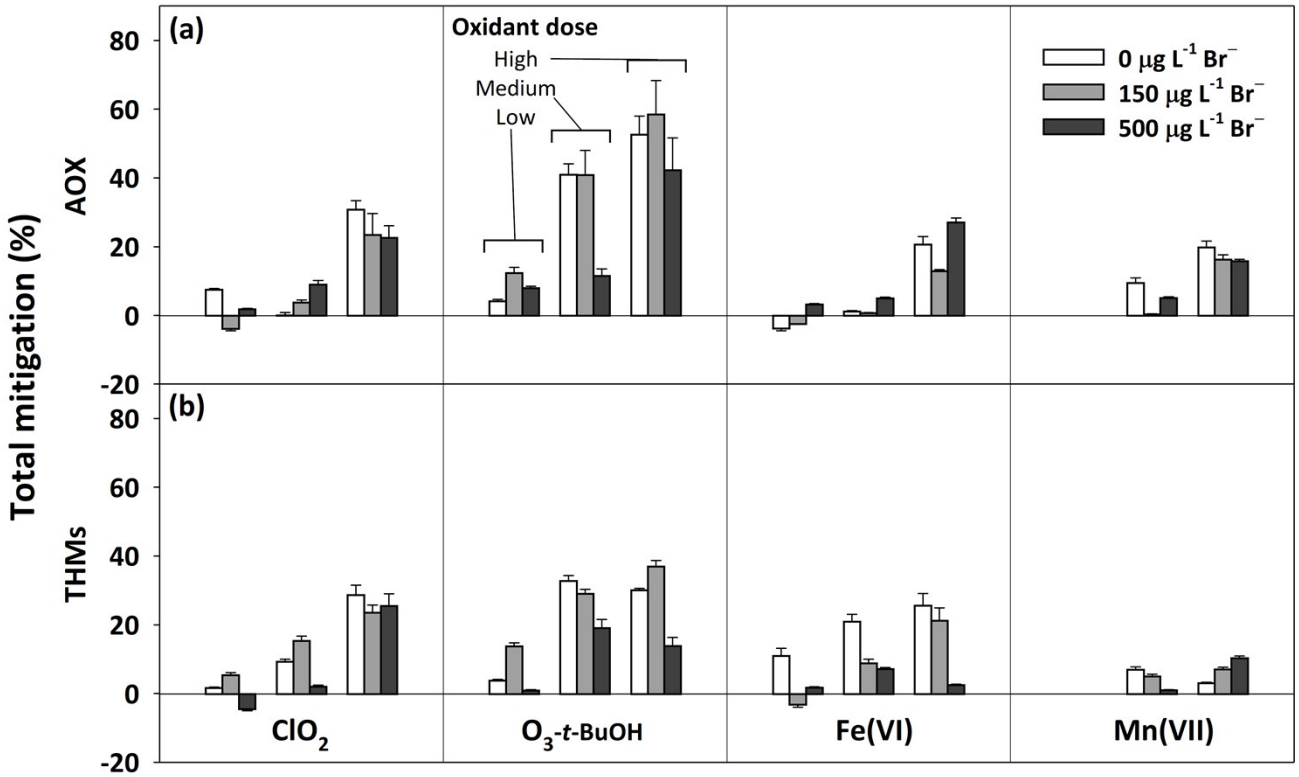


**Figure S5** Chlorination of SRNOM: Impact of bromide on the total (a) AOX and (b) THM mitigation by pre-oxidation with $ClO_2$, $O_3$-*t*-BuOH, Fe(VI) and Mn(VII). The % mitigation is presentend relatively to the DBP formation without pre-oxidation. A negative mitigation represents an increase in DBP formation. Pre-oxidant doses: [$ClO_2$] = 3.5–39.3 µM, [$O_3$-*t*-BuOH] = 2.0–94.3 µM, [Fe(VI)] = 2.5–50 µM, [Mn(VII)] = 1–8.6 µM. Chlorine dose = 85 µM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 8, 72 h. Error bars represent the range of analytical results for duplicate experiments (except the high dose of Fe(VI) and Mn(VII) for which error bars represent duplicate analysis).

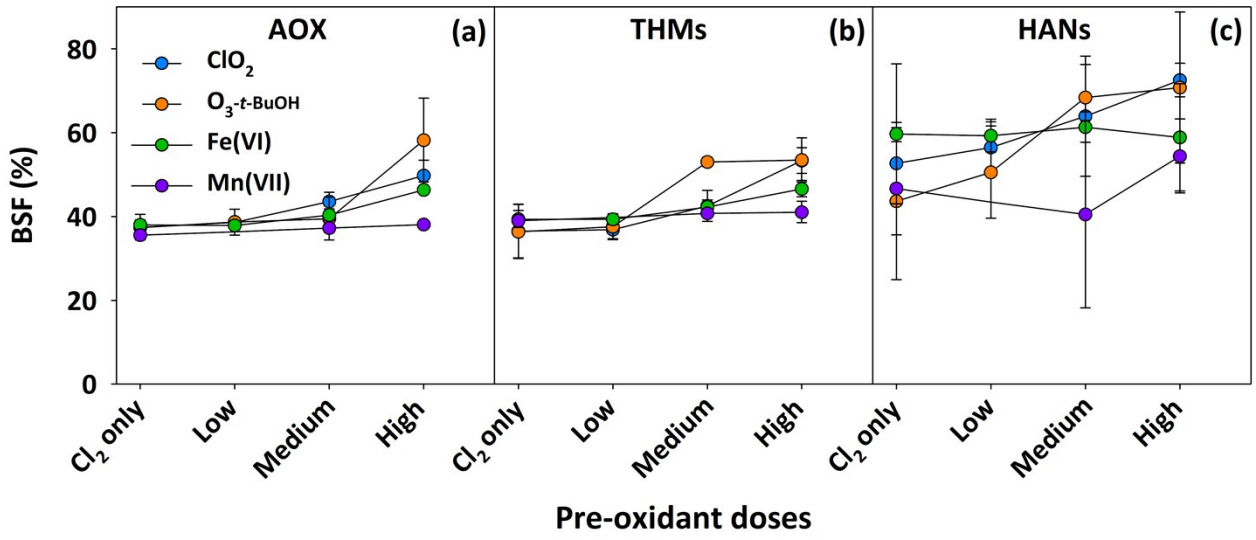


**Figure S6** Bromine Substitution Factors (BSF) in (a) AOX, (b) THMs and (c) HANs after chlorination of SRNOM in presence of 500 µg $L^{-1}$ bromide, without and with pre-oxidation. Pre-oxidant doses: [$ClO_2$] = 3.5–39.3 µM, [$O_3$-*t*-BuOH] = 2.0–94.3 µM, [Fe(VI)] = 2.5–50 µM, [Mn(VII)] = 1–8.6 µM. Chlorine dose = 85 µM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), 72 h. Error bars represent the range of analytical results for duplicate experiments (except the high dose of Fe(VI) and Mn(VII) for which error bars represent duplicate analysis).

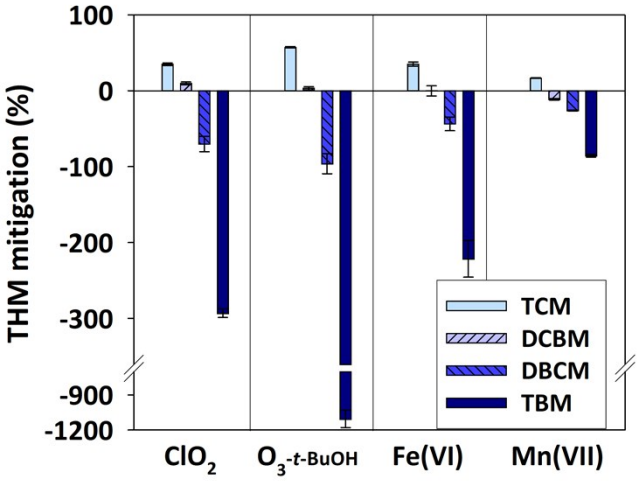


**Figure S7** Chlorination of SRNOM: Mitigation of individual THMs by high doses of pre-oxidants in presence of 150 µg $L^{-1}$ bromide. The % mitigation is presentend relatively to the THM formation without pre-oxidation. A negative mitigation represents an increase in THM formation. Pre-oxidant doses: [$ClO_2$] = 39.3 µM, [$O_3$-*t*-BuOH] = 94.3 µM, [Fe(VI)] = 50 µM, [Mn(VII)] = 8.6 µM. Chlorine dose = 85 µM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), 72 h. Error bars represent the range of duplicate analysis for one experiment.

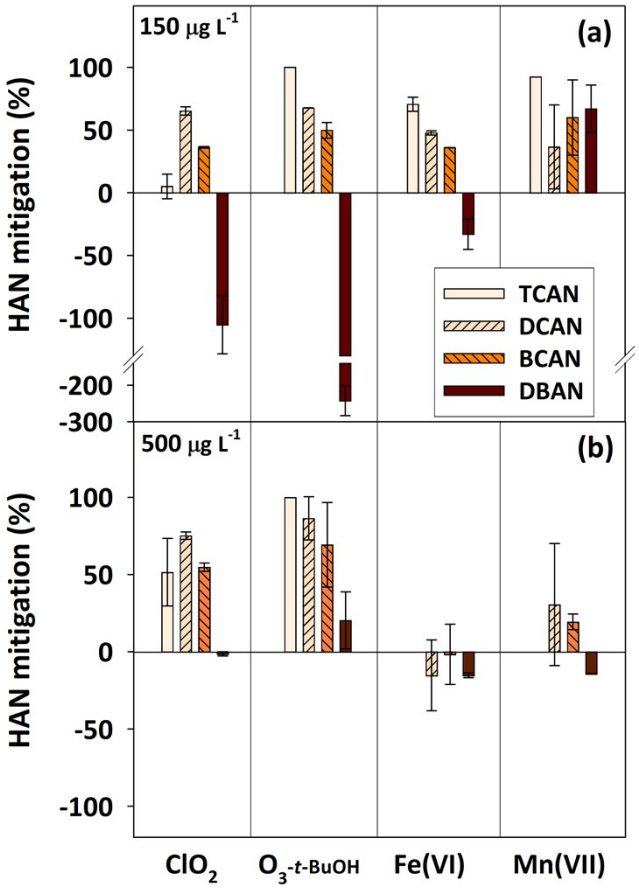


**Figure S8** Chlorination of SRNOM: Mitigation of individual HANs by high doses of pre-oxidants in presence of (a) 150 µg $L^{-1}$ or (b) 500 µg $L^{-1}$ bromide. The % mitigation is presentend relatively to the HAN formation without pre-oxidation. A negative mitigation represents an increase in HAN formation. Pre-oxidant doses: [$ClO_2$] = 39.3 µM, [$O_3$-*t*-BuOH] = 94.3 µM, [Fe(VI)] = 50 µM, [Mn(VII)] = 8.6 µM. Chlorine dose = 85 µM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), 72 h. Error bars represent the range of duplicate analysis for one experiment.

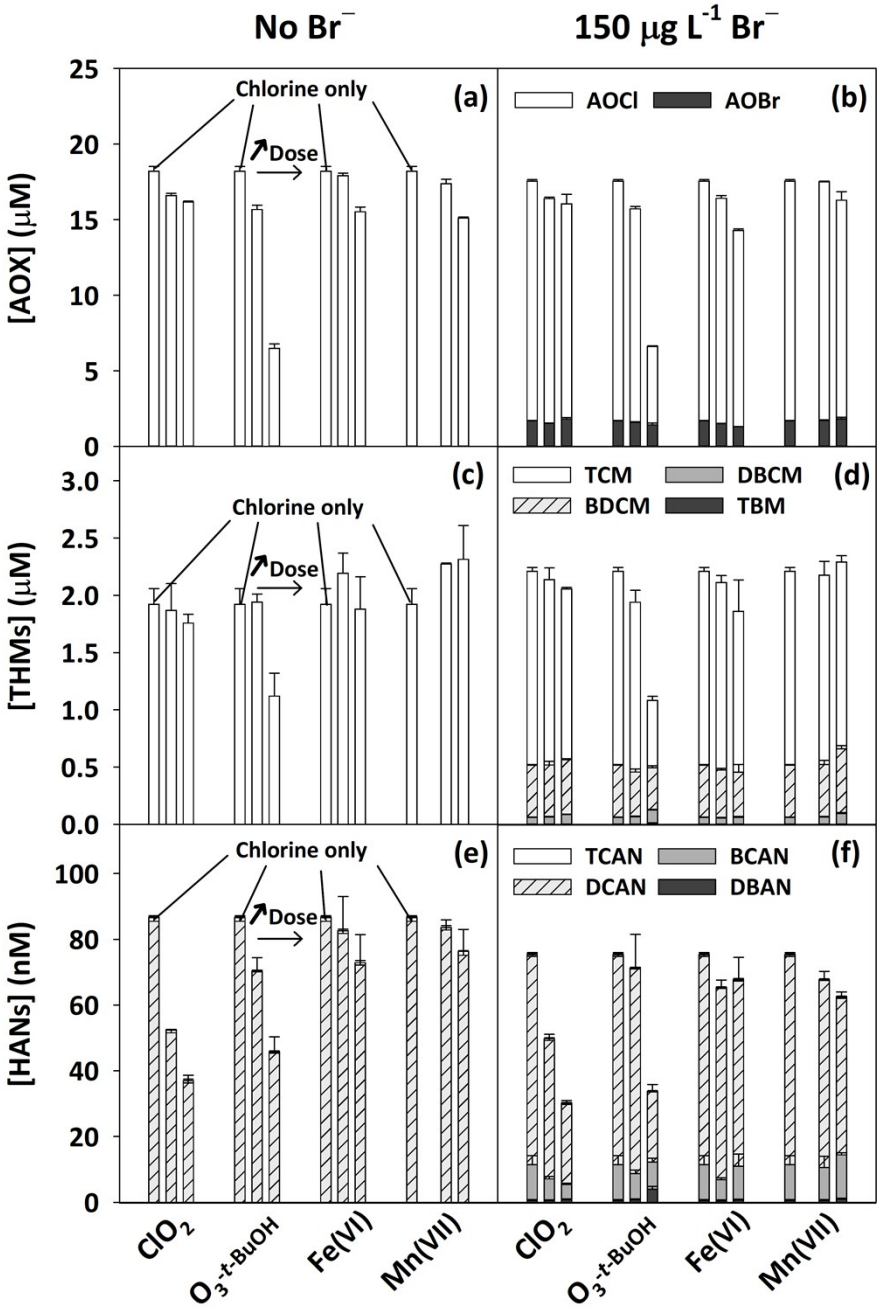


**Figure S9** Formation of (a–b) AOX, (c–d) THMs and (e–f) HANs after chlorination of SRNOM at pH 6.5, without (blank) and with pre-oxidation. For each pre-oxidant, the first bar represents the blank and the following bars the samples pre-oxidized with a low and medium dose. Pre-oxidant doses: [$ClO_2$] = 3.5–15.1 μM, [$O_3$-*t*-BuOH] = 2.0–39.8 μM, [Fe(VI)] = 2.5–14.7 μM, [Mn(VII)] = 1–8.6 μM. Chlorine dose = 85 μM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 6.5 (40 mM phosphate), [$Br^-$] = 0–150 μg $L^{-1}$, 72 h. Error bars represent the range of analytical results for duplicate experiments.

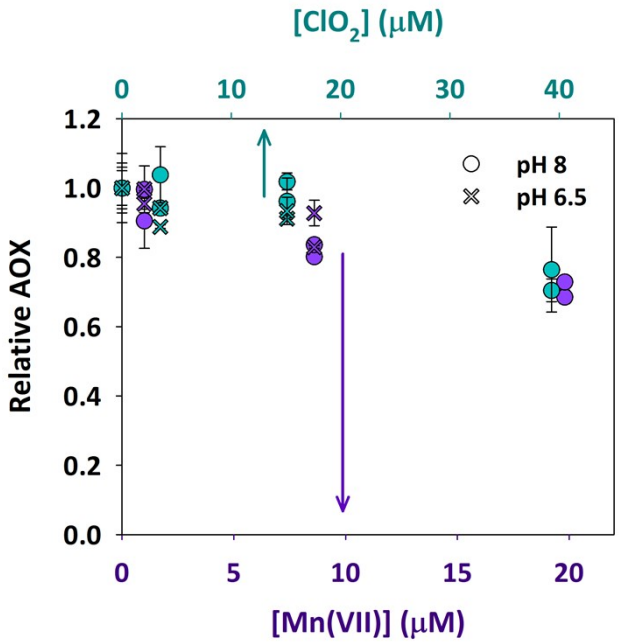


**Figure S10** Chlorination of SRNOM: Relative AOX formation after $ClO_2$ (blue symbols) and Mn(VII) (purple symbols) pre-oxidation at pH 6.5 (crosses) and 8 (circles). Chlorine dose = 85 μM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, [$Br^-$] = 0–150 μg $L^{-1}$, 40 mM phosphate (pH 6.5) or borate (pH 8), 72 h. Error bars represent the range of duplicate analyses for one experiment.

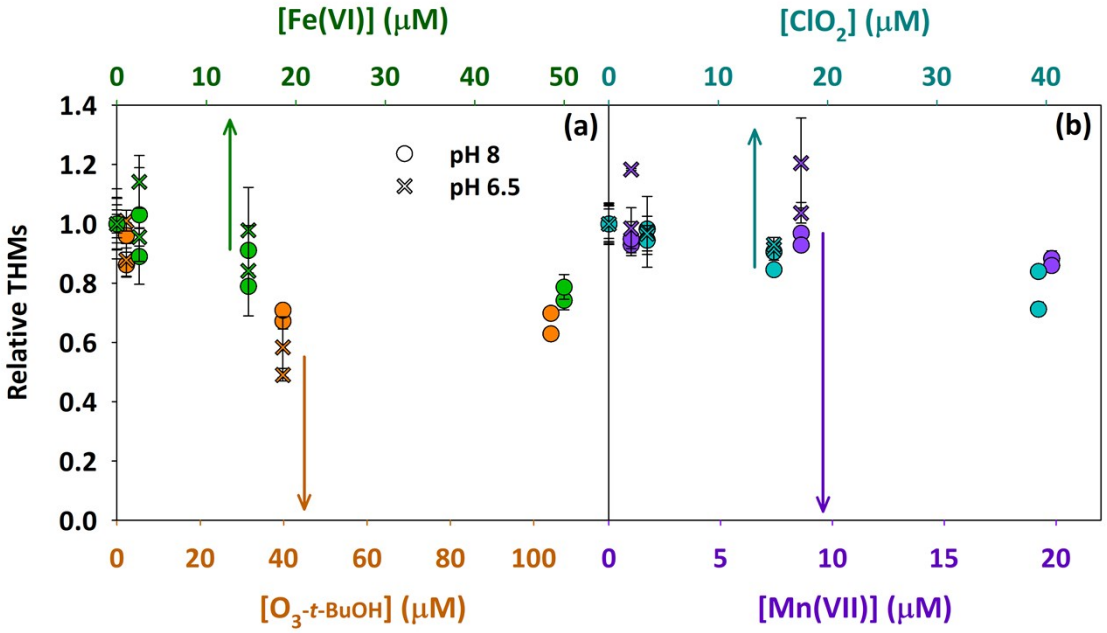


**Figure S11** Chlorination of SRNOM: Relative THM formation after $O_3$-*t*-BuOH (orange symbols), Fe(VI) (green symbols), $ClO_2$ (blue symbols) and Mn(VII) (purple symbols) pre-oxidation at pH 6.5 (crosses) and 8 (circles). Chlorine dose = 85 μM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, [$Br^-$] = 0–150 μg $L^{-1}$, 40 mM phosphate (pH 6.5) or borate (pH 8), 72 h. Error bars represent the range of duplicate analysis for one experiment.

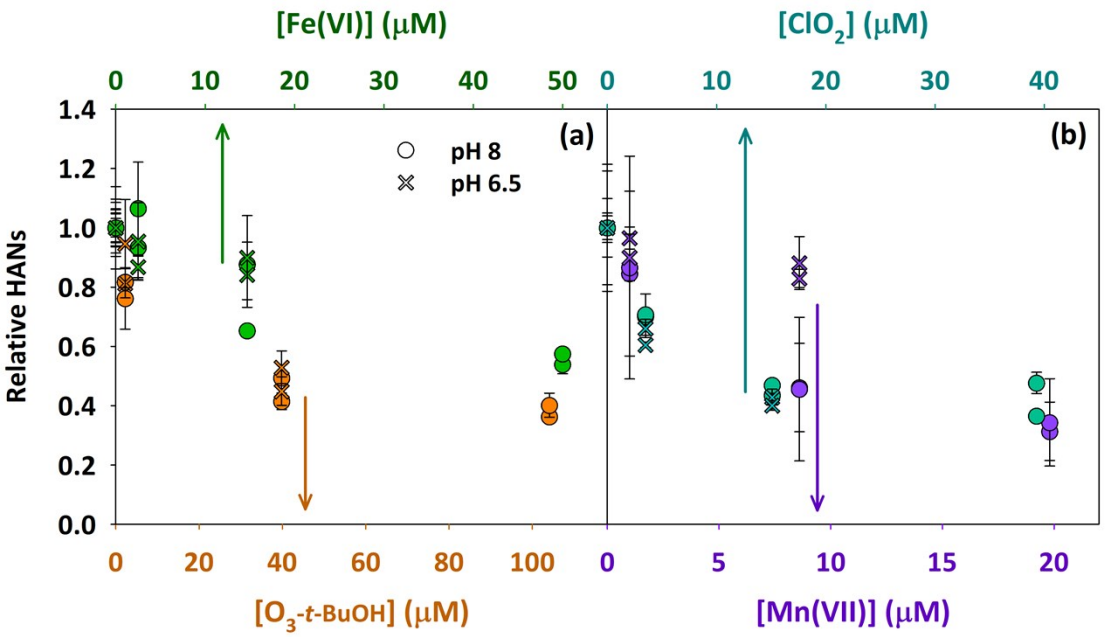


**Figure S12** Chlorination of SRNOM: Relative HAN formation after $O_3$-*t*-BuOH (orange symbols), Fe(VI) (green symbols), $ClO_2$ (blue symbols) and Mn(VII) (purple symbols) pre-oxidation at pH 6.5 (crosses) and 8 (circles)). Chlorine dose = 85 μM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, [$Br^-$] = 0–150 μg $L^{-1}$, 40 mM phosphate (pH 6.5) or borate (pH 8), 72 h. Error bars represent the range of duplicate analysis for one experiment.

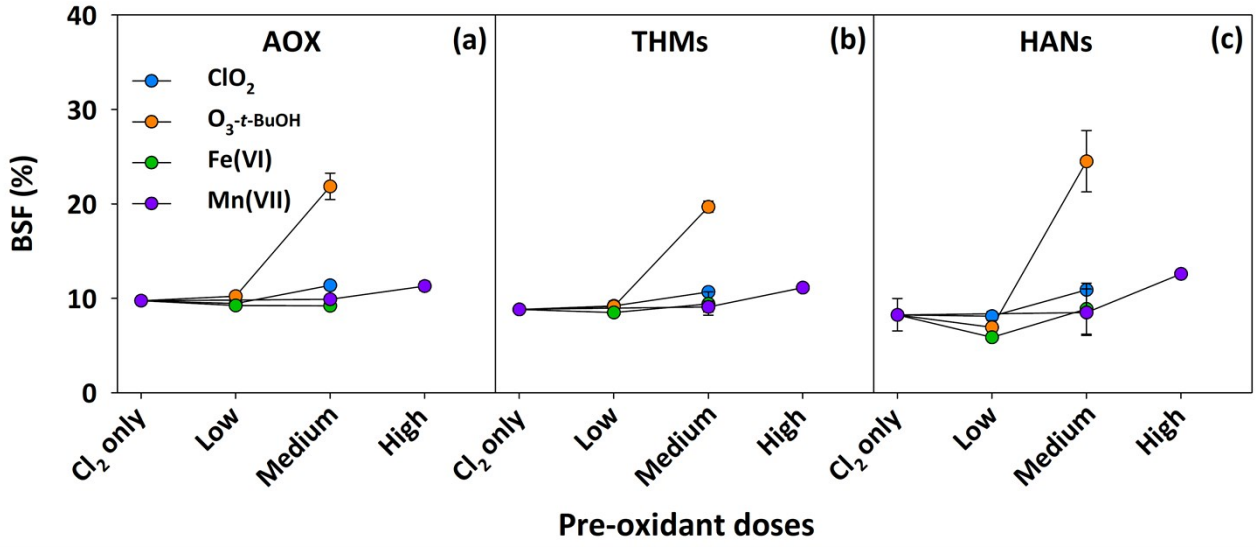


**Figure S13** Bromine Substitution Factor (BSF) in (a) AOX, (b) THMs and (c) HANs after chlorination of SRNOM in presence of 150 μg $L^{-1}$ bromide at pH 6.5, without and with pre-oxidation. Pre-oxidant doses: [$ClO_2$] = 3.5–39.3 μM, [$O_3$-*t*-BuOH] = 2.0–94.3 μM, [Fe(VI)] = 2.5–50 μM, [Mn(VII)] = 1–8.6 μM. Chlorine dose = 85 μM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 6.5 (40 mM phosphate), 72 h. Error bars represent the range of analytical results for duplicate experiments.

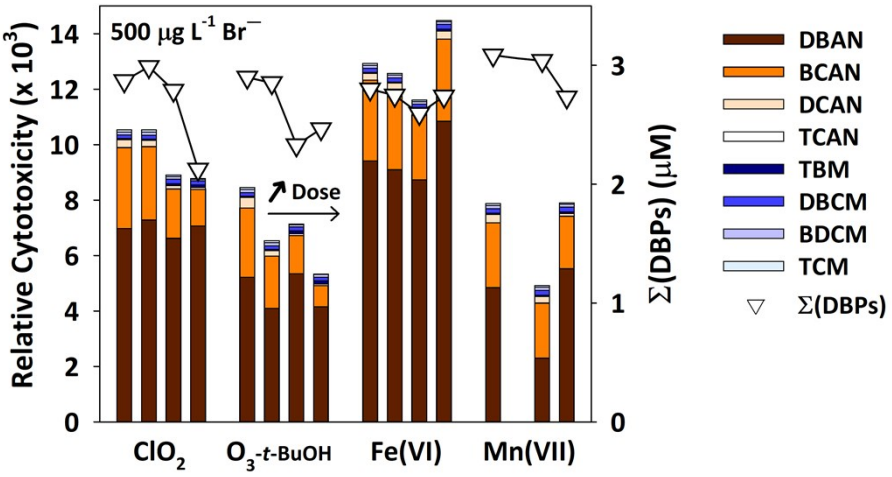


**Figure S14** Chlorination of SRNOM: Calculated relative cytotoxicity (bars) compared to DBP formation (triangles) after chlorination in presence of 500 µg $L^{-1}$ bromide. Pre-oxidant doses: [$ClO_2$] = 3.5–39.3 µM, [$O_3$-*t*-BuOH] = 2.0–94.3 µM, [Fe(VI)] = 2.5–50 µM, [Mn(VII)] = 1–8.6 µM. Chlorine dose = 85 µM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), 72 h. For more clarity, error bars are not shown.

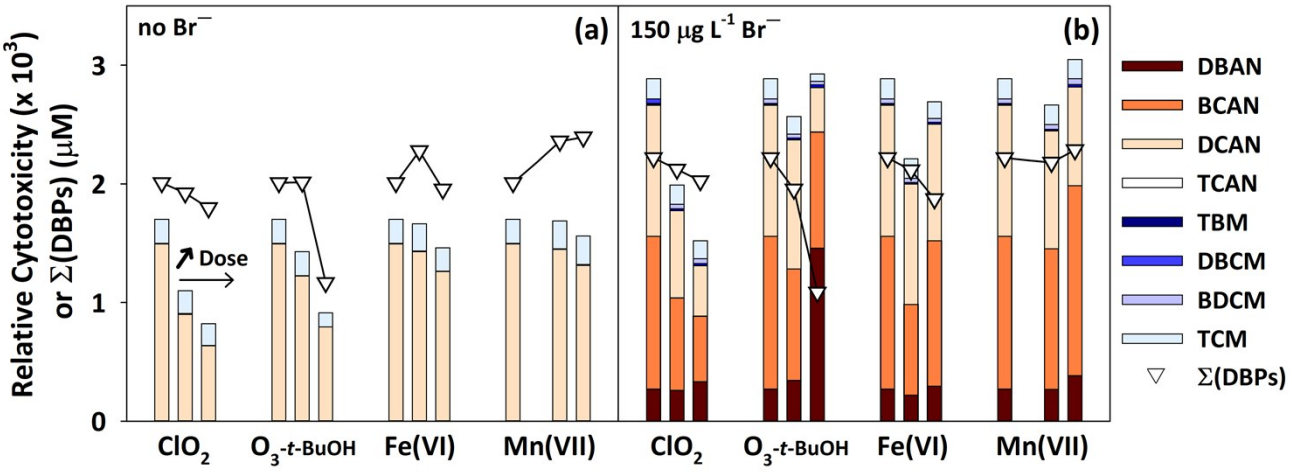


**Figure S15** Chlorination of SRNOM: Calculated relative cytotoxicity (bars) compared to DBP formation (triangles) after chlorination at pH 6.5, (a) without bromide and (b) with 150 µg $L^{-1}$ bromide. Pre-oxidant doses: [$ClO_2$] = 3.5–15.1 µM, [$O_3$-*t*-BuOH] = 2.0–39.8 µM, [Fe(VI)] = 2.5–14.7 µM, [Mn(VII)] = 1–8.6 µM. Chlorine dose = 85 µM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 6.5 (40 mM phosphate), 72 h. For more clarity, error bars are not shown.

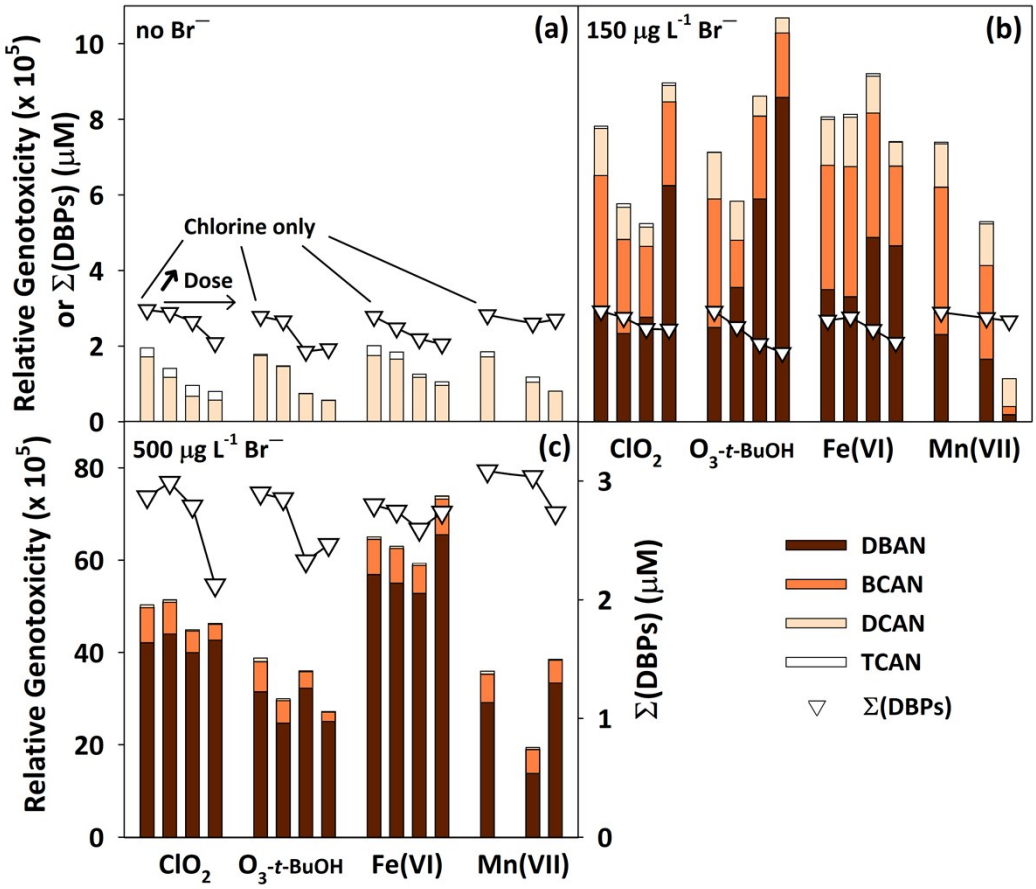


**Figure S16** Chlorination of SRNOM: Calculated relative genotoxicity (bars) compared to DBP formation (triangles) after chlorination and (a) without bromide or (b) with 150 μg $L^{-1}$ or (c) 500 μg $L^{-1}$ bromide. Pre-oxidant doses: [$ClO_2$] = 3.5–39.3 μM, [$O_3$-*t*-BuOH] = 2.0–94.3 μM, [Fe(VI)] = 2.5–50 μM, [Mn(VII)] = 1–8.6 μM. Chlorine dose = 85 μM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), 72 h. For more clarity, error bars are not shown.

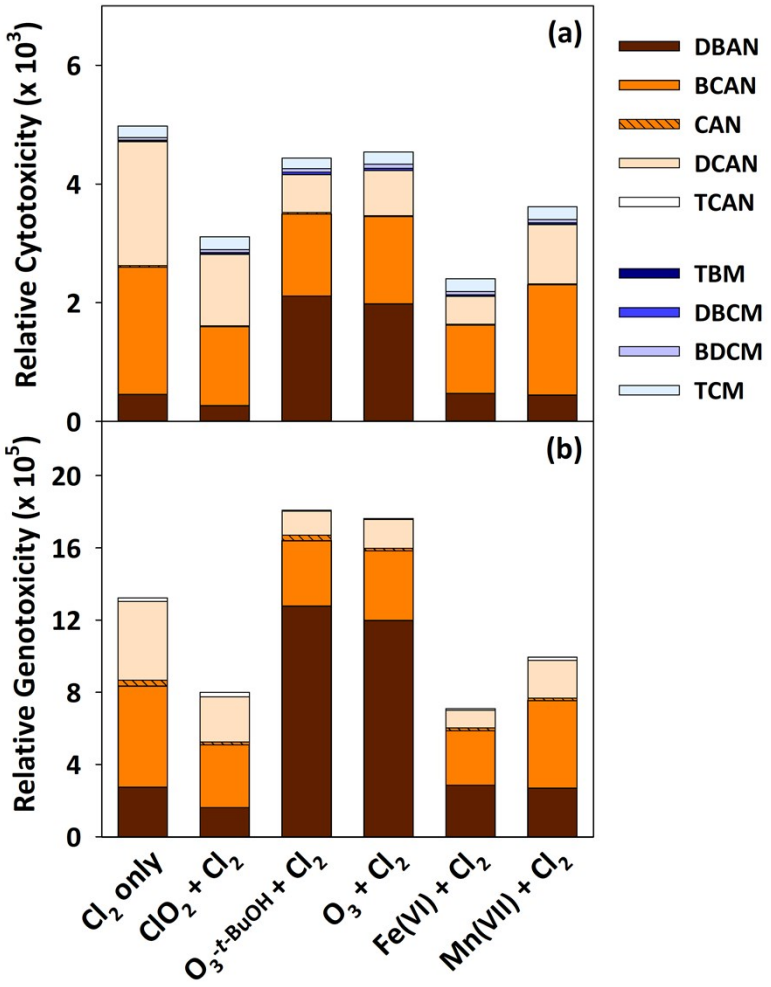


**Figure S17** (a) Relative calculated cytotoxicity and (b) genotoxicity after chlorination of a real water (W20), without ($Cl_2$ only) and with pre-oxidation. Pre-oxidant doses: [$ClO_2$] = 10 µM, [$O_3$-*t*-BuOH] = [$O_3$] = 30 µM, [Fe(VI)] = 24 µM, [Mn(VII)] = 10 µM. Chlorine dose = 155 µM (12.4 mg$Cl_2$ $L^{-1}$), 72 h. The water characteristics are given in the main manuscript (Table 1). For more clarity, error bars are not shown.

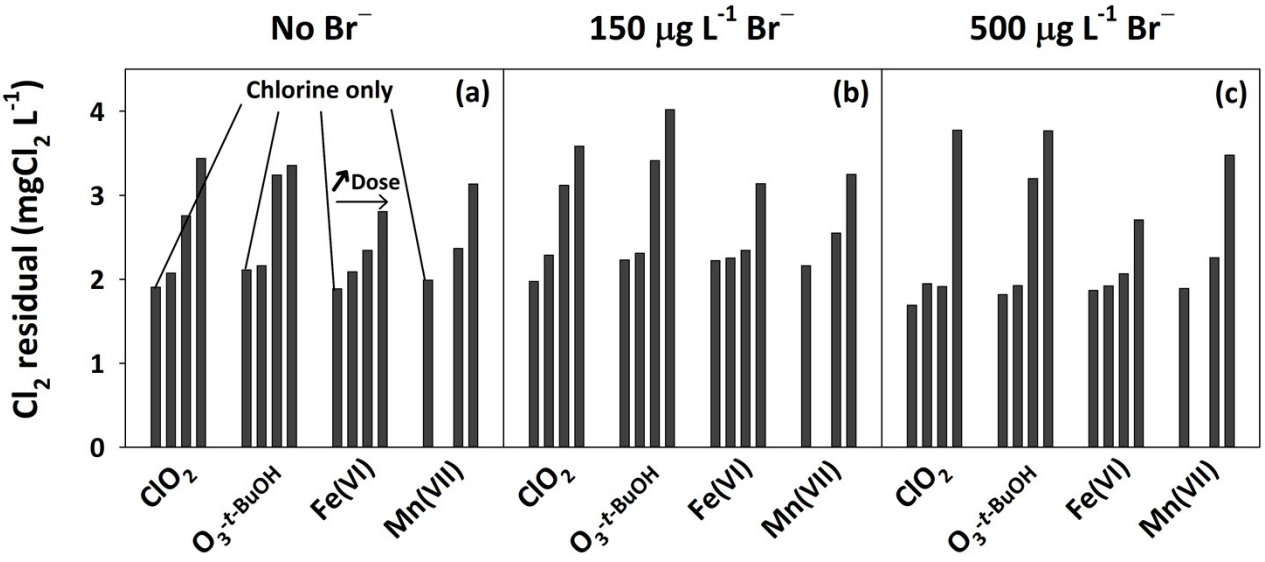


**Figure S18** Chlorination of SRNOM: Impact of pre-oxidation on chlorine residual (HOCl+HOBr) (a) without bromide and (b) with 150 μg $L^{-1}$ or (c) 500 μg $L^{-1}$ bromide. Pre-oxidant doses: [$ClO_2$] = 3.5–39.3 μM, [$O_3$-*t*-BuOH] = 2.0–94.3 μM, [Fe(VI)] = 2.5–50 μM, [Mn(VII)] = 1–8.6 μM. Chlorine dose = 85 μM (6.0 mg$Cl_2$ $L^{-1}$), [SRNOM] = 3 mgC $L^{-1}$, pH 8 (40 mM borate), [$Br^-$] = 0–500 μg $L^{-1}$, 72 h.

## References

1 S. Allard, J. W. A. Charrois, C. A. Joll and A. Heitz, Simultaneous analysis of 10 trihalomethanes at nanogram per liter levels in water using solid-phase microextraction and gas chromatography mass-spectrometry, *J. Chromatogr. A*, 2012, **1238**, 15-21.

2 I. Kristiana, C. Joll and A. Heitz, Analysis of halonitriles in drinking water using solid-phase microextraction and gas chromatography–mass spectrometry, *J. Chromatogr. A*, 2012, **1225**, 45-54.