

Supporting Information Section

CHANGES IN NOM FLUORESCENCE CAUSED BY CHLORINATION AND THEIR ASSOCIATIONS WITH DISINFECTION BY-PRODUCTS FORMATION

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Details of the experimental and analytical methods

Experimental methods

Chlorination experiments water were conducted at different reaction temperatures (3 ± 1 , 20 ± 1 and $34\pm 1^\circ\text{C}$) in the dark in 1.6 L PTFE sampling bags, which were used to prevent the loss of volatile DPBs when samples were taken at different reaction times (10 minutes to 3 days). Controlled temperature rooms were used to conduct the experiments. The samples were chlorinated with sodium hypochlorite at pH 7.0 in the presence of 0.03 mol/L phosphate buffer. Initial chlorine doses were 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 mg Cl_2 per mg DOC. Requisite amounts of Na_2SO_3 or NH_4Cl were added to quench the residual chlorine. Quenched chlorinated samples were stored at 4°C for no more than 10 days before being analysed for DBPs concentrations.

Analytical methods

Chlorine concentrations were determined using the standard N,N-diethyl-p-phenyldiamine (DPD) colorimetric method. UV absorbance spectra were measured using a 5 cm quartz cell on a Perkin-Elmer Lambda 18 spectrophotometer. All spectra were normalized to a 1 cm cell length.

A Perkin-Elmer LS-50B fluorometer, with a 1 cm cell length, was used for fluorescence measurements. The emission wavelengths were scanned from 340 to 600 nm with a bandwidth of 0.5 nm, at 320 nm of excitation. No inner filter corrections were made during the examination of the fluorescence spectra since NOM concentrations were too low for inner filter effects to be important and also because all emission spectra were always normalized to obtain parameters of interest for this study (namely, I_{500}/I_{450} and $\lambda_{0.5}^{em}$).

TOC was analyzed using an O.I. Analytical 1010 total organic carbon analyzer. Concentrations of THMs, other volatile and semi-volatile DBPs were determined using standard analytical procedures (EPA methods 551.1 and 552.2) and a Perkin-Elmer AutoSystem gas chromatograph equipped with an electron capture detector. Other aspects of these analyses are described in reference (14) in the main manuscript.

Table S1. Regression coefficients for correlations between differential fluorescence indexes and, on the other hand, major halogenated DBPs or chlorine consumption. Chlorinated Ancipa Inlet D water at pH7, different chlorine doses, reaction times and temperatures.

Parameter	R² value for $\Delta\lambda^{\text{em}}_{0.5}$	R² value for $\Delta(I_{500}/I_{450})$
ΔCl_2	0.91 (power fit)	0.94 (power fit)
CHCl_3	0.90 (power fit)	0.95 (power fit)
CHBrCl_2	0.87 (power fit)	0.92 (linear fit)
CHClBr_2	0.80 (linear fit)	0.88 (linear fit)
$\text{CHCl}_3(\%)$	0.82 (linear fit)	0.80 (power fit)
$\text{CHBrCl}_2(\%)$	0.81 (power fit)	0.79 (expon. fit)
$\text{CHClBr}_2(\%)$	0.74 (power fit)	0.72 (power fit)
TTHM	0.92 (power fit)	0.95 (power fit)
CH	0.85 (power fit)	0.89 (power fit)
DCAN	0.93 (power fit)	0.95 (power fit)
BCAN	0.88 (power fit)	0.94 (linear fit)
DBAN	0.74 (linear. fit)	0.81 (linear fit)
DCAN(%)	0.69 (power fit)	0.61 (power fit)
BCAN(%)	0.61 (expon.fit)	0.56 (power fit)
DBAN(%)	0.59 (power fit)	0.54 (power fit)
THAN	0.93 (power fit)	0.95 (power fit)
DCAA	0.89 (expon. fit)	0.92 (expon. fit)
TCAA	0.92 (power fit)	0.96 (power fit)
BCAA	0.84 (expon. fit)	0.91 (expon. fit)
BDCAA	0.81 (power fit)	0.88 (power fit)
DCAA(%)	0.81 (ln fit)	0.86 (ln fit)
TCAA(%)	0.83 (ln fit)	0.85 (ln fit)
BCAA(%)	0.80 (power fit)	0.82 (power fit)
DBAA(%)	0.87 (power fit)	0.84 (power fit)
$\text{X}_2\text{AA}(\%)$	0.82 (ln fit)	0.87 (ln fit)
$\text{X}_3\text{AA}(\%)$	0.83 (ln fit)	0.84 (ln fit)
THAA	0.90 (power fit)	0.95 (power fit)

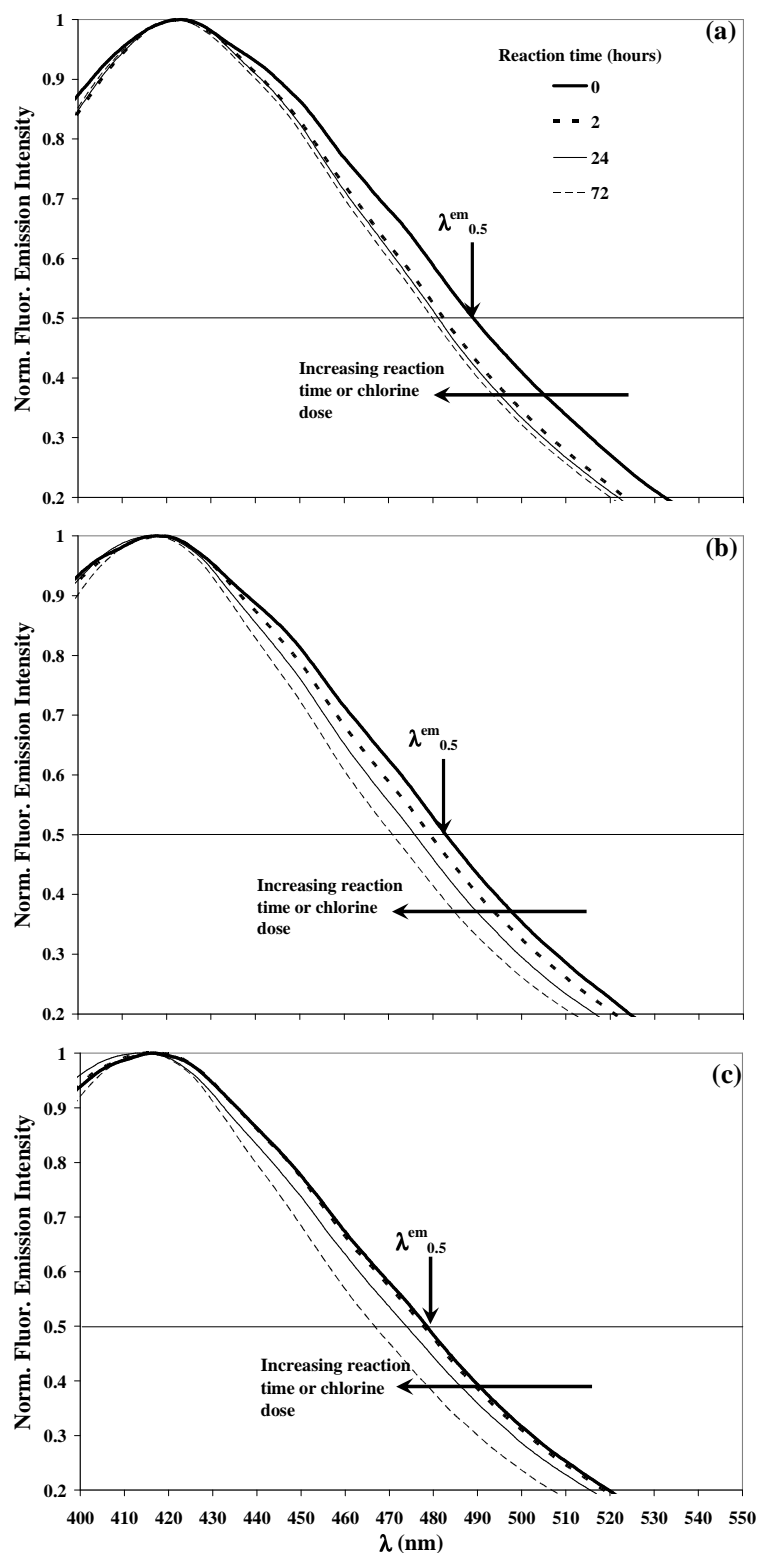


Figure S1. Normalized fluorescence emission spectra for chlorinated Potomac Inlet (a), DS (b) and MF (c) waters at pH 7.0, chlorine to DOC ratio 2.00 mg/mg, reaction times from 10 minutes to 3 days and temperature 20°C.

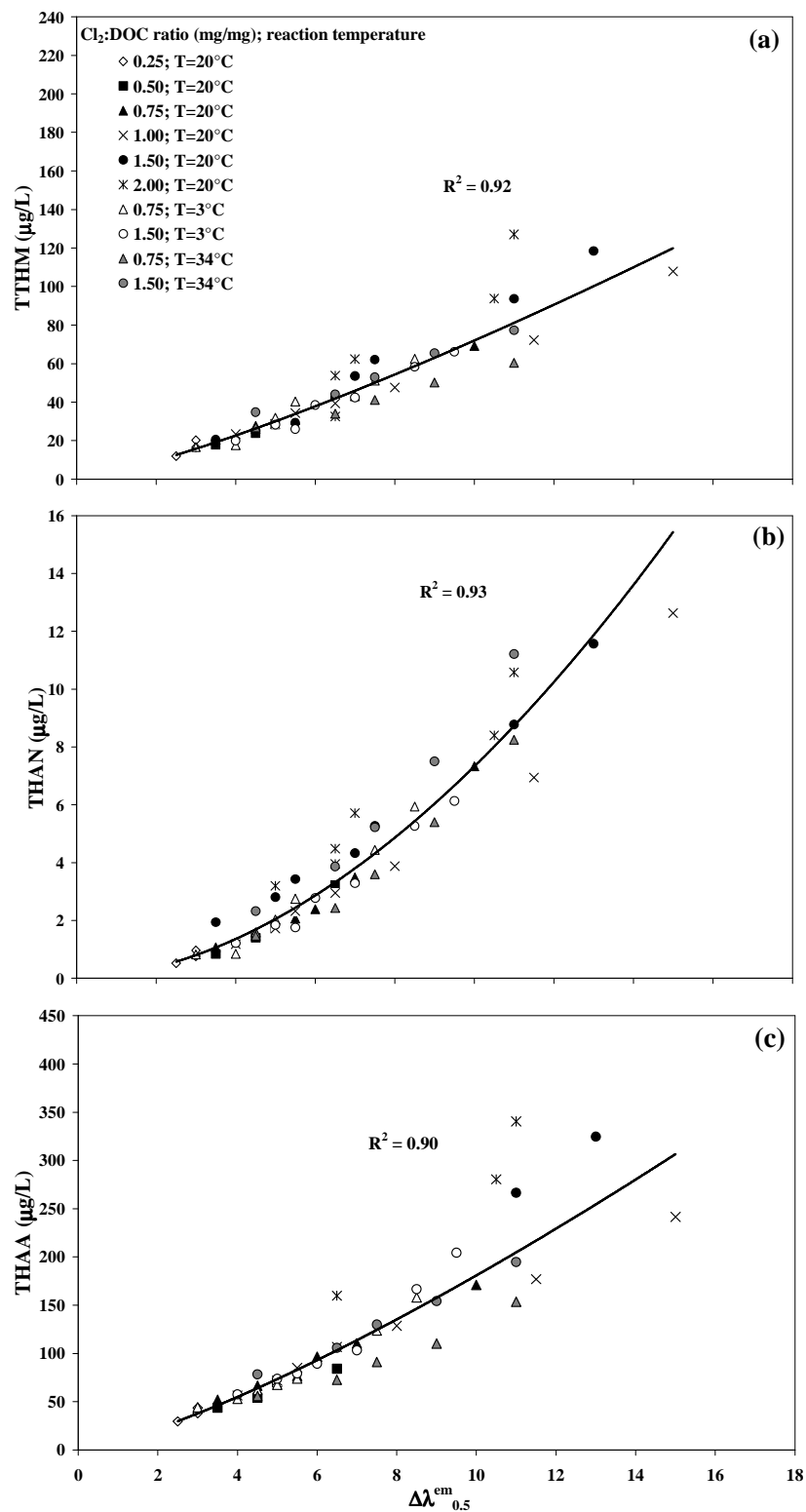


Figure S2. Correlations between $\Delta\lambda_{0.5}^{em}$ values and concentrations of TTHM (a), THAN (b) and THAA (c). Chlorinated Ancipa Inlet D water at pH 7.0, chlorine to DOC ratios from 0.25 to 2.00 mg/mg, reaction times from 10 minutes to 3 days and temperatures from 3°C to 34°C .

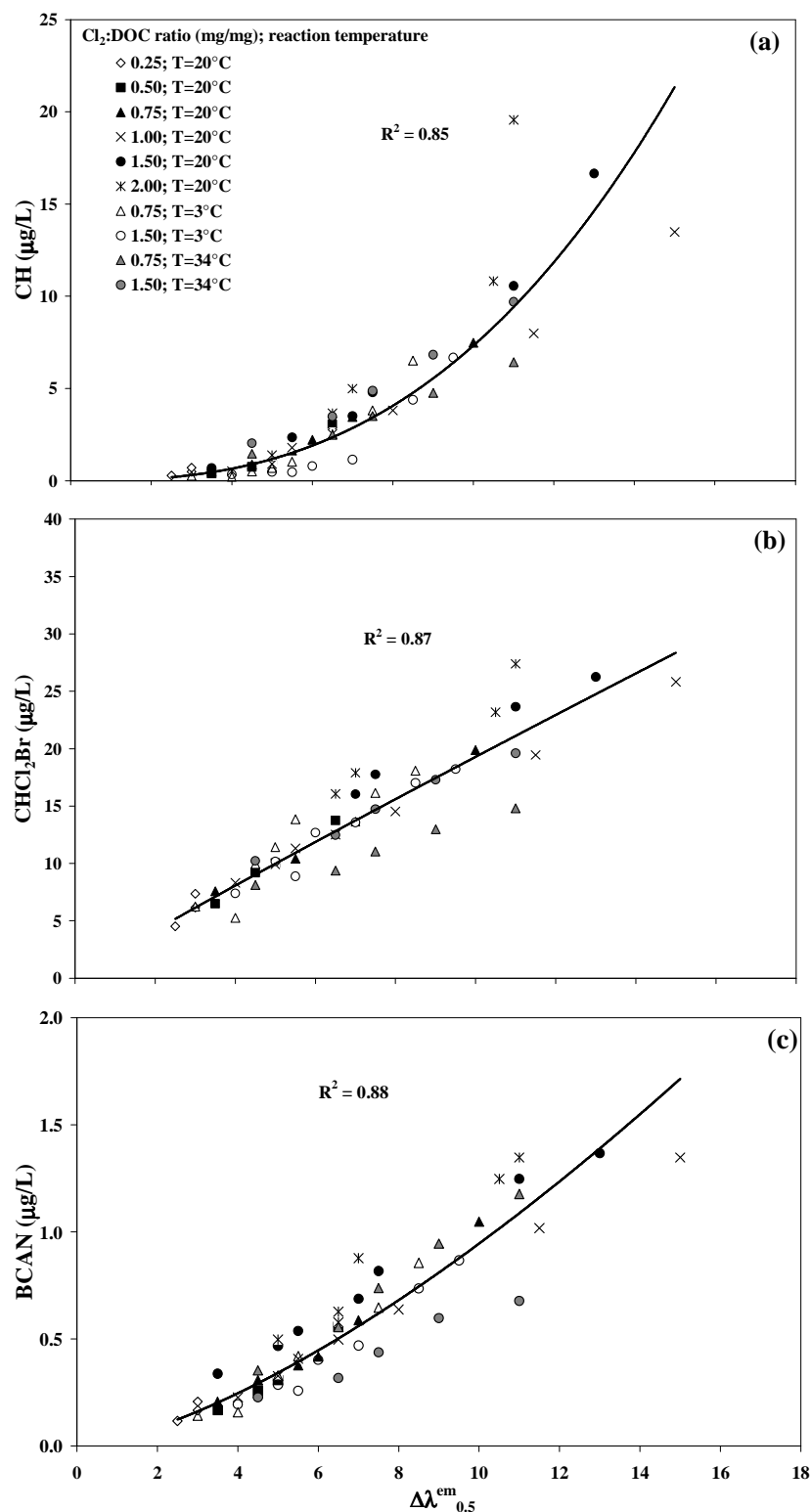


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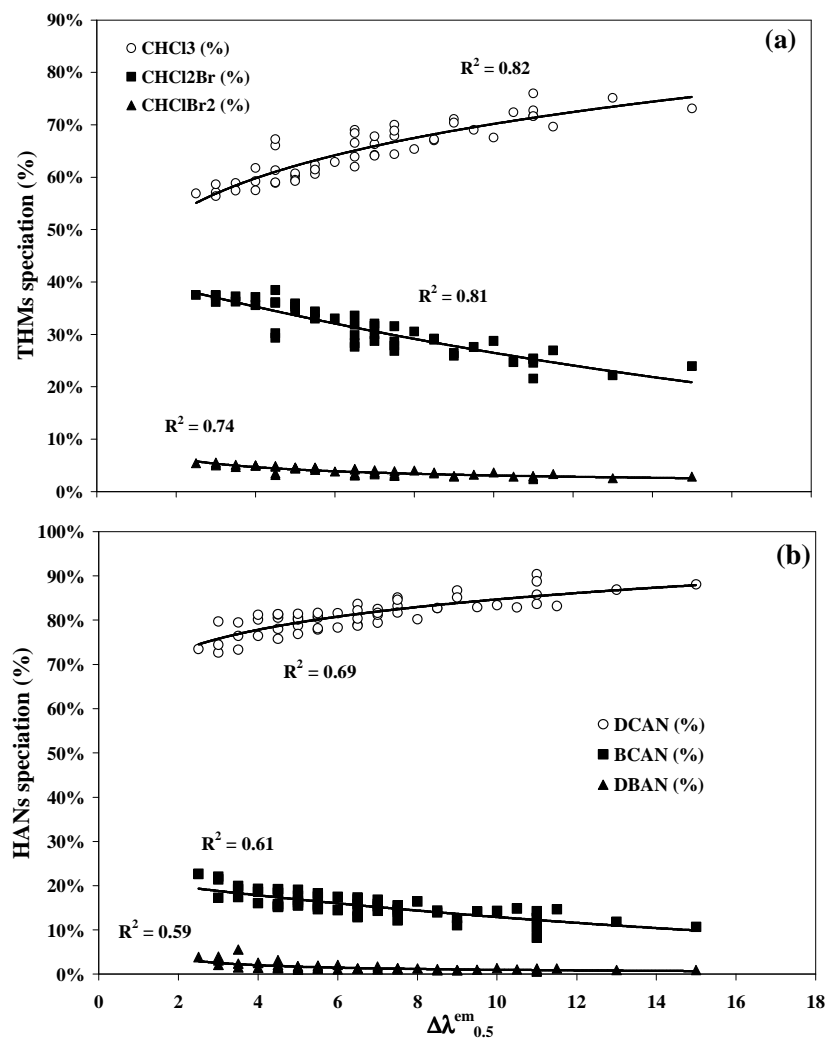


Figure S4. Correlations between $\Delta\lambda^{em}_{0.5}$ values and speciation of THMs (a) and HANs (b). Chlorinated Ancipa Inlet D water at pH 7.0, chlorine to DOC ratios from 0.25 to 2.00 mg/mg, reaction times from 10 minutes to 3 days and temperatures from 3°C to 34°C.

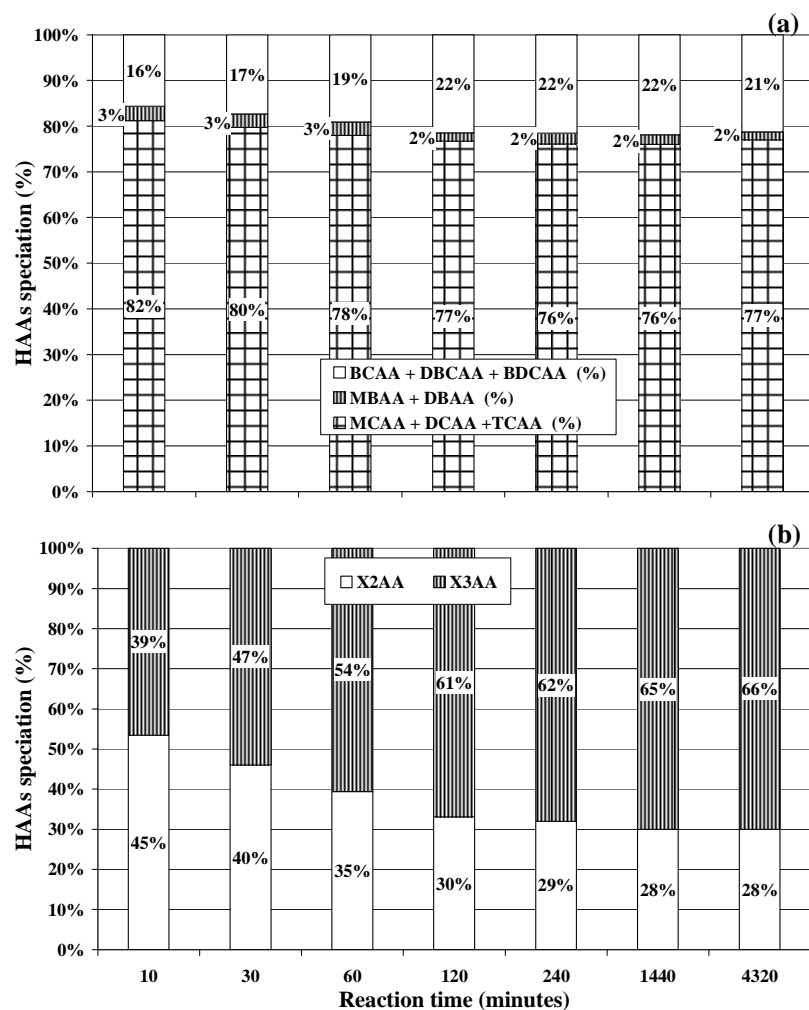


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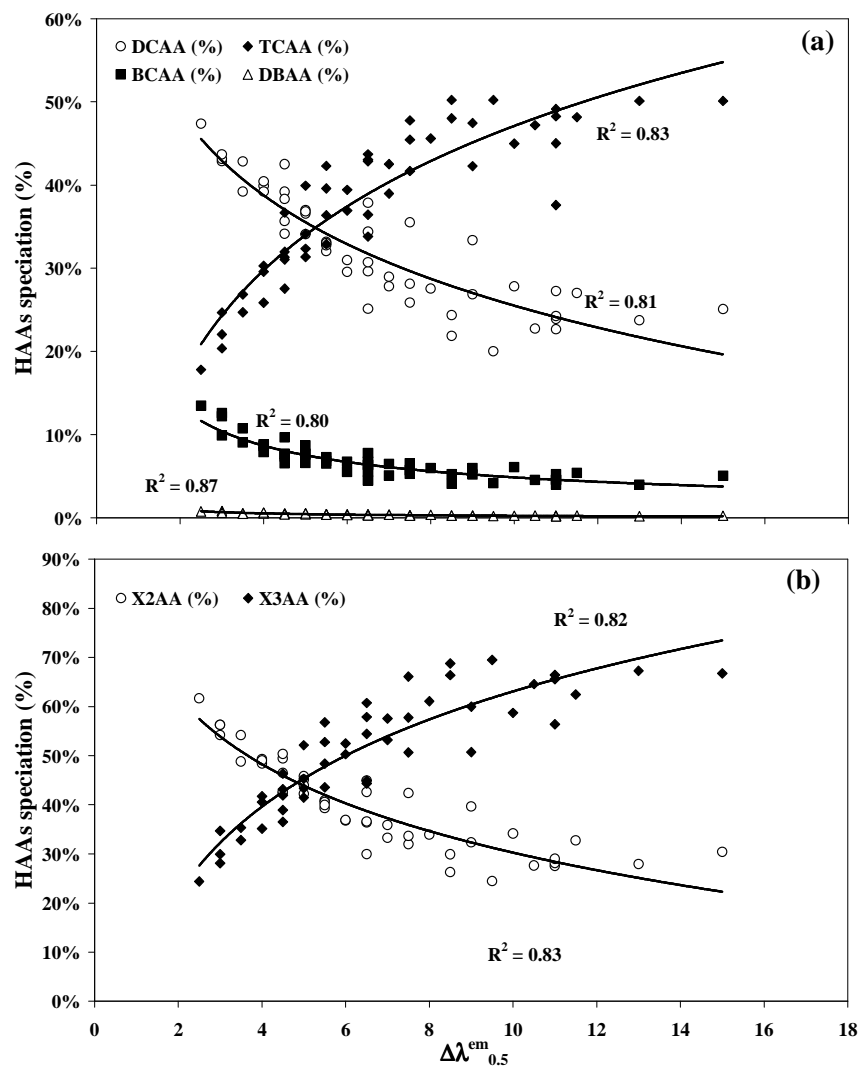


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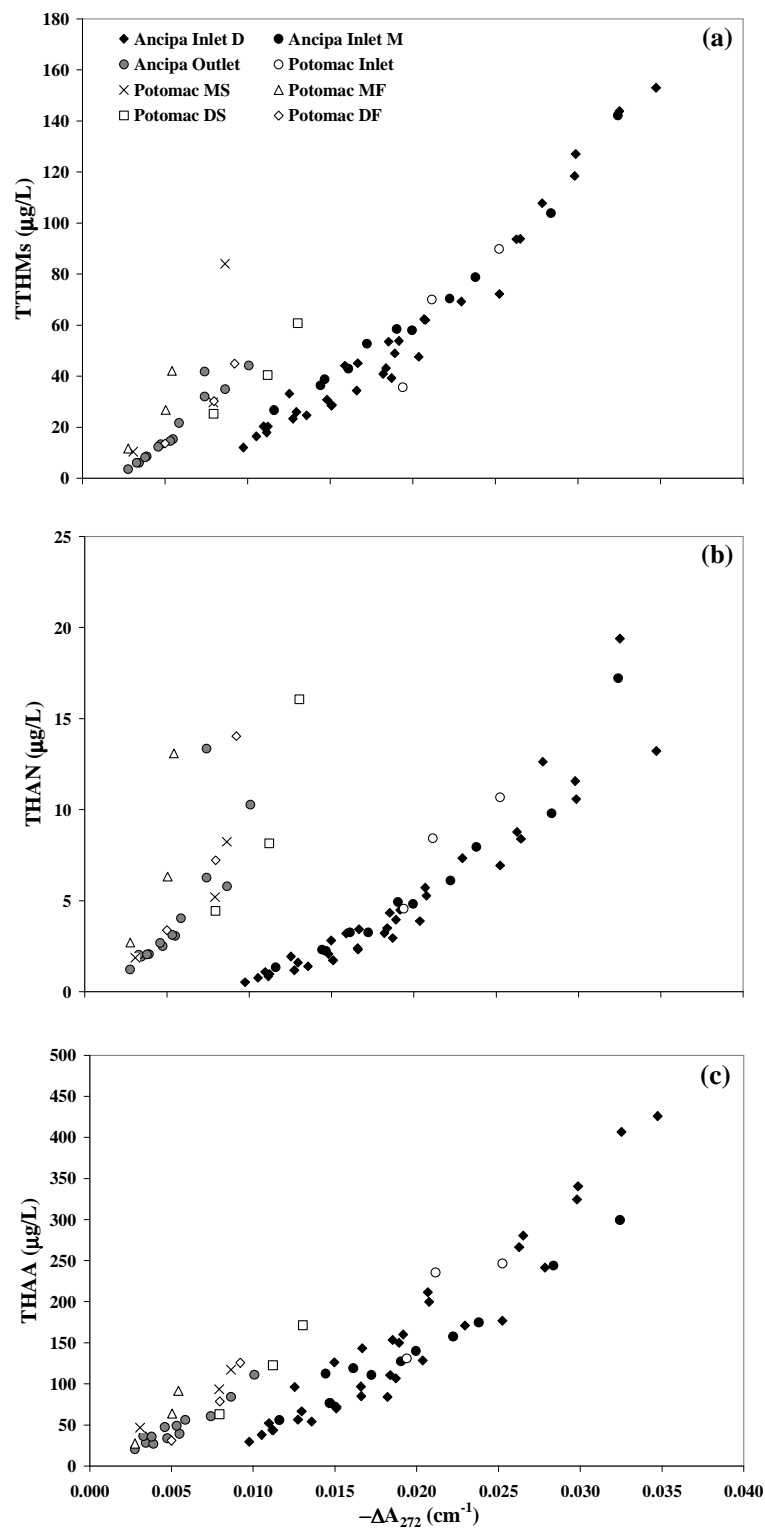


Figure S7. Correlations between $-\Delta A_{272}$ values and concentrations of TTHM (a), THAN (b) and THAA (c). Chlorinated Ancipa and Potomac waters at pH 7.0, chlorine to DOC ratios from 0.25 to 2.00 mg/mg, reaction times from 10 minutes to 3 days and temperatures from 3°C to 34°C.

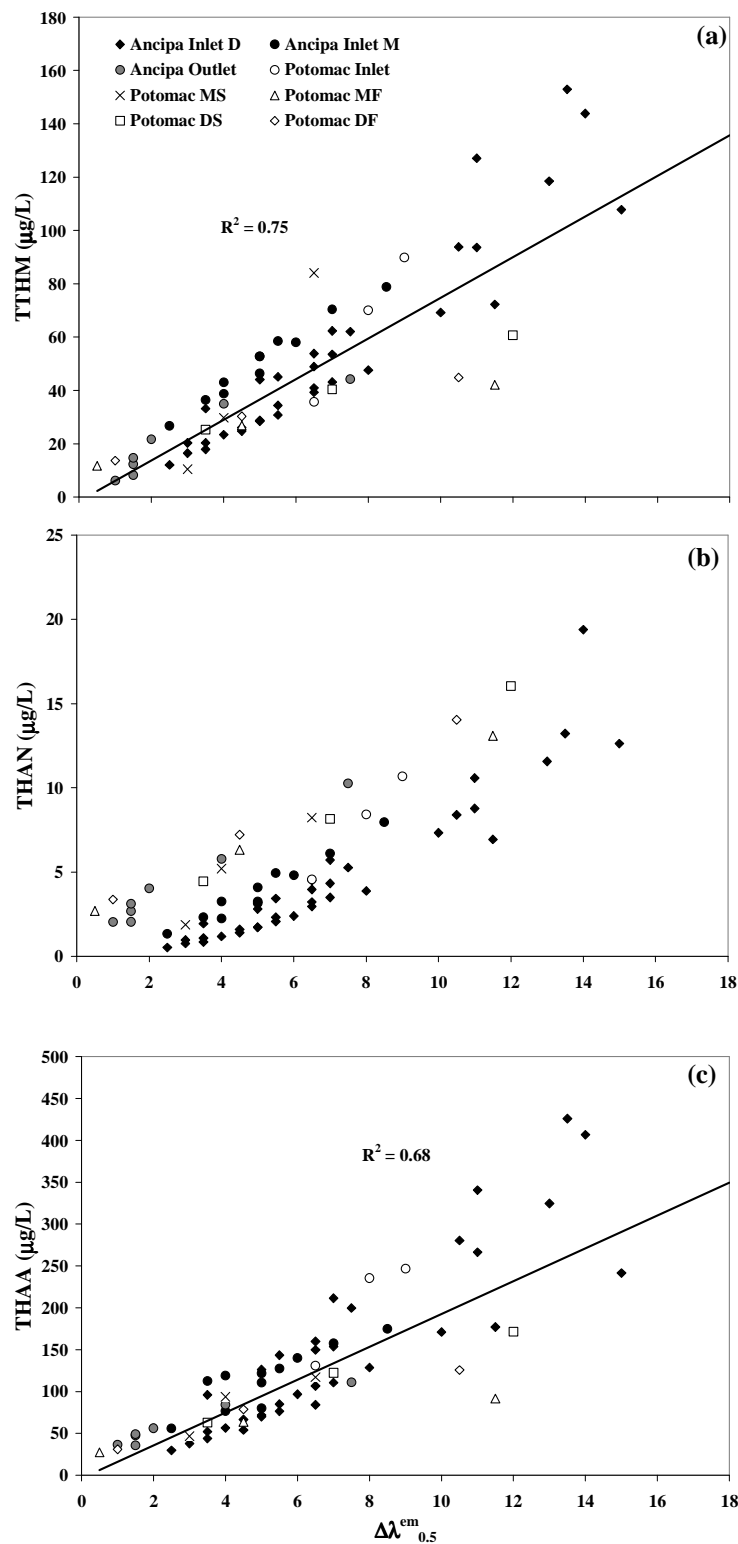


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