# Supplementary Information

# Assessing Disinfection Byproduct Risks for Algal Impacted Surface Waters and the Effects of Peracetic Acid Pre-Oxidation

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**Text S1 Materials**

Sodium hypochlorite (4–4.99% chlorine), 1,2-dibromopropane (97%), EPA 551B halogenated volatiles mix (2000 μg/mL each component in acetone), and peracetic acid (32% PAA, 40–45% acetic acid, <6% hydrogen peroxide ($H_2O_2$)) were obtained from Sigma Aldrich. Acetonitrile (HPLC grade, 99.99%), boric acid (99.8%), sodium hydroxide (99.1%), potassium iodide (100.2%) and sodium sulfate (100.5%) were purchased from Fisher Chemical. Tert-butyl methyl ether (MTBE, ≥97%) was obtained from Honeywell Fluka. Potassium chloride (≥99%) was purchased from Macron. Ammonia salicylate, ammonia cyanurate, and N,N-Diethyl-p-phenylenediamine (DPD) total and free chlorine Permachem reagents were obtained from Hach Company. Hydrochloric acid (2.000 N) was purchased from BDH Chemicals. Sodium thiosulfate anhydrous ($Na_2S_2O_3$) (>97%) was purchased from EMD Millipore. Milli-Q water was used to prepare all aqueous solutions.

**Text S2 Method development for peracetic acid pre-oxidation experiments**

Method development for PAA pre-oxidation included four steps. First, the ratio of sodium thiosulfate ($Na_2S_2O_3$) to PAA needed to quench the reaction was determined. Unlike other disinfection experiments where excess reductant can be used for quenching, PAA pre-oxidation experiments require minimal residual $Na_2S_2O_3$ such that it would not add significant chlorine demand in the subsequent chlorination step in uniform formation conditions (UFC) tests. $Na_2S_2O_3$ also reacts with hydrogen peroxide ($H_2O_2$), but at a much slower rate ($k = 2.3 \times 10^{-2}\ M^{-1}\ s^{-1}$).[1] A series of $Na_2S_2O_3$ doses were tested on three PAA of different concentrations (Table S3). The results suggest that a quenching molar ratio of 0.22:1 ($Na_2S_2O_3$:PAA) would fully quench PAA, leaving a small $H_2O_2$ residual. Second, the potential effects of residual hydrogen peroxide during sample storage (i.e., the time needed to determine the chlorine dose for UFC tests on PAA pre-oxidized samples) on DBP formation was examined. A lake sample was divided into two portions. One was spiked with 2 mg/L $H_2O_2$. Both samples sat in the fridge for 48 h (i.e., the typical storage time of PAA pre-oxidized samples) before being subjected to UFC tests. The results from triplicate analysis are shown in Figure S2, which suggest that the residual $H_2O_2$ during the storage of PAA pre-oxidized samples did not affect DBP formation in subsequent UFC tests. Third, the chlorine demand of $H_2O_2$ was verified. The chlorine residual in a mixture of $H_2O_2$ (5 mg/L) and NaOCl (19.5 mg/L as $Cl_2$) after 20 minutes was 7.53 mg/L, corresponding to 1.15:1 (NaOCl:$H_2O_2$) molar ratio in their reaction. This is within 15% of the theoretical molar ratio of $H_2O_2$ to chlorine of 1:1 ($OCl^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2$).[2] This chlorine demand of $H_2O_2$ is considered in the chlorine dosing determination in the subsequent UFC tests (equation 3 in the main text). Fourth, the potential formation of DBPs from a $Na_2S_2O_3$-quenched PAA solution was examined. A mixture of PAA (6 mg/L) and $Na_2S_2O_3$ (2.8 mg/L) was prepared and then chlorinated, using excess chlorine (25 mg/L) for 24 h, and analyzed for DBPs. All DBPs were under the detection limit.

In addition, we verified that the addition of PAA and $Na_2S_2O_3$ did not contribute to fluorescence signals of the samples. The fluorescence of a mixture of PAA (6 mg/L) and thiosulfate (2.8 mg/L), diluted to 1 mg/L DOC, was measured. The resulting excitation emission matrix (EEM) (Figure S3) showed that it had negligible difference from that of Milli-Q water. The dilution factor used in EEM analysis for PAA pre-oxidized samples was calculated based on the DOC value prior to PAA addition in order to minimize sample holding time (needed for DOC measurement). This procedure had the drawback of resulting in slight variation in the DOC level of the samples subjected to EEM analysis. However, most samples were between 1.0–1.4 mg C/L after dilution, except for two as high as 2.8 mg C/L. These different DOC levels were accounted for later in the comparison of EEMs between PAA pre-oxidized samples and their controls.

**Table S1.** Sampling depths for Lake D samples.

| Sample ID | Depth 1 (m) | Depth 2 (m) | Depth 3 (m) | Depth 4 (m) | Total depth (m) |
|---|---|---|---|---|---|
| D1 | 0.25 | 0.8 | 1.5 | 2.5 | 3.05 |
| D2 | 0.25 | 1.0 | 2.0 | 3.0 | 3.65 |
| D3 | 0.25 | 1.8 | 3.6 | 5.6 | 6.10 |
| D4 | 0.25 | 2.5 | 5.0 | 7.5 | 8.08 |
| D5 | 0.25 | 1.3 | 2.6 | 4.1 | 4.57 |
| D6 | 0.25 | 0.8 | 1.5 | 2.5 | 3.05 |

**Table S2.** Chlorine doses used in UFC tests for samples from Lakes A, B, and C.

| Sample ID | Chlorine Dose (mg/L as $Cl_2$) | Free Chlorine Residual[a] (mg/L as $Cl_2$) | Total Chlorine Residual[a] (mg/L as $Cl_2$) |
|---|---|---|---|
| A1 | 7.7 | 1.1 | 1.8 |
| A2 | 9.5 | 1.1 | 2.0 |
| A3 | 9.5 | 0.9 | 1.7 |
| A4 | 9.2 | 1.2 | 2.0 |
| A5 | 8.6 | 1.2 | 1.9 |
| A7 | 6.7 | 1.0 | 1.6 |
| A9 | 9.0 | 0.8 | 1.8 |
| A11 | 9.9 | 1.1 | 2.7 |
| A13 | 6.8 | 0.7 | 1.4 |
| B1 | 11.9 | 0.9 | 2.4 |
| B2 | 10.1 | 0.9 | 1.8 |
| B3 | 6.1 | 0.8 | 1.5 |
| B4 | 10.2 | 0.9 | 1.8 |
| B5 | 6.6 | 1.0 | 1.6 |
| B7 | 10.9 | 1.2 | 1.8 |
| B11 | 86.4 | 1.0 | 6.6 |
| B13 | 9.9 | 0.9 | 1.9 |
| C1 | 11.2 | 1.2 | 2.6 |
| C2 | 11.5 | 1.1 | 2.6 |
| C3 | 11.4 | 1.1 | 2.4 |
| C4 | 10.2 | 1.1 | 2.4 |
| C5 | 9.8 | 1.0 | 2.2 |
| C7 | 11.2 | 0.8 | 1.7 |
| C9 | 13.1 | 1.3 | 2.8 |
| C11 | 13.8 | 0.7 | 1.8 |
| C13 | 12.6 | 1.2 | 2.2 |

[a]After 24 h.

**Table S3.** Sodium thiosulfate quenching doses tested on PAA and the resulting molar ratio.

| PAA (mg/L) | $Na_2S_2O_3$ (mg/L) | PAA residual (mg/L) |
|---|---|---|
| 1 | 0.35 | 0.5 |
| | 0.375 | 0.4 |
| | 0.4 | 0.3 |
| | 0.425 | 0.1 |
| | 0.45 | <MDL |
| 5.5 | 2.4 | 0.41 |
| | 2.5 | 0.2 |
| | 2.6 | <MDL |
| | 2.7 | <MDL |
| 6 | 2.1 | 0.794 |
| | 2.4 | 0.501 |
| | 2.7 | <MDL |
| | 3.1 | <MDL |

[a] <MDL: Below the method detection limit (MDL) of 0.1

**Table S4**. PAA pre-oxidation and chlorination disinfection conditions.

| Sample | Dosing Condition[a] | PAA Dose (mg/L) | Exposure Time (hr) | PAA Residual (mg/L) | PAA Exposure[b] (mg hr $L^{-1}$) | $H_2O_2$ Residual (mg/L) | Chlorine Dose (mg/L as $Cl_2$) | Free Chlorine Residual[c] (mg/L as $Cl_2$) |
|---|---|---|---|---|---|---|---|---|
| D1 | Control | | | | | | 9.5 | 0.7 |
| | Low | 2 | 2 | 1.8 | 3.8 | 1.8 | 12.4 | 1.2 |
| | High | 6 | 6 | 3.6 | 28.7 | 1.1 | 12.1 | 1.2 |
| D2 | Control | | | | | | 11.6 | 1.3 |
| | Low | 2 | 2 | 1.8 | 3.8 | 1.7 | 11.8 | 1.1 |
| | Med | 6 | 6 | 4.8 | 10.8 | 1.7 | 12.4 | 1.3 |
| | High | 6 | 6 | 3.1 | 27.3 | 1.8 | 12.7 | 1.3 |
| D3 | Control | | | | | | 8.2 | 1.0 |
| | Low | 2 | 2 | 1.5 | 3.5 | 1.5 | 8.3 | 1.0 |
| | Med | 6 | 6 | 3.9 | 9.9 | 1.6 | 9.2 | 1.3 |
| | High | 6 | 6 | 3.0 | 26.9 | 1.5 | 9.1 | 1.1 |
| D4 | Control | | | | | | 14.9 | 1.1 |
| | Low | 2 | 2 | 1.0 | 3.0 | 1.7 | 15.5 | 1.2 |
| | Med | 6 | 6 | 2.4 | 8.4 | 1.6 | 15.2 | 1.2 |
| | High | 6 | 6 | 1.9 | 23.8 | 1.7 | 14.9 | 0.7 |
| D5 | Control | | | | | | 8.9 | 1.0 |
| | Low | 2 | 2 | 1.6 | 3.6 | 0.3 | 8.5 | 0.7 |
| | Med | 6 | 6 | 4.3 | 10.3 | 0.2 | 9.1 | 1.1 |
| | High | 6 | 6 | 3.2 | 27.6 | 0.3 | 10.4 | 1.2 |
| D6 | Control | | | | | | 10.0 | 1.2 |
| | Low | 2 | 2 | 1.7 | 3.7 | 1.3 | 10.2 | 0.9 |
| | Med | 6 | 6 | 4.6 | 10.6 | 1.4 | 11.0 | 1.1 |
| | High | 6 | 6 | 3.4 | 28.2 | 1.6 | 11.1 | 0.8 |

[a]PAA dosing conditions: no PAA (control), initial dose of 2 mg/L with a contact time of 2 h (low), 6 mg/L with 2 h (medium), and 6 mg/L with 6 h (high);
[b]Calculation of PAA exposure is discussed in Section 2.5;
[c]After 24 h.

**Table S5.** DBP formation, yields, and calculated cytotoxicity by UFC tests for samples from lakes A, B, and C.

| Sample ID | DBP Formation (μg/L) | | | | DBP Yield (μg/mg C) | | | | Calculated Cytotoxicity (×$10^{-3}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | THMs | HANs | HKs | TCNM | THMs | HANs | HKs | TCNM | THMs | HANs | TCNM |
| A1 | 97.3 | 6.5 | 0.46 | 4.5 | 22.4 | 1.5 | 0.11 | 1.0 | 0.08 | 1.25 | 0.05 |
| A2 | 94.4 | 7.7 | 0.58 | 9.0 | 19.9 | 1.6 | 0.12 | 1.9 | 0.08 | 1.50 | 0.10 |
| A3 | 98.0 | 7.3 | 0.62 | 7.0 | 13.9 | 1.0 | 0.09 | 0.99 | 0.08 | 1.44 | 0.08 |
| A4 | 90.3 | 6.8 | 0.49 | 7.5 | 19.6 | 1.5 | 0.11 | 1.6 | 0.08 | 1.41 | 0.08 |
| A5 | 91.8 | 6.9 | 0.49 | 7.8 | 20.4 | 1.5 | 0.11 | 1.7 | 0.08 | 1.43 | 0.09 |
| A7 | 111 | 9.5 | 1.0 | 9.1 | 27.9 | 2.4 | 0.26 | 2.3 | 0.10 | 1.81 | 0.10 |
| A9 | 118 | 15.4 | 1.3 | 7.8 | 22.4 | 2.9 | 0.25 | 1.5 | 0.10 | 2.86 | 0.09 |
| A11 | 120 | 24.4 | 2.0 | 9.3 | 26.9 | 5.5 | 0.45 | 2.1 | 0.10 | 4.83 | 0.11 |
| A13 | 91.0 | 13.3 | 1.8 | 6.1 | 24.5 | 3.6 | 0.49 | 1.6 | 0.08 | 2.56 | 0.07 |
| B1 | 124 | 14.4 | 1.2 | 5.2 | 36.2 | 4.2 | 0.35 | 1.51 | 0.11 | 3.30 | 0.06 |
| B2 | 107 | 8.8 | 0.50 | 2.1 | 28.4 | 2.3 | 0.13 | 0.55 | 0.09 | 1.90 | 0.02 |
| B3 | 94.5 | 7.3 | 0.37 | 1.9 | 20.7 | 1.6 | 0.08 | 0.41 | 0.08 | 1.66 | 0.02 |
| B4 | 115 | 9.9 | 0.44 | 2.6 | 23.8 | 2.1 | 0.09 | 0.54 | 0.10 | 2.28 | 0.03 |
| B5 | 133 | 8.7 | 1.2 | 0.27 | 18.6 | 1.2 | 0.16 | 0.04 | 0.11 | 2.53 | 0.00 |
| B7 | 92.2 | 9.1 | 0.81 | 2.4 | 19.6 | 1.5 | 0.16 | 0.21 | 0.08 | 2.67 | 0.03 |
| B11 | 372 | 81.2 | 11.4 | 6.8 | 31.1 | 6.8 | 0.95 | 0.57 | 0.34 | 12.84 | 0.08 |
| B13 | 111 | 87.2 | 1.2 | 9.7 | 21.1 | 16.6 | 0.23 | 1.8 | 0.10 | 17.09 | 0.11 |
| C1 | 150 | 23.5 | 0.72 | 1.5 | 21.7 | 3.4 | 0.11 | 0.21 | 0.13 | 4.51 | 0.02 |
| C2 | 152 | 24.0 | 0.60 | 0.92 | 19.5 | 3.1 | 0.08 | 0.12 | 0.13 | 4.59 | 0.01 |
| C3 | 132 | 11.4 | 0.91 | 0.42 | 20.3 | 1.8 | 0.14 | 0.06 | 0.11 | 2.10 | 0.00 |
| C4 | 109 | 9.6 | 0.86 | 0.64 | 17.4 | 1.5 | 0.14 | 0.10 | 0.09 | 1.82 | 0.01 |
| C5 | 140 | 14.6 | 0.52 | 0.80 | 18.2 | 1.9 | 0.07 | 0.10 | 0.12 | 2.84 | 0.01 |
| C7 | 102 | 10.8 | 1.1 | 1.5 | 13.9 | 1.5 | 0.15 | 0.21 | 0.09 | 2.13 | 0.02 |
| C9 | 135 | 33.4 | 1.6 | 1.8 | 14.5 | 3.6 | 0.17 | 0.19 | 0.12 | 6.21 | 0.02 |
| C11 | 120 | 19.6 | 1.4 | 2.0 | 16.2 | 2.0 | 0.19 | 0.29 | 0.10 | 3.15 | 0.02 |
| C13 | 111 | 13.8 | 1.3 | 1.7 | 14.2 | 2.1 | 0.16 | 0.21 | 0.10 | 3.39 | 0.02 |

**Table S6.** Pearson's r and Spearman's ρ correlation coefficients between the yields of different DBPs for samples from Lakes A, B, and C. A strong correlation is considered to be r, ρ ≥ |0.5| with $p \leq 0.05$. Statistically significant correlations are in bold text.

| | | THMs | | HANs | | TCNM | |
|---|---|---|---|---|---|---|---|
| | | r | ρ | r | ρ | r | ρ |
| Lake A | HANs | **0.712** **p = 0.032** | **0.833** **p = 0.005** | | | | |
| | TCNM | **0.704** **p = 0.034** | 0.617 p = 0.077 | 0.501 p = 0.170 | 0.6 p = 0.088 | | |
| | HKs | **0.707** **p = 0.033** | **0.867** **p = 0.002** | **0.909** **p = 0.001** | **0.967** **p < 0.001** | 0.454 p = 0.219 | 0.655 p = 0.058 |
| Lake B | HANs | 0.04 p = 0.926 | **0.738** **p = 0.037** | | | | |
| | TCNM | 0.421 p = 0.300 | **0.762** **p = 0.028** | **0.801** **p = 0.017** | **0.976** **p < 0.001** | | |
| | HKs | 0.55 p = 0.158 | 0.429 p = 0.289 | 0.289 p = 0.487 | 0.548 p = 0.160 | 0.128 p = 0.763 | 0.524 p = 0.183 |
| Lake C | HANs | 0.225 p = 0.507 | 0.233 p = 0.546 | | | | |
| | TCNM | -0.45 p = 0.225 | -0.317 p = 0.406 | 0.199 p = 0.607 | 0.317 p = 0.406 | | |
| | HKs | -0.628 p = 0.070 | -0.633 p = 0.067 | -0.1685 p = 0.665 | 0.083 p = 0.831 | 0.578 p = 0.103 | 0.467 p = 0.205 |
| All Lakes | HANs | 0.271 p = 0.181 | **0.573** **p = 0.002** | | | | |
| | TCNM | **0.452** **p = 0.021** | **0.577** **p = 0.002** | 0.329 p = 0.101 | 0.307 p = 0.127 | | |
| | HKs | **0.580** **p = 0.002** | 0.386 p = 0.051 | **0.401** **p = 0.043** | **0.527** **p = 0.006** | 0.253 p = 0.213 | 0.332 p = 0.098 |

**Table S7.** DBP formation and calculated cytotoxicity by UFC tests after PAA pre-oxidation for samples from Lake D.

| Sample ID | Dosing Condition[a] | DBP Formation (μg/L) | | | | Calculated Cytotoxicity ($\times 10^{-3}$) |
|---|---|---|---|---|---|---|
| | | THMs | HANs | HKs | TCNM | |
| D1 | Control | 151.4 | 21.2 | 14.4 | 6.32 | 8.84 |
| | Low | 135.8 | 23.1 | 22.8 | 6.79 | 8.74 |
| | High | 120.9 | 24.7 | 100.4 | 8.61 | 9.16 |
| D2 | Control | 166.7 | 22.5 | 23.1 | 6.28 | 8.67 |
| | Low | 162.6 | 26.0 | 63.8 | 6.73 | 11.55 |
| | Med | 139.4 | 22.5 | 81.2 | 8.06 | 8.36 |
| | High | 105.1 | 21.8 | 63.3 | 7.35 | 7.86 |
| D3 | Control | 104.4 | 10.0 | 0.67 | 0.50 | 2.13 |
| | Low | 101.5 | 10.3 | 0.51 | 0.50 | 2.05 |
| | Med | 95.9 | 10.4 | 1.1 | 0.75 | 2.05 |
| | High | 88.5 | 11.3 | 1.1 | 0.76 | 2.18 |
| D4 | Control | 100.8 | 21.8 | 0.88 | 0.65 | 4.08 |
| | Low | 95.7 | 24.1 | 0.96 | 0.62 | 4.54 |
| | Med | 90.3 | 23.7 | 1.2 | 0.84 | 4.49 |
| | High | 94.0 | 23.3 | 0.9 | 0.81 | 4.40 |
| D5 | Control | 138.9 | 21.7 | 19.7 | 6.53 | 8.80 |
| | Low | 119.6 | 18.6 | 22.1 | 7.30 | 7.30 |
| | Med | 122.7 | 21.0 | 25.7 | 7.02 | 7.36 |
| | High | 115.2 | 23.8 | 29.5 | 7.55 | 8.63 |
| D6 | Control | 121.4 | 10.6 | 1.7 | 0.75 | 2.20 |
| | Low | 126.9 | 11.3 | 0.48 | 0.60 | 2.37 |
| | Med | 112.2 | 12.3 | 0.76 | 0.63 | 2.49 |
| | High | 116.9 | 13.1 | 0.63 | 0.71 | 2.65 |

[a]PAA dosing conditions: no PAA (control), initial dose of 2 mg/L with a contact time of 2 h (low), 6 mg/L with 2 h (medium), and 6 mg/L with 6 h (high)

**Table S8**. Excitation-emission matrix region volumes for PAA pre-oxidized samples. Regions I-V represent the fluorescence from tyrosine-like (I), tryptophan-like (II), fulvic-like (III), soluble microbial product-like (IV), and humic-like (V) moieties. The volumes are normalized to 1 mg C/L DOC (Text S2).

| Sample ID | Dosing Condition | I | II | III | IV | V |
|---|---|---|---|---|---|---|
| D3 | Control | 42574 | 81548 | 291830 | 62648 | 313830 |
| | Low | 29584 | 59076 | 228868 | 54427 | 295795 |
| | Med | 27718 | 52654 | 238395 | 49088 | 289082 |
| | High | 33537 | 54617 | 221522 | 49437 | 258282 |
| D4 | Control | 25811 | 60386 | 288690 | 59287 | 379830 |
| | Low | 19937 | 44066 | 240738 | 44969 | 318716 |
| | Med | 34404 | 79725 | 372159 | 72681 | 474564 |
| | High | 29083 | 57373 | 286341 | 52622 | 359873 |
| D5 | Control | 25696 | 44500 | 159320 | 49795 | 238670 |
| | Low | 14083 | 22712 | 80357 | 22861 | 114046 |
| | Med | 26518 | 42735 | 150007 | 41347 | 207324 |
| | High | 15946 | 23384 | 77551 | 20391 | 91944 |
| D6 | Control | 38249 | 69134 | 235050 | 67029 | 319120 |
| | Low | 34129 | 57861 | 219226 | 58624 | 301780 |
| | Med | 63032 | 135442 | 280830 | 108884 | 349113 |
| | High | 38662 | 65269 | 211971 | 57121 | 237010 |

**Figure S1.** Lake D sampling sites.

**Figure S2.** The effects of $H_2O_2$ residual during sample storage time between PAA quenching and UFC chlorination on the potential DBP formation of dissolved organic matter

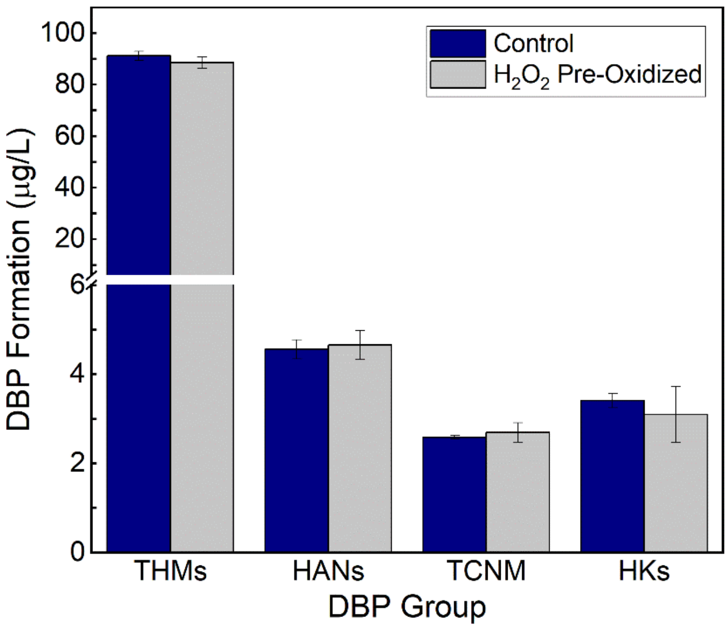


**Figure S3.** The fluorescence EEM of a mixture of PAA (6 mg/L) and thiosulfate (2.8 mg/L), diluted to 1 mg/L DOC. Intensity scale is similar with EEMs in main text Figure 6 for comparison.

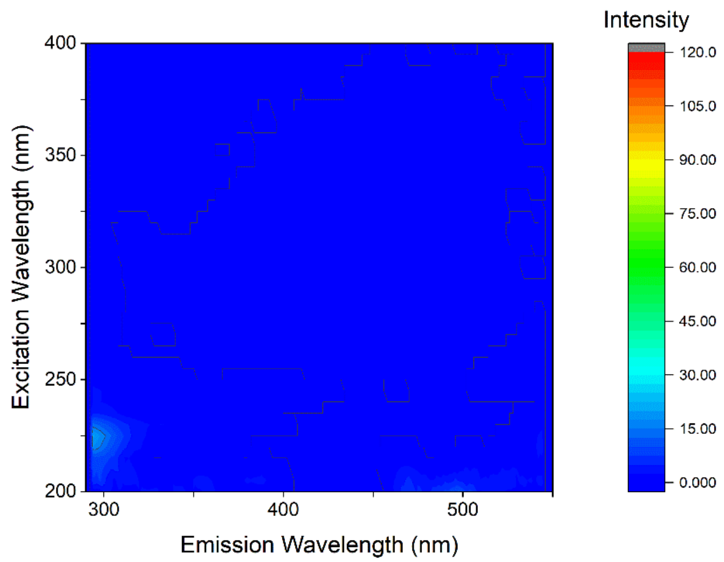


**Figure S4.** Variation in DBP formation in UFC tests and the corresponding calculated cytotoxicity for (a, b) Lake B and (c, d) Lake C Samples. HKs were not included in the calculated cytotoxicity due to unavailability of $LC_{50}$. Corresponding data are shown in Table S5.

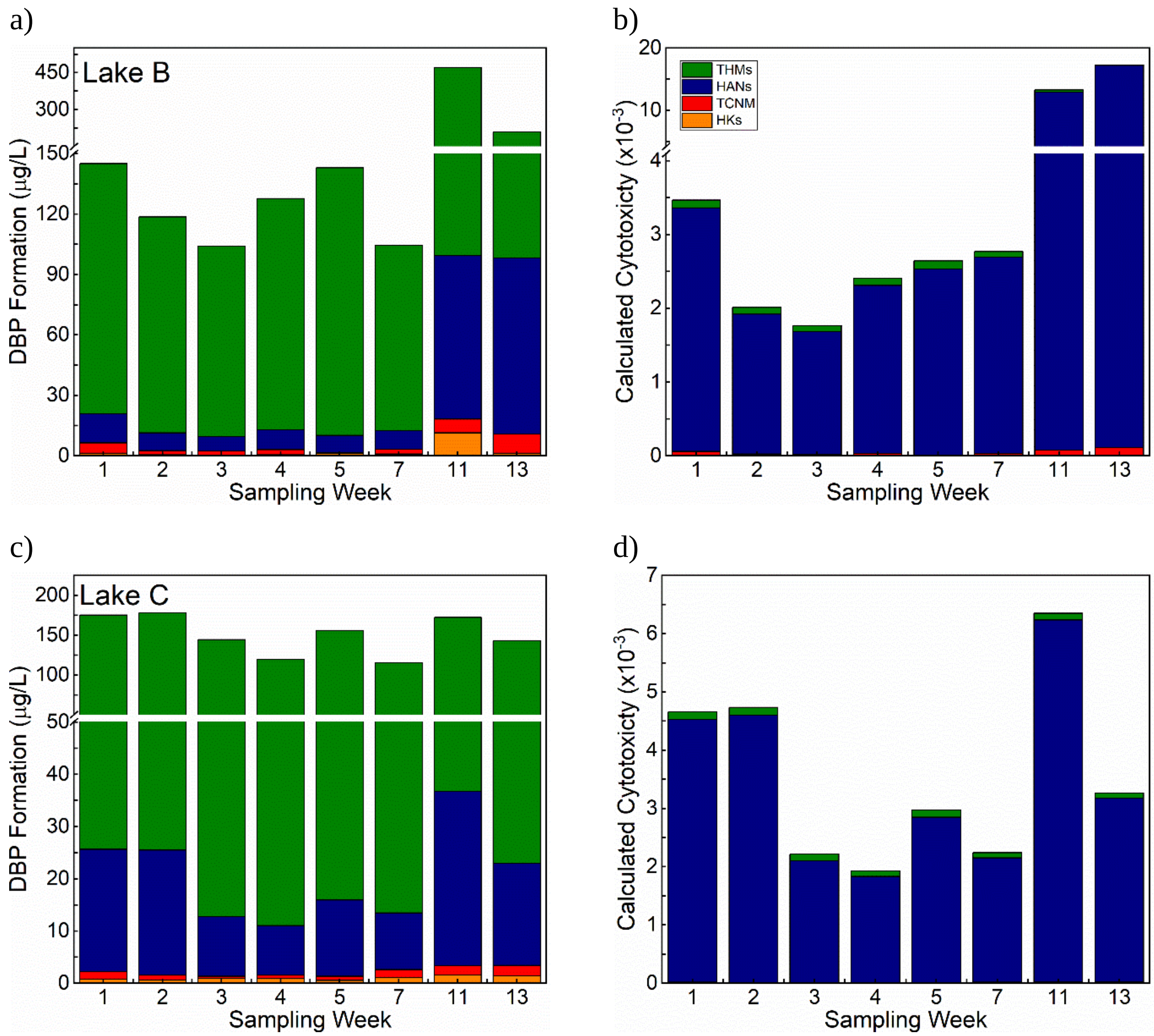


**Figure S5.** Correlation between HAN formation in UFC tests and the calculated cytotoxicity for all samples from Lakes A, B, and C.

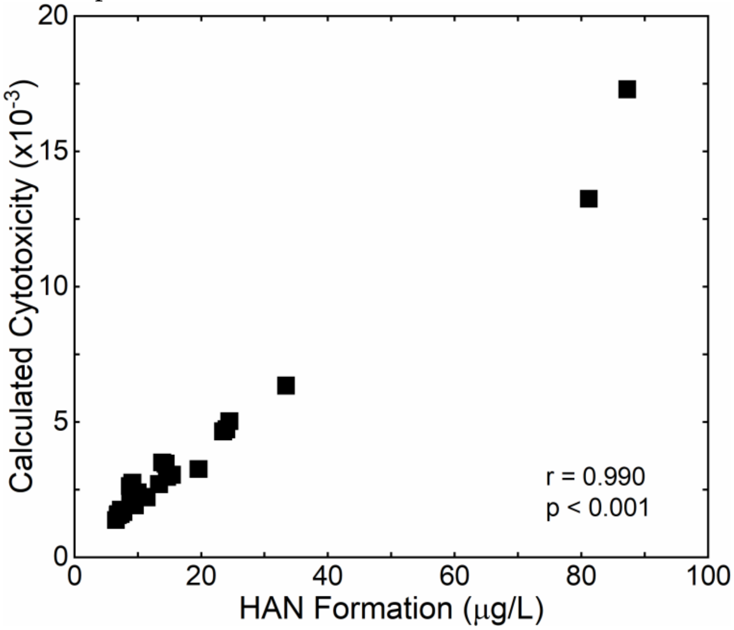


**Figure S6.** Variability in the yields of (a) THMs, (b) HANs, (c) TCNM, and (d) HKs, for UFC tests on Lake A, B and C samples.

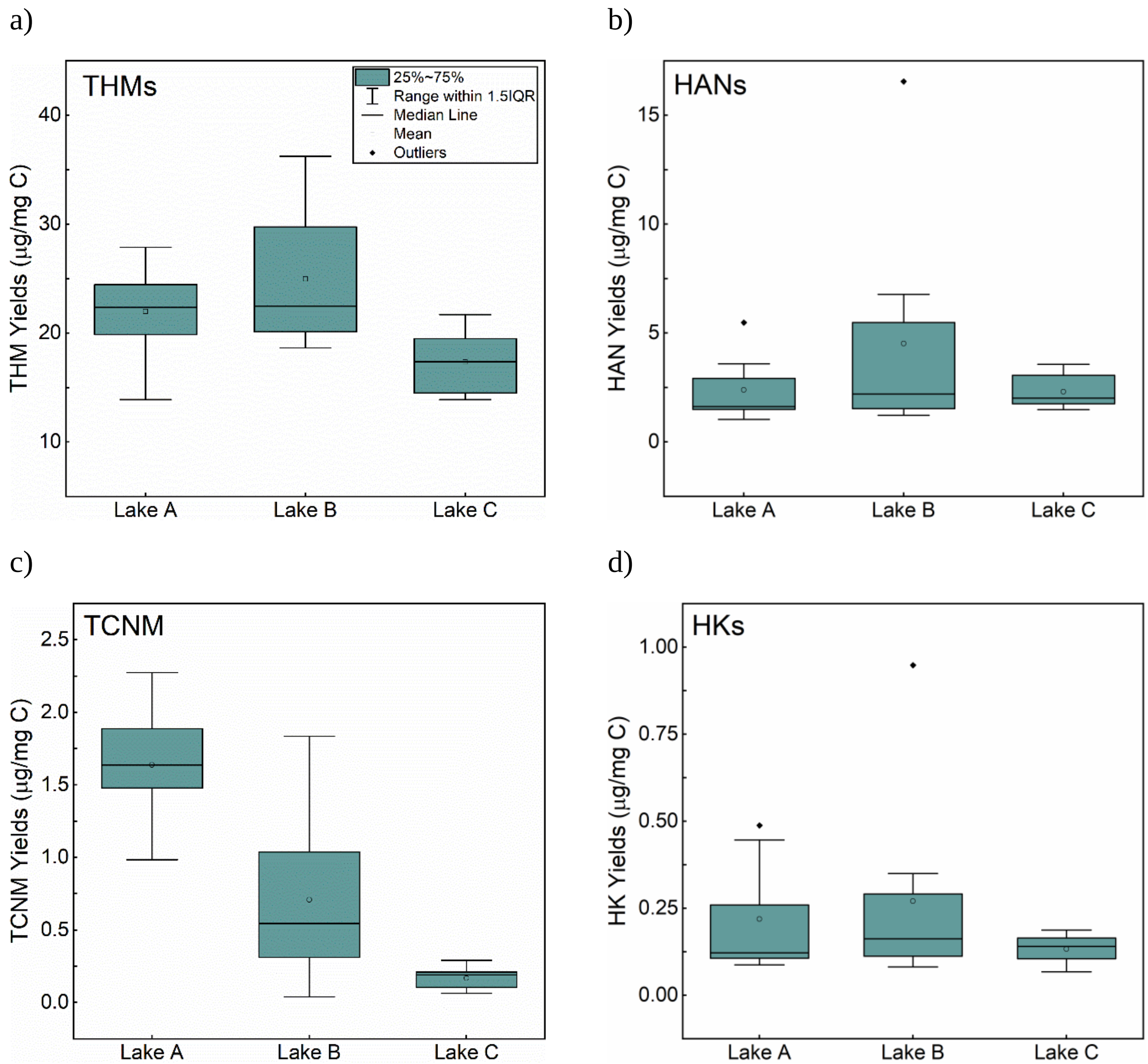


**Figure S7**. Variability in the concentration of organic nitrogen species (a) nitrate ($NO_3$-N), (b) nitrite ($NO_2$-N), and (c) ammonia ($NH_3$-N) for the Lake A, B, and C samples.

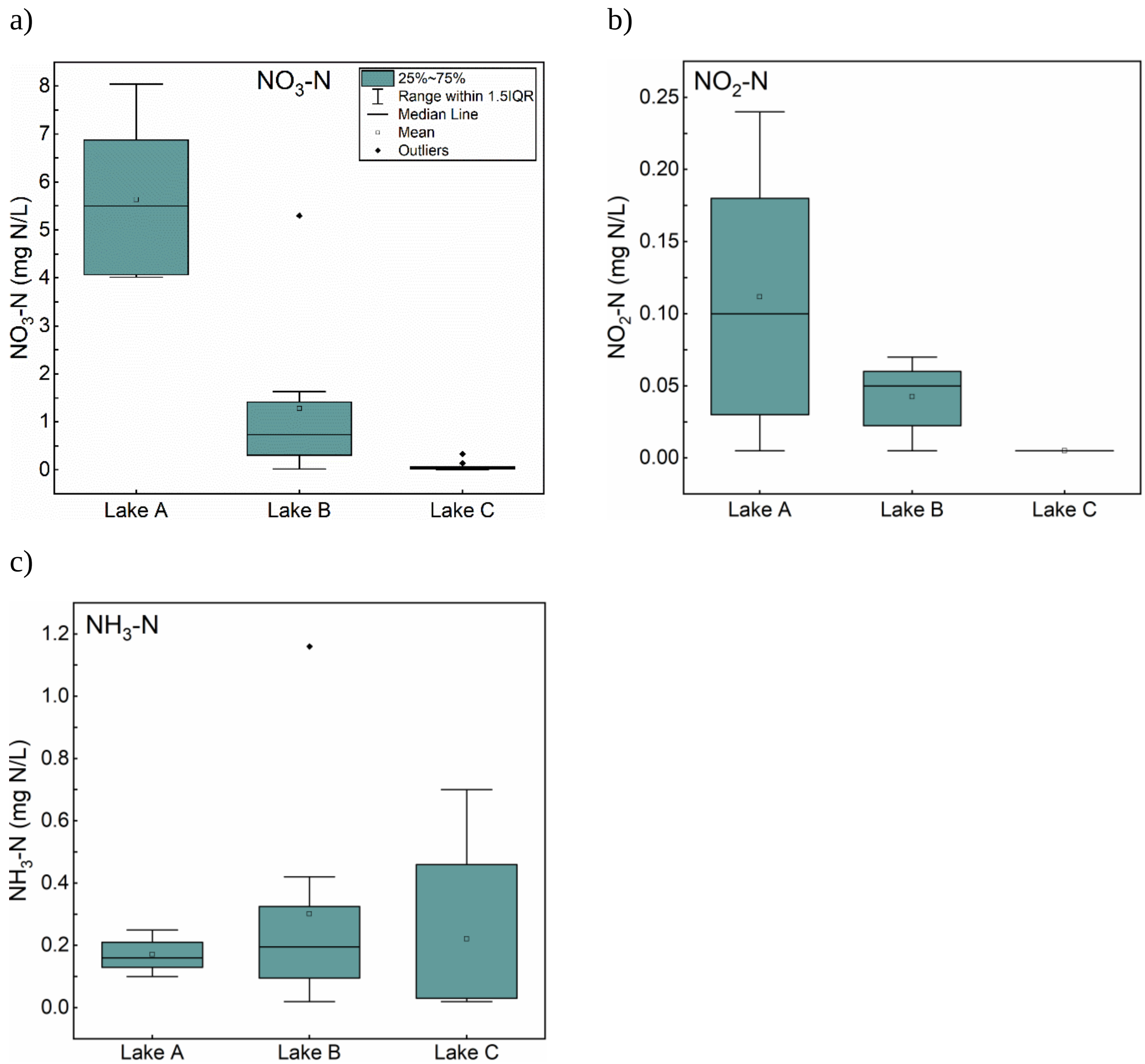


**Figure S8.** Relationship between total chlorophyll concentrations and the non-normalized formation of (a) THMs, (b) HANs, (c) TCNM, and (d) HKs in UFC tests. Correlation statistics are reported in main text Table 2.

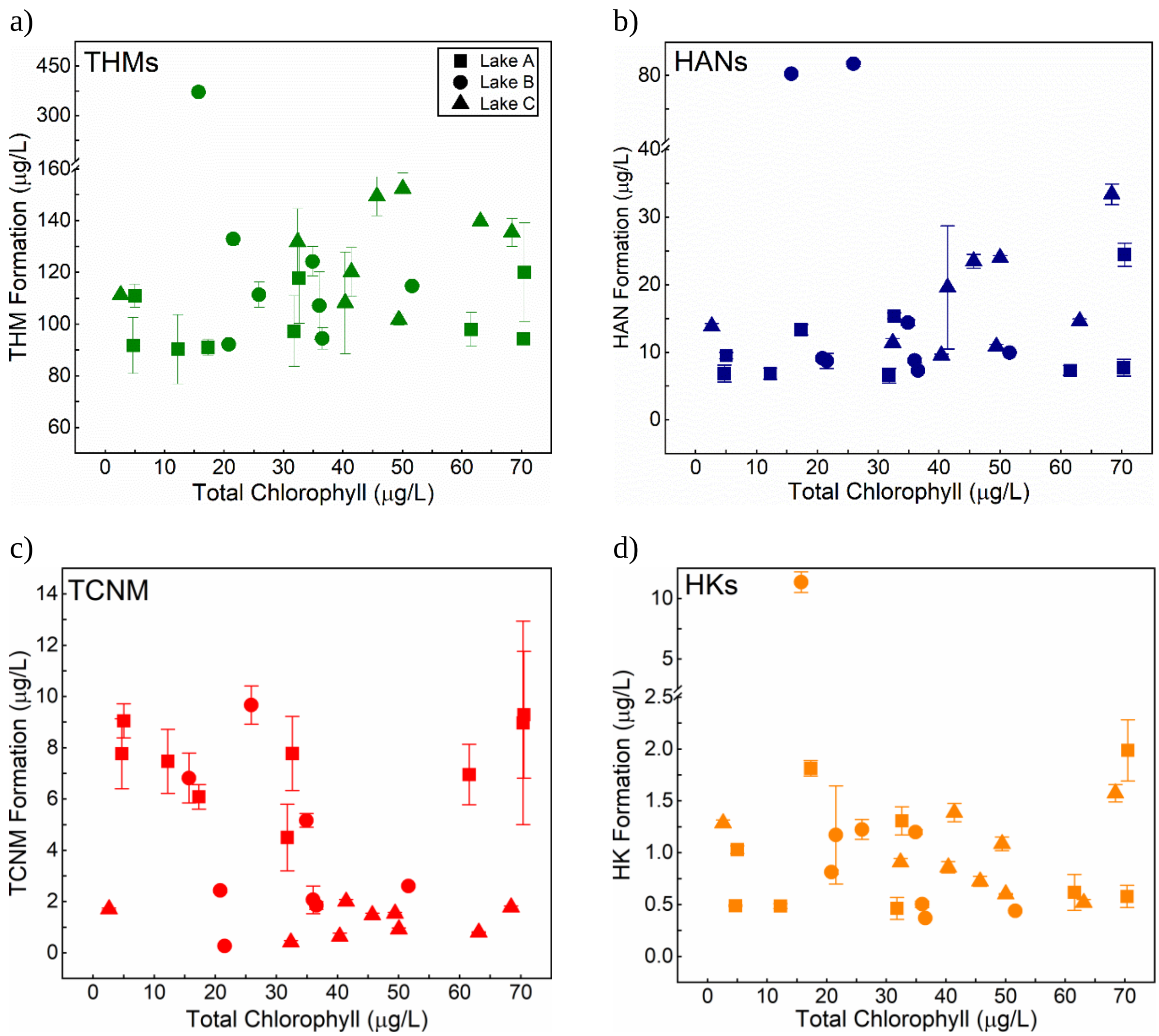


**Figure S9.** Relationship between $NO_2$-N concentrations and the yields of (a) THMs, (b) HANs, (c) TCNM, and (d) HKs in UFC tests. Samples with $NO_2$-N concentrations below the detection limit (all Lake C samples) are not plotted, however they were assigned a value of half the detection limit for statistical analyses. Correlation statistics are reported in main text Table 2.

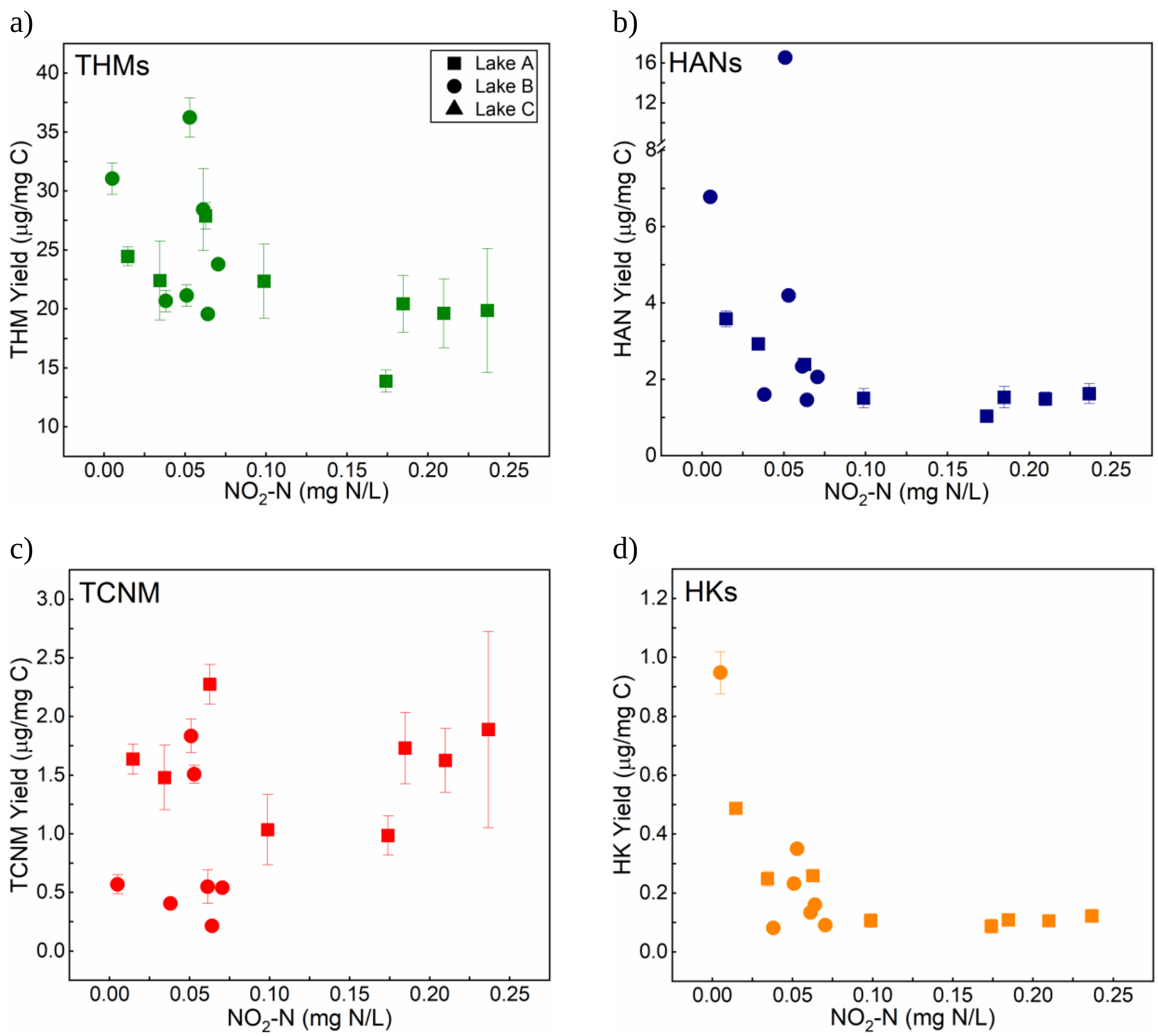


**Figure S10.** Relationship between $NO_3$-N concentrations and the yields of (a) THMs, (b) HANs, (c) TCNM, and (d) HKs in UFC tests. Correlation statistics are reported in main text Table 2.

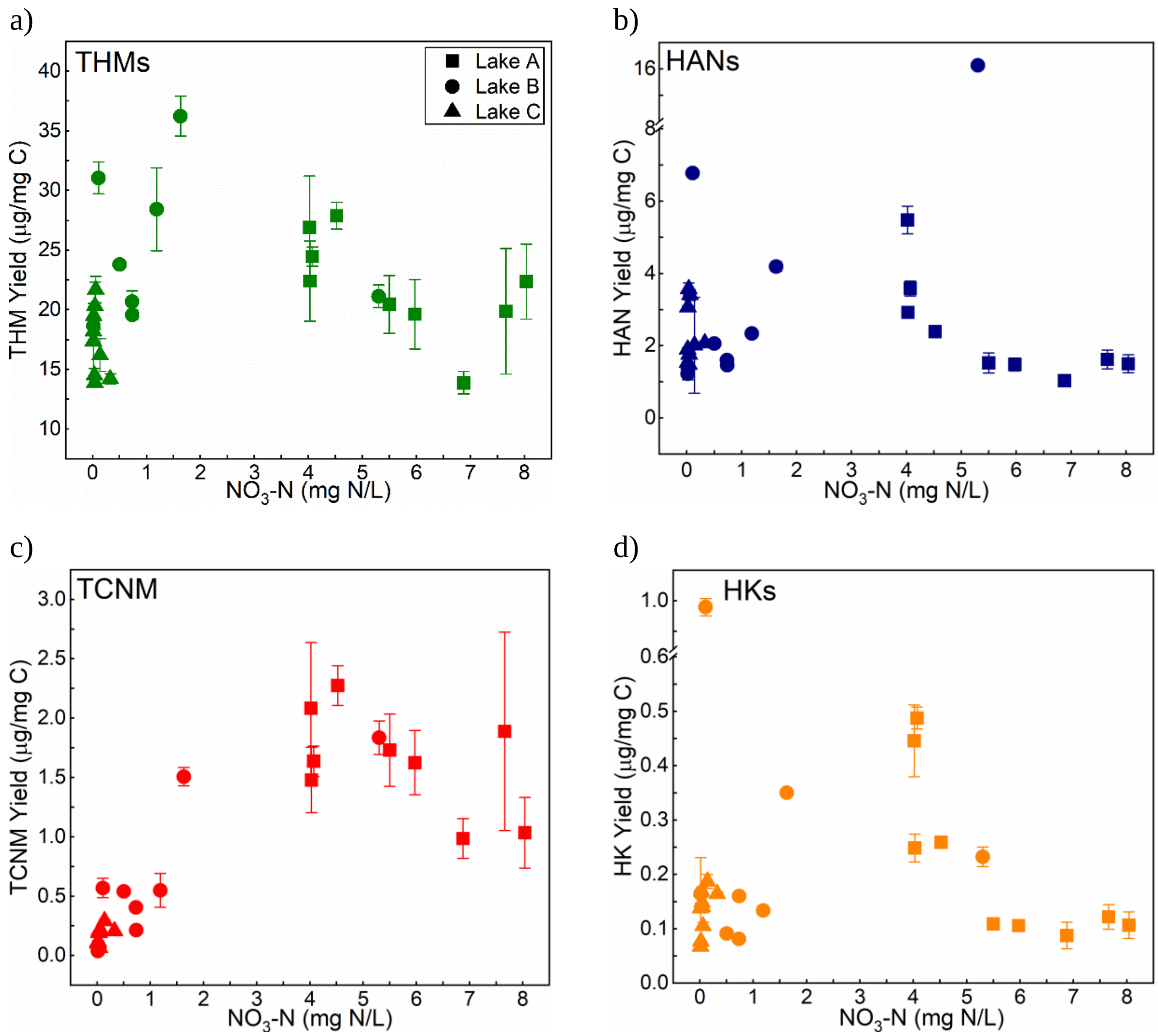


**Figure S11.** Relationship between SUVA values and the yields of (a) THMs, (b) HANs, (c) TCNM, and (d) HKs in UFC tests. Correlation statistics are reported in main text Table 2.

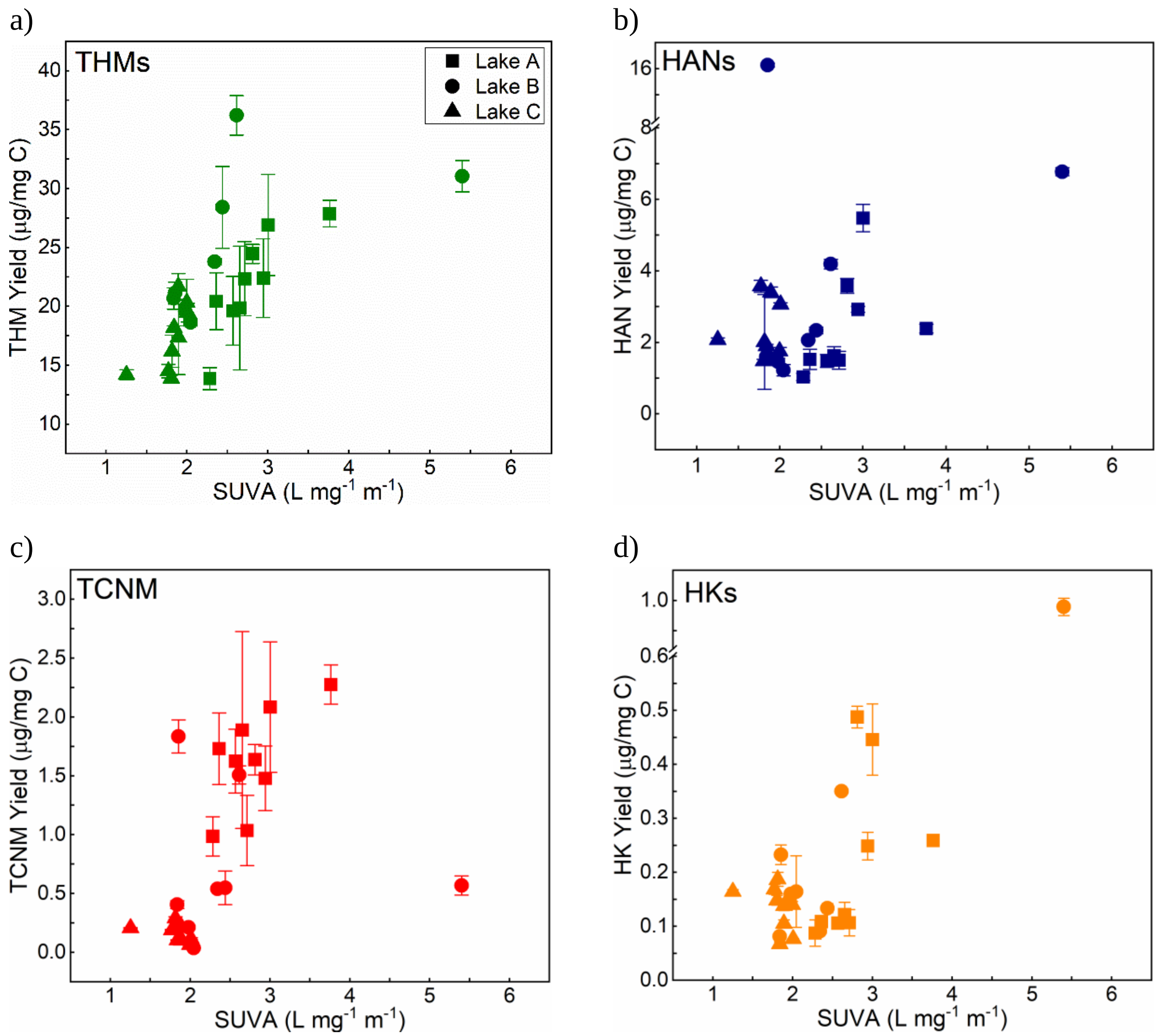


**Figure S12**. Relationship between DON concentrations and the yields of (a) THMs, (b) HANs, (c) TCNM, and (d) HKs in UFC tests. DON was calculated as the difference between total nitrogen and the sum of the inorganic nitrogen species. Samples with DON concentrations below detection limit are not included. Correlation statistics are reported in main text Table 2.

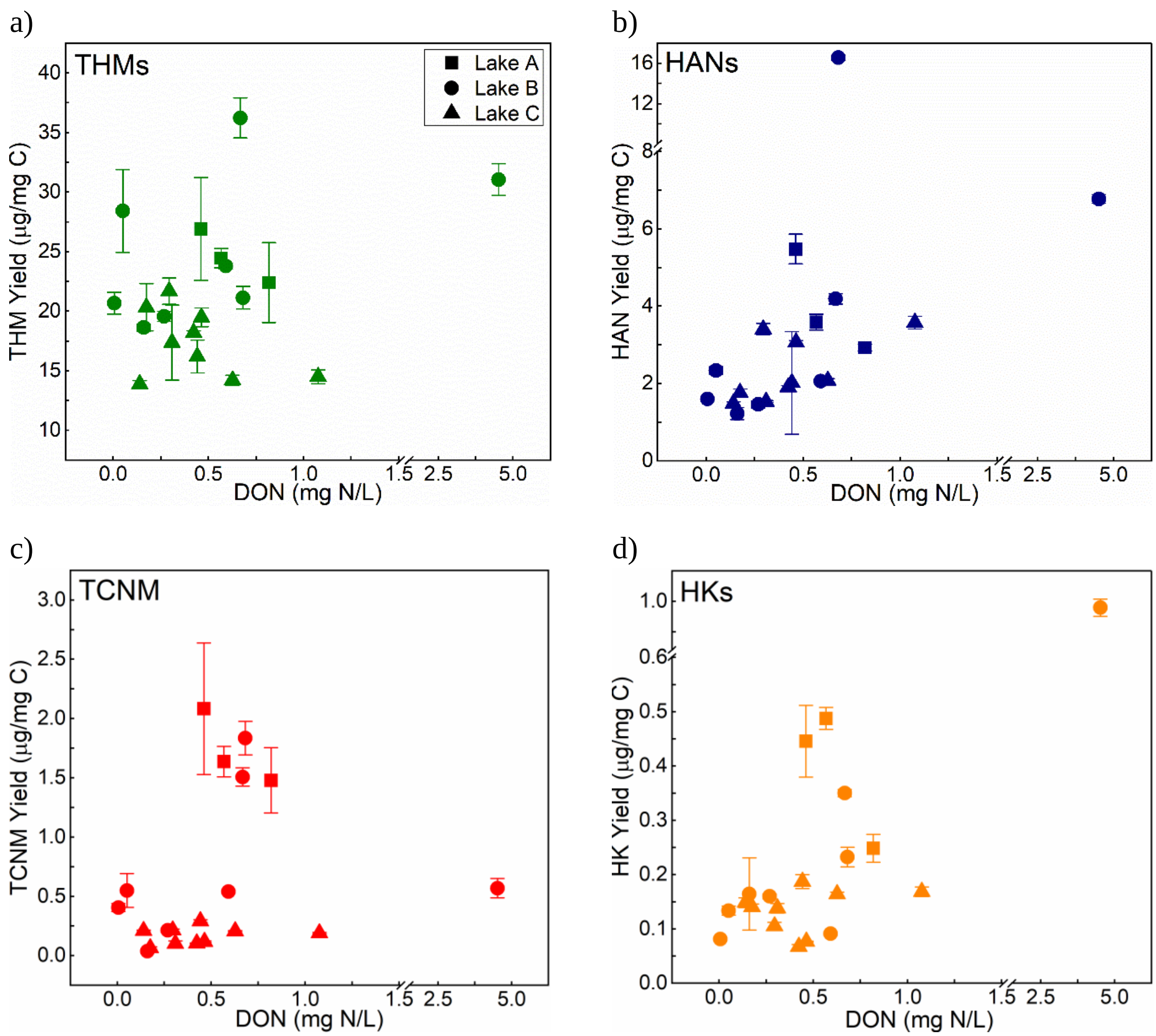


**Figure S13**. Relationship between DOC concentrations and the non-normalized formation potential of (a) THMs, (b) HANs, (c) TCNM, and (d) HKs in UFC tests. Correlation statistics are reported in main text Table 2.

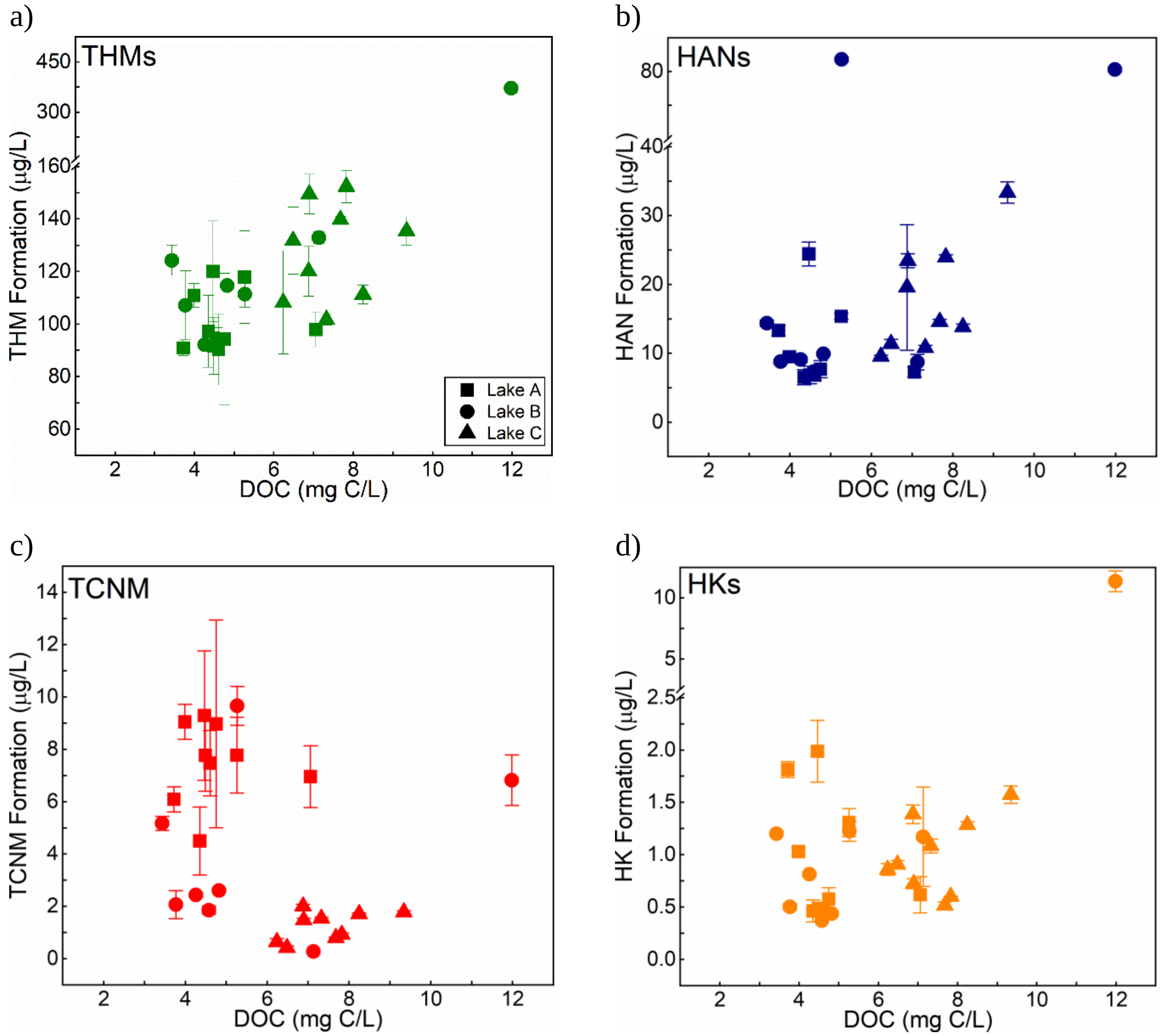


**Figure S14**. Relationship between $NH_3$-N concentrations and (a) THM, (b) HAN, (c) TCNM, and (d) HK yields using uniform formation conditions. Correlation statistics are reported in main text Table 2.

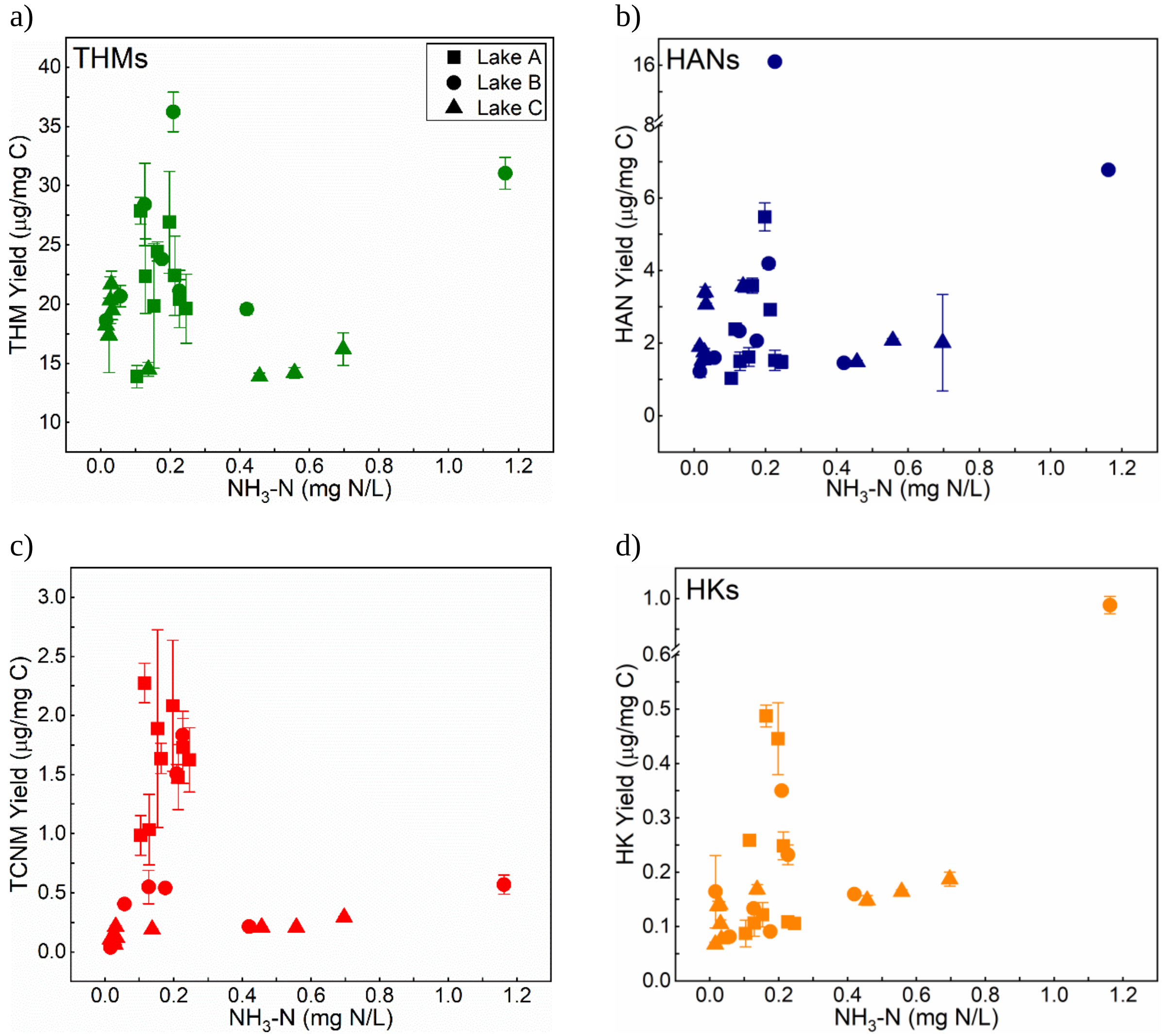


**Figure S15**. Change in the yields of (a) THMs, (b) HANs, (c) TCNM, and (d) HKs in six samples from Lake D by PAA pre-oxidation. Three PAA dosing conditions were evaluated: initial dose 2 mg/L with contact time 2 h (low), 2 mg/L with 6 h (med), 6 mg/L with 6 h (high). PAA decay was considered in the calculation of exposure for each sample (section 2.5). ΔDBP Yield. = (DBP concentration after UFC tests of the PAA pre-oxidized sample / Adjusted DOC of the PAA pre-oxidized sample) – (DBP concentration after UFC test of the corresponding control / DOC of the corresponding control). Adjusted DOC was calculated by subtracting the DOC contributed by PAA and acetic acid from the measured DOC for each PAA pre-oxidized sample.

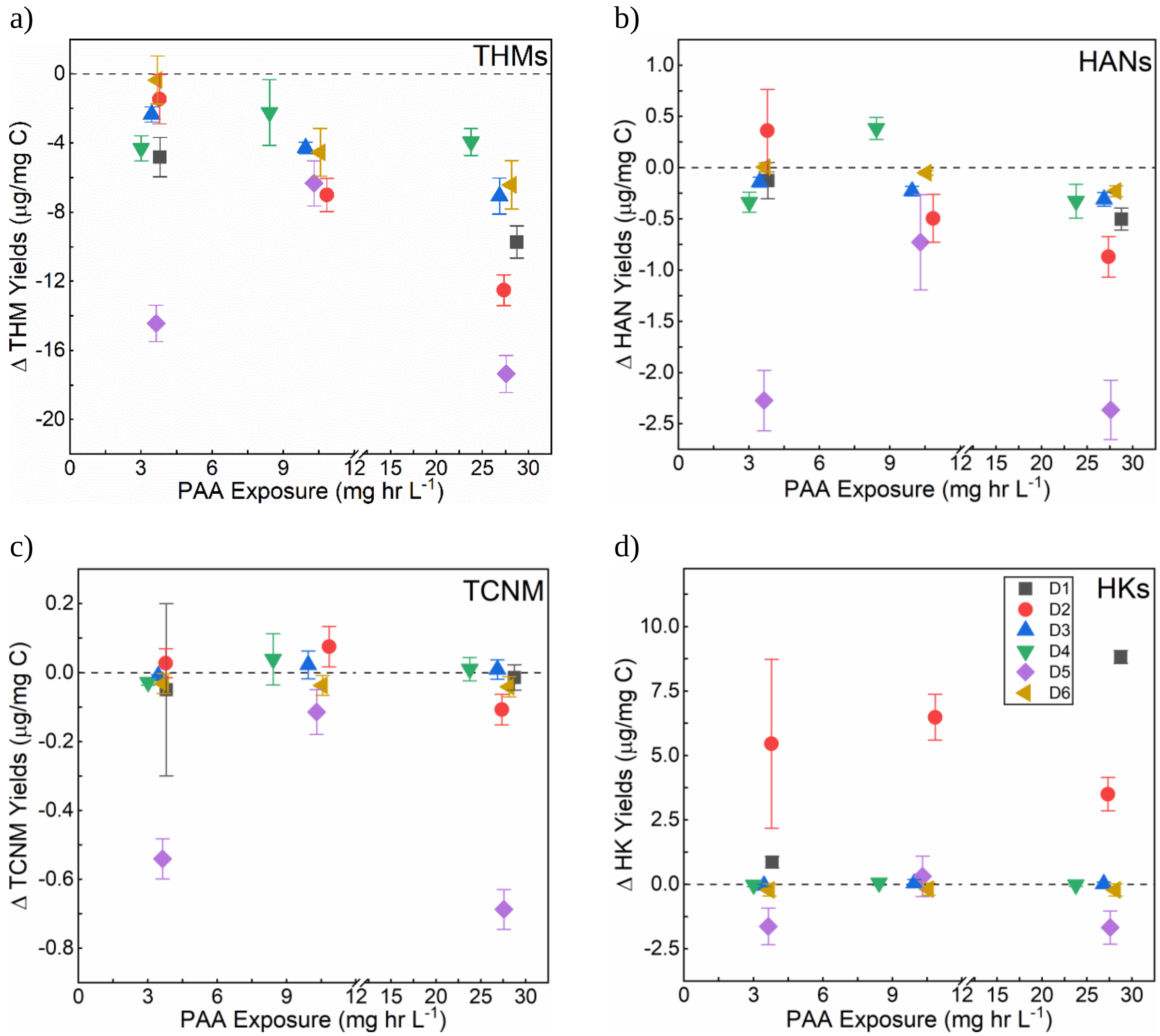
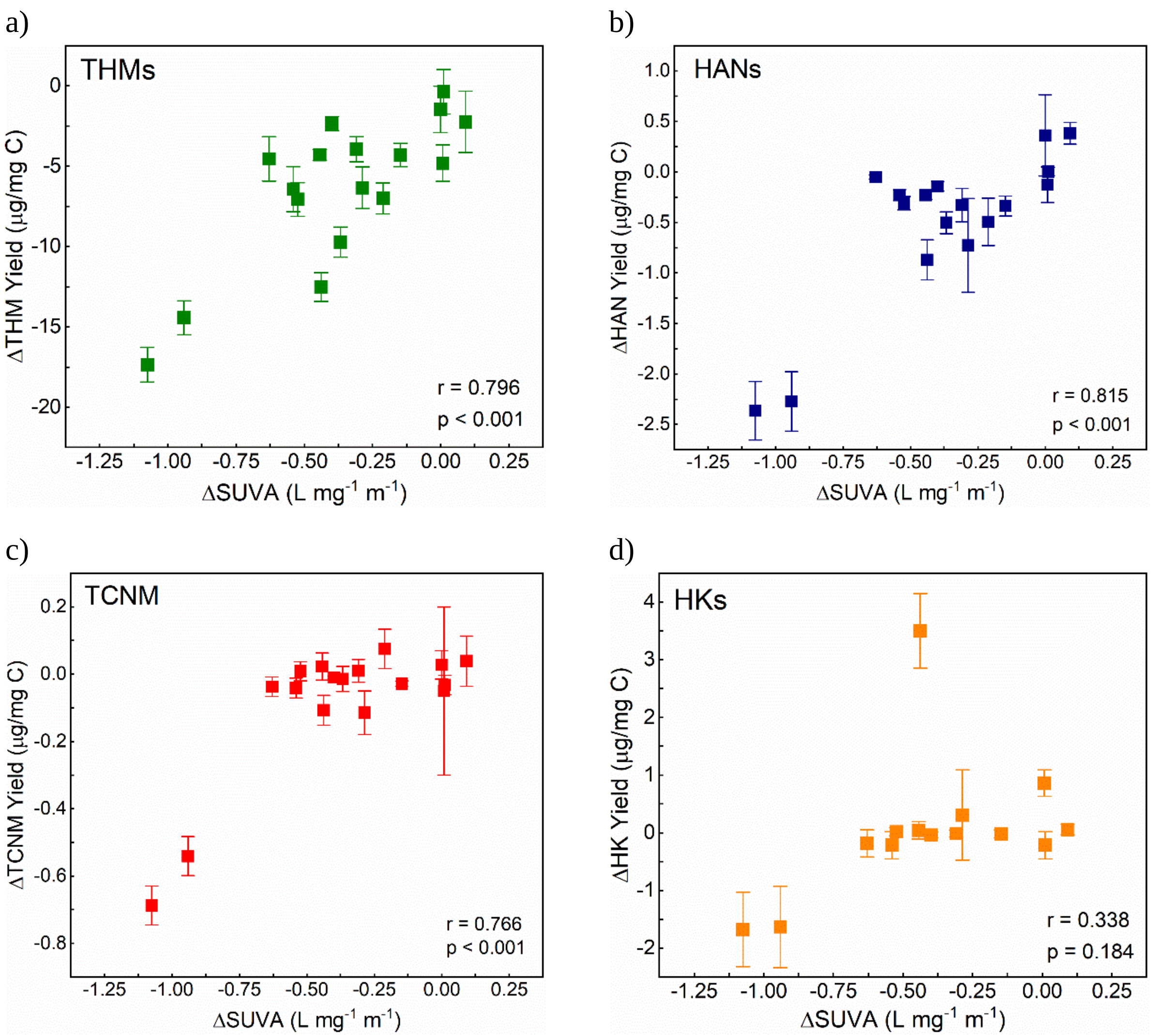


**Figure S16**. Relationship between the change in SUVA and the change in the yields of (a) THM, (b) HAN, (c) TCNM, and (d) HK in UFC tests by PAA pre-oxidation. For the PAA pre-oxidized samples, the DBP yields and SUVA were both calculated using the adjusted DOC (i.e., the DOC contributed by PAA and acetic acid was subtracted).



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