Supporting information for:

## Differences in photochemistry between seawater and freshwater for two natural organic matter samples

Laura T. Stirchak,<sup>1</sup> Kyle J. Moor,<sup>2</sup>, Kristopher McNeill,<sup>2</sup>, and D. James Donaldson\*<sup>1,3</sup>

- 1. Department of Chemistry, University of Toronto
- 2. Institute for Biogeochemistry and Pollutant Dynamics, ETH Zurich
- 3. Department of Physical and Environmental Sciences, University of Toronto

\*author for correspondence. Email: jdonalds@chem.utoronto.ca

Excitation spectra of NOM with different concentrations of NaCl and IO
Emission spectra of NOM with different concentrations of NaCl and IO
Absorption spectra of NOM with Mg <sup>2+</sup> and IO
Fluorescence Intensity (I <sub>fl</sub> ) versus pH
Emission spectra of SRNOM with CO <sub>2</sub> <sup>3-</sup> and SO <sub>4</sub> <sup>2-</sup>
Emission spectra of NOM with Fe <sup>3+</sup>
Excitation and emission spectra of NOM with Mg <sup>2+</sup>
Water corrected anisotropy spectra for AHA with NaCl and IO
Changes to [TMP] with time to determine k <sub>eff</sub>
k <sub>f</sub> versus [NaCl] or [IO]
$k_{\rm f}$ versus [Mg <sup>2+</sup> ] for AHA
Report of k <sub>f</sub> , k <sub>d</sub> , and k <sub>O2</sub> for all 3 NOM samples with solutes

## Experimental details for AHA

Aldrich Humic Acid (AHA), derived from coal,<sup>1</sup> was purchased as the sodium salt from Sigma Aldrich and was used without purification. Although this commercial product has been reported to contain many impurities,<sup>1–3</sup> we used it without purification since our purpose was to use AHA as a "benchmark" NOM proxy. Stock AHA solutions for the optical experiments were made with 11mg/L AHA using Milli-Q deionized water. Solutions with NaCl, IO, NaHCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub> and FeCl<sub>3</sub> were all prepared in the same way as the solutions with NRNOM and SRNOM. All absorption, fluorescence and anisotropy experiments were run using the same set-up as those with NRNOM and SRNOM.

The AHA solutions for the triplet NOM production were also made with 1mg/L AHA and were prepared in the same way as the other two NOM sample solutions. The TMP experimental set-up was also the same.

The experimental set-up for the time-resolved <sup>1</sup>O<sub>2</sub> phosphorescence measurements was the same as with NRNOM and SRNOM. Stock AHA solutions were made with 33mg/L AHA and all subsequent solutions were prepped following the details in the main manuscript.



Figure S1: Excitation plots of SRNOM, NRNOM and AHA with NaCl (a-c) and Instant Ocean (df). NaCl solutions were run in a concentration range of 0.05M to 2.0M. IO solutions were made with the same weight concentration as the NaCl solutions, resulting in a concentration range of 2.9g/L to 116g/L. All excitation spectra were collected using an emission wavelength of 480nm. NRNOM solutions were run in a smaller concentration range as the SRNOM and AHA studies showed that changes to the fluorescence intensity were not dependent on NaCl or IO concentration.



Figure S2: Emission plots of SRNOM, NRNOM and AHA with NaCl (a-c) and Instant Ocean (d-f). NaCl solutions were run in a concentration range of 0.05M to 2.0M. IO solutions were made with the same weight concentration as the NaCl solutions, resulting in a concentration range of 2.9g/L to 116g/L. All emission spectra were collected using an excitation wavelength of 405nm. NRNOM solutions were run in a smaller concentration range as the SRNOM and AHA studies showed that changes to the fluorescence intensity were not dependent on NaCl or IO concentration.



Figure S3: Absorbance plots for SRNOM (a), NRNOM (b), and AHA (c) with different concentrations of MgCl<sub>2</sub> and IO. The inserted photos are a zoomed in section of the absorbance spectra between 350 and 500nm.



*Figure S4: The relationship between pH and maximum fluorescence intensity of NRNOM, SRNOM and AHA. The pH of the NOM solutions was changed by adding 0.2M NaOH dropwise to the solutions.* 



Figure S5: Emission spectra of SRNOM and with a) NaHCO<sub>3</sub> and b) NaSO<sub>4</sub>. All emission spectra were collected using an excitation wavelength of 405nm. The concentrations of the two solutes matched their concentrations in the IO solutions.



Figure S6: Emission spectra of SRNOM, NRNOM and AHA with  $Fe^{3+}$ . SRNOM and AHA solutions with  $FeCl_3$  were made at 0.062, 0.31 and 0.62 $\mu$ M, which correspond to the 5.8, 29 and 58g/L IO solutions. Solutions at 0.5 and 1 $\mu$ M FeCl<sub>3</sub> were run with NRNOM as the fluorescence intensity did not show dependence on the concentration of  $Fe^{3+}$ .



Figure S7: Excitation (a-c) and emission (d-f) spectra of SRNOM, NRNOM and AHA with  $Mg^{2+}$ . All magnesium solutions were run between 7.8mM and 78.2mM, which correspond to the 5.8, 29 and 58g/L IO solutions.



Figure S8: Difference spectra of the fluorescence anisotropy of AHA measured in the presence of 100 mM NaCl minus that measured without added NaCl (a-c) and those measured in the presence and absence of added IO (d-f) minus those without added IO.



Figure S9: Plots depicting the loss of TMP, as the  $ln(C \setminus C_0)$ , over time for SRNOM (a), NRNOM (b), and AHA (c). The slopes of these plots were used to determine  $k_{eff}$  as a function of magnesium concentration.



Figure S10: The plots of  $k_f$  for SRNOM (a), NRNOM (b,) and AHA (c) versus the concentrations of NaCl (green circles) and IO (blue triangles).



Figure S11: Plot of  $k_f$  versus the concentration of magnesium for AHA.

	$k_{\rm f}$ (us <sup>-1</sup> )	$k_{\rm d}$ (us <sup>-1</sup> )	$k_{02}$ (M <sup>-1</sup> s <sup>-1</sup> )
SRNOM	1.455	0.273	$1.13 \times 10^9$
0.0228M Mg <sup>2+</sup>	1.285	0.281	1.01 x10 <sup>9</sup>
0.1143M Mg <sup>2+</sup>	1.283	0.273	1.01 x10 <sup>9</sup>
0.228M Mg <sup>2+</sup>	1.220	0.280	9.64 x10 <sup>8</sup>
0.68M NaCl	1.095	0.270	8.51 x10 <sup>8</sup>
1.9M NaCl	0.799	0.3012	6.21 x10 <sup>8</sup>
0.3M IO	1.084	0.268	8.47 x10 <sup>8</sup>
1.5M IO	0.913	0.260	7.14 x10 <sup>8</sup>
3.0M IO	0.634	0.276	$4.95 \text{ x} 10^8$
NRNOM	1.631	0.273	1.26 x10 <sup>9</sup>
0.0228M Mg <sup>2+</sup>	1.627	0.263	1.25 x10 <sup>9</sup>
0.1143M Mg <sup>2+</sup>	1.488	0.267	1.14 x10 <sup>9</sup>
0.228M Mg <sup>2+</sup>	1.230	0.256	9.42 x10 <sup>8</sup>
0.68M NaCl	1.180	0.245	9.13 x10 <sup>8</sup>
0.3M IO	1.678	0.244	1.33 x10 <sup>9</sup>
1.5M IO	1.081	0.246	8.6 x10 <sup>8</sup>
3.0M IO	0.821	0.249	6.53 x10 <sup>8</sup>
AHA	1.724	0.278	1.36 x10 <sup>9</sup>
$0.0\overline{228M}$ Mg <sup>2+</sup>	1.377	0.299	$1.06 \text{ x} 10^9$
0.1143M Mg <sup>2+</sup>	1.277	0.293	$9.83 \times 10^8$
$0.228M Mg^{2+}$	1.446	0.264	$1.11 \text{ x} 10^9$

0.68M NaCl	1.289	0.261	9.99 x10 <sup>8</sup>
0.3M IO	1.300	0.287	$1.0 \text{ x} 10^9$
1.5M IO	1.058	0.272	8.15 x10 <sup>8</sup>
3.0M IO	0.926	0.238	7.13 x10 <sup>8</sup>

Table S1:  $k_{f}$ ,  $k_d$  and calculated  $k_{O2}$  rate constants for all three NOM samples with  $Mg^{2+}$ , NaCl and IO.

## References

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- 2 J. I. Kim, G. Buckau, G. H. Li, H. Duschner and N. Psarros, Characterization of humic and fulvic acids from Gorleben groundwater, *Fresenius*. J. Anal. Chem., 1990, **338**, 245– 252.
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