Temperature Dependence of the Reaction Between the Hydroxyl Radical and Organic Matter

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Supplemental Information

In this Supplemental Information, we have included the following: estimation of average molecular weight from SEC, SEC for EfOM samples, NOM isolate characterization data, estimated average molecular weights, a discussion of the temperature dependence of competing reactions, and all temperature dependent $k_{OM-HO\cdot}$ measured in this study.

Estimation of Average Molecular Weight (AMW). AMW was estimated by integrating the SEC from 100 to 18,000 Da. The lower limit of 100 Da was chosen because no polyethylene glycols below 100 Da were used in SEC calibration, and an interference from nitrite in the EfOM samples. Though this is an approximate estimation of AMW (Equation 1), previous work by our group and others has utilized the same calibration method; thus, allowing for comparison.

$$AMW = \frac{\sum MW \times TOC}{\sum TOC}$$

Equation 1

Temperature Dependent Rate Constants for the Reaction of HO[•] with HCO₃⁻, CO₃²⁻, NH₃, and SCN⁻. Temperature dependent rate constants were used for all hydroxyl radical scavengers at each temperatures are shown below [1-3]. The Arrhenius form of the competing reactions are:

Using the measured temperature during experiments, and with R as 8.314 J mol⁻¹ K⁻¹, we were able to calculate the temperature dependent scavenging rates of all non-OM species. These temperature dependent scavenging rates were then subtracted from the observed pseudo first order rate constant k[X] (where [X] = [HCO₃⁻] + [CO₃²⁻] + [NH₃] + [OM]) to yield the pseudo first order rate constant k[OM], from which the molar carbon concentration of OM was factored out to give the bimolecular reaction rate constant, *k*_{OM-HO[•]}.

43 **Table S. 1. Characterization Data of DOM Isolates Used^a.**

Sample	ESHA	SRFA	PLFA
Cat. No.	1S102H	1S101F	1R109F
% H ₂ O	8.2	8.8	0.32
% Ash	0.88	0.46	1.25
% C	58.13	52.44	52.47
% H	3.68	4.31	5.39
% O	34.08	42.2	31.38
% N	4.14	0.72	6.51
% Carboxyl	18	20	17
% Aromatic	50	24	12
% Heteroaliphatic	6	11	8
% Aliphatic	16	33	61

44 ^aData obtained from International Humic Substances Society (IHSS) website
 45 (<http://www.ihss.gatech.edu/>).

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Figure S. 2. SEC of EfOM samples A-C. These SEC are typical for EfOM samples.).

Conditions: buffer (2.4 mM NaH₂PO₄, 1.6 mM Na₂HPO₄, and 25 mM Na₂SO₄ adjusted to pH 6.8 ± 0.1), 1.0 mL/min flow rate, 2.0 µL/min acid and oxidizer flow rate. UV₂₅₄ detection (top) and DOC detection (bottom).

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65 **Table S. 3. AMW estimations and $k_{(\text{OM-HO}\cdot)}$ values.**

Sample	AMW (Da)	$k_{(\text{OM-HO}\cdot)} \times 10^8 (\text{M}_\text{C}^{-1}\text{s}^{-1})$ 20 °C
ESHA	3100	1.21 ± 0.09
SRFA	2800	2.06 ± 0.09
PLFA	2400	6.90 ± 0.53
Sample C	2200	6.79 ± 0.11
Sample A	2100	7.39 ± 0.06
Sample B	2100	9.37 ± 0.07

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68 **Table S. 4. Temperature Dependent rate data for all samples**

Sample	Temperature (°C)	$k_{(\text{OM-HO})} \times 10^8 (\text{M}_\text{C}^{-1} \text{s}^{-1})$
ESHA	8.7	0.593 ± 0.11
	24.4	1.21 ± 0.09
	32.6	1.51 ± 0.13
	42.0	2.36 ± 0.12
SRFA	9.0	1.58 ± 0.03
	20.6	2.06 ± 0.09
	31.4	2.57 ± 0.29
	43.3	3.06 ± 0.10
PLFA	9.2	5.26 ± 0.20
	14.7	5.92 ± 0.36
	20.5	6.90 ± 0.53
	29.9	8.30 ± 0.69
	37.6	9.42 ± 0.40
Sample A	9.7	5.56 ± 0.23
	19.2	7.39 ± 0.06

Sample B	30.9	9.02 ± 0.33
	39.6	10.44 ± 0.05
	9.4	7.25 ± 0.28
	15.2	9.29 ± 0.54
	19.4	9.37 ± 0.07
Sample C	31.1	10.98 ± 0.04
	39.6	11.80 ± 0.04
	9.3	5.45 ± 2.16
	15.0	6.27 ± 0.21
	19.4	6.79 ± 0.11
	29.7	9.18 ± 0.80
	36.6	9.91 ± 0.31

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