Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplementary information:

Feedbacks between microphysics and kinetics in the temperature dependent reactivity of ozone with bromide in aqueous secondary organic matter

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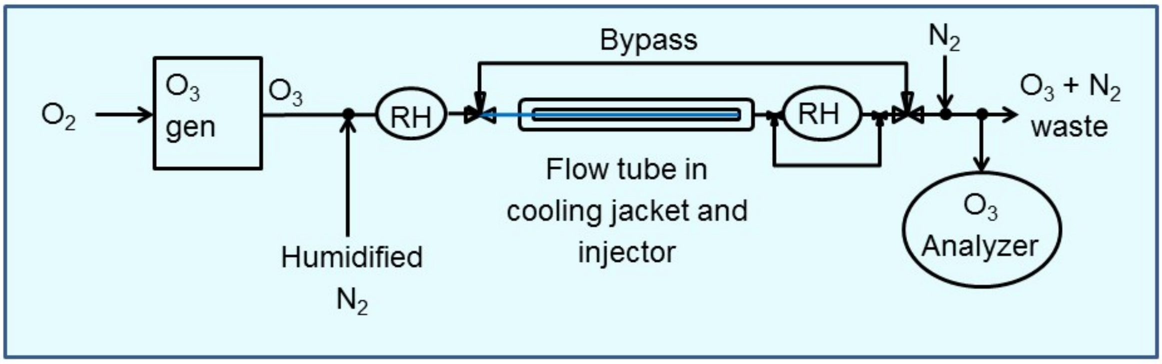
Experimental setup



SI. Figure S1 . Schematic of the coated wall flow tube experimental setup. RH = relative humidity sensors

Gas diffusion correction factor [1,2]

$$C_{gd} = \frac{1}{1 + \gamma_{obs} \times \frac{0.75 + 0.28Kn}{Kn\,(1 + Kn)}} \qquad \text{SI1}$$

Where Kn is the knudsen number (descriptor for the flow regime) and C_{gd} is the gad diffusion correction factor

$$Kn = \frac{6D_{gO3}}{w_{O3} \cdot h} \qquad \text{SI2}$$

Where D_{gO3} is the gas phase diffusion coefficient of ozone,[3,4] w_{O3} is the mean thermal velocity of ozone, and h is the characteristic length, in this case the diameter of the flow tube.

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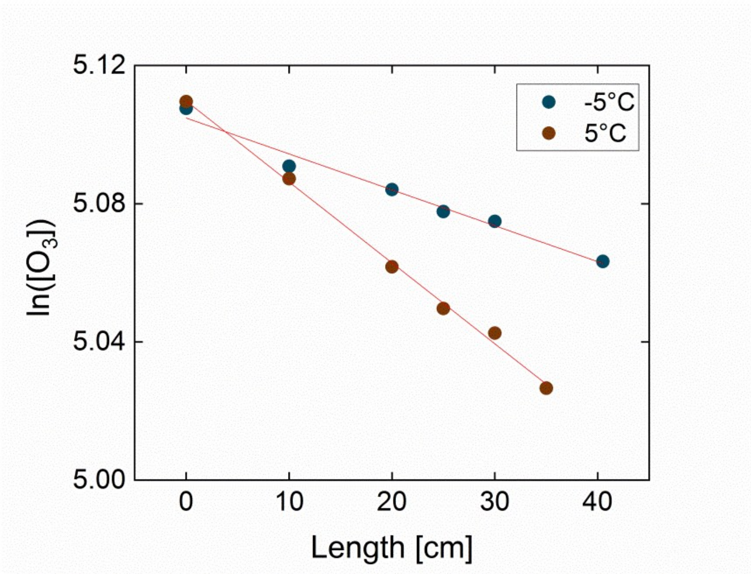
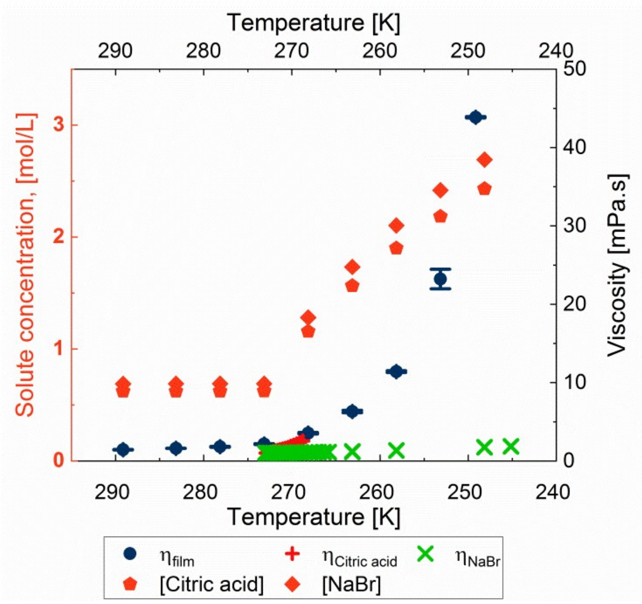
Test of first order kinetics



SI. Figure S2 Plot of ln([O3]) exiting the flow tube as a function of length of the coated wall flow tube exposed at -5°C and 5°C. The observed linear trend indicates that reactive loss of ozone follows first order kinetics with respect to Br^-

Temperature dependence of viscosity



SI. Figure S3 Comparison between measured viscosity in the mixture in the film (blue circles ● ± s.d.) and viscosity data for NaBr (+) and citric acid solutions (×).[5] ◆ is the equilibrium concentration of NaBr in the film as calculated using the AIOMFAC model; ◀ is the equilibrium concentration of citric acid in the film as calculated using the AIOMFAC model.[6]

Parameterization of the second order bulk reaction rate coefficients

The bulk uptake coefficient was parameterized using Liu et al.'s measurements at different temperatures and pHs.[7] Below we present the Arrhenius representation of the rate coefficients for the reactions presented in the paper (R1-R5).

$$k_b^{II} = \frac{k_1\left(\frac{k_2}{k_{-1}}[H^+] + \frac{k_3}{k_{-1}}\right)}{1 + \frac{k_2}{k_{-1}}[H^+] + \frac{k_3}{k_{-1}}} \quad (1)$$

Where,

$k_1 = 2.05\times10^{13}$ exp(-6916/T);

$k_2 = 1.50\times10^{39}$ exp(-23863/T);

$k_3 = 1.60\times10^{36}$ exp(-23515/T);

$k_{-1} = 4.20\times10^{41}$ exp(-26714/T);

Summary tables of parameters and uncertainty analysis

SI Table S 1 Estimated solubility parameters at temperatures of study

T [K]	H_{water} [mol/Latm]	H_{NaBr} [mol/Latm]	$H_{salt\ in}$ [mol/Latm]	$H_{salt-in(T-ind)}$ [mol/Latm]	$H_{salt-out}$ [mol/Latm]	$H_{mix\_salt\ out}$ [mol/Latm]	$H_{mix\_salt-in(T-ind)}$ [mol/Latm]	$H_{mix\_salt-in}$ [mol/Latm]
289.15	1.50E-02	1.01E-02	1.51E-02	1.16E-02	1.01E-02	9.75E-03	9.94E-03	1.16E-02
283.15	1.81E-02	1.21E-02	1.82E-02	1.16E-02	1.22E-02	1.18E-02	1.12E-02	1.39E-02
278.15	2.12E-02	1.43E-02	2.14E-02	1.16E-02	1.44E-02	1.38E-02	1.24E-02	1.64E-02
273.15	2.51E-02	1.68E-02	2.53E-02	1.16E-02	1.71E-02	1.64E-02	1.40E-02	1.94E-02
268.15	2.99E-02	1.40E-02	3.07E-02	1.18E-02	1.59E-02	1.48E-02	1.26E-02	2.10E-02
263.15	3.59E-02	1.26E-02	3.74E-02	1.20E-02	1.63E-02	1.46E-02	1.22E-02	2.42E-02
258.15	4.33E-02	1.18E-02	4.58E-02	1.22E-02	1.76E-02	1.51E-02	1.20E-02	2.88E-02
253.15	5.27E-02	1.15E-02	5.65E-02	1.23E-02	1.96E-02	1.63E-02	1.20E-02	3.51E-02
248.15	6.46E-02	1.15E-02	7.03E-02	1.25E-02	2.25E-02	1.80E-02	1.22E-02	4.34E-02

SI Table S 2: Estimated diffusivities (D) applied to Figure 3

T [K]	D_{water} cm^2/s	D_{NaBr} cm^2/s	D_{mix} cm^2/s
289.15	1.56E-05	1.47E-05	1.18E-05
283.15	1.36E-05	1.25E-05	1.01E-05
278.15	1.21E-05	1.10E-05	8.74E-06
273.15	1.06E-05	9.60E-06	6.82E-06
268.15	9.35E-06	8.09E-06	4.28E-06
263.15	8.17E-06	6.83E-06	2.49E-06
258.15	7.11E-06	5.79E-06	1.30E-06
253.15	6.15E-06	4.92E-06	5.94E-07
248.15	5.29E-06	4.21E-06	3.02E-07

SI Table S 3: Values of other parameters used in the study models

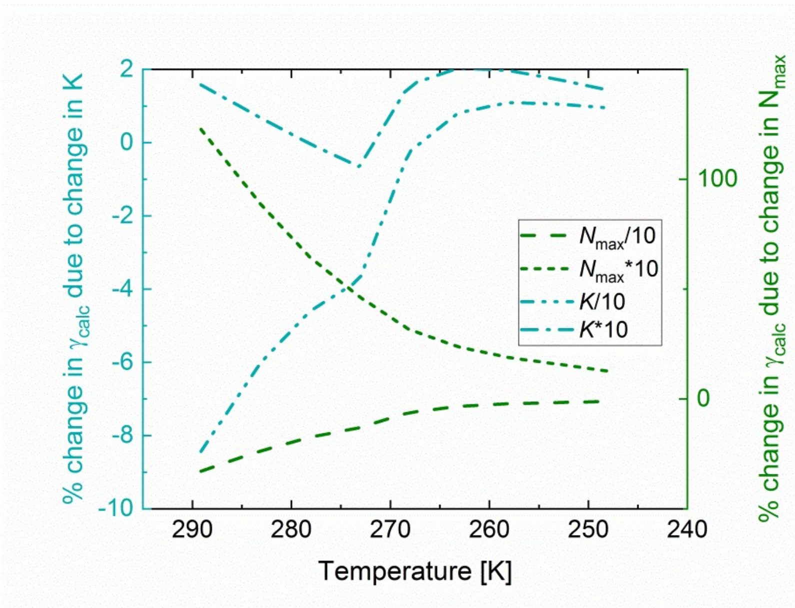
a is the activity of bromide (Br-) and citric acid (CA) in the film; k_b^{II} is the 2nd order rate coefficient; l_{rd} is the reacto diffusive length; t_{film} is the calculated film thickness; k_s^{I} is the *pseudo*-first order surface reaction rate coefficient; K is the surface adsorption coefficients.

T [K]	$a_{[Br-]}$ M	$a_{[CA]}$ M	pH	k_b^{II} [$M^{-1}s^{-1}$]	l_{rd} [μm]	t_{film} [μm]	O_3 [#/cm^{-3}]	k_s^{I} [s^{-1}]	K [cm^3]
289.15	0.59	0.09	2.0	388	2.3	13	4.31E+12	3.31E-02	6.43E-12
283.15	0.59	0.09	2.1	258	2.6	13	4.41E+12	1.69E-02	6.76E-12
278.15	0.58	0.08	2.1	180	2.9	13	4.49E+12	9.43E-03	7.06E-12
273.15	0.57	0.08	2.1	123	3.1	13	4.57E+12	5.15E-03	7.38E-12
268.15	1.27	0.19	1.9	92	1.9	6	4.65E+12	2.75E-03	7.74E-12
263.15	2.04	0.30	1.8	62	1.4	4	4.74E+12	1.43E-03	8.12E-12
258.15	2.87	0.42	1.7	40	1.1	3	4.83E+12	7.29E-04	8.54E-12
253.15	3.76	0.52	1.7	25	0.8	2	4.93E+12	3.61E-04	9.00E-12
248.15	4.69	0.62	1.6	15	0.7	2	5.03E+12	1.74E-04	9.51E-12

SI Table S 4: Uncertainty analysis and sensitivity of the bulk (Γ_{bulk}) and total (γ_{calc}) uptake coefficients to the bulk uptake parameters

	Diffusivity (D)			Aqueous bulk rate coefficient (k_b^{I})			Solubility (H)		
T [K]	% error	% Change in Γ_{bulk}	% Change in γ_{calc}	% error	% Change in Γ_{bulk}	% Change in γ_{calc}	% error	% Change in Γ_{bulk}	% Change in γ_{calc}
289.15	5	3	2	22	11	7	20	19	12
283.15	5	3	2	22	11	8	20	19	14
278.15	5	3	2	22	11	9	20	19	16
273.15	5	2	2	22	11	9	20	20	17
268.15	6	3	3	25	12	11	21	20	19
263.15	7	4	3	27	13	13	23	22	21
258.15	8	4	4	31	15	14	27	26	25
253.15	9	4	4	34	17	16	35	34	32
248.15	10	5	5	39	19	19	51	49	47

Sensitivity of γ_{calc} to surface parameters



SI. Figure S4 Sensitivity of γ_{calc} to N_{max} and K presented as % change in γ_{calc} as a function of temperature. The *green dash* lines represent changes to γ_{calc} due to change in N_{max}. The *cyan dash-dot* lines represent changes with change in K. $\left(K = 6 \times 10^{13} \cdot exp(\frac{686}{T})\right)$

Increase in K leads to increase in surface coverage. Since the model is already close to maximum coverage, 10 times increase in K does not significantly increase surface coverage. However, decrease in K by a factor of 10 significantly decreases surface coverage and more strongly at the warmer temperatures than at the lower temperatures. As a result, there is a much stronger effect on the $\gamma_{calc.}$.

Uncertainty consideration and error propagation

- Bulk uptake coefficients

$$\Gamma_{bulk} = \frac{4HRT}{\omega_{O_3}} \times \sqrt{D_{O3l} \times k_b^I} = \frac{4HRT}{\omega_{O_3}} \times \sqrt{D_{O3l} \times k_b^{II} \times \alpha_{Br^-}}$$

Let $a = \sqrt{D_{O3l}}$; $b = \sqrt{k_b^{II}}$; $c = \sqrt{\alpha_{Br^-}}$; $A = \frac{4RT}{\omega_{O_3}}$;

Let $P = H \times a \times b \times c$;

Then, $\Gamma_{bulk} = AP$; where A is a considered as a constant at each T,

By error propagation,

$$\frac{\delta a}{|a|} = \frac{1}{2}\frac{\delta D_{O3l}}{|D_{O3l}|}; \frac{\delta b}{|b|} = \frac{1}{2}\frac{\delta k_b^{II}}{|k_b^{II}|}; \frac{\delta b}{|b|} = \frac{1}{2}\frac{\delta \alpha_{Br^-}}{|\alpha_{Br^-}|};$$

$$\frac{\delta P}{|P|} = \frac{\delta \Gamma_{bulk}}{|\Gamma_{bulk}|} = \sqrt{\left(\frac{\delta H}{|H|}\right)^2 + \left(\frac{\delta a}{|a|}\right)^2 + \left(\frac{\delta b}{|b|}\right)^2 + \left(\frac{\delta c}{|c|}\right)^2};$$

- Surface uptake coefficients

$$\Gamma_{surf} = \frac{4 \cdot k_s \cdot K \cdot N_{max}}{\omega_{O_3} \cdot \left(1 + K \cdot [O_3]_g\right)}$$

$$\frac{\delta \Gamma_{surf}}{|\Gamma_{surf}|} = \sqrt{\left(\frac{\delta k_s}{|k_s|}\right)^2 + \left(\frac{\delta N_{max}}{|N_{max}|}\right)^2 + \left(\frac{\delta K}{|K|}\right)^2 + \left(-1\frac{\delta K}{|K|}\right)^2};$$

- Total calculated uptake coefficients

$$\frac{\delta \gamma_{calc}}{|\gamma_{calc}|} = \sqrt{\left(\frac{\delta \Gamma_{surf}}{|\Gamma_{surf}|}\right)^2 + \left(\frac{\delta \Gamma_{bulk}}{|\Gamma_{bulk}|}\right)^2};$$

$$\gamma_{calc\_upper} = \gamma_{calc}\left(1 + \frac{\delta \gamma_{calc}}{|\gamma_{calc}|}\right);$$

$$\gamma_{calc\_lower} = \gamma_{calc}\left(1 - \frac{\delta \gamma_{calc}}{|\gamma_{calc}|}\right);$$

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