Modification of Ozone Deposition and I$_2$ Emissions at the Air-Aqueous Interface by Dissolved Organic Carbon of Marine Origin

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Supporting Information

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Figure S1. Experimental set up used to investigate ozone uptake by iodide

in PBS, pH 8, and quantify gaseous molecular iodine emission.

Figure S2. Pseudo first order ozone uptake to iodide PBS (pH8). Empty diamonds, 5 x 10^{-6} M^{1}; filled diamonds, 1 x 10^{-5} M [I$^-$].The y error bars are calculated from the propagation of the quoted MFC error (2.5%), the calibration error and the standard deviation of replicate analyses.

Table S1. Calculated reaction rate constants, λ, for DOC + O$_3$ reactions in seawater at 298K.

Supporting Information

Description of the parallel resistance approach of the ozone uptake potential of seawater, figures S1-S2 and table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

The parallel resistance approach

The ozone uptake potential of seawater can be considered as a mechanism involving two layers, an overlying air and surface water layer. The overlying air layer offers an aerodynamic resistance (r_a) to ozone deposition from the air to seawater and the surface water layer provides an aqueous phase resistance (r_s). The total resistance (r_t) is the sum of the resistances in these layers, as shown in equation (1), which is related to the deposition velocity (v_d) by equation (7), in manuscript[2-3]. The term r_a is determined by mixing in the atmosphere and will be similar in value to the corresponding resistance to the transfer of heat and other trace gases[4]. Being relatively insoluble, atmospheric ozone deposition is determined (~95%) by r_s in the surface seawater which is a function of the chemical loss rate (λ, s^{-1}) in seawater [5-6], where H is the dimensionless Henry's law constant, D is the molecular diffusivity of O_3 in water (m^2 s^{-1}), k_i is the second order kinetic rate constant and C_i is the reactant concentration, equations 8 and 9, in manuscript. Considering equation (1), it follows that the ozone deposition rate is dependent on the assumed value for the (pH dependent) O_3 + I^- reaction rate constant k_1 as well as competing reactions for O_3 in surface seawater.

$$r_t = r_a + r_s \qquad (1)$$

The aerodynamic resistance (r_a) of the experimental system was determined from the ozone deposition velocity over 0.02 M [I⁻] solutions, wherein r_s is considered negligible. At an ozone concentration of 70 ppbv and a flow rate of 0.2 L min^{-1} (i.e. the same experimental conditions as used throughout the study), r_a was determined as 7.7 m^{-1} s.

Equation (8), in manuscript, represents the deposition velocity due solely to molecular gas-transfer including molecular diffusion and chemical reactions, and is applicable in laboratory conditions or when wind speed is low. Wanninkhof (1992)[7] assumed that deposition was also controlled by interactions between wind-induced turbulent transport and chemical enhancement, and Chang et al. (2004)[8] proposed a general formula for r_s to account for this as follows:

$$r_s = H / (\alpha k_w + (\lambda D)^{1/2}) \qquad\qquad (2)$$

where k_w is the gas-transfer velocity, a function of wind speed at 10 m height, and α the chemical enhancement factor.

Note that whilst the parallel resistance approach to oceanic ozone deposition is used extensively, improved models have been developed more recently that describe the dependencies of deposition on atmospheric and oceanic processes from a more fundamental perspective [9].
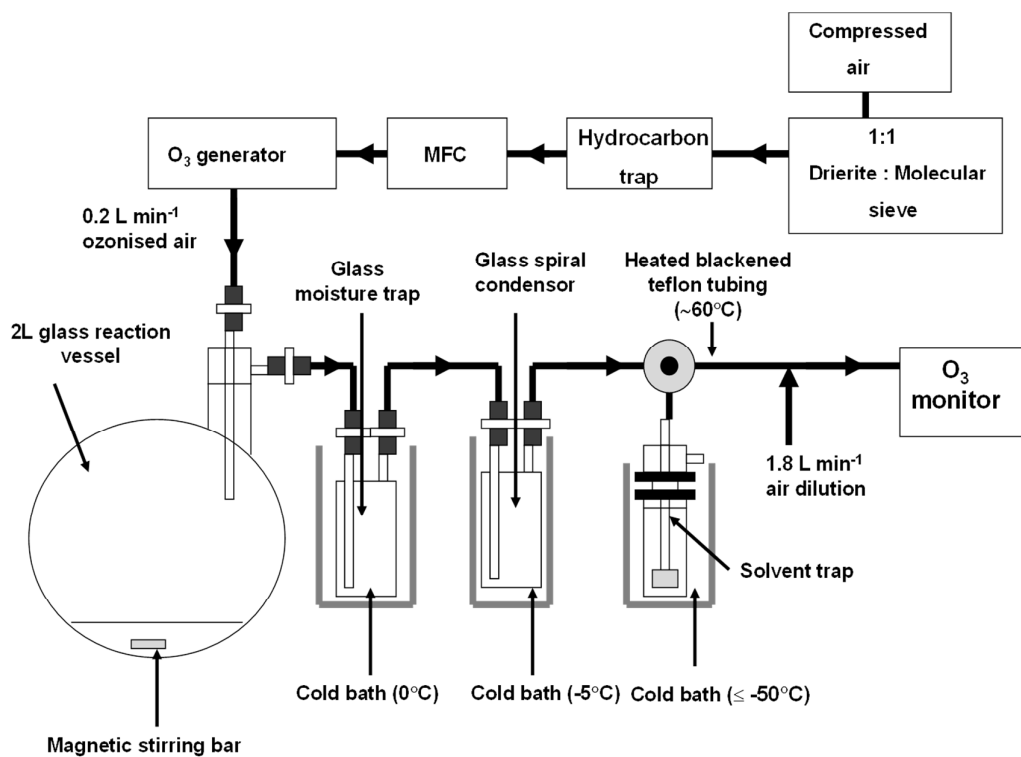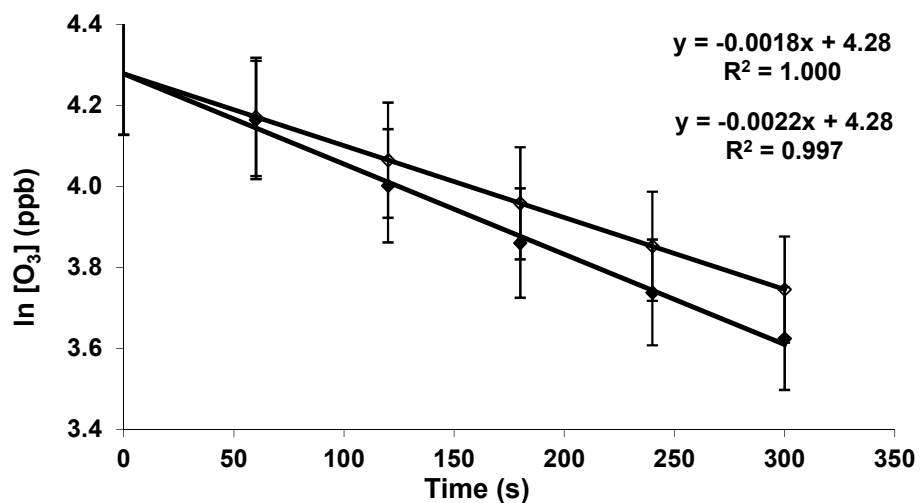
3 way adjustable tap

Gas transfer lines (PFA, covered with black tape)

MFC   Mass flow controller

Figure S1. Experimental set up used to investigate ozone uptake by iodide in PBS (pH 8, 293 K) and quantify gaseous molecular iodine emission.

Figure S2. Pseudo first order ozone uptake to iodide PBS (pH8). Empty diamonds, 5×10^{-6} M [I⁻]; filled diamonds, 1×10^{-5} M [I⁻]. The *y* error bars are calculated from the propagation of the quoted MFC error (2.5%), the calibration error and the standard deviation of replicate analyses.

Compound	Molarity $(10^{-9}\,\text{mol dm}^{-3})$	k $(\text{mol}^{-1}\text{dm}^3\,\text{s}^{-1})$	$\lambda\ (\text{s}^{-1})$	References
DMS	5(0.04 – 316)	8.6×10^8	4.3 (0.04 – 272)	10-11
Ethene	0.5	1.8×10^5	1.8×10^{-4}	12-13
Propene	0.2	8.0×10^5	3.2×10^{-4}	12-13
Isoprene	0.05	4.0×10^5	2×10^{-5}	14
Chlorophyll a	2000 – 10,000	6×10^7	120 – 1200*	15
Phenol	2.34	1.3×10^3	3.0×10^{-6}	16-17
Phenolate	0.23	1.4×10^9	0.32	16-17
P-cresol	0.14	3.0×10^4	0.56	16, 18
TOTAL			(126 – 1473)	

Table S1. Calculated reaction rate constants, λ, for DOC + O_3 reactions in seawater at 298K.

* Calculated assuming *Chl a* concentrations were free to react at the surface of solution.

Supporting Information References

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