



Photochemical oxidation of dimethylsulphide to dimethylsulphoxide in estuarine and coastal waters



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HIGHLIGHTS

- We observed 1:1 M conversion of DMS to DMSO in estuarine waters.
- This suggests that DMS photo-oxidation occurred via the CDOM sensitised ¹O₂ pathway.
- Photochemical rate constants decreased ~10-fold from river to seawater.
- Rate constants were strongly correlated with CDOM absorption coefficients (a₃₅₀).
- a₃₅₀-normalised rate constants increased ~10-fold from river to seawater.

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ABSTRACT

Dimethylsulphide (DMS) photo-oxidation and dimethylsulphoxide (DMSO) photoproduction were estimated in 26 laboratory irradiations of coastal samples from NE England (Tyne estuary) and W Scotland (Loch Linnhe and River Nant at Taynuilt). Pseudo-first order rate constants of DMS photo-oxidation (0.038 h⁻¹ to 0.345 h⁻¹) and DMSO photo-production (0.017 h⁻¹ to 0.283 h⁻¹) varied by one order of magnitude and were lowest in the coastal North Sea. Estuarine samples (salinity *S* < 30) had a mean DMSO yield of 96 ± 16% (*n* = 14), consistent with 1:1 M conversion via photosensitised oxidation by singlet oxygen. Photochemical rate constants were strongly correlated with coloured dissolved organic matter (CDOM) absorption coefficients at 350 nm, a₃₅₀. Variations in a₃₅₀ explained 61% (R² = 0.61, *n* = 26) and 73% (R² = 0.73, *n* = 17) of the variability in DMS photo-oxidation and DMSO production, respectively. However, CDOM normalised photochemical rate constants increased strongly towards coastal waters exhibiting lowest CDOM absorbance, indicating water samples of marine character (*S* > 30) to be most reactive with respect to DMS photo-oxidation. Estimates of water column averaged DMS photo-oxidation rate constants, obtained by scaling to mean daily irradiance (July, NE England) and mid-UV underwater irradiance, were 0.012 d⁻¹, 0.019 d⁻¹, and 0.017 d⁻¹ for upper estuary (*S* < 20), lower estuary (20 < *S* < 30) and coastal waters (*S* > 30), at the lower end of previous observations. Comparing our water column averaged DMS photo-oxidation rate constants with estimated DMS losses via air-sea gas exchange and previously reported biological consumption implies that DMS photochemical removal is of only minor importance in our study area.

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1. Introduction

Dimethylsulphide (DMS) is an important biogenic trace gas implicated in the regulation of global climate. Marine DMS emissions may account for ~20–35 Tg (S) a⁻¹ globally (Simo and Dachs, 2002; Kloster et al., 2006; Lana et al., 2011; Land et al., 2014) and likely dominate the southern hemisphere tropospheric sulphur budget (12 Tg (S) a⁻¹; Stern, 2006; Lana et al., 2012; Land et al., 2014). A marine DMS-climate feedback loop was first proposed

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by Charlson et al. (1987), in which gas to particle conversion of phytoplankton-derived DMS in the marine boundary layer produces sulphate aerosols that act as cloud condensation nuclei, thereby impacting Earth's radiation balance via changes to cloud albedo. While some recent modelling studies imply a rather weak marine DMS-climate feedback (Carslaw et al., 2010; Quinn and Bates, 2011), others support the notion that cloud condensation nuclei abundance may be controlled by DMS-derived and other secondary aerosols (Lana et al., 2012). Considerable uncertainty regarding the contribution of DMS to indirect aerosol forcing (Carslaw et al., 2013; Woodhouse et al., 2013) illustrates the need for further studies of biogeochemical DMS cycling.

Marine DMS is primarily derived from the enzymatic breakdown of dimethylsulphonio-propionate (DMSP), an algal osmolyte and cryoprotectant (Simó, 2001). Sea surface DMS losses are usually dominated by microbial consumption or photodegradation, with only minor contributions from air-sea exchange (Archer et al., 2002; Toole et al., 2006; Vila-Costa et al., 2008; Galí and Simó, 2015). Results from ^{35}S -DMS tracer experiments indicate that microbial DMS consumption in surface waters primarily yields dimethylsulphoxide (DMSO) (Del Valle et al., 2007b). By contrast, the DMSO yield from DMS photo-oxidation apparently varies between shelf seas (25%), polar waters (39%) and the open ocean (14%) (Kieber et al., 1996; Hatton, 2002; Toole et al., 2004). Even so, DMSO concentrations frequently exceed those of DMS (Lee et al., 1999), possibly due to a lack of photochemical removal (Toole et al., 2004), slow microbial consumption (Tyssebotn et al., 2017), significant biological production (Del Valle et al., 2007a) or an aggregate of all three.

Laboratory studies established that aqueous solutions of dialkylsulphides undergo photosensitised oxidation to their respective sulphoxides (e.g. Sysak et al., 1977), involving singlet oxygen ($^1\text{O}_2$) formation via chromophoric photosensitisers, and 1:1 M conversion to the sulphoxide. Brimblecombe and Shooter (1986) showed that marine chromophoric dissolved organic matter (CDOM) sensitises DMS photo-oxidation, consistent with singlet oxygen ($^1\text{O}_2$) formation via electronically excited triplet states in natural CDOM (Zepp et al., 1985). However, Brimblecombe and Shooter (1986) did not report DMSO concentrations, and subsequent work reported low DMSO yields, particularly in open ocean waters (Kieber et al., 1996; Hatton, 2002; Toole et al., 2004), that are not consistent with the $^1\text{O}_2$ pathway. Positive correlations of DMS photo-oxidation rates with nitrate concentrations imply that reactive intermediates deriving from nitrate photolysis are also involved in DMS photo-degradation (Bouillon and Miller, 2004; Toole et al., 2004). Their likely contribution, as estimated from relationships between photo-oxidation rate constants and in-situ nitrate concentrations, appears to be rather variable between contrasting open ocean waters of the subpolar South Pacific (35%; Toole et al., 2004) and NE Pacific (81%; Bouillon and Miller, 2004). By implication, these results suggest highly variable contributions from CDOM related pathways of DMS photo-oxidation (19–65%). Data on the relationship between DMS photo-oxidation rate constants and nitrate concentrations remain scant. However, a recent meta-analysis of both available and unpublished apparent quantum yields of DMS photo-oxidation suggested that photochemical DMS removal is primarily controlled by CDOM nature and abundance, while the overall contribution of nitrate related pathways is likely limited to ~20–25% (Galí et al., 2016). Concurrent studies of the effects of CDOM and nitrate on DMS photo-oxidation are needed to further constrain the roles of contrasting photodegradation pathways at regional scales.

Due to their characteristically high DMS concentrations, coastal waters are thought to be disproportionately large contributors to global marine DMS emissions (Uher, 2006). UV light absorption by

CDOM, a proxy for the photosensitisation capacity of natural waters (Zepp et al., 1985) is also high in coastal waters (Stedmon and Nelson, 2014). Given the high levels of natural photosensitisers, it is plausible to assume that CDOM related DMS photo-degradation, including CDOM sensitised photo-oxidation by $^1\text{O}_2$, is important in controlling coastal DMS concentrations and sea-to-air flux. In this paper we evaluate the results of irradiation experiments using estuarine and coastal waters collected along the UK northeast and northwest coasts. DMS photo-degradation and DMSO photo-production were quantified, with the DMSO yield used to diagnose photosensitised DMS oxidation by $^1\text{O}_2$. Rate constants for DMS photo-oxidation and concurrent DMSO production were compared to spectral CDOM absorbance in the UV and visible domains to test for predictive relationships between photochemical DMS removal and proxies of the photo-sensitisation capacity of natural waters.

2. Methods

2.1. Study areas and sampling

A total of 16 surface water samples were collected from the Tyne estuary, NE England, and adjacent North Sea waters, and a further 2 samples were obtained from Loch Linnhe and the River Nant at Taynuilt, W Scotland (Table 1, Fig. 1). Both study areas receive river discharge rich in dissolved organic carbon (DOC) due to extensive blanket peat coverage in their catchments (Hope et al., 1997; Joint Nature Conservation Committee, 2011). The Tyne estuary is a ria type, macrotidal estuary of 33 km length, receiving a mean freshwater discharge of $\sim 45 \text{ m}^3 \text{ s}^{-1}$ from the River Tyne (Manning, 2012). Loch Linnhe is a large Scottish sea loch of fjordic character, extending approximately 60 km in length from its north-eastern end to the coastal waters of the Inner Hebrides to the southwest. Loch Linnhe is connected with Loch Eil and, via River Lochy, with Loch Lochy to the north, receiving significant runoff ($112.5 \text{ m}^3 \text{ s}^{-1}$), dominated by River Lochy discharge ($59.5 \text{ m}^3 \text{ s}^{-1}$) to its northern end (Manning, 2012). The Lochy and Tyne rank among the 10 largest UK rivers by discharge (National River Flow Archive, <http://nrfa.ceh.ac.uk/>). The River Nant is a small Scottish river of ~ 10 km length discharging freshwater from Loch Nant into Loch Etive, which connects with Loch Linnhe at Connel, Argyll and Bute, Scotland.

Surface water samples for subsequent irradiation experiments were collected in 25 L high density polyethylene (HDPE) carboys pre-cleaned with laboratory detergent, (Decon 90), 10% HCl, and “Milli-Q” analytical grade laboratory water (Millipore Q185, 18.2 Ohm Milli-Q, Millipore System Inc., USA). Tyne estuary and adjacent North Sea samples were immediately transferred to our Newcastle laboratory and pressure filtered (Gelman, No. 15207, stainless steel, <0.7 bar N_2) with sequential inline filtration (Pall Corp.: $0.7 \mu\text{m}$, 142 mm diameter TCLP glass fibre filter; Sartorius, $0.2 \mu\text{m}$ Sartopore 2 Gamma capsule filter). Loch Linnhe and River Nant samples were filtered by tangential flow (Millipore, Pellicon, $0.2 \mu\text{m}$ cassette filter) at Dunstaffnage Marine Laboratory in Oban. All filtration was completed on the day of sampling, usually within 4 h of collection. Samples were dark stored at 5°C in HDPE carboys, prior to their irradiation during the following 16 days (Table 1). Loch Linnhe and River Nant samples were transferred to Newcastle for irradiation.

2.2. Irradiation experiments

DMS concentrations often decreased to <0.2 nM for river waters and <1 nM for sea waters during storage. Therefore, prior to irradiation (in Newcastle) and immediately following their re-filtration

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