

Ubiquity of algal dimethylsulfoxide in the surface ocean: Geographic and temporal distribution patterns

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Abstract

We carried out analyses of dimethylsulfoxide (DMSO) in surface–sea particulate samples collected between 1995 and 2003 in the Arctic, Antarctica, Sub-polar North Atlantic, Sargasso Sea, Sub-tropical NE Atlantic, W and E Mediterranean Seas, Black Sea, the coastal North Sea and the coastal Mediterranean Sea. Particulate DMSO (DMSO_p) was found to co-occur with particulate dimethylsulfoniopropionate (DMSP_p), with concentrations in the range 1–40 nM for the former and 6–340 nM for the latter. The two compounds were significantly correlated, which suggests that they both have a common origin in phytoplankton. Conversely, no significant correlation was found between DMSO_p and chlorophyll-*a* concentrations (which spanned more than 2 orders of magnitude: 0.04–13 mg m⁻³), suggesting that DMSO production, like that of DMSP, is taxon-dependent. DMSO_p concentrations were generally lower than concurrent DMSP_p concentrations and accounted for 8–50% (on average ca. 20%) of the intracellular dimethylated sulfur pool (DMSP+DMSO). There was a trend towards higher relative proportions of DMSO in warmer waters, and lower proportions in colder waters. This pattern with temperature was particularly apparent along an annual series in the coastal NW Mediterranean, and along a transect from cold productive waters through warm oligotrophic waters in the NW Atlantic. This is the most comprehensive dataset on DMSO_p reported so far, which shows that this compound is as ubiquitous as DMSP_p in the surface ocean.

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1. Introduction

Dimethylated sulfur occurs in the ocean mainly in the forms of the volatile dissolved compound dimethylsulfide (DMS) and the dissolved and particulate pools of the non-volatile compounds dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide (DMSO). While the particulate pools are clearly dominated by DMSP on

most occasions, the dissolved pools are dominated generally by DMSO (Hatton et al., 2004). Overall, dimethylated sulfur species represent major players in oceanic sulfur biogeochemistry and oceanic biosphere–atmosphere interactions (Simó, 2001). Evasion of volatile DMS from the sea surface is the main natural source of sulfur to the global troposphere (Bates et al., 1992), and its subsequent atmospheric oxidation is a major source of aerosols and cloud condensation nuclei over the oceans (Andreae and Crutzen, 1997), with potential climatic implications on a global scale (Charlson et al., 1987). In the water column, dimethyl-

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lated sulfur (mostly DMSP) represents an important fraction of organic sulfur in phytoplankton (Matrai and Keller, 1994) and a major carrier for sulfur among trophic levels of the food web (Kiene et al., 2000; Simó et al., 2002; Simó, 2004). Finally, within the phytoplankton cell, DMSP and derivatives are suggested to play important physiological functions, such as osmoregulation, cryoprotection, sulfur and carbon overflow under unbalanced growth, scavenging of oxygen free radicals, and chemical signaling (see e.g. Kiene et al., 1996; Stefels, 2000; Welsh, 2000; Wolfe, 2000; Sunda et al., 2002; Hatton et al., 2004).

Although there is an increasing tendency to consider DMS, DMSP and DMSO as a group of compounds so tightly interrelated that need to be studied altogether, there is an overwhelmingly larger body of knowledge of the oceanic distribution and dynamics for DMS and DMSP than for DMSO. This is largely because the occurrence of DMS and DMSP in seawater and marine organisms was discovered earlier, but it is due also to the intrinsic difficulties in the analysis of DMSO at nanomolar levels (Simó, 1998).

While the body of data on aqueous DMSO is steadily enlarging (an excellent compilation of current knowledge can be found in the review by Hatton et al., 2004), much less is known about its particulate pool (DMSO_p). It was first reported by Andreae (1980), but later it was revealed that the analytical method was determining all or part of the co-occurring DMSP as DMSO. The first direct evidence (free of known interferences) for the existence of DMSO_p was provided by Simó et al. (1998a). Work with algal cultures and size-fractionated marine seston led these authors to suggest that DMSO was being produced by phytoplankton. Lee et al. (1999) measured significantly higher concentrations of DMSO_p than dissolved DMSO (DMSO_d) in the Saguenay Fjord, which they interpreted as an indication of direct biosynthesis by phytoplankton. Later, Simó et al. (2000) observed an increase in DMSO_d after a whole seawater sample had been treated with chloroform. As dissolved DMSP also increased, the authors interpreted that chloroform was inducing the release of both compounds from the algal cells, and, consequently, there was a pool of intracellular DMSO associated with intracellular DMSP.

Since those pioneering papers, only a few further reports of the occurrence of DMSO_p in the marine environment have been published (Lee et al., 2001; Bouillon et al., 2002; Hatton, 2002; Besiktepe et al., 2004). Even such a short body of data was enough for Sunda et al. (2002) to suggest that DMSO acts as an efficient scavenger of reactive oxygen species in phy-

toplankton. The distribution of DMSO_p in the marine environment, whether it is widespread or not, and how it compares with the distribution of DMSP_p, remain largely unresolved. Also unresolved is its temporal variability and controlling factors. This field information is needed in parallel to lab work aimed at asking which organisms produce DMSO and what its function in the cell is.

Here we report on the concentrations of DMSO_p in marine particles from a variety of oceanic regions and coastal sites (mostly in the North Atlantic and adjacent continental seas), and in different seasons. Some previously published data are included to complete the inventory. The spatial and temporal distributions of DMSO_p are compared with those of chlorophyll-*a* and DMSP_p, and related to seawater temperature.

2. Methods

2.1. Sampling, filtration and storage

Samples used in this study were collected between 1995 and 2003 during oceanographic cruises to the Arctic, Antarctica, Sub-polar North Atlantic, Sargasso Sea, Sub-tropical NE Atlantic, W and E Mediterranean Seas, Black Sea, and boat trips to the coastal North Sea (Simó et al., 1998a,b) and the coastal Mediterranean



Fig. 1. Approximate locations of the samples reported in this study. 1: coastal NW Mediterranean; 2: Alboran Sea (W Med); 3: E Mediterranean; 4: Black and Marmara Seas; 5: coastal North Sea; 6: Arctic (Atlantic sector); 7: NE Atlantic; 8: Canary Basin; 9: Gulf of Maine and George's Bank; 10: Sargasso Sea; 11: North Carolina shelf; 12: Antarctic (Peninsula). The open triangle (13) corresponds to the study by Riseman and DiTullio (2004) in the Equatorial Pacific.

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