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Research Article

Particulate dimethylsulphoxide and dimethylsulphoniopropionate in phytoplankton cultures and Scottish coastal waters

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Abstract. Dimethylsulphoniopropionate (DMSP), an algal compatible solute, has for many years been considered to play a key role in dimethylsulphide (DMS) production, influencing the concentrations of DMS in sea water available to be transferred to the atmosphere. However, in recent years it has been shown that dimethylsulphoxide (DMSO) can also be produced directly within the cells of marine phytoplankton. The exact role DMSO plays in cells is still subject to debate, but it is thought that it may act as an antioxidant or cryoprotectant. Whatever the reason, it has been suggested that release through algal mortality and permeative loss of DMSO from cells may contribute to dissolved DMSO concentrations and as such this pathway must also be considered an important component of DMS biogeochemistry. Experiments were conducted to investigate the intracellular concentrations of DMSO and the ratio of DMSP:DMSO in a range of phytoplankton species and in natural samples. Results indicate that prymnesiophytes and dinoflagellates are the main producers, generating relatively higher concentrations of particulate DMSO than diatoms. Results from both laboratory and field experiments show that there is a strong relationship between DMSOp and DMSPp, with DMSO generally representing between 10 and 20 % of the intracellular sulphur pool. Field data also indicates that dissolved DMSO concentrations in surface waters were not significantly correlated with those for particulate DMSO, but were significantly correlated with DMS concentrations.

Key words. Particulate dimethylsulphoxide; dimethylsulphoniopropionate; dimethylsulphide; phytoplankton.

Introduction

In the marine environment, interest in dimethylsulphoxide (DMSO) and dimethylsulphoniopropionate (DMSP) focuses primarily on the role these compounds play in the production and removal of dimethylsulphide (DMS), which is considered to be one of the most important biogenic sulphur compounds in the marine environment (Hatton et al., 2004 and others). The sea-to-air flux of DMS accounts for one quarter of global sulphur emissions and is the principal natural source of atmospheric sulphur from the marine environment and a key component of the biogeochemical sulphur cycle (Liss et al., 1997). Furthermore, a proposed phytoplankton-cloud-climate feedback loop, whereby DMS derived cloud condensation nuclei affect the Earth's radiation balance through increased albedo (Charlson et al., 1987) has stimulated considerable research into this gas.

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Oceanic DMS emissions to the atmosphere are partly a function of its concentrations in surface waters, which in turn are regulated by marine microorganisms. DMS is thought to be formed mainly from the enzymic breakdown of DMSP, a compatible solute produced by marine algae to maintain their osmotic balance in seawater (Vairavamurthy et al., 1985; Dacey and Wakeham, 1986). It has also been suggested that DMSP may be produced as a cryoprotectant (Kirst et al., 1991; Lee and de Mora, 1999), an antioxidant (Sunda et al., 2002), a methyl donor for a variety of biochemical processes (Cantoni and Anderson, 1956; Ishida, 1968; Kiene et al., 2000) or a grazing deterrent (Wolfe et al., 1997; 2002). Furthermore it has been hypothesised that DMSP may be produced as an overflow mechanism enabling cells to keep cysteine and methionine concentrations at a level that is low enough to prevent feedback mechanisms and allow continued sulphate assimilation even under nitrogen-limited conditions (Stefels, 2000). However, recent studies now indicate that intracellular DMSO could also fulfil some of these cellular functions (Sunda et al., 2002, Lee and de Mora, 1999; Hatton et al., 2004; Simó and Vila-Costa, 2006).

Although DMS, DMSP and DMSO are a group of tightly interrelated compounds, DMS and DMSP have typically been studied in isolation, leading to greater understanding of the oceanic distribution and dynamics for these compounds than for DMSO (Hatton et al., 2004; Simó and Vila-Costa, 2006). This primarily stems from the fact that, until a decade ago, the analysis of DMSO at the concentration ranges found in marine waters was problematic (Hatton et al., 1994). Initially measurements were made for dissolved DMSO (DMSOd) from a range of geographical regions. These studies showed that DMSOd levels can exceed those of both DMS and dissolved DMSP (DMSPd) in euphotic waters, and depth integrated DMSO levels are significantly higher than those of other DMS-related compounds, making it the dominant dimethylated sulphur species throughout the water column (Hatton et al., 1998). Although some of this work allowed progress to be made in addressing the role of photochemical and bacterial oxidation of DMS, it has been the subsequent measurements of particulate DMSO (DMSOp) that have allowed a deeper understanding of the role this compound may play. This includes demonstrating that the anaerobic formation of DMSO can occur in sedimenting faecal pellets (Hatton, 2002; Hatton et al., 2004) and most interestingly the discovery that DMSO can be produced directly by marine phytoplankton (Simó et al., 1998).

The possibility that algae could directly produce DMSO had been considered for many years, following the detection of DMSO in various fruits and vegetables (Pearson et al., 1981) and the large pool of DMSO observed in surface sea waters (Lee and de Mora, 1996). However, the production of DMSO by marine microalgae was not confirmed until the late nineties when laboratory culture of both *Amphidinium carterae* and *Emiliania huxleyi* were shown to produce 0.3 and 0.1 pg DMSO cell^{-1} respectively during logarithmic growth (Simó et al., 1998). Since these initial results showing DMSO associated with phytoplankton (Simo et al., 1998) a number of measurements have been made for DMSOp (Lee et al., 1999a; Lee et al., 2001; Bouillon et al., 2002; Hatton, 2002; Hatton et al., 2004; Riseman and DiTillio, 2004; Simó and Vila-Costa, 2006). It had been suggested that the ability to synthesise DMSO may be present in a wider range of marine phytoplankton species than those shown to produce DMSP (Lee et al., 1999a; Bouillon et al., 2002). The notion of ubiquitous DMSOp production was based on a stronger correlation between DMSOp and chlorophyll *a* compared to that for particulate DMSP (DMSPp) and chlorophyll *a* (Lee et al., 1999a; Bouillon et al., 2002). However, positive correlations between chlorophyll *a* and DMSOp have not been consistently observed (Lee et al., 2001; Simó and Vila-Costa, 2006) and more recent studies have hypothesised that, like DMSP, DMSO production may be taxon-dependent (Simó and Vila-Costa, 2006). It should be noted, however, that very few measurements have been made for DMSO in phytoplankton cultures and the particulate pool of DMSO continues to be under-represented in DMS research limiting our ability to draw any major conclusions about algal production of DMSO.

The interactions occurring between DMS and DMSO may be key to our understanding of DMS biogeochemistry (Lee et al., 1999b), yet the role DMSO plays in the marine sulphur cycle is still poorly resolved and may remain significantly underestimated. This study seeks to address the question of DMSO production by marine phytoplankton with the analysis of a range of phytoplankton cultures and seawater samples. Particulate DMSO concentrations are provided for 20 clonal algal cultures and compared to particulate DMSP values. Concomitant analysis of dissolved fractions provides further insight into the role and fate of DMSO in the marine sulphur cycle.

Materials and methods

Phytoplankton cultures

Phytoplankton cultures were obtained from the Culture Collection of Algae and Protozoans (CCAP) or personal collections of Drs. David Green and Mark