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Annual cycle of dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide (DMSO) related to phytoplankton succession in the Southern North Sea

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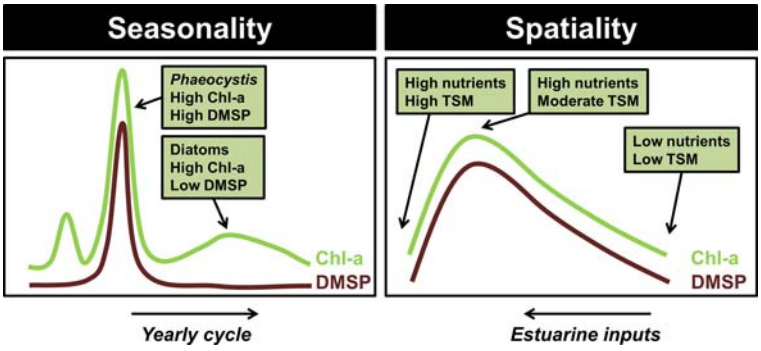
HIGHLIGHTS

- Annual in-situ data set of DMSP, DMSO and DMS in the Belgian Coastal Zone
- High seasonal and spatial variation of DMSP and DMS linked to phytoplankton succession
- High DMSO concentration linked to high suspended particulate matter

GRAPHICAL ABSTRACT



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ABSTRACT

The influence of abiotic and biotic variables on the concentration of dimethyl sulfide (DMS), dimethylsulfoniopropionate (DMSP), and dimethylsulfoxide (DMSO), were investigated during an annual cycle in 2016 in the Belgian Coastal Zone (BCZ, North Sea). We reported strong seasonal variations in the concentration of these compounds linked to the phytoplankton succession with high DMS(P,O) producers (mainly *Phaeocystis globosa*) occurring in spring and low DMS(P,O) producers (various diatoms species) occurring in early spring and autumn. Spatial gradients of DMS and DMSP were related to those of phytoplankton biomass itself related to the inputs of nutrients from the Scheldt estuary. However, the use of a relationship with Chlorophyll-*a* (Chl-*a*) concentration is not sufficient to predict DMSP. Accounting for the phytoplankton composition, two different DMSP versus Chl-*a* correlations could be established, one for diatoms and another one for *Phaeocystis* colonies. We also reported high nearshore DMSO concentrations uncoupled to Chl-*a* and DMSP concentrations but linked to high suspended particulate matter (SPM) presumably coming from the Scheldt estuary as indicated by the positive relationship between annual average SPM and salinity.

1. Introduction

Dimethylsulfoniopropionate (DMSP) and dimethylsulfoxide (DMSO) are sulfur (S) containing organic molecules produced by some species of phytoplankton, macroalgae and angiosperms (Keller

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et al., 1989; Hatton and Wilson, 2007; Borges and Champenois, 2017) and the primary precursors of dimethylsulfide (DMS). DMS emissions from the oceans play an important role in the global S cycle, contributing to approximately 40% of the biogenic S emissions (Wang et al., 2015) and could act on climate through the formation of atmospheric aerosols and the modification of cloud albedo (Charlson et al., 1987). However, the significance of this feedback on climate remains uncertain (Quinn and Bates, 2011; Green and Hatton, 2014). DMS emissions depend directly on surface water DMS concentration which is regulated by marine microorganisms and abiotic processes such as photo-oxidation. When released in the water through exudation, lysis of senescent cells, grazing or viral attack, DMSP and DMSO are involved in a complex chain of phytoplanktonic and bacterial processes leading, among others, to their transformation into DMS (Stefels et al., 2007). Although DMSP and DMSO are produced by phytoplankton, correlating DMS production with phytoplankton biomass (generally expressed in term of Chlorophyll *a*) is challenging (Kettle et al., 1999) because DMSP and DMSO production are species-specific and vary with environmental conditions (e.g. Stefels et al., 2007). Therefore, DMS concentration in seawater is controlled mainly by phytoplankton composition rather than by algal biomass or production (Masotti et al., 2010).

Since the compilation of DMSP content by 123 phytoplankton species by Keller et al. (1989), we know that Dinophyceae and Haptophyceae are the major DMSP producers and diatoms lower DMSP producers with a few exceptions. Similarly, the biogenic production of DMSO is specific and generally correlated to DMSP production (Hatton and Wilson, 2007). There are different sources of specific variability in DMSP and DMSO production including growth stage, salinity, temperature, nutrient limitation and light related to several potential physiological functions of these molecules as osmoregulator (Vairavamurthy et al., 1985), cryoprotectant (Kirst et al., 1991), antioxidant (Sunda et al., 2002), methyl donor (Kiene et al., 2000), grazing deterrent (Wolfe et al., 1997) and overflow mechanism in nitrogen-limiting conditions (Stefels, 2000). DMSP is also a source of carbon (C) and S for heterotrophic organisms (Kiene and Linn, 2000a) and acts as a chemical cue for higher trophic level organisms (Steinke et al., 2002). These physiological functions are not necessarily exclusive (Harada and Kiene, 2011) and phytoplankton cells may use several of them.

In the Belgian Coastal Zone (BCZ) of the North Sea, the phytoplankton succession is characterized by a first diatom bloom in late February-early March, followed by a huge biomass peak of *Phaeocystis globosa* in April–May before summer and autumn diatom blooms (Lancelot et al., 2005) The prymnesiophyte *Phaeocystis globosa* (referred hereafter as *Phaeocystis*) forms extensive blooms representing 95% of the phytoplankton spring community biomass (Rousseau et al., 1990, 2000) and their colonies are estimated as responsible for around 80% of the total annual DMSP production in this zone (Gypens et al., 2014). The area is a permanently well-mixed and eutrophied coastal zone under the influence of the Scheldt and the Rhine rivers. The modification of C and nutrient river loads to the BCZ observed since the 1950's led to important changes of primary production, phytoplankton dominance, and CO_2, CH_4 and DMS concentrations and emissions (Gypens et al., 2009; Gypens and Borges, 2014; Borges et al., 2017).

Seasonal variations DMSP and DMS have been previously studied in the Southern North Sea (SNS) based on field measurements and model applications (Turner et al., 1988; Kwint and Kramer, 1996; van den Berg et al., 1996; Stefels et al., 1995; van Duyl et al., 1998; Archer et al., 2002; Gypens et al., 2014). All of these studies reported a marked seasonal cycle in DMS(P) with a maximum in spring (April–May) corresponding to the *Phaeocystis* bloom followed by a decrease to low winter values. Generally, particulate DMSP (DMSPp) (the intracellular DMSP) represents the main part of the total DMSP (DMSPt) measured in the field, the dissolved DMSP (DMSPd) being quickly consumed or transformed into DMS, DMSO or others degradation products. In the Wadden Sea, van Duyl et al. (1998) measured concentration of DMSPp of about 1650 nmol L^{-1}, and found a significant correlation between DMSPp and the abundance of *Phaeocystis* cells. Turner et al. (1996) reported maximal values of DMSPp and DMS in the SNS of respectively 450 nmol L^{-1} and 25 nmol L^{-1} in May with large concentration gradients over short distances. In the SNS, Liss et al. (1994) have also reported DMS concentrations between 3 and 49 nmol L^{-1} during the *Phaeocystis* bloom. In the BCZ, the maximal DMSPp, DMSPd and DMS concentrations simulated by Gypens et al. (2014) respectively reached 580, 210 and 28 nmol L^{-1} during the *Phaeocystis* bloom. DMS fluxes follow the patterns of DMS concentrations and are highest closest to the coast and between May and July (Turner et al., 1996; Gypens et al., 2014).

Only a few studies focused on DMSO concentrations in the North Sea because of the later evidence of the existence of particulate DMSO (DMSOp) until recent years (Simó et al., 1998) and its importance for the S cycle (Hatton et al., 2004; Green and Hatton, 2014). Unlike DMS and DMSP that are usually restricted to the euphotic zone, DMSO is ubiquitous and dominant throughout the water column (Hatton et al., 2004). As DMSOp production is also taxon-specific and limited to the same taxons that produce DMSPp (Simó and Vila-Costa, 2006), DMSOp peaks are concomitant or follow those of DMSPp (Hatton and Wilson, 2007). Similarly, a strong relationship exists between DMS and DMSO in surface waters (Hatton et al., 1996, 2004) but no correlation has been found between DMSOp and DMSOd (Hatton and Wilson, 2007); the latter being often greater than DMSOp and DMSPd, because it passively diffuses across cellular membranes unlike DMSP. DMSOd also originates from photochemical and microbial oxidation of DMS (Hatton, 2002).

The current study presents the annual cycle of DMSP, DMSO and DMS concentrations measured in the BCZ on a regular grid of fixed stations during the year 2016. The study site is characterized by a high variability in abiotic parameters (salinity, temperature and light), and primary production throughout the year and by a similar phytoplankton taxonomic succession from one year to another (Rousseau et al., 2002). In order to improve understanding of biotic and abiotic controls on DMS(P,O) distribution in the area, the present study aims to: (1) determine the extent and patterns of spatial and seasonal variations in DMSP, DMSO and DMS concentrations related to changing physico-chemical environmental conditions; (2) determine how these concentrations vary in function of phytoplankton abundance and diversity; and (3) compare DMSP cellular content measured in seawater and in laboratory cultures for key-species of the studied phytoplankton succession.

2. Material and methods

2.1. Field sampling

Annual monitoring of a range of physical, chemical and biological parameters was carried out at nine fixed stations regularly sampled as part of national water quality monitoring programs by the VLIZ (Vlaams Instituut voor de Zee) and located along three nearshore-offshore transects covering the BCZ (Fig. 1). Samples were collected between January and December 2016, bi-monthly during spring-summer phytoplankton blooms (mid-February to end of June) and monthly during the rest of the year on the *RV Simon Stevin*. Single samples were carried out at 3 m depth with a 4 L Niskin bottle connected to a conductivity-temperature-depth (CTD) probe (Sea-bird SBE25) for further analysis of phytoplankton diversity and abundance, Chlorophyll *a* (Chl-*a*) and DMS(P,O) concentrations. Salinity, temperature and nutrient data were retrieved from the data collected at the same stations and during the same cruises by the VLIZ in the frame of the LifeWatch sampling campaigns (http://rshiny.lifewatch.be/Station%20data/) (VLIZ, 2017). The surface incident Photosynthetic Active Radiation (PAR) was calculated from the daily global solar radiation data collected at the Oostende station of the Royal Meteorological Institute of Belgium.