Atmospheric Environment 136 (2016) 1–15

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Relationships linking primary production, sea ice melting, and biogenic aerosol in the Arctic

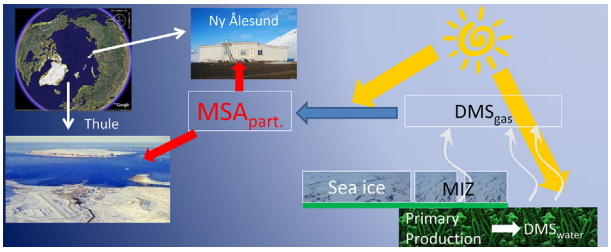
S. Becagli [a, *], L. Lazzara [b], C. Marchese [c], U. Dayan [d], S.E. Ascanius [e], M. Cacciani [f], L. Caiazzo [a], C. Di Biagio [g, h], T. Di Iorio [g], A. di Sarra [g], P. Eriksen [i], F. Fani [b], F. Giardi [a], D. Meloni [g], G. Muscari [l], G. Pace [g], M. Severi [a], R. Traversi [a], R. Udisti [a]

[a] Department of Chemistry, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Florence, Italy
[b] Department of Biology, University of Florence, Via Madonna del piano 6, 50019, Sesto Fiorentino, Florence, Italy
[c] Département de Biologie, Chimie et Géographie, Université du Québec à Rimouski, 300 Allée des Ursulines, Rimouski, Québec, G5L 3A1, Canada
[d] Department of Geography, The Hebrew University of Jerusalem, 91905, Jerusalem, Israel
[e] Danish Meteorological Isntitute, Qaanaaq, Greenland
[f] Physics Department, Sapienza University of Rome, Italy
[g] ENEA, Laboratory for Earth Observations and Analyses, Rome, 00123, Italy
[h] LISA, UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot Institut Pierre Simon Laplace Créteil, France
[i] Danish Meteorological Institute, Copenhagen, Denmark
[l] Istituto Nazionale di Geofisica e Vulcanologia, INGV, Rome, 00143, Italy

HIGHLIGHTS

- MSA is measured at Ny Ålesund (78.9°N, 11.9°E) and Thule Air Base (76.5°N, 68.8°W).
- Primary production (PP) is calculated by a bio-optical model in the surrounding seas.
- PP explains about the 30% of MSA variability in both the Arctic sites.
- MSA and sea ice melting are correlated (slope: 39 ng $m^{-3}$of MSA/10^6 km^2).
- MSA and ice free marginal ice zone are correlated (slope: 56 ng $m^{-3}$of MSA/10^6 km^2).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 November 2015
Received in revised form
1 April 2016
Accepted 4 April 2016
Available online 8 April 2016

Keywords:
MSA
Primary production
Arctic
Marginal sea ice

ABSTRACT

This study examines the relationships linking methanesulfonic acid (MSA, arising from the atmospheric oxidation of the biogenic dimethylsulfide, DMS) in atmospheric aerosol, satellite-derived chlorophyll *a* (Chl-*a*), and oceanic primary production (PP), also as a function of sea ice melting (SIM) and extension of the ice free area in the marginal ice zone (IF-MIZ) in the Arctic. MSA was determined in PM_{10} samples collected over the period 2010–2012 at two Arctic sites, Ny Ålesund (78.9°N, 11.9°E), Svalbard islands, and Thule Air Base (76.5°N, 68.8°W), Greenland. PP is calculated by means of a bio-optical, physiologically based, semi-analytical model in the potential source areas located in the surrounding oceanic regions (Barents and Greenland Seas for Ny Ålesund, and Baffin Bay for Thule). Chl-*a* peaks in May in the Barents sea and in the Baffin Bay, and has maxima in June in the Greenland sea; PP follows the same seasonal pattern of Chl-*a*, although the differences in absolute values of PP in the three seas during the blooms are less marked than for Chl-*a*. MSA shows a better correlation with PP than with Chl-*a*, besides,

* Corresponding author.
E-mail address: silvia.becagli@unifi.it (S. Becagli).

http://dx.doi.org/10.1016/j.atmosenv.2016.04.002

Sea ice melting
Chlorophyll

the source intensity (expressed by PP) is able to explain more than 30% of the MSA variability at the two sites; the other factors explaining the MSA variability are taxonomic differences in the phytoplanktonic assemblages, and transport processes from the DMS source areas to the sampling sites. The taxonomic differences are also evident from the slopes of the correlation plots between MSA and PP: similar slopes (in the range 34.2–36.2 ng $m^{-3}$of MSA/(gC m^{-2} d^{-1})) are found for the correlation between MSA at Ny Ålesund and PP in Barents Sea, and between MSA at Thule and PP in the Baffin Bay; conversely, the slope of the correlation between MSA at Ny Ålesund and PP in the Greenland Sea in summer is smaller (16.7 ng $m^{-3}$of MSA/(gC m^{-2} d^{-1})). This is due to the fact that DMS emission from the Barents Sea and Baffin Bay is mainly related to the MIZ diatoms, which are prolific DMS producers, whereas in the Greenland Sea the DMS peak is related to an offshore pelagic bloom where low-DMS producer species are present. The sea ice dynamic plays a key role in determining MSA concentration in the Arctic, and a good correlation between MSA and SIM (slope = 39 ng m^{-3} of MSA/10^6 km^2 SIM) and between MSA and IF-MIZ (slope = 56 ng m^{-3} of MSA/10^6 km^2 IF-MIZ) is found for the cases attributable to bloomings of diatoms in the MIZ. Such relationships are calculated by combining the data sets from the two sites and suggest that PP is related to sea ice melting and to the extension of marginal sea ice areas, and that these factors are the main drivers for MSA concentrations at the considered Arctic sites.

1. Introduction

Dimethyl sulfide (DMS) produced by marine phytoplankton is the most abundant form of sulfur released from the ocean (Stefels et al., 2007). The precursor of DMS is dimethylsulfoniopropionate (DMSP) which is one of the most relevant phytoplanktonic metabolic compounds, it is mainly produced by Prymnesiophyceae (prymnesiophytes, particularly the coccolithophores *Phaeocystis* spp. and *Emiliania huxleyi*, Keller et al., 1989), Dinophyceae (dinoflagellates, as recently reviewed by Caruana and Malin, 2014), and polar sea-ice diatoms (Kirst et al., 1991; DiTullio et al., 1998). In high-latitude marine areas, DMSP is also produced by sea-ice algae (Levasseur et al., 1994; Arrigo et al., 2012; Boetius et al., 2013) and by the microalgal assemblage in the marginal ice zone (MIZ, the boundary between the open ocean and ice-covered seas Perrette et al., 2011). DMSP is then enzymatically converted into DMS by both microalgae and by heterotrophic bacteria, further it can be uptaken by bacteria and some microalgae (Vila-Costa et al., 2006; Spielmeyer et al., 2011; Ruiz-González et al., 2012), or finally encounter photolysis into other compounds, including MSA. A positive correlation between phytoplankton biomass and DMS, and its derived compound MSA as well (Sharma et al., 2012; Vallina and Simo, 2007), is commonly found: under the so-named 'bloom-dominated regime' DMS conditions (Toole and Siegel, 2004), DMS pattern depends both on microalgal concentration, physiological state and taxonomic composition.

Furthermore, DMS production is related to the physiological state of the cells, increasing under stressed conditions, i.e. stationary/senescent phase (Laroche et al., 1999; Zhuang et al., 2011), grazing (Wolfe and Steinke, 1996), viral lysis (Hill et al., 1998), high UV (which conversely inhibits bacterial DMS uptake; Toole et al., 2006), nutrient-limitation (Sunda et al., 2002) and Fe-limitation (Bucciarelli et al., 2013), named the 'stressed-forced regime' DMS conditions by Toole and Siegel (2004). The 'stressed-forced regime' is typical of temperate seas and the DMS production (and then MSA in atmosphere) are found to be correlated to stress factors such as solar radiation dose, and/or to the specific production index or assimilation number (P^B; i.e. the rate of photosynthetic carbon assimilation per weight of chlorophyll a, Vallina and Simo, 2007; Becagli et al., 2013). Besides, the two DMS regime conditions can co-exist or the latter may follow the "bloom-dominated regime" also in polar sea (Galí and Simó, 2010).

The oceanic DMS flux, estimated using surface ocean DMS concentration data in conjunction with corresponding air-sea exchange coefficients for DMS, has been estimated to be in the range 18–34 Tg yr^{-1} (Lana et al., 2011), accounting for 10–40% of the total sulfur flux (Simó, 2001).

Once in the atmosphere, DMS is oxidized to sulfate and methanesulfonate (MSA) by means of photochemical reactions involving both the heterogeneous and the homogeneous phases (Gondwe et al., 2004). These oxidized sulfur compounds can directly act as cloud condensation nuclei (CCN) or increase the hygroscopicity of already formed particles, enhancing their capability to form CCN (Petters and Kreidenweis, 2007). In this way, the particles formed from DMS oxidation should exert a negative (mitigation) feedback on the solar irradiation - cloud albedo – surface temperature loop at global scale (CLAW hypothesis, Charlson et al., 1987), even though there has been little evidence to support this hypothesis on a regional scale (Quinn and Bates, 2011).

MSA also serves as a tracer for aerosol oceanic sources and changes in MSA may reflect changes in the availability of such sources.

The decline in sea ice extent, coverage and thickness observed in the Arctic over the past decades (e.g., Serreze et al., 2007), and its possible summer disappearance projected within a few decades (Stroeve et al., 2008; Wang and Overland, 2009), is expected to lead to an increase of primary production (PP), both at the local and regional scales (Gradinger, 1995; Loeng et al., 2005; Arrigo et al., 2008; Bélanger et al., 2013). As a consequence of the increased PP the annual DMS flux from the Arctic Ocean is predicted to increase by up to 80% by 2080 (Gabric et al., 2005), possibly as a consequence of changes in phytoplankton productivity associated with shoaling of the mixed layer resulting from sea ice melting.

Several studies have been performed to understand the relation between MSA and the parameters related to biogenic production (Clorophyll-a, hereafter Chl-*a*, sea ice extent) from present day observations and from ice core data in both hemispheres (e.g. Sharma et al., 2012; Isaksson et al., 2005, O'Dwyer et al., 2000; Curran et al., 2003; Abram et al., 2013; Becagli et al., 2009). However, cause and effect associations among, MSA in the atmosphere, changes in sea ice extent, and phytoplankton productivity are yet to be established because several other processes in addition to the source strength play an important role in determining the concentration of MSA at the sampling site. Such processes are the DMS sea-atmosphere exchange, the oxidation efficiency, and the transport processes from the source area to the sampling site (Park et al., 2013; Sharma et al., 2012; Gondwe et al., 2003, 2004).

Moreover, the previous studies do not generally address the role