

## Relationships between methansulfonic acid in PM<sub>10</sub> sampled at two Arctic sites (Ny Ålesund, Thule) and primary production and marginal ice zone in the surrounding seas.

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Keywords: MSA, sea ice, primary productivity, Arctic.

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Recent studies (e.g. Boyce et al 2010) suggest that global marine primary production is declining over the last century and it is expected to decrease again with global warming. Nevertheless, such a decline was not observed in Arctic waters (Bélanger et al., 2013, Behrenfeld et al., 2006) for which despite some regional differences (i.e. North Water Polynya), an increasing trend in primary production is expected as an answer to global warming. An important parameter affecting Arctic primary production is sea ice (e.g. Arrigo et al., 2012). The decline in sea ice extent, coverage and thickness observed in the Arctic over the past decade, and its eventual disappearance during summer, is expected to promote increased primary production, both in situ and as areal average (Bélanger et al., 2013). The biogenic productivity and atmospheric particulate are correlated by dimethylsulfide (DMS) emission by phytoplankton. Once in the atmosphere, DMS is oxidized to produce H<sub>2</sub>SO<sub>4</sub> and methanesulfonic acid (MSA). These oxidised sulfur compounds can act as precursor of cloud condensation nuclei or they can increase the size of particles on which they condense, enhancing the particle hygroscopicity, in turn enhancing their CCN activity

This study examines the relationships between MSA in the atmospheric particulate, sampled in two Arctic sites (Ny Ålesund, Svalbard islands 78.9°N, 11.9°E, and Thule, Greenland 76.5°N, 68.8°W) over the period 2010-2012, and satellite chlorophyll (Chl-a) and related primary production (PP) in the potential source areas located in the surrounding oceanic areas (Barents and Greenland Seas for Ny Ålesund, and Baffin Bay for Thule).

Primary Production and Chl-a follows the same seasonal pattern, nevertheless the differences in absolute values of PP in the three seas during the blooms are less marked than that of Chl-a. This is due to the eco-physiological variability of phytoplankton, e.g. photo-adaptation processes (different amounts of Chl- a in the cell as function of light availability), nutrient limitation and metabolic adaptations. Indeed, PP depends on Chl-a concentration, but its main limiting factor is the photosynthetic active radiation.

The source area of MSA at Ny Ålesund is mainly the Barents Sea, as confirmed by the significant correlation obtained during spring and summer period between MSA and PP, conversely the linear regression

MSA-PP in Greenland Sea is significant only in summer. Transport processes play an important role in determining MSA concentration at the sampling sites, for instance, at Ny Ålesund, anomalous high MSA concentrations were measured in condition of intense transport processes of air masses from the Barents Sea. At Thule a significant correlation between MSA and PP in Baffin Bay over the examined period is obtained. Back trajectories analysis show that Baffin Bay is the dominant source area of MSA at Thule.

The MSA vs PP slopes are similar for Barents Sea and Baffin Bay and they are higher than Greenland Sea, these differences are due to taxonomic differences in the phytoplanktonic assemblages. Indeed, MSA at both sites is mainly related to MIZ coccolithophores and ice diatoms that are prolific producers of DMS. Conversely, in the Greenland Sea DMS peak is mainly related to off-shore blooms, of coccolithophores and flagellates.

Significant correlations are found between MSA at Ny Ålesund and Thule and sea ice coverage melting and marginal sea areas extension in Barents Sea and Baffin Bay respectively, suggesting that source intensity (i.e. primary production) is related to sea ice melting and the extension of marginal sea ice areas and these factors are the main driver for MSA concentration in the considered Arctic sites. Besides, in Barents Sea and Baffin Bay, sea ice plays a role in triggering phytoplankton activity at the ice-edge, and the MSA increasing trend is related to the timing of sea ice melting. Conversely, as previously mentioned for the Greenland Sea the off-shore bloom is independent from sea ice melting, and MSA at Ny Ålesund and marginal ice areas (and melting) do not show to correlate.

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