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Methanesulfonic acid in a Svalbard ice core as an indicator of ocean climate

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Abstract. Methanesulfonic acid (MSA) is an atmospheric oxidation product of dimethyl sulfide, produced by marine biota. MSA preserved in a Svalbard glacier between 1920 and 1996 is compared with the sea surface temperature (SST) and sea-ice extent of the surrounding ocean over the same period. On decadal timescales high MSA concentrations are found to be associated with warm SST and reduced sea-ice extent. MSA appears to be influenced by climatic changes related to variations in the import of warm Atlantic Water to the Barents Sea. Atlantic Water plays an important role in the Arctic climate system, therefore MSA concentrations may indirectly reflect larger-scale changes in the region and may be useful as a proxy for past climate.

Introduction

Methanesulfonic acid (MSA) in the snow deposited on a glacier forms a stratigraphic record of atmospheric concentrations. The only source of MSA appears to be the atmospheric oxidation of dimethyl sulfide (DMS), which is emitted by marine biota [*Saltzman et al.*, 1983, 1986]. The MSA record has therefore been used as an indicator of the strength of the marine biogenic source of DMS [*Ivey et al.,* 1986; *Saigne and Legrand,* 1987]. MSA concentrations in the ice will be affected by (i) conditions at the source location influencing primary productivity, phytoplankton species, and air-sea exchange of DMS, (ii) atmospheric conditions influencing the oxidation pathways of DMS or altering the source location, (iii) conditions at the glacier. Thus variations in air and sea temperatures, precipitation patterns, sea-ice conditions, winds and ocean currents can affect MSA concentrations, and all these parameters are intimately linked through the complex interactions of the climate system. It has been suggested that the sulfur cycle itself actively contributes to climate regulation through the role of the sulfur aerosol in cloud formation [*Charlson et al.*, 1987]. Although sulfate is the major component of the cycle, MSA makes a significant contribution in the marine atmosphere [*Bates et al.*, 1992].

Here we examine the MSA record for the period from 1920 to 1996 in an ice core taken from a glacier on Svalbard (Fig. 1). During this period observations of sea-ice extent and ocean temperature are available for the region around Svalbard, and these are compared with MSA concentrations. By contrast with the century timescale of observational timeseries, Arctic glaciers contain a record extending back several thousand years. If changes in MSA concentration are correlated with changes in climate then ice cores can give information about climate on these long timescales.

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Climatic conditions around Svalbard

The climate around Svalbard is mild for its latitude due to the presence of warm Atlantic Water flowing northward in a continuation of the Gulf Stream (Fig. 1). The current splits south of Svalbard and one branch flows to the west of Svalbard, through the Fram Strait and into the Arctic Ocean. A second branch flows eastward into the Barents Sea where it forms a tongue of warm, saline surface water [*Matishov et al.*, 1998].

Sea-ice is another important component of the Arctic environment. Ice cover strongly affects exchanges between the atmosphere and the ocean, and thus climate. Ice also affects marine biota [*Clarke and Ackley*, 1984]. Thick ice prevents the growth of phytoplankton, but in spring and summer the melting ice creates a highly productive environment in which a fresh surface layer inhibits vertical mixing, holding phytoplankton in the euphotic zone. Combined with long daylight hours this leads to high rates of photosynthesis. For example, in the Arctic Ocean the highest concentrations of DMS are found in open water at the ice edge, and the lowest concentrations beneath heavy pack ice [*Leck and Persson*, 1996a, b]. The sea-ice extent around Svalbard varies on seasonal, annual and decadal timescales. As shown in Fig. 1, at the end of a severe winter sea-ice can extend several degrees south of Svalbard, whilst in other winters the ocean around Svalbard is almost ice-free [*Vinje*, 2000].

Mean sea level pressure fields from the NCEP reanalysis (accessible via FTP from ncardata.ucar.edu/pub/reanalysis/monthly) imply easterly geostrophic winds over the region around Svalbard, stronger in winter and weaker in summer. This suggests that the Barents Sea to the east of Svalbard will be an important source of the MSA in snow deposited on Svalbard.

Results

MSA

In 1997 a 124 m long ice core was retrieved from Lomonosovfonna, the highest ice field on Svalbard at 1230 masl (Fig. 1). Radar measurements indicated a total ice depth of 126.5 m, and temperature measurements from the borehole indicated that the ice was below the melting point. The top 36 m of the core were sampled at high resolution [*Isaksson et al.*, 1998] and dated using two independent methods [*E. Isaksson et al.,* manuscript in preparation, 2000]. The

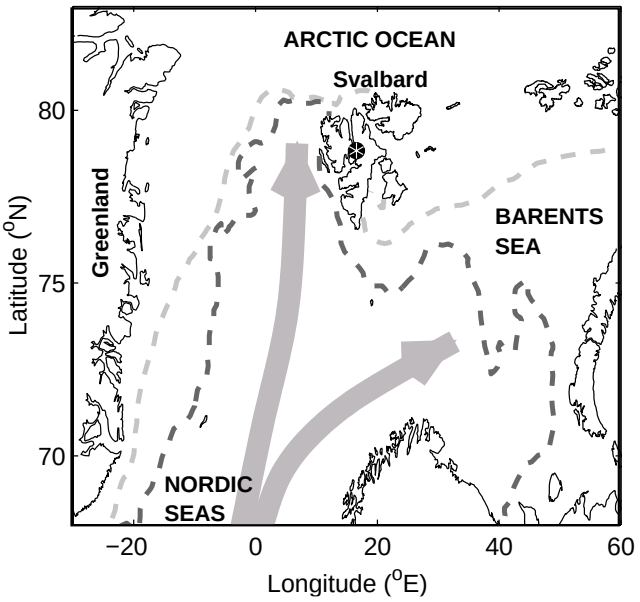

Figure 1. Svalbard and the surrounding region. The ice core drilling site at Lomonosovfonna on Svalbard is marked *. Arrows show the northward flow of warm Atlantic water into the Arctic Ocean and the Barents Sea. Broken lines mark the end-of-winter ice edge positions in 1980 (dark grey) and 1995 (light grey).

first method used the seasonal variation of the different ion records, and by counting the layers and using the ^{137}Cs peak from 1963 (at 18.50–18.95 m depth) as a reference layer, the ice core was dated back to 1920. The second method assumed a constant accumulation rate of 36 g cm^{-2} yr^{-1} with thinning by pure shear [*Nye*, 1963]. The methods give ages which agree to within three years at 36 m depth.

MSA concentration in 280 samples was determined by suppressed ion chromatography, as described by *Jauhiainen et al.* [1999]. The precision of the method and total uncertainty at the 5 ng g^{-1} level were 7% and 21% respectively and the accuracy was confirmed by an interlaboratory comparison test between three laboratories (p-value 0.227 at 95% confidence). The detection limit of MSA was 0.3 ng g^{-1}. MSA was not found in blank samples prepared by freezing pure water in PE measuring cylinders, which were handled in the same way as the ice core samples.

Annual mean MSA concentrations have large interannual and interdecadal variability (Fig. 2a), with a mean of 7.1 ng g^{-1} and a standard deviation of 7.5 ng g^{-1}. For our analysis of variability on decadal and longer timescales, the annual values were smoothed with a five-year running mean.

There are some clear differences from MSA in Greenland ice cores over the same period. The accumulation rate at the 20D site in southern Greenland [*Whung et al.*, 1994] is similar to that at Lomonosovfonna, but MSA concentrations in the 20D core are less than half those at Lomonosovfonna. This is also true for the central Greenland GISP site [*Legrand et al.*, 1997] where there is a lower accumulation rate. Both the Greenland sites have a recent decrease in MSA (starting around 1900 in southern Greenland and 1945 in central Greenland), whereas MSA in the Lomonosovfonna core exhibits no significant trend over the twentieth century.

Sea surface temperature

Timeseries of sea surface temperature (SST) in selected seasons were calculated for regions to the east and west of Svalbard. The time of year of the timeseries depended upon the available data. Hydrographic stations were selected that had been repeated at least 20 times and SST was defined as the average temperature over the upper 50 m. For each set of stations annual averages were calculated and the resulting timeseries were smoothed with a five-year running mean.

In the Barents Sea, in the area 72–76°N, 30–40°E, which lies in the main path of Atlantic Water inflow, timeseries of winter (January to March) and summer (July to September) SST were calculated using data from *Matishov et al.* [1998] (Fig. 2b). Data were available in 32 and 39 years

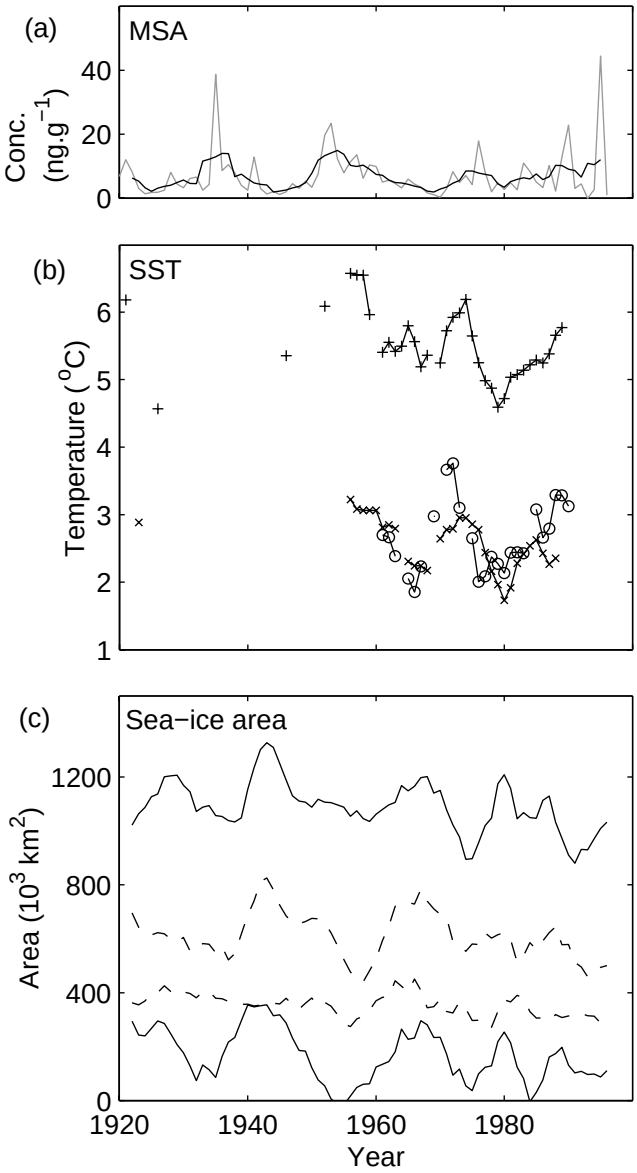

Figure 2. (a) Annual mean (grey) and five-year running mean (black) of MSA concentration. (b) Five-year running means of SST in the Barents Sea in summer (+) and winter (×), and west of Svalbard in autumn (o). (c) Five-year running means of sea-ice extent in April and August to the east (full lines) and west (broken lines) of Svalbard.

for winter and summer respectively. Before 1955 the data is sparse, although there are indications of high SST at the start of the 1920s and increasing SST from the mid-1940s to the mid-1950s. The timeseries are nearly continuous after 1955 and SST variability corresponds closely to that of MSA, with a decrease in SST from 1955 to 1970, a peak in 1974, and a gradual increase after 1980. High MSA concentrations are associated with warm conditions in the Barents Sea with correlation coefficients (significant at the 99% confidence level) of $R = 0.55$ for winter SST and $R = 0.58$ for summer SST.

To the west of Svalbard data from 30 years between 1959 and 1992 from the Norwegian Polar Institute were used to calculate autumn (September to November) SST (Fig. 2b). Comparing with Fig. 2a, MSA appears to lag the SST and the correlation coefficient, $R = 0.23$, is not significantly different from zero. Higher coefficients are obtained when the SST timeseries is lagged, the maximum, $R = 0.69$ (significant at the 99% confidence level), occurring with a lag of three years. This time-lag suggests that ocean conditions to the west of Svalbard and MSA concentrations may be indirectly linked by the larger scale ocean circulation.

Sea-ice

Vinje [2000] derived a 400 year record of sea-ice area in the Svalbard region from ships' logbooks. Here we use timeseries of ice extent in regions to the east and west of Svalbard in winter (April) and summer (August) of each year, smoothed with a five-year running mean. Fig. 2c shows that the variations of ice extent are similar in these two regions and in different seasons, and a comparison with Fig. 2a indicates an inverse relationship with MSA concentration. The correlations of MSA concentration with the sea-ice extent are all significant at the 99% confidence level, with coefficients of $R = -0.51$ and $R = -0.56$ for winter sea-ice extent to the east and west of Svalbard respectively, and of $R = -0.66$ and $R = -0.37$ for summer sea-ice extent to the east and west of Svalbard. High MSA concentrations are thus associated with reduced ice extent, and the strongest correlation is with summer ice extent in the Barents Sea.

Discussion

It is difficult to unravel the climatic parameters affecting MSA concentrations in an ice core. Sea surface temperatures, air temperatures, wind fields and sea-ice extent are not mutually independent and they can all influence the concentration of MSA in the ice on Svalbard, probably through more than one route. Prevailing easterly winds suggest the Barents Sea as the main source of MSA in snow deposited on Svalbard and concentrations in the ice core do appear to be more strongly linked with conditions in the Barents Sea than with conditions to the west.

No consistent picture emerges from studies of the links between sea-ice, SST, and MSA in ice cores. In the Antarctic a positive correlation between MSA in a snow core from Newall Glacier (a coastal site) and sea-ice in the Ross Sea was found [*Welch at al.*, 1993] and this was explained in terms of increased growth of phytoplankton in heavy ice years, giving high atmospheric MSA concentrations [*Bunt*, 1963], [*Bunt and Wood*, 1963]. A negative correlation between MSA in a core from a relatively coastal site on the Antarctic Peninsula, and the sea-ice in Scotia Bay in the South Orkney Island [*Pasteur et al.*, 1995] was explained by lower local DMS emission during heavy sea-ice years due to the specific circulation conditions in the Weddell Sea. In the Northern Hemisphere, on Greenland, *Whung et al.* [1994] found a negative correlation between North Atlantic SST and MSA in an ice core from the 20D site, and *Legrand et al.* [1997] found a positive correlation between sea-ice and MSA in an ice core from the GRIP site.

The variation of MSA in the Svalbard ice core is very different from that in the Greenland ice cores, demonstrating that trends over the Arctic region are not uniform. In contrast to the Greenland ice cores we find a negative correlation with sea-ice extent and a positive correlation with SST, i.e., high MSA concentrations are associated with years when the surrounding ocean is warm and has reduced sea-ice extent. SST and sea-ice extent are strongly linked, so it is not clear from this correlation analysis which has the most important influence on MSA. In the Arctic Ocean, however, sea-ice and sea-ice meltwater are seen to strongly affect DMS production [*Leck and Persson*, 1996a]. Possible links between reduced sea-ice extent and high MSA are the larger area of open water available for biological production, and the longer period of time for which ice-free water is present in years with reduced sea-ice extent.

Atlantic Water in the Barents Sea is derived from the same source as the Atlantic Water which flows to the west of Svalbard and into the Arctic Ocean (Fig. 1), and both carry the signal of the Atlantic Water variability. Thus the MSA concentrations which correlate with SST in the Barents Sea are also reflecting larger-scale variability in the ocean circulation in the Nordic Seas and Arctic Ocean, an important component of the region's climate system. The signals to the east and west of Svalbard will be out of phase if there is a difference in the times taken by Atlantic Water to travel to these two regions and this could explain the time-lag between the signal in SST west of Svalbard and the signal in MSA.

The remainder of the core, estimated to cover the last thousand years, is currently being analysed. Future work will include an investigation of the complete MSA record from the core in relation to the reconstructed 400 year record of Barents Sea ice extent [*Vinje*, 2000].

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