

## Sulfate source apportionment in the Ny-Ålesund (Svalbard Islands) Arctic aerosol

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Received: 25 November 2015 / Accepted: 26 February 2016 / Published online: 28 March 2016  
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**Abstract** Daily PM10 aerosol samples were collected at the Gruvebadet observatory, Ny-Ålesund (Svalbard Islands), during the spring-summer 2014 Italian Arctic Campaign. A total of 136 samples were analysed for ion (inorganic anions and cations, selected organic anions) composition aiming to evaluate the seasonal pattern of sulfate, as a key component of the Arctic haze. Ionic balances indicated a strong sulfate seasonality with mean spring concentration about 1.5 times higher than that

measured in summer. The spring and summer aerosol was almost neutral, indicating that ammonia was the major neutralizing agent for atmospheric acidic species. The linear regression between sulfate from potential acidic sources (non-sea salt sulfate and non-crustal sulfate) and ammonium indicated that the mean sulfate/ammonium ratio was intermediate between semi- $(\text{NH}_4\text{HSO}_4)$  and complete  $((\text{NH}_4)_2\text{SO}_4)$  neutralization. Using sea-salt sodium as sea-spray marker, non-sea-salt calcium as crustal marker and methanesulfonic acid as biogenic marker, a detailed source apportionment for sulfate was carried out. The anthropogenic input (calculated as the differences between total sulfate and the sum of sea-salt, crustal and biogenic contributes) was found to be the most relevant

This peer-reviewed article is a result of the multi and interdisciplinary research activities based at the Arctic Station “Dirigibile Italia”, coordinated by the “Dipartimento Scienze del Sistema Terra e Tecnologie per l’Ambiente” of the National Research Council of Italy.

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contribution to the sulfate budget in the Ny-Ålesund aerosol in summer and, especially, in spring. In this last season, crustal, sea-salt, biogenic and anthropogenic sources accounted for 3.3, 12.0, 11.5 and 74.8 %, respectively.

**Keywords** Arctic aerosol · Sulfate sources · Anthropogenic input · Biogenic emissions · Spring-summer pattern

## 1 Introduction

Atmospheric aerosol plays a key role in the complex feedback processes between climate forcings and environmental responses, through the interaction with the solar irradiance. Such interaction involves direct effects, by scattering and absorption processes (RF<sub>air</sub>—radiation forcing by aerosol-radiation interaction) and indirect effects on Earth albedo (RF<sub>aci</sub>—radiation forcing by aerosol-cloud interaction), because atmospheric particles act as cloud condensation nuclei (IPCC 2013). By considering scattering and absorption processes of several aerosol components, the IPCC (2013) Report estimates that the RF<sub>air</sub> effect accounts for an overall cooling forcing of about  $-0.35 \text{ W/m}^2$ , with a large uncertainty ( $\pm 0.5 \text{ W/m}^2$ ). A similar cooling forcing ( $-0.4 \text{ W/m}^2$ ) is also exerted by the RF<sub>aci</sub> effect, with an even higher uncertainty (IPCC 2013). Such uncertainties are so large, with respect to the averaged RF<sub>air</sub> and RF<sub>aci</sub> values, to make uncertain also the sign of the forcing. This is particularly true for polar aerosol because, in the Polar Regions, the negative forcing by the surface albedo (snow cover and sea ice) is higher than that produced by cloud coverage and scattering processes, so leading to a positive aerosol forcing. Besides, size distribution and chemical composition data on polar aerosol have scarce spatial and temporal coverage, due to the little number of monitoring sites and logistic difficulties. Indeed, just few stations are carrying out continuous measurements on Arctic aerosol. These sites include: Alert

(Canadian Arctic), Station Nord (Northern Greenland), Zeppelin (Svalbard Islands), Barrow (Alaska), Karasjok and Svanvic (Northern Norway), Oulanka (Northern Finland) and Janiskoski (Northern Russia) (Quinn et al. 2007). The chemical characterization of aerosol collected in these stations revealed that the Arctic atmosphere is characterized by the so-called “Arctic haze”, mainly occurring in spring. This phenomenon was at the beginning attributed to natural processes affecting the atmosphere transparency but, since late 1970s, the anthropogenic origin of the Arctic haze (via atmospheric transport of contaminants from polluted continental areas) was established by the chemical composition of the atmospheric particulate (see Quinn et al. 2007, for references). The Arctic haze is mainly composed by a mixture of sulfate, organic particulate matter, ammonium, nitrate, dust, black carbon and heavy metals (Li and Barrie 1993; Quinn et al. 2002, 2007), in particles especially distributed in the accumulation mode (Tunved et al. 2013).

As sulfate is the dominant component in the Arctic haze, several studies were carried out to understand the inter- and intra-annual trends of sulfur-cycle compounds in the Arctic aerosol (e.g., Hara et al. 2003; Scheuer et al. 2003; Quinn et al. 2007; VanCuren et al. 2012; Nguyen et al. 2013) and in ice cores drilled in northern hemisphere (e.g., Isaksson et al. 2005; Goto-Azuma and Koerner 2001). In particular, extensive data set of aerosol chemical composition are available for the Zeppelin Station (Ny-Ålesund,  $78^{\circ}54' 29'' \text{ N}$ ,  $11^{\circ}52' 53'' \text{ E}$ , 474.0 m a.s.l.) at the WEB site [ebas.nilu.no](http://ebas.nilu.no) (e.g., Aas et al. 2015).

Since 2010, an Italian infrastructure (Gruvebadet observatory) was installed in Ny-Ålesund (Svalbard Islands), aiming to study the physical and chemical properties of the Arctic aerosol (Viola et al. 2013; Udisti et al. 2013; Calzolari et al. 2014; Moroni et al. 2015; Bazzano et al. 2015). At the Gruvebadet observatory, aerosol samples were collected in the spring-summer period at different resolution by several sampling devices, including PM<sub>10</sub> samplers and multi-stage impactors.

Here, we report the record of spring-summer sulfate concentrations measured at daily resolution during the 2014 Italian Arctic Campaign. Particular effort was made to identify and quantify the natural and anthropogenic sources of sulfate particulate reaching Ny-Ålesund, by using specific markers for sea spray, crustal and biogenic sources (anthropogenic contribution was evaluated by difference with respect to the total sulfate content).

To our knowledge, this is the first complete source apportionment of sulfate in the Arctic aerosol.

Results here reported can be useful in evaluating the relevance of the impact of anthropogenic aerosol on the critical Arctic ecosystem and in improving climate models based on aerosol-solar irradiation feedback processes.

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## 2 Methodology

### 2.1 Sampling area

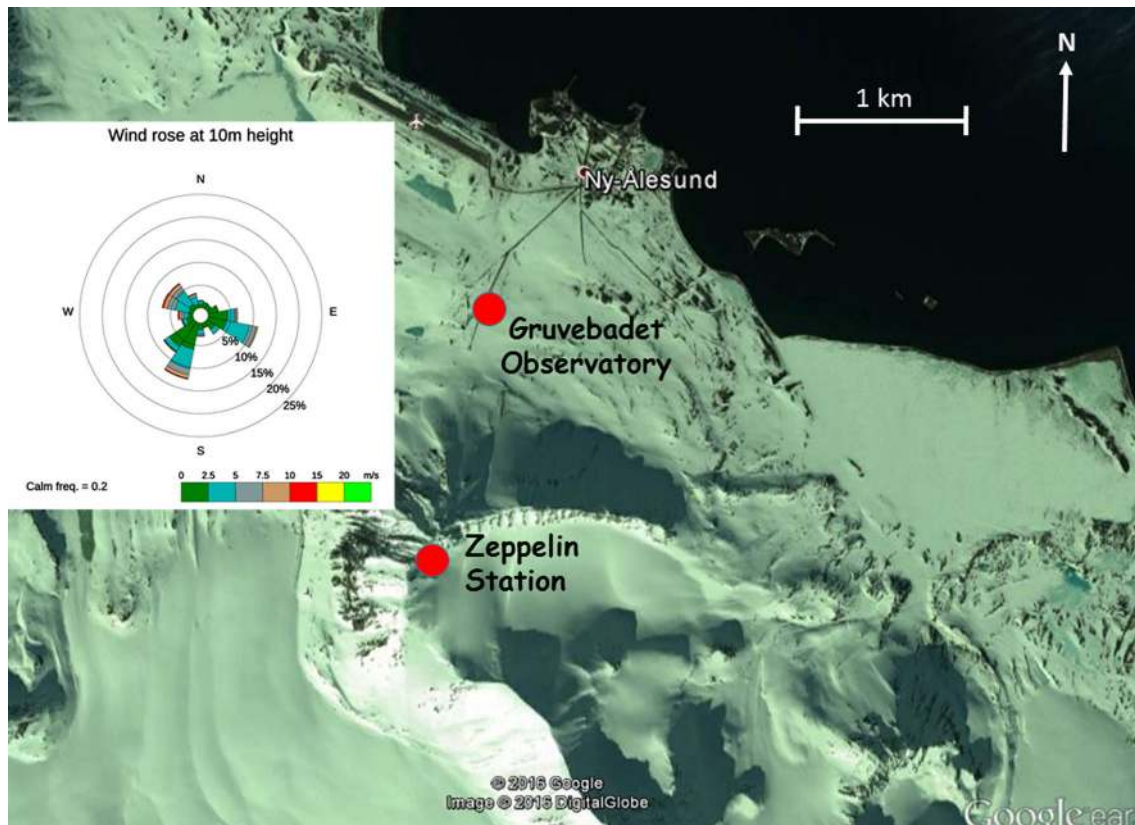
The spring-summer 2014 campaign was carried out at the Gruvebadet Observatory (GVB), located at about 50 m a.s.l., 800 m south-west from the Ny-Ålesund village (78°55′N, 11°56′E), Svalbard Islands. Ny-Ålesund is located in the Kongsfjorden fiord that develops in the north-west south-east direction, so that dominant winds are channelled in the same direction. In this way, the geographical position of the GVB observatory guarantees for the lowest impact from local emissions. Besides, around GVB, especially in the north-east side overlooking the Ny-Ålesund village, a clean area was established and snow mobile traffic and other potentially contaminant activities were forbidden.

Figure 1 shows the Ny-Ålesund area satellite view, where the Zeppelin Station and Gruvebadet Observatory are marked. In the same figure, the wind direction and speed mean values are reported for the period April–September 2014. The wind rose was obtained from Amundsen-Nobile Climate Change Tower measurements (CCT, Mazzola et al. 2016). The CCT is located about

1 km away from Gruvebadet, in the West direction. The two most frequent flows are those from the Kongsvegen glacier (direction E-SE) and from the Brøggerbreen glaciers (direction S-SW). The third notable flow is again along the fiord, but coming from the open sea (direction W-NW), and it is mostly present during summer. These results are consistent with those from Maturilli et al. (2013), obtained from another nearby meteorological station. It is important to note that the contribution of wind coming from the Ny-Ålesund village is practically absent, therefore excluding a significant local anthropogenic contamination of the aerosol samples.

### 2.2 Aerosol sampling

Aerosol samples were continuously collected on daily basis (00:01–23:59, Universal Time Coordinated—UTC) from 31 March to 09 September 2014, by a Tecora SkyPost low-volume sampler, equipped with a PM<sub>10</sub> (particulate matter smaller than 10 μm aerodynamic equivalent diameter— a.e.d.) head. Samplings were carried out in actual conditions: pressure and temperature were continuously monitored to maintain a constant flow rate of 38.3 L/min (EN 12341 European rules), corresponding to a 24 h air volume



**Fig. 1** Satellite view of the Ny-Ålesund area with wind rose for the period April–September 2014. The sites of Gruvebadet and Zeppelin are also marked

of about 55 m<sup>3</sup>. Particulate matter was collected on Teflon filters (Pall R2PJ047, 47 mm diameter, 2 μm nominal porosity). After sampling, filters were individually sealed in pre-washed (Milli-Q water, 18.3 MΩ) polystyrene filter containers and stored at −20 °C until analysis. PM<sub>10</sub> mass was measured by weighing the filters with a microbalance (0.01 mg sensitivity) before and after exposure. The filters were conditioned at low humidity (silica gel) and controlled temperature (25 ± 1 °C) for at least 24 h before the weighing. A sample loss occurred in the periods 19th Apr–7th May and 07th–12th August due to system failures. During the 2014 campaign, a total of 136 samples were collected.

At the analysis time, one half of each PM<sub>10</sub> Teflon filter was extracted in about 10 ml Milli-Q water (accurately evaluated by weighing) by ultrasonic bath for 20 min, for ionic content determination. Every filter manipulation was carried out under a class-100 laminar-flow hood, to minimize contamination risks. Inorganic anions and cations, as well as selected organic anions, were simultaneously measured by using a three Dionex ion-chromatography system, equipped with electrochemical-suppressed conductivity detectors. The sample handling during the IC injection was minimized by using a specifically-designed Flow-Injection Analysis (IC-FIA) device (Morganti et al. 2007). Cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) were determined by using a Dionex CS12A-4 mm analytical column with 20 mM H<sub>2</sub>SO<sub>4</sub> eluent. Inorganic anions (Cl<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup> and C<sub>2</sub>O<sub>4</sub><sup>2−</sup>) were measured by a Dionex AS4A-4 mm analytical column with a 1.8 mM Na<sub>2</sub>CO<sub>3</sub>/1.7 mM NaHCO<sub>3</sub> eluent. F<sup>−</sup> and some organic anions (acetate, glycolate, formate and methanesulfonate) were determined by a Dionex AS11 separation column by a gradient elution (0.075–2.5 mM Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> eluent). A six-standard calibration curve was daily used for quantification. Further details are reported in Udisti et al. (2004) and Becagli et al. (2011).

Here, only sulfate data are in depth discussed, referring to sodium, calcium, ammonium and methanesulfonic acid just as ancillary measurements. PM10 atmospheric load (by filter weighing) and ions concentrations will be discussed in a further paper.

### 2.3 Calculation of the ion fractions

Ny-Ålesund aerosol contains not-negligible contributions of sea salt and crustal components, so that Na<sup>+</sup> and Ca<sup>2+</sup>, which originate from both these sources, cannot be used as univocal sea spray and crustal markers, respectively. To quantify the sea-salt (ss-) and non-sea-salt (nss-) contributions of these elements in every sample, we used a simple equation system (Becagli et al. 2012; Udisti et al. 2012):

$$\text{tot-Na}^+ = \text{ss-Na}^+ + \text{nss-Na}^+$$

$$\text{tot-Ca}^{2+} = \text{ss-Ca}^{2+} + \text{nss-Ca}^{2+}$$

$$\text{ss-Na}^+ = \text{tot-Na}^+ - 0.562 \text{ nss-Ca}^{2+}$$

$$\text{nss-Ca}^{2+} = \text{tot-Ca}^{2+} - 0.038 \text{ ss-Na}^+$$

where 0.562 represents the Na<sup>+</sup>/Ca<sup>2+</sup> weight-to-weight (w/w) ratio in the crust (Bowen 1979), and 0.038 is the Ca<sup>2+</sup>/Na<sup>+</sup> w/w ratio in seawater (Nozaki 1997).

The sea-salt fraction of sulfate (ss-SO<sub>4</sub><sup>2−</sup>) was calculated by multiplying the ss-Na<sup>+</sup> (as sea spray marker) concentration by 0.253 (indicating the SO<sub>4</sub><sup>2−</sup>/Na<sup>+</sup> w/w ratio in seawater—Bowen 1979).

The non-sea-salt fraction of sulfate (nss-SO<sub>4</sub><sup>2−</sup>) was calculated by subtracting the ss-SO<sub>4</sub><sup>2−</sup> contribution from the tot-SO<sub>4</sub><sup>2−</sup> concentrations.

The crustal fraction of sulfate (cr-SO<sub>4</sub><sup>2−</sup>) was estimated by multiplying the nss-Ca<sup>2+</sup> (as crustal marker) content by 0.59 (SO<sub>4</sub><sup>2−</sup>/Ca<sup>2+</sup> w/w ratio in the uppermost Earth crust—Wagenbach et al. 1996).

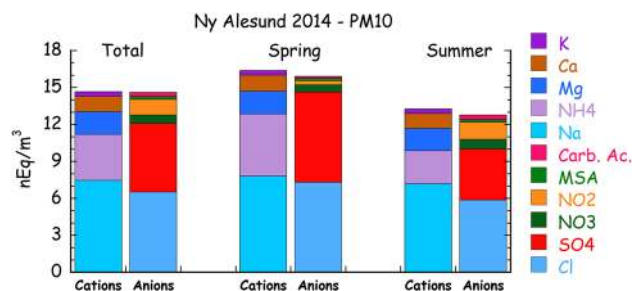
The sulfate contribution from marine phytoplanktonic activity (via atmospheric oxidation of dimethylsulfide—DMS-emitted from micro-algal population) was estimated by multiplying the methanesulfonate (MSA—as specific marker of marine biogenic emissions) concentration by 3.0 (see, Sect. 3.3).

## 3 Result and discussion

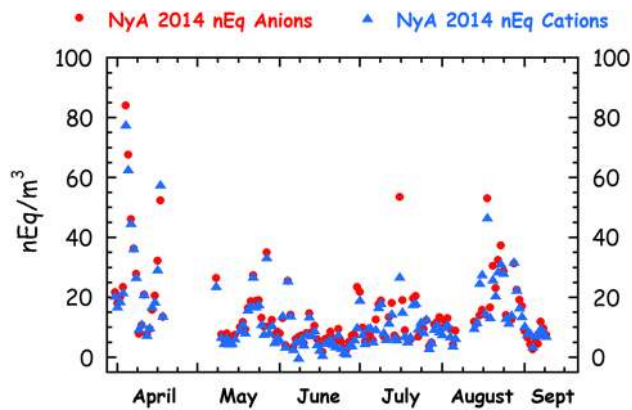
### 3.1 Ionic balances

Figure 2 shows the ionic balances (expressed as nEq/m<sup>3</sup>) of the PM<sub>10</sub> aerosol samples collected in Ny-Ålesund during the spring-summer 2014 campaign (136 samples).

The ionic composition is dominated by two main components: sea spray (marked by Na<sup>+</sup>, Cl<sup>−</sup>, Mg<sup>2+</sup> and, partially, SO<sub>4</sub><sup>2−</sup>) and secondary aerosol (marked by sulfate, ammonium, nitrate and nitrite). The all-period (total) plot shows that Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> were the major cations, accounting for 51 and 25 % of the cation content,



**Fig. 2** Ionic balances (in nEq/m<sup>3</sup>) for all-period (total) and seasonal aerosol samples collected at Ny-Ålesund during the 2014 campaign

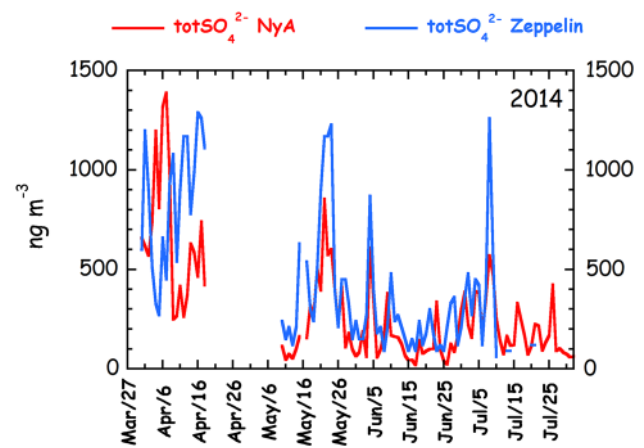


**Fig. 3** Ny-Ålesund PM<sub>10</sub> anions (red dot) and cations (blue triangle) budget (nEq/m<sup>3</sup>) along the sampling period

respectively. In the same way, chloride and sulfate dominate the anion budget (45 and 38 %, respectively). Such components, however, are not equally distributed in the spring and summer samples, showing a sharp seasonal pattern. Indeed, sulfate and ammonium show the highest contribution (both in absolute quantity and in ion percentage) in spring. In this season, NH<sub>4</sub><sup>+</sup> accounts for 30 % of the cation budget, while SO<sub>4</sub><sup>2-</sup> reaches a contribution as high as 46 % of the anion content. In particular, sulfate accounts for 19 % (5.6 nEq/m<sup>3</sup>), 23 % (7.3 nEq/m<sup>3</sup>) and 16 % (4.1 nEq/m<sup>3</sup>) of the total ion content (anions plus cations) in all-period, spring and summer samples, respectively. All-period and seasonal ionic balances show that anions and cations are almost balanced, indicating a quite completely neutralized aerosol. Figure 3 shows the anions and cations sums (as nEq/m<sup>3</sup>) for all the collected samples. Besides experimental errors (cumulative uncertainties evaluated around 10 %), anions and cations are also balanced day by day, with very few exceptions (4–5 April, 15 July, 18 August), when a significant free acidity is evident (especially on 15 July). This evidence means that acidic species, such as H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, were almost neutralized by ammonia, to give ammonium salts, in the atmosphere during the transport from the source areas to the deposition site.

### 3.2 Total sulfate profile

Figure 4 shows the temporal profile of total sulfate measured at the GVB (this paper) and Zeppelin (Aas et al. 2015) sites in the period 31 March–09 September 2014. Unfortunately, continuous daily Zeppelin data are available just up to 10 July, so that the comparison can be carried out only for the late spring to early summer period. Besides, we have to note that Zeppelin data are more representative of free tropospheric circulation (474 m a.s.l.), while the measurements at GVB (50 m a.s.l.) are strongly related to



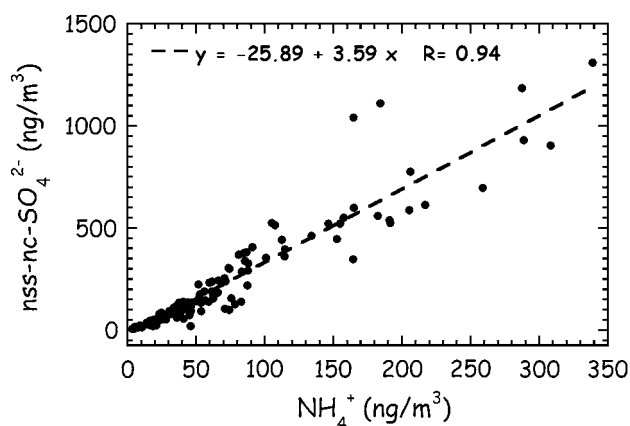
**Fig. 4** Comparison between the total sulfate atmospheric concentrations at Ny-Ålesund (red line) and Zeppelin (blue line) in the spring-mid summer 2014

the Planetary Boundary Layer (PBL) dynamics, so that the aerosol concentrations are affected by the height of the mixing layer. In spite of the different sampling cut-off (PM<sub>10</sub> for NyA and Total Suspended Particulate—TSP—for Zeppelin), the sulfate profiles match quite well in the summer (May–early July), even if the sulfate spikes around 21 May, 04 June and 08 July show significantly higher concentrations at the Zeppelin site. On the contrary, spring profiles are quite different, possibly due to the different aerosol atmospheric load below and above the PBL in such period, when the vertical atmospheric structure is well layered.

### 3.3 Sulfate/ammonium relationship

To evaluate the neutralizing effect of ammonia on H<sub>2</sub>SO<sub>4</sub>, we studied the relationship between the concentrations of NH<sub>4</sub><sup>+</sup> and of the sulfate species mainly originated in acidic form. Sea-salt sulfate originates mainly as Na<sub>2</sub>SO<sub>4</sub>, and crustal sulfate as CaSO<sub>4</sub>. Therefore, their contribution has to be subtracted from the total sulfate content. By using ss-Na<sup>+</sup> as sea spray marker and nss-Ca<sup>2+</sup> as crustal indicator, the ss-SO<sub>4</sub><sup>2-</sup> and cr-SO<sub>4</sub><sup>2-</sup> fractions were calculated, following the equations shown in Sect. 2.3, and their values were removed from the tot-SO<sub>4</sub><sup>2-</sup> concentration, then obtaining the nss-nc-SO<sub>4</sub><sup>2-</sup> fraction. By plotting nss-nc-SO<sub>4</sub><sup>2-</sup> vs. NH<sub>4</sub><sup>+</sup> concentrations, it was possible to evaluate if NH<sub>3</sub> is a relevant neutralizing agent for H<sub>2</sub>SO<sub>4</sub> and to estimate the neutralization level.

Figure 5 shows that nss-nc-SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> concentrations are significantly correlated (linear regression;  $R = 0.94$ ,  $n = 136$ ), so demonstrating that sulfate is present in the Ny-Ålesund aerosol as ammonium salt. The slope of the linear regression (3.59) represents an intermediate value between the SO<sub>4</sub><sup>2-</sup>/NH<sub>4</sub><sup>+</sup> ratios of 2.66



**Fig. 5** Linear relationship between  $\text{nss-nc-SO}_4^{2-}$  and  $\text{NH}_4^+$  concentrations in 2014 Ny-Ålesund aerosol samples

(corresponding to the w/w ratio in  $(\text{NH}_4)_2\text{SO}_4$  salt) and 5.33 ( $\text{SO}_4^{2-}/\text{NH}_4^+$  w/w ratio in  $\text{NH}_4\text{HSO}_4$ ). Therefore, the sulfate is present in both these species in spring-summer 2014 Ny-Ålesund aerosol.

Figure 6 shows the temporal trend of the  $\text{nss-nc-SO}_4^{2-}/\text{NH}_4^+$  w/w ratio along all the sampling period. It is evident that  $\text{nss-nc-SO}_4^{2-}$  is contemporaneously present both as completely  $(\text{NH}_4)_2\text{SO}_4$  or partially  $\text{NH}_4\text{HSO}_4$  neutralized form in the majority of samples, with a significant exception for a short transport event occurred on 15–16 August 2014. In these days, the  $\text{nss-nc-SO}_4^{2-}/\text{NH}_4^+$  w/w ratio reaches values as high as 6.31, indicating the presence of sulfate in acidic form ( $\text{H}_2\text{SO}_4$ ).

### 3.4 Sulfate biogenic contribution

As above discussed, the  $\text{nss-nc-SO}_4^{2-}$  fraction can be attributed to the sum of the species originated in acidic form. The main sources of  $\text{H}_2\text{SO}_4$  are the anthropogenic emissions and the marine biogenic activity. While source markers of anthropogenic emissions are difficult to interpret, the contribution of the phytoplanktonic metabolic processes can be evaluated by using MSA as their univocal marker. Therefore,

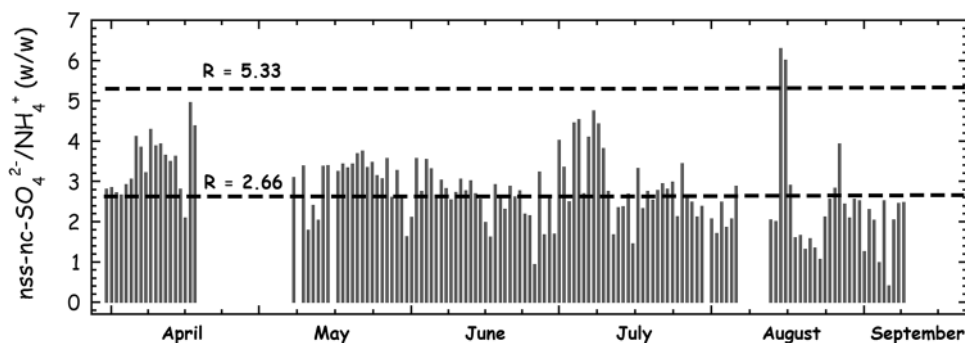
the anthropogenic impact on the sulfate budget was evaluated by subtracting the biogenic sulfate ( $\text{bio-SO}_4^{2-}$ ) fraction from the  $\text{nss-nc-SO}_4^{2-}$  concentrations.

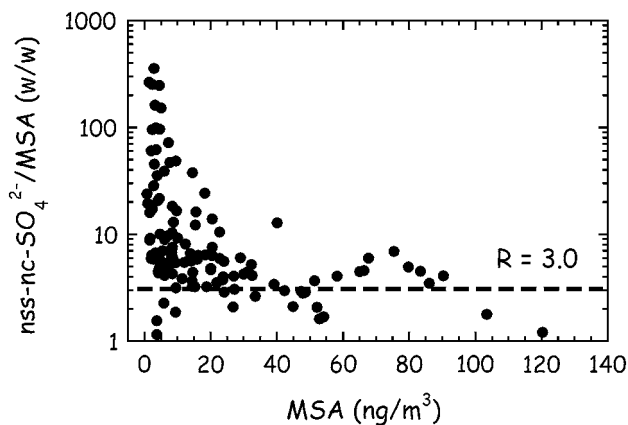
Phytoplanktonic metabolic processes produce dimethylsulfoniopropionate (DMSP) as an osmolyte. DMSP is broken down by marine microbial species to form two major volatile sulfur compounds: methanethiol ( $\text{CH}_3\text{SH}$ ) and dimethylsulfide ( $\text{DMS-CH}_3\text{-S-CH}_3$ ). While methanethiol is rapidly assimilated by bacteria into sulfur-proteins, DMS bacteria uptake is slower and this compound, scarcely soluble in seawater, is emitted into the atmosphere, where it is oxidized to methanesulfonic acid (MSA) and  $\text{H}_2\text{SO}_4$  (Bates et al. 1992; Saltzman 1995; Kettle and Andreae 2000). On global scale, the MSA and  $\text{H}_2\text{SO}_4$  aerosol originated from marine biogenic emissions affects the Earth's radiative budget by direct (solar irradiation scattering) and indirect (they act as cloud condensation nuclei and affect surface albedo) way (e.g., Kaufman et al. 2002; Gondwe et al. 2003). For these effects, the marine biogenic emissions are believed to play a relevant negative feedback on climate change (CLAW hypothesis, Charlson et al. 1987). A strong relationship between aerosol MSA and marine primary productivity was found by Becagli et al. (2013), in the Southern Mediterranean Sea. Besides,  $\text{nss-SO}_4^{2-}$  from marine biogenic emissions was used by Wolff et al. (2006), as a specific marker to reconstruct marine biogenic activity for the last 800 kyr by ice core analysis.

While  $\text{H}_2\text{SO}_4$  at present in the Arctic is originated mainly from anthropogenic emission, MSA is a univocal marker of the biogenic emissions. Therefore, the  $\text{bio-SO}_4^{2-}$  fraction can be evaluated if the  $\text{SO}_4^{2-}/\text{MSA}$  ratio from DMS oxidation is known. Unfortunately, this ratio is highly variable and it depends from latitude, air temperature and photochemistry efficiency (e.g., Bates et al. 1992; Barone et al. 1995; Hynes et al. 1986; Leck et al. 2002; Turnipseed et al. 1996).

To understand the relationship between MSA and  $\text{SO}_4^{2-}$  from biogenic emission, we plotted the  $\text{nss-nc-SO}_4^{2-}/\text{MSA}$

**Fig. 6** Temporal trend of the  $\text{nss-nc-SO}_4^{2-}/\text{NH}_4^+$  w/w ratio along the 2014 Ny-Ålesund campaign (see text for values interpretation)





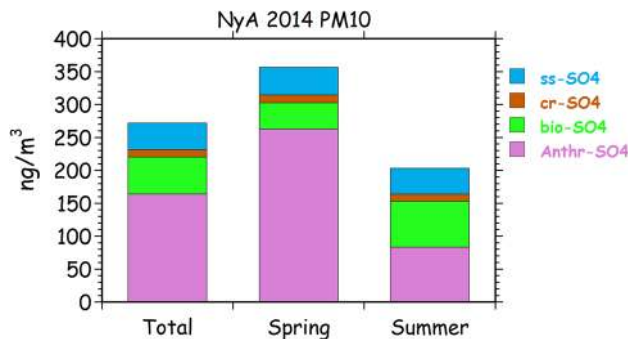
**Fig. 7** Relationship between the  $\text{nss-nc-SO}_4^{2-}/\text{MSA}$  w/w ratio and MSA concentration in all-period 2014 Ny-Ålesund aerosol samples

w/w ratio vs. MSA concentration measured in the  $\text{PM}_{10}$  samples, aiming to find a limit ratio when MSA (i.e. biogenic contribution) is high. Figure 7 shows that the  $\text{nss-nc-SO}_4^{2-}/\text{MSA}$  ratio tends to be 3.0. This value is similar to other values measured in Polar Regions during summer campaigns. Teinilä et al. (2003) found  $\text{nss-SO}_4^{2-}/\text{MSA}$  ratios ranging from 77 to 3.8 at ground level in Ny-Ålesund. In the same site, by using multistage impactor data, Teinilä et al. (2004) calculated a value around 5 in the sub micrometric fraction. In central Arctic Ocean, Chang et al. (2011) found a value of 4, while Leck and Persson (1996) calculated a ratio = 4.5 in the sub micrometric aerosol fraction. Values closer to that we have observed as biogenic limiting value were reported at Alert (Canada) by Norman et al. (1999) ( $\text{nss-SO}_4^{2-}/\text{MSA} = 2.6$ ) and by Li and Barrie (1993) ( $\text{nss-SO}_4^{2-}/\text{MSA} = 1.7$ ). In East Antarctic Plateau (Concordia Station), by using the same approach, Udisti et al. (2012) found the value of 2.6 for a multi-year aerosol database. The ratio = 3.0 evaluated in the 2014 GVB data set is very close to that obtained by the AOE-96 box-model (mean  $\text{nss-SO}_4^{2-}/\text{MSA} = 3.1$ , Karl et al. 2007), and slightly higher than those calculated by a chemical transport model (1.5–2.6; Gondwe et al. 2006).

By using the  $\text{SO}_4^{2-}/\text{MSA}$  ratio = 3 in biogenic aerosol originated in the Arctic sea areas, the  $\text{bio-SO}_4^{2-}$  fraction can be evaluated by multiplying the MSA concentrations, measured in the Ny-Ålesund aerosol samples, by this value.

### 3.5 Sulfate anthropogenic fraction

Following the above discussion, the anthropogenic contribution to the sulfate budget ( $\text{anthr-SO}_4^{2-}$ ) in every aerosol sample is evaluated by subtracting the sum of the  $\text{ss-SO}_4^{2-}$ ,  $\text{cr-SO}_4^{2-}$  and  $\text{bio-SO}_4^{2-}$  fractions from the  $\text{tot-SO}_4^{2-}$  concentration.



**Fig. 8** All-period and seasonal contribution of sea salt, crustal, biogenic and anthropogenic fractions to the sulphate budget in 2014 Ny-Ålesund aerosol

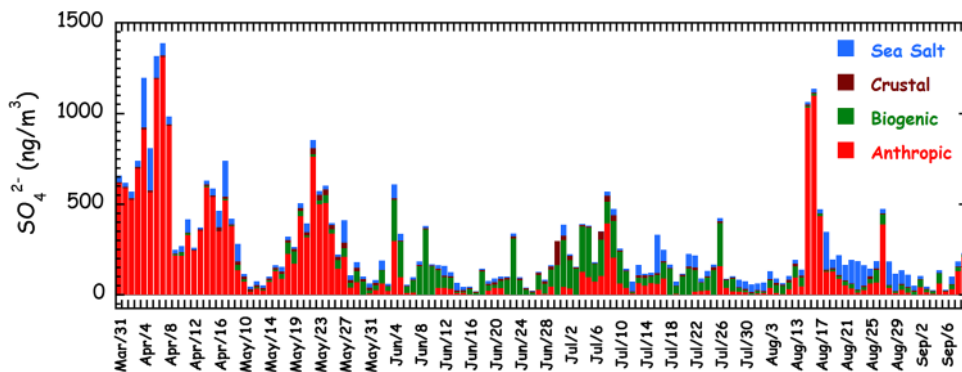
**Table 1** Sulfate source apportionment ( $\text{ng/m}^3$ ) for Ny-Ålesund summer-spring  $\text{PM}_{10}$  samples

	All period	Spring	Summer
Anthrop. sulfate	163.7	262.4	83.4
Biogenic sulfate	56.4	40.3	69.5
Sea-salt sulfate	40.6	42.2	39.3
Crustal sulfate	11.2	11.6	10.8

Figure 8 and Table 1 shows the mean values of the contribution of the four sulfate fractions to the sulfate budget in all period and in spring and summer samples. In all-period samples, ss-, cr-, bio- and anthr-sulfate fractions account for 15.2, 4.2, 21.2 and 61.2 % of the total sulfate budget, respectively. It is evident that the anthropogenic emissions play a dominant role in the sulfate atmospheric concentration at Ny-Ålesund, with a minor, but significant, contribution from sea spray and biogenic sources. On the contrary, the crustal contribution is quite low. More interesting information can be retrieved by the seasonal pattern. In the spring samples, the anthropogenic contribution is very high (covering the 74.8 % of the sulfur budget), so demonstrating the effect of “Arctic haze” transport events, which are more probable and intense in this season (Quinn et al. 2007), due to the inefficient pollutants dispersal, slow removal rates and isentropic transport into the Arctic as low-pressure systems run-up against quasi-stationary Siberian high (Barrie 1986). In summer, the impact of the anthropogenic source is lower (42 %), with a contribution comparable to that coming from biogenic emissions (35 %), which reaches absolute and percentage values about two times higher than those measured in spring.

The ss-contribution is quite constant (as absolute concentration) in the two seasons, but the percentage contribution is significantly higher in summer (19.8 %) than in spring (12.0 %).

**Fig. 9** Temporal trend of the contribution of sea salt, crustal, biogenic and anthropogenic fractions to the sulphate budget in 2014 Ny-Ålesund aerosol



The crustal source plays a minority role. The all-period contribution is 4.2 % of the sulfate budget. Likewise  $\text{ss-SO}_4^{2-}$ , the absolute concentrations of  $\text{cr-SO}_4^{2-}$  are similar in spring and summer, but summer percentage is higher (5.5 %, with respect to 3.3 % in spring), due to the larger sulfate atmospheric concentrations in spring, especially caused by anthropogenic Arctic haze transport.

Figure 9 shows the temporal distribution of the four sulfate fractions along all the sampling period. A dominant anthropogenic contribution is visible in the aerosol samples from 31 March to end of May, in the period 03–10 June and during a sharp event on 15–16 August. Scheuer et al. (2003) showed that, as the spring season progresses, surface haze diminishes and sulfate starts to decline. In summer, sulfate aerosol is efficiently removed from the atmosphere by low-level clouds and wet deposition processes (Scheuer et al. 2003). Sea spray sulfate is especially large in sporadic spring events and, consistently, in the period 17–31 August. The biogenic sources are relevant from early June to the end of July. The sulfate crustal fraction is visible (but scarcely relevant) in the period 19–25 May and in sporadic samples in late June–early July (especially in the 30 June sample). The higher summer values are possibly due to the contribution of local dust after the snow coverage melting.

In conclusion, the anthropogenic sources was found to be the major contribution to the sulfate budget in Ny-Ålesund aerosol, especially in spring, when the Arctic haze transport events are more frequent and intense.

## 4 Conclusions

A 4-term source apportionment of sulfate aerosol was accomplished on 136 PM10 filters collected on daily basis at Ny-Ålesund, Svalbard Islands, during the spring-summer 2014 campaign. The sea spray contribution was calculated from  $\text{ss-Na}^+$ , used as sea spray marker; crustal fraction was evaluated by using  $\text{nss-Ca}^{2+}$  as crustal marker; the biogenic contribution was derived by MSA, as univocal

phytoplanktonic emission indicator (via DMS atmospheric oxidation). Anthropogenic sulfate was obtained as a difference between the sum of the previously cited contributions and the total sulfate atmospheric concentration in every sample.

The sulfate probably emitted in acidic form (anthropogenic plus biogenic) was plotted as a function of ammonium, to evaluate the neutralization level from atmospheric ammonia. The linear regression was highly significant ( $R = 0.94$ ;  $n = 136$ ) and indicated that the mean sulfate/ammonium ratio was intermediate between semi- ( $\text{NH}_4\text{HSO}_4$ ) and complete ( $(\text{NH}_4)_2\text{SO}_4$ ) neutralization. This is in agreement with the spring and summer ionic balances, where anion equivalent were completely counterbalanced by cations, avoiding the necessity to insert  $\text{H}^+$  or  $\text{HCO}_3^-$  equivalents to compensate possible unbalances.

Sulfate source set showed a clear seasonal pattern. The anthropogenic fraction was dominant (74.8 % of the total sulfate budget) in spring (up to the end of May), probably due to Arctic haze transport events, and in two short transport events (early July and mid-August). Biogenic emissions were the main sulfate source from early June to early August, accounting for 35.0 % in the summer samples. Sea salt aerosol contributed for about 20 % in summer, while spring values were lower (12.0 %). The crustal fraction was always low, with a relatively higher contribution in summer (5.5 %).

To our knowledge, this is the first complete source apportionment of sulfate in the Arctic aerosol.

Results here reported can be useful in evaluating the relevance of the impact of anthropogenic aerosol on the critical Arctic ecosystem and in improving climate models based on aerosol-solar irradiation feedback processes.

**Acknowledgments** This study was partially funded by the Italian Ministry of University and Research (MIUR) within the framework of the PRIN-2009 project 20092C7KRC\_002. The logistic assistance of the Polar Support Unit of the CNR Department of Earth and Environment (POLARNET) is gratefully acknowledged. This work was also partially supported by Italian MAE (Ministry of Foreign Affairs), within a bilateral cooperation program, in the framework of the Italy-South Korea agreement 2013–2015.



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