Atmospheric Aerosol at the Svalbard Islands in Year 2010. A Preliminary Analysis of Multielemental Data from Size-Segregated Samples: (I) Sea-Salt Components

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INTRODUCTION AND EXPERIMENTAL

The Arctic Ocean region plays a critical rôle in the Global Change phenomena, due in particular to the progressive reduction of the sea-ice coverage and the related positive feedback effects on the climate system. The radiative transfer through the atmosphere has a central part in this connection, so that monitoring of the relevant atmospheric parameters in this region is essential. The knowledge of the chemistry involving both natural atmospheric components and pollutants is also important. In the above context, we should mention in particular the considerable direct and indirect role of aerosol in both radiative and chemical processes.

The Svalbard Islands are located in an ideal position in the Arctic region to perform a systematic monitoring of the atmospheric parameters. In connection with the above outline, the "Dirigibile Italia" collaboration has started a sampling and measuring campaign concerning several atmospheric parameters, at the site Gruvembadet, Ny Alesund (lat. 78' 55" 37º N, long. 11' 55" 58º E) during year 2010. In particular, aerosol sampling has been performed continuously during the period March 19 – September 15, with a 12-stage SDI impactor and a 48 hours duration. Altogether, 42 size segregated samples with their blanks were collected on Nuclepore membranes. The full aerodynamic range varied from 40 nm to 12 μm.

Subsamples and blanks were submitted (in vacuum) to absolute PIXE analysis at LNL, with the "FISAMB" set-up, with a spatially uniform 1.8 MeV proton beam [1]. Typical intensity was 12 nA; a Canberra hyperpure Germanium X-ray detector, with 140 eV of resolution at Mn Kα line, and Gupix spectra analysis software were used.

Here and in the two other reports; labeled respectively II and III, we present preliminary results concerning two samples: GB17 and GB02. The first sample displays almost exclusively sea-salt elements and S-compounds, whereas the second is much more complex. The present report is dedicated to the sea-salt part of both samples. The aim of the present work is to check the adequacy of our sampling, analytical and data handling methods in the peculiar environmental conditions. We note however that these methods were already successfully used in an Antarctic coastal site [2, 3].

METHODS OF DATA HANDLING

18 Blanks are available for the first set of 26 size-segregated aerosol samples. All the corresponding Nuclepore membranes belong to the same commercial set. For each element, the mean M value and the standard deviation σ of the areal density (ng cm^{-2}) distribution of the blanks were determined. An iterative procedure discarded in most cases 1 or 2 values exceeding M + 2σ. An effective MDL was defined as $MDL_{eff} = M+2\sigma$ and measured aerosol areal densities Δ, ng cm^{-2}, were accepted if larger than MDL_{eff}. The value of M was subtracted from Δ, to get real aerosol areal density δ. The value of σ was quadratically added to the Gupix error in the evaluation of the overall error on δ. When $\Delta < MDL_{eff}$ a conventional value $\delta = \sigma \pm \sigma$ was adopted. The Gupix MDL and the Gupix error alone were used for a limited number of elements.

The following definitions are used:
D_a, particle aerodynamic diameter, μm; D_i^g, geometric mean diameter, μm, of SDI stage *i*, st_i; δ_i, areal density, ng·cm^{-2}, st_i; ΔM_i, volume concentration, ng·m^{-3}, st_i; D_i^T, aerodynamic cut diameter, μm, st_i.

The quantities characterizing the EMSD's are:

$$\left(\frac{\Delta M}{\Delta \ln D_a}\right)_i \equiv \left(\frac{\Delta M_i}{\left(\ln D_{i+1}^T - \ln D_i^T\right)}\right); \qquad (1)$$

The lognormal fitting procedure makes use of a combination of functions of the form:

$$\frac{dM}{d\left(\ln D_a\right)}(D_a) = y_0 + \frac{A}{\sqrt{2\pi} D_a \ln\sigma_g} \exp\left\langle -\frac{\left(\ln D_a - \ln \overline{D}_a\right)}{3\ln^2 \sigma_g}\right\rangle; \qquad (2)$$

Each size mode is therefore represented by four parameters: y0, ng·m^{-3}; $X_0 = \overline{D_a}$; w = lnσ; A, ng·m^{-3}.

All the above considered diameters are in fact divided by 1 μm and therefore adimensional.

LOGNORMAL REPRESENTATION OF ELEMENTAL MASS SIZE DISTRIBUTIONS, EMSD'S, FOR SEA-SALT ELEMENTS

Sample GB17.

It should preliminarily be noted that no element distinct from the sea-salt elements is significantly present in this sample, with the exception of Fe. The problem is therefore here to correctly represent a "pure" sea-salt component, plus the sulphur compounds considered in paper II. Figures 1, 2 and 3 display the EMSD's of four elements: Na, Cl, K and Ca.

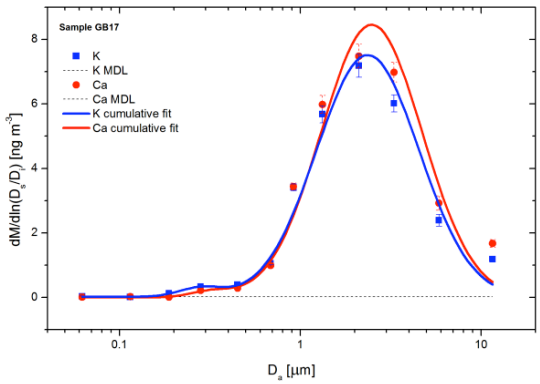

Fig. 1. EMSD of K and Ca for sample GB17.

Fig. 1 displays together the EMSD's of K and Ca and shows that their centers X_0 and, respectively, their widths w have well compatible values, whereas the value of the ratio A_{Ca} / A_K is compatible with the standard sea-salt value. These two elements appear thus as good reference elements in this case.

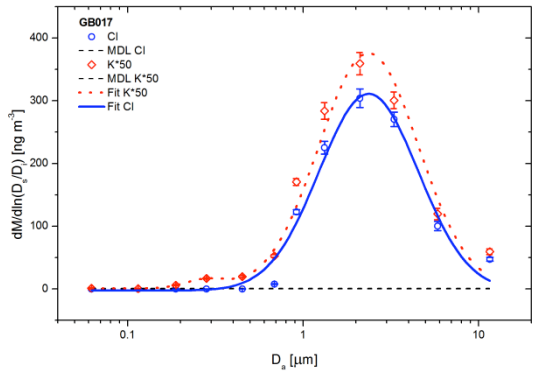

Fig. 2. EMSD of K and Cl for sample GB17.

Fig. 2 displays together the EMSD's of Cl and K. The values of K are multiplied by 50, the value of the Cl/K sea-salt ratio. A standard fitting procedure gives rise to poor results for Cl. We therefore decided to "visually" build up an EMSD for Cl maintaining the parameters X_0 and w of the K EMSD and adjusting the value of the parameter A. The value of A_{Cl} differs by one standard deviation from that of A_K (multiplied by 50). Fig. 3 displays together the EMSD's of Na and Cl. In order to facilitate a comparison (and supposing that only the sea-salt source is present for these two elements), we use the symbol Cl(Na) to denote the EMSD of Na multiplied by the Cl/Na sea-salt ratio. The ratio Cl(Na)/Cl measures the attenuation of Cl(Na) with respect to Cl and varies in a regular way between 0.80 (stage 7) and 0.50 (stage 12). At stage 6, Cl(Na)/Cl = 3.30, possibly indicating an effect of Cl^- depletion around the corresponding diameters. We note that the behavior of Cl(Na)/Cl can be conveniently represented by an exponential function of the areal density ($ng \cdot cm^{-2}$) of Cl, in the size range including the four stages between 7 and 10. In these conditions, we use the Cl EMSD, multiplied by the sea-salt Na/Cl ratio, to evaluate the "final" Na EMSD, over the whole size range.

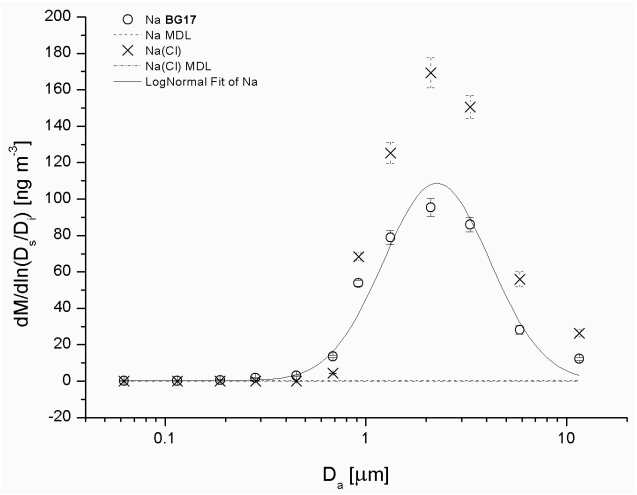

Fig. 3. EMSD of Na and Cl for sample GB17.

Sample GB2.

The properties of this sample are more complex than those of sample GB17. The presence of a significant crustal-like component is indicated by the analysis of the data in paper III. It is therefore expected that contributions from this component be present in the EMSD's of elements Mg, K and Ca. Fig. 4 displays together the MSD's of Cl and Cl(Na). Both Cl-depletion (at low diameters: Da ≤ D8) and Na absorption attenuation (at high diameters: Da ≥ D9) are clearly observed.

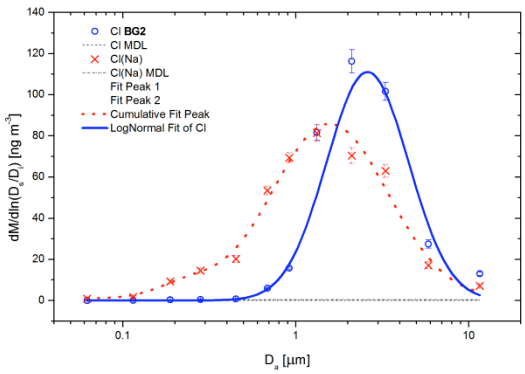

Fig. 4. EMSD of Cl and Cl(Na) for sample GB2.

In these conditions we build-up a (new) reference distribution, Cl(Na)corr, by means of a combination of Cl(Na) and Cl EMSD's in the following way: Cl(Na)corr coincides with Cl, for Da ≥ D9; coincides with Cl(Na), for Da ≤ D5; is evaluated by interpolation in the interval D6 ≤ Da ≤ D8. Once this function is build-up, the sea-salt contributions to Mg, K and Ca EMSD's can be evaluated. This work is being performed now.

[1] P. Mittner et al, Nucl. Instr. Meth., B 109-110 (1996) 375.
[2] F. Chiminello et al., Proc. 16th ICNAA, Kyoto (2004), p.649.
[3] P. Mittner et al., Proc. Int. Polar Year, Olso (2010).