

Soluble/insoluble (dilute-HCl-extractable) fractionation of Cd, Pb and Cu in Antarctic snow and its relationship with metal fractionations in the aerosol

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Abstract. A chemical fractionation methodology for determination of the (water) soluble and the insoluble (dilute-HCl-extractable) fractions of Cd, Pb and Cu in Antarctic snow was set-up and verified for the additivity of the two fractions detected. Molten samples were filtrated and the water-insoluble fraction was extracted by dilute ultrapure HCl (pH ~1.5). Metal determinations were carried out in the two fractions by square wave anodic stripping voltammetry. The total metal concentrations in samples collected in the 2000-2001 austral summer in a clean area (Faraglione Camp) in the neighbourhood of the Mario Zucchelli Italian Station were of the order of Cd 10-20 pg g^{-1} , Pb 20-40 pg g^{-1} , Cu 60-120 pg g^{-1} with an approximate equidistribution between soluble and insoluble fractions. These fractionations compare well (and show a quite consistent temporal trend) with those observed in the aerosol samples collected in the same area/period and confirm the close relationship between metal distributions in snow/ice and in the aerosol. At the station metal concentrations increase due to anthropic contribution and the distribution changes with Cd predominantly present in the soluble fraction (~80%), while Pb and Cu are more concentrated in the insoluble fraction, 70-80% and ~70%, respectively.

Key words: Cd, Pb, Cu, Antarctic snow, soluble/insoluble fractionation, voltammetry.

Introduction

Atmospheric aerosol represents a primary source of soluble and insoluble particulate matter¹, which, in different ways, depending on soluble/insoluble distribution, plays a key role in the terrestrial climatic system, interacting with the solar radiation transfer through the atmosphere².

The global climatic and environmental changes which occurred in past glacial/interglacial cycles were always accompanied by substantial variations in the content of the particulate matter dispersed in the atmosphere and, at the same time, in the load of dust trapped in the Antarctic ice. Thus these events are always accompanied by considerable changes in the total content of chemical substances in the ice; even more considerable is the change in the distribution between soluble and insoluble phases, as shown by the observed variations in the dust content of deep Antarctic ice cores^{3,4}.

Variations in soluble ionic species concentrations have been ascribed to substantial changes in polar vortex

size, in the strength of atmospheric circulation and in the relative contribution of the different sources of aerosol (continental, biogenic, marine) to polar regions in different climatic conditions^{5,6}. Similarly dust deposited in polar regions is subjected to considerable spatial and temporal variations in concentration, dimensional and mineralogical distributions of particles. High dust levels in glacial periods have been related to increment of continental aridity and to changes in transport pathways in the atmosphere^{7,8}.

Although the solubility depends on the chemical nature of particles and on the operative dissolution conditions^{9,10}, the discrimination between the soluble and the insoluble fractions of impurities deposited on the polar ice caps represents an important tool to be used both in measurements carried out in snow/ice and in aerosols to identify the sources of chemical substances and to detect the changes that have taken place in the sources due to the climatic changes of the past.

As regards trace heavy metals, there is at present no information available in the literature with reference to the distribution between the soluble and the insoluble

fractions in snow and ice, possibly due to difficulties in the treatment and analysis of samples under uncontaminated conditions and with sufficient sensitivity^{11,12}.

This work describes the set-up of the voltammetric determination of the soluble/insoluble fractionation of Cd, Pb and Cu in Antarctic snow and compares results with data previously obtained with the same procedure on aerosol samples collected at the same site. A preliminary evaluation of the relationship between aerosol and snow with respect to the stated chemical fractionation will be also presented.

Materials and Methods

During the 2000-2001 austral summer, in the period January-February 2001, five snow samples were collected in the area of the "Mario Zucchelli" Italian Station (MZS), Victoria Land, Antarctica, three of them at the clean site of the Faraglione Camp (Campo Faraglione), about 3 km south of the station, and two at the station itself, with wind direction from the sea and from the station, respectively (Fig. 1). Sample collections were carried out directly into polyethylene sampling bottles (previously decontaminated according to a procedure described elsewhere¹³), while wearing polyethylene gloves and clean room garments. Snow samples were stored and transported to Italy frozen (at -25 °C) until analysis.

The sample treatments and voltammetric analysis for heavy metal determinations were performed in a clean chemistry laboratory ISO 14644-1 Class 6, with areas at ISO Class 5 under laminar flow cabinets. Here the samples were melted and divided into two aliquots. The first aliquot was filtrated through a 0.45 µm pore size filter. The filtrate was then acidified with ultrapure HCl (Romil, Cambridge, England) (2 mL acid 34-37% in 1000 ml melted snow, pH ~1.5) for the determination of the water-soluble metal contents, while the particulate matter collected on the filter was extracted with an acidified solution at pH ~1.5 (2 mL ultrapure acid in 1000 ml Milli-Q water, Millipore, Bedford, MA, USA, for the determination of the water-insoluble, HCl-extractable metal fractions (in the following simply insoluble fractions). The second aliquot was merely acidified with ultrapure HCl (2 mL acid in 1000 ml melted snow, pH ~1.5) for the determination of the total (dilute-HCl-extractable) metal concentrations.

The voltammetric analysis of samples was carried out by Square Wave Anodic Stripping Voltammetry (SWASV) using a polarographic analyzer system from Metrohm (Herisau, Switzerland) including a 746/747 VA Trace Analyzer equipped with an Ultra Trace electrode on which a Thin Mercury Film was deposited as working Electrode (TMFE). The main instrumental parameters were as follows: deposition potential -975 mV vs. Ag/AgCl, 3 mol L⁻¹ KCl; deposition time 2-5 min; potential scan from -900 mV to 0 mV with SW amplitude 25 mV, SW frequency 100 Hz, step height 8 mV, step

time 150 ms.

The accuracy of measurements was controlled and assured by analyzing the certified reference material NASS-5 (National Research Council of Canada) for trace metals in seawater.

Results and Discussion

Data and measurement additivity

Figure 1 shows the results obtained at the two sites (Faraglione Camp and Mario Zucchelli Station) in terms of the soluble and insoluble (dilute-HCl-extractable) fractions, and the total extractable concentrations which were both computed as soluble plus insoluble fractions and experimentally measured.

The quantitativity of the sequential extraction and the additivity of the soluble and insoluble fractions to obtain the total (computed) metal concentrations are clearly demonstrated by the results. In fact it can be seen that the computed and measured total concentrations show generally consistent values, with very few exceptions.

Faraglione Camp Site

At the Faraglione Camp values for "measured" total extractable metals averaged 12.7 pg g⁻¹ for Cd (min-max 9.8-16.3 pg g⁻¹), 32.2 pg g⁻¹ for Pb (23.2-39.9 pg g⁻¹) and 91 pg g⁻¹ for Cu (61-123 pg g⁻¹). These values are in the same order of magnitude as metal concentrations previously reported for the coastal area of Victoria Land^{14,15}.

Concerning fractionations it can be observed that metals are generally approximately equidistributed between the soluble and the insoluble fractions or with a slightly higher proportion of the soluble fraction. Indeed this fraction varies, on average, in the ranges (percentages referred to the "computed" total content): Cd 55%-76%, Pb 44%-68%, Cu 47%-59%.

Relationship with aerosol

From the data obtained at the Faraglione Camp, an interesting observation can be made if we consider the temporal sequences in the metal fractionations in snow (soluble fraction: Cd 76%, 55%, 55%; Pb 45%, 68%, 44%; Cu 47%, 59%, 52%). In fact these fractionations are fully consistent (and show quite similar temporal trends) with those observed in the aerosol collected in the same period¹⁶ (soluble fractions in temporal sequence: Cd 78%, 70% and 42%; Pb 52%, 70% and 49%; Cu 33%, 64%, 64% (Fig. 1). This fact led us to conclude that in Antarctica soluble/insoluble fractionations of heavy metals in snow are closely related (quite similar) to their distributions in the aerosol (comparison in Fig. 1).

Moreover, even more importantly, a direct comparison between the snow metal concentrations obtained here and the aerosol metal concentrations

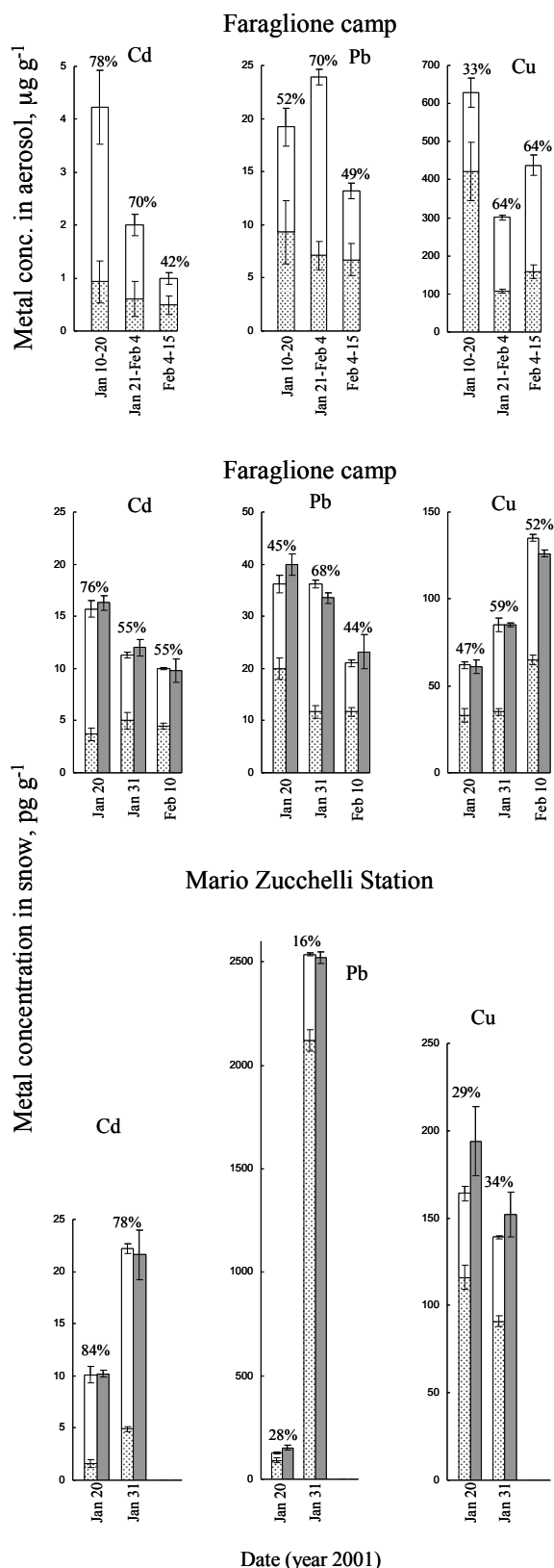


Fig. 1. Soluble (white) / insoluble (dotted) fractionation and total concentration (grey) of Cd, Pb and Cu in snow and aerosol¹⁶ collected at Victoria Land, Antarctica. Percentages of soluble fractions are referred to the total computed metal concentrations. Error bars \pm SD from at least three measurements. Note the different scale of Pb in snow of MZS from that at Faraglione Camp.

reported previously¹⁶ can be carried out (see Fig. 1). In particular passing from the aerosol to the snow we observe a dilution factor of the order of one million times, i.e. from concentrations of the order of $\mu\text{g g}^{-1}$ to pg g^{-1} . More precise values cannot be computed from the available data since aerosol values refer to average concentrations from ~ 10 -day periods of sampling while the snow samples refer to single snowing events.

Mario Zucchelli Station Site

Cadmium data obtained at the Mario Zucchelli Station show no great differences from those obtained at the Faraglione Camp. A total content of 10.2 pg g^{-1} is observed with the wind direction from the sea, which increases to 21.6 pg g^{-1} with the wind direction from the station. Conversely the soluble/insoluble distribution changes significantly with the soluble fraction which predominates with percentages of 84% and 78%, respectively.

For lead, the total contents in samples collected at the station are very much higher than those detected at the Faraglione Camp, and a considerable difference is observed with respect to the wind direction. With a wind direction from the sea the total lead content was 152 pg g^{-1} , which is about 5 times higher than the values obtained at the Faraglione Camp. When the wind came from the station, a value of 2.52 ng g^{-1} (2520 pg g^{-1}) was observed, which is about 100 times higher than those found at the Faraglione Camp. Also the soluble/insoluble distribution changes considerably, with a substantial increase in the insoluble fraction, from 32-56% at the Faraglione Camp, to 72% and 84% at the station with wind direction from the sea and from the station, respectively. Both the net increase of Pb and its predominance in the insoluble fraction at the site very close to the station are evidence of anthropic contamination of the metal by the human activity at the station itself.

In the case of copper, passing from the Faraglione Camp to the station again the total concentration increases but to a much lower extent than that observed for Pb. Moreover in this case no substantial differences are observed in relation to the wind direction. In particular the total copper concentration increased to 194 pg g^{-1} and 152 pg g^{-1} for the samples collected with wind direction from the sea and from the station, respectively, (~ 2 times higher than at the Faraglione Camp) while the insoluble fractions increased to 71% and 66% for the same two samples with respect to the value of 41-53% of the Faraglione Camp. These results show a contamination contribution from the station also for Cu, although at much lower degree than that for Pb, and only a small change in the soluble/insoluble distribution with respect to the clean area of the Faraglione Camp.

Conclusion

An approximate equidistribution is observed between the soluble and the insoluble fractions of the three metals Cd, Pb and Cu in the snow of a clean area (Faraglione Camp) in the neighbourhood of the Italian Antarctic scientific station "Mario Zucchelli". This distribution alters significantly when the site of the station with high anthropic contribution is considered. In the latter case, besides the general increment of concentrations, the distribution also changes considerably, with a predominance of the insoluble fraction for Pb (70-80%) and Cu (~70%) and of the soluble fraction for Cd (~80%).

From the present preliminary measurements it appears that the metal fractionation in snow is quite well related to the same fractionation in the aerosol and, although more systematic studies are required to obtain precise snow/aerosol relationships, the methodology described and set-up here could be of help in the interpretation of ice core data in terms of reconstruction of global past atmospheric processes and changes.

References

- Prospero JM, Charlson RJ, Mohnen V, Jaenicke R, Delany AC, Moyers J, Zoller W, Rahn K. The atmospheric aerosol system. *Rev Geophys* 1983; 21:1607-1629.
- Li X, Maring H, Savoie D, Voss K, Prospero JM. Dominance of mineral dust in aerosol light-scattering in North Atlantic trade winds. *Nature* 1996; 380:416-419.
- Laj P, Ghermandi G, Cecchi R, Maggi V, Riontino C, Hong S, Candelone J-P, Boutron C. Distribution of Ca, Fe, K, and S between soluble and insoluble material in the Greenland Ice Core Project ice core. *Rev Geophys* 1997; 102:26615-26623.
- Marino F, Ghermandi G, Maggi V. Elemental characterization of insoluble atmospheric aerosol in EPICA ice core samples, using PIXE analyses. *Terra Antarctica Reports* 2003; 8:95-100.
- Fuher KA, Neftel A, Anklin M, Maggi V. Continuous measurements of hydrogen peroxide, formaldehyde, calcium, and ammonium concentrations along the new GRIP ice cores from Summit, central Greenland. *Atmos Environ Part A* 1993; 27:1873-1885.
- Mayewsky PA, Meeker LD, Whitlow S, Twickler MS, Morrison MC, Bloomfield P, Bond GC, Alley RB, Gow AJ, Meese DA, Grootes PM, Ram M, Taylor KC, Wumkes W. Changes in atmospheric circulation and ocean ice cores over the North Atlantic during the last 41.000 years. *Science* 1994; 263:1747-1751.
- De Angelis M, Barkov NI, Petrov VN. Aerosol concentration over the last climatic cycle (160 kyr) from an Antarctic ice core. *Nature* 1987; 325:318-321.
- Petit JR, Mounier L, Jouzel J, Korotkevich YS, Kotlyakov VI, Lorius C. Palaeoclimatological and chronological implications of the Vostok core dust record. *Nature* 1990; 343:56-59.
- Colin JL, Jaffrezo JL, Gros JM. Solubility of major species in precipitation: Factors of variation. *Atmos Environ Part A* 1990; 24:537-544.
- Losno R, Colin JL, LeBris N, Bergametti G, Lim B, Jickells TD. Aluminium solubility in rainwater and molten snow. *J Atmos Chem* 1993; 17:29-43.
- Boutron CF. Historical reconstruction of the earth's past atmospheric environment from Greenland and Antarctic snow and ice cores. *Environ Rev* 1995; 3:1-28.
- Planchon FAM, Van De Velde K, Rosman KJR, Wolff EW, Ferrari CP, Boutron CF. One hundred fifty-years record of lead isotopes in Antarctic snow from Coast Land. *Geochim Cosmochim Acta* 2003; 67:693-708.
- Annibaldi A, Truzzi C, Illuminati S, Scarponi G. Recent sudden decrease of lead in Adriatic coastal seawater during the years 2000-2004 in parallel with the phasing out of leaded gasoline in Italy. *Mar Chem* 2009; 113:238-249.
- Barbante C, Turetta C, Capodaglio G, Scarponi G. Recent decrease in the lead concentration of Antarctic snow. *Int J Environ Anal Chem* 1997; 68:457-477.
- Scarponi G, Barbante C, Cescon P. Differential pulse anodic stripping voltammetry for ultratrace determination of cadmium and lead in Antarctic snow. *Analisis* 1994; 22:M47-M50.
- Annibaldi A, Truzzi C, Illuminati S, Bassotti E, Scarponi G. Determination of water-soluble and insoluble (dilute-HCl-extractable) fractions of Cd, Pb and Cu in Antarctic aerosol by square wave anodic stripping voltammetry. Distribution and summer seasonal evolution at Terra Nova Bay (Victoria Land). *Anal Bioanal Chem* 2007; 387: 977-998.