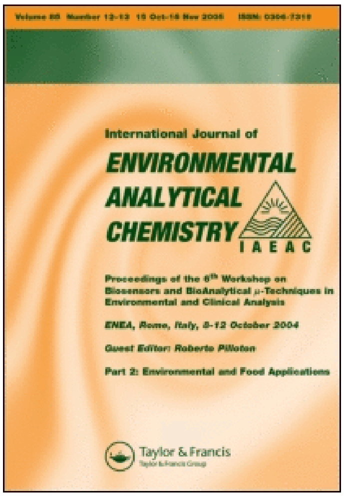

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Distribution of Macro-and Macro-Components in the Water Column of the Antarctic Ross Sea and in Surface Antarctic Snow

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DISTRIBUTION OF MACRO- AND MICRO-COMPONENTS IN THE WATER COLUMN OF THE ANTARCTIC ROSS SEA AND IN SURFACE ANTARCTIC SNOW

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Sample of Antarctic Ross Sea water were collected during the 1990/91 Italian Antarctic expedition: near the coast (74°40' S, 164°07' E) both with and without pack ice above the water column, and in the open ocean (70°53' S, 177°21' E) at different depths. In addition to alkaline and alkaline-earth elements, Se(IV), total inorganic Se, V, Cd, Pb and Cu were determined along the water column depth.

In the open sea the concentrations of the macro components increased by ca, 3% from 0 to 500 m in depth and then decreased lightly (1%) for all these analytes from 500 to 1500 m. Both soluble selenium (IV) and total inorganic Se, increased with increasing depth whereas the concentration of V was fairly constant when normalized to the sodium concentration of V. The dilution effect due to the pack ice under the water column could no longer be measured at a depth of 25 m.

Surface snow samples collected during the same expedition at varying distances from the sea, showed that the ionic concentration ratios relating to sodium are from two to five times higher than in sea water for potassium, two to four times for calcium, six to ten for magnesium, about 10^4 for lead and cadmium, and 10^5 for copper. In particular, it was found that alkaline and alkaline-earth elements exhibited the highest concentrations at a station 10 Km from the sea (100 m a.s.l.) and the lowest ones at a station 60 Km from the sea (700 m a.s.l.). No precise correlation was generally found among the normalized concentrations of heavy metals at the various sampling stations. For instance, the highest concentrations of lead, cadmium and copper were found at the last station, they were about 2.5 or 9 times higher than in the former, according to whether absolute or relative (to sodium) concentrations were considered.

KEY WORDS: Antarctica, sea water, snow, metals.

INTRODUCTION

This work is part of a series of research activities carried out in Terra Nova Bay with the aim of describing and characterising this Antarctic area from the environmental chemistry standpoint.

Two different matrices were considered. Firstly, sea water, to characterize the water column in terms of macro- and micro- components, in connection with the distance from the sea and the presence of pack ice over the sampling place. Secondly, surface, snow, with the target of further supporting the hypothesis that sea water aerosols are not the main factors causing the chemical content of snow.

As the samples were collected during the summer, when it rarely snows, the salt content in such samples refers to a larger exposition time to the atmosphere than for the deeper layers relating to the winter. All the findings however relate to the summer climate.

Since it is assumed that the chemical content in snow is not as homogeneously distributed as it is in sea water samples, the relative concentrations of some components (normalized to sodium concentration) are expected to play a very important role in data interpretation in addition to absolute ones.

Following the above considerations, samples of surface snow collected in Antarctica during the 1991/1992 Italian expeditions were analysed for Na, K, Ca, Mg and NH_4 in addition to Cd, Pb and Cu.

EXPERIMENTAL

Instrumentation. A Dionex model DX300 Ionic Chromatography (Dionex, Sunnyvale, CA, USA) equipped with an injection valve model 9126 Reodyne; a Pulsed Electrochemical Detector (PED) working in conductivity mode; a Dionex Micro Membrane Suppressor (CMMS II: 4 mm for sea water samples; 2 mm for snow samples) were employed. The separations were carried out on an Ionpac CS11 (250 mm × 2 mm i.d.) for snow samples, and on an Ionpac CG12 (50 mm × 4 mm i.d.) and and Ionpac CS12 (250 mm × 4 mm i.d.) for sea water samples. The loop volume was 50 µL. An AutoIon 450 for data acquisition and processing was used.

A DQP-1 pump (Dionex, Sunnyvale, CA, USA) was used for the preconcentration of snow samples (2 ml of samples) on an Ionpac CG11 (50 mm × 2 mm i.d.), and an AutoIon 450 for data acquisition and processing. Different cation exchange and C18 columns were used according to the solutes to be eluted.

A PAR MOD. 174 polarographic analyser, equipped with an AutoIon 450 for data acquisition and processing, was employed in the differential pulse mode. The electrochemical cell was equipped with a platinum wire counter-electrode and saturated calomel (SCE) and hanging drop mercury (HDME) as reference and working electrodes, respectively.

Reagents. All reagents were Suprapure grade materials. All standards, samples and reagents were prepared and stored in pre-cleaned polyethylene containers conditioned according to a procedure for trace element determination described elsewhere[1].

Sampling stations and sampling techniques

Sea water. Sea water samples were collected during the 1990–91 expedition by a go-flow system with teflonated bottles. Samples were taken in two sites (Figure 1) in order to obtain an oceanic profile (Station A: 70°53' S, 177°21' E) and a coastal one (Station B-Gerlache Inlet: 74°40' S, 164°07' E). Two series of samples were collected at Station B: before pack ice melting, through a hole in the ice, and after pack ice melting.

Immediately after sampling, sea water samples were filtered through a 0.45 µm pore size membrane filter, acidified at pH 2 and stored at 4°C. Cleaned and conditioned high-density polyethylene containers were used.

Snow. Surface snow samples were collected during the 1991–92 expedition in three sites (Figure 2): Priestley Glacier (station 03/SN/SUP/A/: 74°08' S, 162°48' E, about 700 m a.s.l.); Snowy Point (station 11/SN/SUP/A: 74°04' S, 165°19' E, about 100 m a.s.l.) and Kay Island (station 14/SN/SUP/A: 74°38' S, 163°45' E, about 100 m a.s.l.). After discarding about the first 2 cm layer, the snow samples were collected manually at

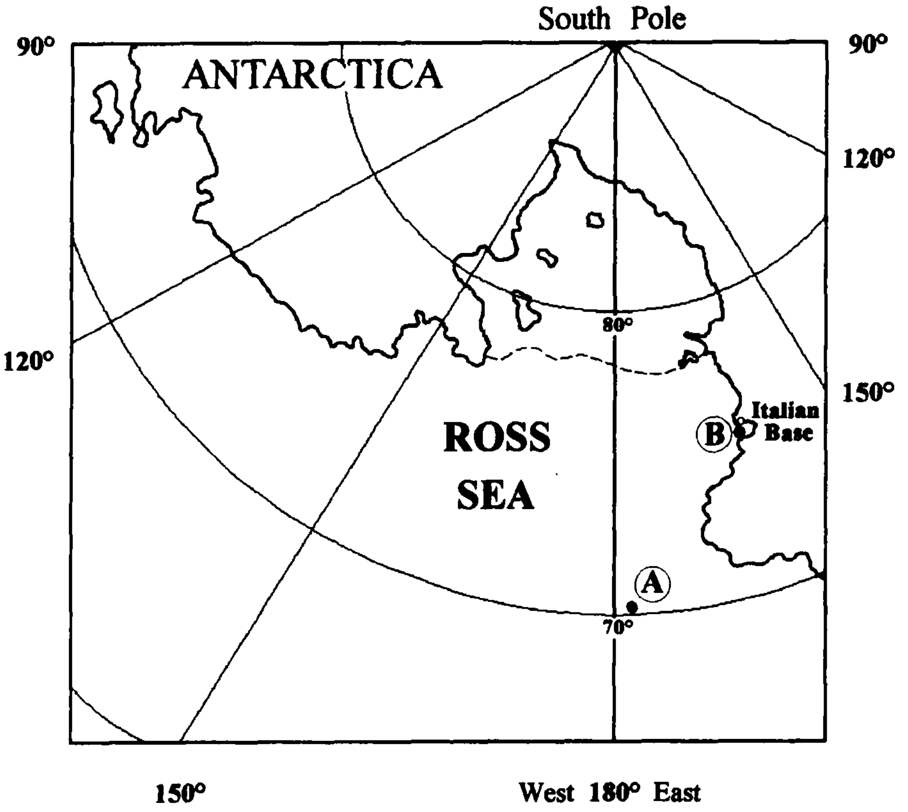

Figure 1 Location of sampling stations of sea water samples collected during the 1990/91 Italian expedition in Antarctica: **A** off shore and **B** in shore sampling stations. In station **B** (Gerlache Inlet) samples were collected before and after ice pack melting.

each station for a maximum depth of about 5 cm and a total volume of ca. 1 litre using a precleaned teflon scraper and precleaned sample wide-necked containers (1000 ml, high density polyethylene).

To prevent contamination the sampling procedure was always carried out against wind direction, around 500 m from the transportation means. All samples were stored at –20°C and analysed in our laboratory in Italy immediately after melting.

Procedures

Alkaline and alkaline earth elements

a) *Sea water.* Using an ion chromatographic (I.C.) procedure previously described[2], lithium, sodium, potassium, magnesium and calcium were determined on the same run after a 50-fold dilution of the sample: a 15 mM HCl was used in the isocratic elution mode on a CS12 Dionex column (250 mm × 4 mm i.d.).

Concentrations were estimated on three replicates by using for each set of measurements an external three point calibration plot. Concentrations of the analytes in

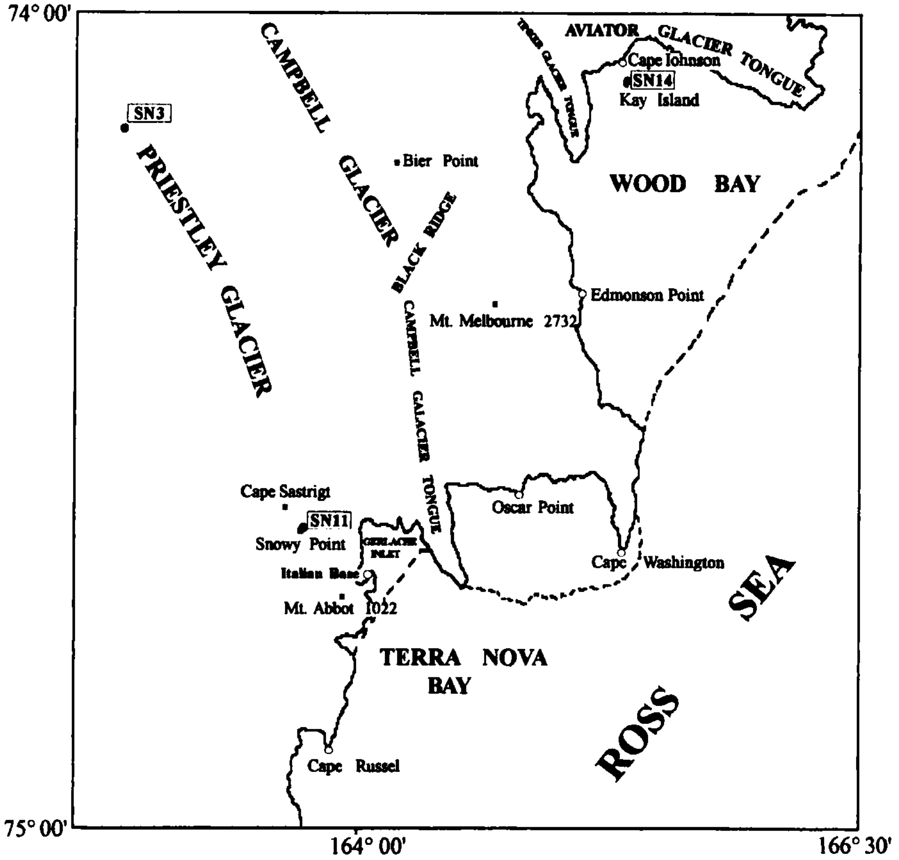

Figure 2 Location of sampling stations of snow samples collected during the 1991/92 Italian expedition in Antarctica.

the standard solution were arranged so that the signal of the sample for each analyte was around the middle of the plot. The concentrations, % relative confidence intervals (% R.I.C.), as obtained by regression analysis at a confidence level of $\alpha = 0.05$, around the mean value, were: Li: 4.6–5.4, Na: 0.03, K: 0.6–0.7, Mg: 0.3, Ca: 0.5.

b) *Snow.* After a preconcentration step on a CG11 Dionex Column[2], a 40 mM HCl mixed with 2 mM 2,3-Diamminopropionic monohydrochloride acid (DAP-HCl, NovaChimica, MI) eluent solution and a 40 mM HCl mixed with 8 mM DAP-HCl solution were used in a step gradient mode. The step gradient elution was changed after 5 minutes.

Blank contributions, due to release from the walls of the containers or from the laboratory environment, were made insignificant by making the whole chromatographic chain operate in an air-tight closed loop. Before each set of measurements a few runs with pure water were performed to wash out the system. Blank concentrations (nM) were: Na: 5, NH_4: 3, K: 0.3, Mg: 0.08, Ca: 0.5. Concentrations were estimated by regression analysis using, as for sea water, an external three point calibration plot.

Total soluble lead, cadmium and copper

These elements were determined both in sea water and snow by differential pulse anodic stripping voltammetry (DPASV), after UV decomposition of the organic matter present in the sample[3]. The estimated d.l. were: $2.7 \cdot 10^{-2}$ nM (3 $ng.l^{-1}$) for Cd, $2.9 \cdot 10^{-2}$ nM (6 $ng.l^{-1}$)for Pb and $3.1 \cdot 10^{-1}$ nM (20 $ng.l^{-1}$) for Cu. The blank contributions due to reagents were typically below d.l. for all the elements considered.

In order to quantify the extent of sample-container exchanges, samples of pure water were analyzed for the above elements before and after their trip from our laboratory in Pisa to the Antarctic Italian Base and return.

The mean values together with their R.I.C.s ($\alpha = 0.05$), before and after the trip, were: 10.1 ± 16.5% and 11.5 ± 13.6% $ng \cdot l^{-1}$ for Pb, 29.3 ± 18.7% and 30.4 ± 20.1% for Cu. The cadmium content was always found far below the detection limit. The % r.s.d. values relevant to subsamples or to parallel samples were found to coincide and equal to: Cd 3%, Pb 4.5% and Cu 6%. Mean concentration values were estimated by regression analysis using a two-point standard addition method.

Se(IV) and total inorganic Se in sea water

Se(IV) was determined by differential pulse cathodic stripping voltammetry (DPCSV) according to the procedure initially proposed by Baltensperger[4]. Since the organic content in the sample affects the sensitivity of the method, ultraviolet irradiation of the sample, at pH 2 in the presence of 50 µl H_2O_2 for 60 ml sample, was found useful to perform before analysis. In these conditions we found that H_2O_2 decomposes organic substances such as humic acids or benzene without any contribution of organic selenium to Se(IV). Total inorganic Se was determined as Se(IV) according to the procedure[4,5], after UV reduction of Se(VI) to Se(IV) at pH 10. A two point standard addition procedure was used for concentration estimation. Mean concentrations and relevant % R.I.C. values are shown in Table 2. No blank contribution was found at the Se concentration level measured.

Vanadium

Based on reported procedures[6–8], vanadium, as V(IV + V), was determined by RP-HPLC after its derivatization in the sample by 5-Br-PADAP and H_2O_2, in the presence of Triton X-100, followed by its preconcentration on a C18 chromatographic pre-column. The elution was performed on an analytical Alltima-C18 5 µm Alltech column (250 mm length, 4.6 mm diameter) using a two-step eluent programme.

The peak area was found to vary linearly both with the preconcentration volume and the original concentration in the sample. Blank levels (related to the original samples) were lower than 20 $ng.l^{-1}$ (0.4 nM). The usable linear dynamic range was from 0.8 to 200 nM. Mean values and relevant % R.I.C.s are shown in Table 2.

RESULTS AND DISCUSSION

Sea water. The concentration values for some alkaline and alkaline-earth elements present in the sea water samples are reported in Table 1. This shows of each element: the

Table 1 Ice pack and water column depth effects on alkaline and alkaline-earth element ion concentrations in Antarctic sea water samples gathered at stations A and B (see Figure 1). $\overline{X}_i$: mean concentration (mM) (on three replicates) estimated by regression analysis using an external calibration curve (see text) daily controlled. $R_{i,z} = (\overline{X}_i/\overline{X}_{Na})_z$: normalized concentration of the i analyte, referred to sodium concentration, both measured at the same station Z (R values obtained by the original not rounded untrounched data of $\overline{X}_i$. For an estimation of % R.I.C. ($\alpha = 0.05$) see text.

	$\overline{X}_i$					$(\overline{X}/\overline{X}_{Na})_z = R_{i,z}$			
Sample name	*Li*	*Na*	*K*	*Mg*	*Ca*	*$[Li_i]/[Na_i]$*	*$[K_i]/[Na_i]$*	*$[Mg_i]/[Na_i]$*	*$[Ca_i]/[Na_i]$*
SWA-20	$22.6 \cdot 10^{-3}$	461	9.90	52.2	10.2	$4.9 \cdot 10^{-5}$	0.0214	0.113	0.0221
SWA-150	$22.7 \cdot 10^{-3}$	470	10.1	53.5	10.3	$4.8 \cdot 10^{-5}$	0.0214	0.114	0.0220
SWA-500	$22.7 \cdot 10^{-3}$	473	10.1	53.8	10.4	$4.8 \cdot 10^{-5}$	0.0214	0.114	0.0220
SWA-700	$25.5 \cdot 10^{-3}$	470	10.0	53.3	10.3	$5.4 \cdot 10^{-5}$	0.0213	0.114	0.0220
SWA-1500	$24.3 \cdot 10^{-3}$	468	10.0	53.3	10.3	$5.2 \cdot 10^{-5}$	0.0214	0.114	0.0221
SWB8-0.5	$21.5 \cdot 10^{-3}$	461	9.90	51.6	10.0	$4.7 \cdot 10^{-5}$	0.0215	0.112	0.0218
SWB8-25	$17.8 \cdot 10^{-3}$	464	9.86	52.0	10.1	$3.8 \cdot 10^{-5}$	0.0213	0.112	0.0217
SWB8-250	$16.5 \cdot 10^{-3}$	462	9.94	51.7	10.1	$3.6 \cdot 10^{-5}$	0.0215	0.112	0.0218
PWB6-0.5	$14.7 \cdot 10^{-3}$	421	9.22	48.1	9.30	$3.5 \cdot 10^{-5}$	0.0219	0.114	0.0221
PWB6-25	$24.7 \cdot 10^{-3}$	465	10.1	53.8	10.4	$5.3 \cdot 10^{-5}$	0.0217	0.116	0.0224
PWB6-250	$26.6 \cdot 10^{-3}$	468	10.2	54.4	10.5	$5.7 \cdot 10^{-5}$	0.0218	0.116	0.0223

individual $\overline{X}_i$ mean concentration values (three replicates) for the samples taken at various depths, z; the $R_{i,z} = (\overline{X}_i/\overline{X}_{Na})_Z$ values, i.e. the normalized concentrations of any element related to the concentration of sodium at the same z.

From these data, it was found for all the i solutes, with the exception of lithium, that:

i) in the open ocean the absolute concentrations $\overline{X}_i$ increased from 0 to 500 m; and then decreased to 1500 m, although not significantly from hydrographic view point: owing to the accuracy and precision levels of the chromatographic procedure used it was possible to quantify a decrease in concentration, for all the elements considered, as low as 1%.

ii) near the coast (Station B) the effect of the ice pack under the sea water corresponds to a dilution of sea water of about 7% at 0.5 m under the surface of ice-sea water, which is no longer evident at 25 m.

The reproducibility of R_is among depth for each element is a direct, experimental assessment of the accuracy of the analytical procedures used.

The fact that lithium shows a particular trend, can only be partially explained in terms of a lower accuracy in its determination owing to its low level of concentration and to the fact that its chromatographic peak is adjacent to that of sodium with a concentration ratio of $1{:}10^5$. The erratic behaviour of lithium is supported by the data of concentrations measured at the same station before and after pack ice melting. The lithium concentration increases or decreases with depth, depending on whether the samples were collected before or after ice pack melting, respectively, while the $[Li]_i/[Na]_i$ ratio reaches the highest values at 250 m in depth before melting and 0.5 m after pack ice melting. Interaction with particulate and sediments is considered likely[9].

Accurate measurements of salinity, performed at the same conditions by Innamorati *et al.*[10], are consistent with our findings.

As for the micro-elements V and Se in sea water (see Table 2), in spite of their concentration at nM level, the following findings were obtained:

i) vanadium showed a fairly constant ionic concentration ratio with sodium $(6.7 \pm 0.6) \cdot 10^{-8}$ for all the considered stations. The range of V concentrations observed in

Table 2 Effects of water column depth on ion concentration (nM) of some microcomponents in Antarctica sea water samples collected at stations A and B (see Figure 1). In the case of V and total inorganic Se, measurements were also performed at 0.5 m below sea water level before and after ice pack melting.

% R.I.C. (a = 0.05) values were estimated by regression analysis using two spikes for V and two standard additions for all the other components. Three replicates for each sample.

Sample name	*V*	*R.I.C.%*	*Tot. inorganic Se*	*R.I.C.%*	*Se(IV)*	*R.I.C.%*	*Cu*	*R.I.C.%*	*Pb*	*R.I.C.%*	*Cd*	*R.I.C.%*
SWB8-0.5 A	34.9	1.09	1.11	9.78	–	–	–	–	–	–	–	–
SWB8-0.5 B	–	–	1.00	12.3	–	–	–	–	–	–	–	–
PWB6-0.5 A	27.4	2.91	0.62	15.3	–	–	–	–	–	–	–	–
PWB6-0.5 B	–	–	0.67	16.3	–	–	–	–	–	–	–	–
SWA-20	30.9	0.82	0.95	6.28	0.067	32.5	2.69	14.3	0.84	11.2	0.63	12.8
SWA-700	32.1	1.27	1.64	4.15	0.39	14.5	3.71	17.7	0.97	6.3	0.72	5.7
SWA-1500	27.9	1.65	2.46	2.83	0.48	4.25	3.83	12.2	0.67	10.9	0.59	17.1

Antarctica sea water was comparable with that observed by J. H. Martin[9] in the eastern North Pacific. According to the findings of Morris[11], the concentration of V in oceans is 23 ± 3 nM with no discernible depth-related patterns.

ii) selenium, both as Se(IV) and total inorganic Se, presents an increasing concentration at an increasing depth of the water column, with a trend similar to that observed by Measures *et al.*[12] in the open ocean.

Snow. The chemical content in surface snow samples depends upon many variables which are mutually correlated in a complicated way. The following play an important role:

i) the time of sampling with respect to the onset of precipitation and to the cyclonic storm period or season[13,14];

ii) the scavenging ability[15,16] of the snow with respect to the air;

iii) the exposure time to sunlight between snowing and sampling[17];

iv) the layer of surface snow considered and the type of precipitation such as hoarfrost or snow[17,18]; the distance and the elevation of the sampling point from the sea[19].

In this sense the chemical content of surface snow is expected to change, even significantly, in the same geographical area according to the time, location and depth of the sampling. As a general rule, the determination of traces in snow, such as alkaline and alkaline earth elements down to 10 nM, does not involve serious analytical problems in terms of the accuracy of the estimated mean values. It is in the case of ultratraces, such as heavy metals in snow, where concentrations of the order of 1 nM or less are involved, that there is a considerable probability that one or more samples become inadvertently contaminated during the handling procedure. As a matter of fact, and this is a fundamental preliminary condition, before assigning a precise meaning to the observed variations in the chemical content of snow samples, sound information must be acquired about the overall reproducibility of the procedure steps and on the relevant accuracy, at real concentration levels in the sample.

The literature and our own direct experience show that the occurrence of outliers is always possible, at least at a pg·g^{-1} level, no matter how good the procedures used from sampling to analysis are. Reducing the probability of using outliers is thus the primary goal: this can be achieved by considering many samples collected in the same area or many parallel samples of the same origin collected in few places.

Two enlightening examples will now be discussed concerning the results obtained in Antarctica from two different groups of researchers who are, in our opinion, among the best in obtaining the most accurate data currently possible.

Boutron and Patterson[20] were able, in the case of lead in ice core, to recognize occasional contamination by the profile at each depth of the considered analyte (lead) concentration vs the distance from the centre of the core. In spite of all the care taken, the dependence of lead concentration on the age of the core related to this century has given rise to totally different interpretations according to whether the data related to 1900–1950 or 1950–1980 are considered to be more reliable (max. difference 4 pg·g^{-1}).

Obviously seasonal effects and any short-term changes which may affect surface snow, are no longer evident in core samples in which each sample refers to several years of snow accumulation.

In the case of surface snow, Völkening and Heumann[17], measured several elements on the same Antarctic field using DPASV, whenever possible, and IDMS (Isotopic Dilution Mass Spectrometry). In the case of lead, they found a reproducibility among portions of the same sample within 10% and among parallel samples within 30%, in the DPASV measurements. Considering that the lead concentration was in the range 5–120 $pg{\cdot}g^{-1}$ this reproducibility is very good. When the results obtained by DPASV and by IDMS are compared, some significant differences can be observed for the same samples, apart from the effect of snow aging. For instance, in one case they found 120 $pg{\cdot}g^{-1}$ using DPASV and 178 with IDMS, in another case 4.5 $pg{\cdot}g^{-1}$ with DPASV and 25.8 with IDMS.

As for Cd, some samples with a concentration of ca. 4 $pg{\cdot}g^{-1}$, as found with IDMS, were always under d. l. using DPASV, while for other samples at ca. 1 $pg{\cdot}g^{-1}$ level the two procedures substantially agreed. In addition, the authors disregarded 20% of the results related to the higher concentrations because they found that about 20% of all blank determinations carried out in the Antarctic laboratory, were considerably higher than the mean of blanks due to contamination problems.

Their findings clearly show that the combined effects of sampling date (within one month) and of the sampling origin (within a field of 700×700 m^2) may lead to snow content variations of 3 to 15 times depending on the element considered. In particular, the observed concentration range ($pg{\cdot}g^{-1}$) was 3–40 for lead 0.2–3 for Cd and 11–30 for Cu in surface snow, with an enrichment factor of 3–15 when hoar-frost samples are considered, compared to snow in the same location.

From all the above considerations, some important conclusions can be drawn:

i) no matter how good the sampling and analytical procedures used so far are (see f.i. ref. 21), measured concentrations in snow up to 5–8 $pg{\cdot}g^{-1}$ may contain an unknown amount of bias (provided that the estimation of the mean is statistically correct). Only in the case of cross-core profiles[20] can the effect of sampling contaminations be evidenced; while the other effects including analytical procedure bias remain unknown. Since the latter contributions may not be reproducible among samples, also correlations among data obtained from the same source are uncertain at this $pg{\cdot}g^{-1}$ level.

ii) with reference in particular to the findings[17,18] it is possible to dispute some trends whereby data sets at low $pg{\cdot}g^{-1}$ levels are considered to have been affected by contamination since they are five to ten times higher than other data obtained years before in another Antarctic region.

Any further research performed in different areas of Antarctica and extended over several years, will therefore lead to an improvement in understanding the dependence of the local effects on distance from the sea, elevation and incidental mountain protection against snow precipitation and wind, provided that the procedures used are carefully tested and found suitable.

If concentrations of several analytes are measured in surface or depth snow, additional information can be obtained on the origin of each analyte and, in particular, on whether they are to some extent generated by human activities.

It is generally accepted from the large amount of literature on this topic, that marine salt and atmospheric dust from local sources, only contribute a part of the ion chemistry of the snowfall, the greater part being contributed by gas derived aerosols.

A technique that has proved to be useful for a first step identification of the source of a given trace element *i*, is to normalize their concentrations with respect to a reference element. Frequently, Na is used as an indicator of atmospheric sea salt and Al as an indicator of weathered crustal material. The enrichment factor related to sea water is defined by:

$$EF_{sea,i} = ([I]/[Na])_{sample}/([I]/[Na])_{sea\ water}$$

and likewise when the EF is related to crustal material, the reference element is Al[22].

Under a large sea-air exchange program concerning the aerosol composition at the Enewetak Atoll (Pacific Ocean), Arimoto and Duce[15] were able to distinguish three groups of elements on the basis of their R_{sea} and $R_{crust.}$ values. Elements such as Br, Cl, Mg, K, Ca, Rb, were found to originate from the sea (R_{sea} were near 1); a large group, including Al, Fe, Co, Cr and Cu, were found to have crustal origin ($R_{crust.} < 3$–5); and elements such as Zn, Pb, Cd, Se and I were enriched significantly or predominantly controlled by other influences: an enrichment step was assumed to take place during the period spent in air.

Substantially similar conclusions have recently been reached by other authors[18,23,24] using Fe as a reference element, for the Atlantic Ocean and Antarctica eco-systems. In the case of Antarctica surface snow[18] the $EF_{crust.}$ was in the range: 100–820 for Cd, 32–97 for Pb, 8–20 for Cu and only 0.5–2 for Cr.

The interpretation of these different EF ranges was that the predominance of other influences besides crustal weathering sharply decreases from Cd to Cu, becoming zero for Cr (only terrestrial origin).

Table 3 shows that the highest concentrations of alkaline and alkaline-earth elements were found at station SN11 (100 m elevation, 10 Km from the sea, behind a 500 m hill), and the lowest ones at SN3 (700 m elevation, 60 Km from the sea). The EF inspection shows that none of the salt contents in the samples have a predominant marine origin.

It is worth comparing our normalized values with those calculated by Johnson and Chamberlain original data[25], relating to sampling in Law Dome (East Antarctica) performed in 1986. At 5 Km from the coast and 380 m elevation their EF's with respect to sea water were 1.3 for K, 1.0 for Mg and Ca, which are quite different from our data at SN11. In addition, the EF's for their sampling at 110 Km distance and 1400 m elevation (3.2 for K, 8.1 for Mg and 2.1 for Ca) were comparable with ours for SN14, this showing that the distance from the sea and elevation are not the only determinant factors[26].

The concentrations of heavy metals, were on average 2.5 higher at SN3 than at SN11 or SN14, while the normalized to sodium concentrations were about 10 times higher at SN3. This fact can be interpreted by assuming that during snowing or later before sampling, the air from the interior of the continent, relatively enriched in heavy metals, was mixed with the coastal air, relatively enriched in sodium, in ways which may differ depending on the situation.

The fact that for each heavy metal considered, the concentrations are essentially constant at SN11 and SN14 and consistently lower than at SN3 (the furthest one from the Italian Station), may be seen as a proof that the contamination due to human activities in the base, is quite low, if any.

Table 4, which should not be seen as a comprehensive summary of literature data, shows the interval of concentrations (nM) obtained by various authors, along with information about the depth of the snow layer considered and the concentrations in sea water. For further data, concerning snow and ice see references 17 and 20.

Apart from Landy[27], whose concentration values appear to be quite high, Table 4 highlights that bearing in mind the unpredictable effects of different Antarctic regions and sampling data as well, the ionic concentrations of heavy metals generally increase as both the distance from the surface and the thickness of the snow layer collected decrease. However, they may vary by a factor of ten or more depending on the sampling location, even when a restricted field is considered[17].

Normalized concentrations (with respect to sodium) show no correlation among different sampling sites, thus confirming that sea water aerosol is not the direct cause of heavy metal content in snow. Also, neither the distance from the sea nor the elevation are determinant in sea salt content in surface snow.

Table 3 $\overline{X}_i$ mean concentrations and $R_{i,z}$ normalized concentrations on three replicates of some elements in snow samples gathered (see Figure 2). The EF enrichment factors refer to sea water. (a) and (b) refer to I.C. and DPASV measurements respectively. For an estimation of % R.I.C. ($\alpha = 0.05$) see text.

	Element							
Station i	$[NH4]^a$	$[Na]^a$	$[K]^a$	$[Mg]^a$	$[Ca]^a$	$[Pb]^b$	$[Cu]^b$	$[Cd]^b$
SN3	0.30 (7)	1.64 (14)	0.17 (14)	0.19 (11)	0.06 (15)	$2.7\cdot10^{-4}$ (9)	$3.6\cdot10^{-3}$ (15)	$3.9\cdot10^{-4}$ (7)
SN11	0.70 (2)	8.35 (4)	0.39 (7)	0.62 (5)	0.71 (9)	$1.1\cdot10^{-4}$ (12)	$1.9\cdot10^{-3}$ (17)	$1.2\cdot10^{-4}$ (8)
SN14	2.14 (3)	5.65 (2)	0.34 (4)	0.41 (20	0.25 (5)	$1.3\cdot10^{-4}$ (11)	$1.4\cdot10^{-3}$ (14)	$1.4\cdot10^{-4}$ (6)

	R_i							
Station i	R_{NH4}		R_K	R_{Mg}	R_{Ca}	R_{Pb}	R_{Cu}	R_{Cd}
SN3	$1.8\cdot10^{-1}$		$1.0\cdot10^{-1}$	$1.2\cdot10^{-1}$	$3.7\cdot10^{-2}$	$1.6\cdot10^{-4}$	$2.2\cdot10^{-3}$	$2.4\cdot10^{-4}$
SN11	$8.4\cdot10^{-2}$		$4.7\cdot10^{-2}$	$7.4\cdot10^{-2}$	$8.5\cdot10^{-2}$	$1.3\cdot10^{-5}$	$2.3\cdot10^{-4}$	$1.4\cdot10^{-5}$
SN14	$3.8\cdot10^{-1}$		$6.0\cdot10^{-2}$	$7.3\cdot10^{-2}$	$4.4\cdot10^{-2}$	$2.3\cdot10^{-5}$	$2.5\cdot10^{-4}$	$2.5\cdot10^{-5}$
Sea water			$2.10\cdot10^{-2}$	$1.18\cdot10^{-2}$	$2.20\cdot10^{-2}$	$4.9\cdot10^{-10}$	$6.23\cdot10^{-9}$	$7.47\cdot10^{-10}$

	E.F.							
Station i								
SN3			4.9	9.8	1.7	$3.4\cdot10^{5}$	$3.5\cdot10^{5}$	$3.2\cdot10^{5}$
SN11			2.2	6.3	3.9	$2.7\cdot10^{4}$	$3.7\cdot10^{4}$	$1.9\cdot10^{4}$
SN14			2.9	6.1	2.0	$4.7\cdot10^{4}$	$4.0\cdot10^{4}$	$3.3\cdot10^{4}$

Table 4 Interval of concentration (nM) of Cd, Pb and Cu found in Antarctica snow or sea water by different authors, in different sites and years. For further data concerning snow and ice, see [20] and [17]. The depth column shows the depth intervals from the surface inside which the layers of snow were collected.

Ref.	*Expedition*	*Sample type*	*Depth*	*Cd*		*Pb*		*Cu*	
				min	*max*	*min*	*max*	*min*	*max*
20		Snow core				0.005	0.03		
27	1976	Snow	Depth not specified	3.3		3.9			
17	1987	Snow Hoar-Frost	Surf. (15–30 cm)	0.002 0.13	0.03	0.015 0.9	0.2	0.2	0.5
This work	1991/92	Snow	Surf. (2–5 cm)	0.12	0.39	0.11	0.27	1.4	3.6
28	1990/91	Snow	Surf. 25 cm			0.24 0.011			
29	1988/89	Snow	Surf. (2–5 cm)	0.10	0.27			0.71	1.42
30	1990/91	Flowing Melt waters		0.05	0.21				
31	1989/90	Sea water		0.13	0.28	0.07	0.14	1.49	2.22

Finally, absolute concentrations of some elements in Antarctic surface snow and sea water are comparable as shown in Table 4 for Cd, Pb and Cu. The same was found for Zn, Tl and Fe:

Sample type	Zn	Tl	Fe
Sea water	4[31]	0.06[9]	8[31]
Surface snow	0.5–7.6[17]	0.001[17]	9–27[17]
flow. melt. snow		0.05–0.2[30]	

CONCLUSIONS

In Antarctic sea water it was found that the total inorganic Se concentration increases with depth, while the V concentration remains fairly constant regardless of depth and the presence of ice pack when referred to the same sodium concentration. These trends are similar to those found in oceans.

Regarding snow, from an analysis of literature data and our findings, it may be concluded that the chemical content in Antarctica surface snow may vary significantly even when a restricted field and a limited time interval is considered for sampling. The element contents increase as the distance from the surface and the thickness of the snow layer collected decrease. Thus, whenever problems related to contamination of the sample are avoided, local and seasonal effects due to air-snow interaction are amplified when surface snow is considered.

Owing to the continuous improvements of sampling and analysis procedures, it is likely that the actual bias in the determination of element concentrations in snow, which we estimate to be nowadays of some pg$\cdot$g^{-1} will further be reduced. Incidentally, it is worth observing that absolute concentrations of metals such as Cd, Pb, Cu, Tl, Zn and Fe, in Antarctic surface snow and sea water are comparable in spite of the completely different values of their concentration normalized to sodium.

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