# Trace metals in aerosol at Terra Nova Bay, Antarctica

G. Toscano,<sup>a</sup> A. Gambaro,<sup>\*ab</sup> I. Moret,<sup>ab</sup> G. Capodaglio,<sup>ab</sup> C. Turetta<sup>b</sup> and P. Cescon<sup>ab</sup>

<sup>a</sup> Dipartimento di Scienze Ambientali, Università di Venezia, Calle larga S. Marta,

Dorsoduro 2137, 30123 Venezia, Italy. E-mail: gambaro@unive.it; Fax: +39-041-2578549 <sup>b</sup> Istituto per la Dinamica dei Processi Ambientali del CNR, Dorsoduro 2137, 30123 Venezia, Italy

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Atmospheric particulate with an aerodynamic diameter  $< 10 \ \mu m (PM_{10})$  was sampled continuously during the austral summers of 2000–2001 and 2001–2002 at a coastal site near to the Italian base of Terra Nova, Antarctica. Li, Pb, Cd, U, Ba, Bi, Cs, Rb, Tl, Sr, Al, V, Fe, Cu, Mn, Zn, Co, Ag were determined by inductively coupled sector field mass spectroscopy (ICP-SFMS) after sample digestion by a combination of HF, HNO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> in ultraclean conditions. Quality control of the analytical procedure was carried out by blank control, by evaluating the limits of detection, recoveries and repeatability. Concentrations found are extremely low for most metals, confirming the high purity of Antarctic aerosol. Principal Component Analysis (PCA) highlights high correlations among Pb, Cr, Bi, Cu and Zn concentration values and among Li, U, Ba, Cs, Rb, Al, V, Fe, Mn, Co concentration values permitting the identification of two principal source groups, namely crustal dust and human emission activities. Elements of anthropogenic origins (Pb, Cr, Cu, Zn) were highly enriched with respect to their crustal composition.

## Introduction

Atmospheric aerosol particles affect a great variety of processes in the atmosphere such as solar radiation scattering, visibility and climate, and health effects.<sup>1,2</sup> Moreover in the past few decades it has become apparent that the atmospheric aerosol is an important pathway by which trace elements are transported both locally and on a remote scale. Data on the elemental composition of atmospheric aerosol at a given location are used for the characterization of local air conditions. The nature of regional sources have been often revealed through the evaluation of concentration values and principal component analysis performed on statistically representative data sets.

Particulate matters are emitted into the atmosphere from both natural sources (Earth's crust, oceans, volcanic activity, biosphere)<sup>3–5</sup> and anthropogenic activities (*e.g.* fossil fuel combustion, waste incineration, industrial processes).<sup>6</sup> Elements associated with high-temperature sources such as volcanic processes and mainly anthropogenic processes have most of their total mass on fine particulates<sup>7,8</sup> which have a longer residence time in the atmosphere and can be transported from distant emission sources.

The trace element content of aerosols sampled in the most remote parts of our planet, primarily due to long range transport, would give valuable information on the global transport of particulates and on the contribution of human activities to air pollution. In these areas moreover extremely interesting records of the past history of the atmosphere of our planet are preserved in snow and ice. In this context, several authors have investigated the occurrence of trace metals in pristine Antarctic snow and ice9,10 to show the ancient and recent changes in heavy metal quantities in naturally occurring and man-derived aerosols that reach the Antarctica continent. As yet the actual availability of data on the trace metals composition of Antarctic aerosol is very little and not enough to give the order of magnitude of the level or variability of trace element concentrations in such an interesting area. Mazzera et al.11 found at Hut Point (located less than 1 km from

downtown McMurdo) a  $PM_{10}$  (particles with aerodynamic diameters less than 10 µm) mass concentration of 3.4 µg m<sup>-3</sup> which is an order of magnitude lower than the US National Ambient Air Quality Standards. Moreover Maenhaut *et al.*<sup>12</sup> reported low concentrations (pg m<sup>-3</sup>) for 28 heavy metals in South Pole aerosol samples, and Mittner *et al.*<sup>13</sup> found low concentrations (ng m<sup>-3</sup>) of Na, Mg, Al, Si, S, Cl, K, Ca and Fe in the aerosol from Terra Nova Bay. The accurate determination of low element concentrations is a real analytical challenge and utmost precaution in the sampling as well as ultrasensitive analytical techniques are necessary.

The Antarctic Italian base is sited at Terra Nova Bay  $(74^{\circ}51'42'' \text{ S}, 164^{\circ}07'23'' \text{ E})$  and it provides support for Italian and international research in Antarctica. It is able to host about 100 people during the austral summer with a surface of 5000 m<sup>2</sup> (laboratories, storage, accommodation, plant, services).

In this paper the results obtained from the determination of 16 elements (Li, Pb, U, Ba, Bi, Cs, Rb, Tl, Sr, Al, V, Fe, Cu, Mn, Zn, Co) in Antarctic aerosol are presented and discussed in order to highlight the different possible natural and anthropogenic sources. The samples were collected at a site near the Italian base, on the coast of the Ross Sea, during the austral summers of 2000–2001 and 2001–2002. After a microwave oven digestion, the aerosol samples are analysed by inductively coupled plasma sector field mass spectroscopy (ICP-SFMS). The chemometric method of the PCA was used as a tool for the extraction of the available information from the data.

# Experimental

All the analytical procedures preceding the instrumental measurements (cleaning of filters and all plastic items, sample treatments, preparation of standard solutions) were carried out inside a laminar flow clean bench in class 100 clean chemistry laboratories.



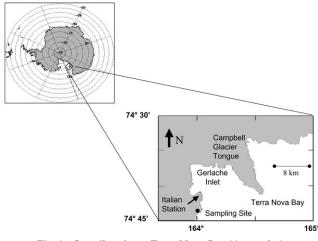


Fig. 1 Sampling site at Terra Nova Bay (Antarctica).

#### Sampling

The sampling was performed at a coastal site (Fig. 1), about 3 km south of the Italian base of Terra Nova Bay  $(74^{\circ}42'56.3'' \text{ S}, 164^{\circ}06'52'' \text{ E})$ , at ground level on the coast and at 57 meters above sea level. Samples were collected over a 10 day period from November 2000 to February 2001 and from November 2001 to February 2002, providing a total of 13 observations and sampling volumes of between 11 000 m<sup>3</sup> and 20 000 m<sup>3</sup> (Table 1).

 $PM_{10}$  was collected by a brushless high volume sampler (Tisch Environmental Inc., Village of Cleves, OH, USA) equipped with cellulose filter (Whatman 41) and operated at a flow rate of ~1.13 m<sup>3</sup> min<sup>-1</sup>. Every two months a calibration is done to check the flow rates.

Several tests were carried out to identify a suitable cleaning procedure of the cellulose filter. The filters were washed with diluted HCl (Merck suprapur) and rinsed with ultrapure water obtained by coupling a Milli-RO with a Milli-Q system (Millipore, Bedford, MA). Afterwards they were dried at room temperature and weighted to five decimal places before and after sampling, while keeping the humidity between 8–10 UR%. The aerosol samples were closed in washed petri dishes inside plastic bags and stored at -20 °C until the analysis.

Table 1 Sampling periods, air volume sampled (m<sup>3</sup>) and  $PM_{10}$  concentrations (µg m<sup>-3</sup>) during 2000/01 and 2001/02 austral summer campaigns

	Sampling periods	Air volume sampled	PM <sub>10</sub>
1a	22/11/2000-02/12/2000	a	a
2a	02/12/2000-12/12/2000	17 089	_
3a	12/12/2000-22/12/2000	15 096	0.5
4a	22/12/2000-02/01/2001	16 326	1.1
5a	03/01/2001-10/01/2001	10 942	1.3
6a	10/01/2001-20/01/2001	15 998	_
7a	21/01/2001-04/02/2001	<i>a</i>	a
8a	04/02/2001-15/02/2001	17 800	_
1b	05/11/2001-17/11/2001	18 568	2.4
2b	17/11/2001-27/11/2001	16 143	2.2
3b	27/11/2001-07/12/2001	16 806	—
4b	07/12/2001-19/12/2001	a	a
5b	23/12/2001-04/01/2002	20 021	3.0
6b	04/01/2002-14/01/2002	16 327	1.6
7b	14/01/2002-25/01/2002	18 003	1.1
8b	25/01/2002 - 04/02/2002	16 226	0.8
<sup>a</sup> Samp	ling lost due to technical difficu	lties during the camp	oaign.

#### Sample preparation and treatment

The filters used for sample collection were initially cut into 4 equal parts using a teflon cutter in a laminar flow clean area and were successively weighted. 5 ml ultrapure HNO<sub>3</sub>, 2 ml H<sub>2</sub>O<sub>2</sub> (30%, Merck, Suprapur), 2.5 ml Milli-Q water and 1 ml ultrapure HF were added to a 1/8 portion of the filters inside a TMF (tretraflouromethoxil) precleaned vessel and were then digested.

The samples were digested by a microwave oven (Milestone model Ethos 1600) through the following five step procedure: step 1: 5 min at 300 W; step 2: 15 min at 0 W; step 3: 5 min at 400 W; step 4: 5 min at 0 W; step 5: 5 min at 500 W.

After digestion the vessels were cooled to room temperature and to each was added 5 ml of saturated  $H_3BO_3$  (Merck, Suprapur) solution to remove the excess of HF that could etch the silica-based injector tube in the ICP torch. Final solutions were transferred into acid cleaned low density polyethylene (LDPE) bottles for the determination of various trace elements. Before every sample digestion a decontamination cycle for the TFM Teflon vessels was carried out using the same quantities of reagents used for the sample and a three step digestion programme (step 1: 5 min at 300 W; step 2: 5 min at 0 W; step 3: 5 min at 400 W).

A reagent blank, composed of the same amounts of chemicals as those used in sample digestion, was included in each sample digestion batch to monitor the cleanliness of microwave digestion and sample handling processes. For the quality controls (see below) blank filters was washed, dried and weighted as the filters used for sampling.

## **ICP-SFMS** analysis

Li, Pb, Cd, U, Ba, Bi, Cs, Rb, Tl, Sr, Al, V, Fe, Cu, Mn, Zn, Co, Ag were determined by double-focusing ICP-SFMS (Finnigan MAT, Bremen, Germany). The instrument has predefined resolution settings of 300 (low-resolution mode), and 3000 (medium-resolution mode). After digestion the samples were transferred to the sample introduction area of the instrument, where they were handled under a clean bench in order to minimize contamination from ambient air. Finally, samples were introduced into the plasma using a Micro Concentric Nebulizer (MCN-100, Cetac Technologies, Omaha, NB). The instrumental conditions and measurements parameters are described in detail elsewhere.<sup>14</sup> The concentration of the elements was obtained by using an external calibration curve.

#### Quality controls

In this analytical determination an important problem is constituted by the low quantities of the metals present in the sampled aerosol compared to the great mass of cellulose material from which the filters are made. Some analytes are present as trace impurities in the cellulose material and could accumulate to a level comparable to that present in the aerosol samples. Moreover due to the large time elapse between the cleaning of the filters in Italy, the sampling in the southern hemisphere, and the analysis of the samples on return to Italy, possible sample contamination must be considered. Therefore, we collected and analysed 5 blank samples to establish baseline concentrations which were subtracted from the concentrations of trace elements in the field samples. Field blanks were obtained by keeping the filters in samplers at the sampling station for a few minutes without any air flowing and then transferring them to a plastic bag without further exposure. Field blanks were used to determine the "limits of detection' (LODs), that were quantified as three times the blank standard deviation.<sup>15</sup> The amounts found (Table 2) ranged from 0.04 ng for Tl to  $8.9 \times 10^3$  ng for Al with individual LODs ranging from 0.09 ng to  $1.2 \times 10^4$  ng, respectively.

 Table 2
 Filter blanks for the complete process of sampling, treatment and analysis, and limit of detections (LODs)

Element	Filter blank <sup>a</sup> /ng	$\mathrm{SD}^b/\mathrm{ng}$	$LOD^c/ng$	$\mathrm{LOD}^d/\mathrm{pg}~\mathrm{m}^{-3}$
Li	1.8	3.5	10.5	0.62
Pb	103	36	108	6.4
U	0.71	0.4	1.2	$7.1 \times 10^{-2}$
Cd	173	80	240	14.1
Ba	156	114	342	20.1
Bi	0.38	0.3	0.9	$5.3 \times 10^{-2}$
Cs	0.18	0.4	1.2	$7.1 \times 10^{-2}$
Rb	8.17	1.9	5.7	0.34
Tl	0.04	0.03	0.09	$5.3 \times 10^{-3}$
Sr	39.1	27	81	4.8
Al	$8.9 \times 10^3$	$3.9 \times 10^3$	$1.2 \times 10^{4}$	$6.9 \times 10^{2}$
V	5.9	2.8	8.4	0.49
Fe	$2.7 \times 10^{3}$	$1.2 \times 10^{3}$	$3.6 \times 10^{3}$	$2.1 \times 10^{2}$
Cu	109	94	282	16.6
Mn	33.3	19	57	3.4
Zn	170	65	195	11.5
Co	2.6	2.2	6.6	0.39
Cr	143	97	291	17.1
Ag	5.7	6.3	18.9	1.11

<sup>*a*</sup> Five repeats. <sup>*b*</sup> Standard deviation. <sup>*c*</sup> LOD calculated as three times the blank standard deviation. <sup>*d*</sup> LOD calculated as pg m<sup>-3</sup> using the average air volume (17 000 m<sup>3</sup>).

The trace metal amounts in the air samples at Terra Nova Bay were generally higher than the LODs. Therefore the majority of trace metal amounts found in the field blanks were generally <20% of the amount found in the sample from the Antarctic station, the values of Ag and Cd in the field blanks were comparable to those in the sample; so these elements were left out of further discussions.

An estimation of the repeatability of the method was obtained by replicate measurements on five aliquots (about 10 mg) of NIST Standard Urban Dust Reference Material (SRM-1648), which were digested with an 1/8 portion of a blank filter. Moreover four portions of the same sample were digested to test the uniformity of particulate collected on the filter. The relative standard deviation ranged between 1% and 3% for the SRM and between 1% and 15% on real samples.

The recovery was tested by the analysis of four aliquots (some mg) of NIST Standard Urban Dust Reference Material

(SRM-1648) and expressed as a percentage of the NIST certified values. The recoveries ranged from 81% for V to 97% for Pb and indicated that no correction for laboratory bias was necessary. These values are in agreement with those reported by Yang *et al.*<sup>16</sup> who found recoveries from 70% to 107% for Fe, Zn, As, Se, Sb for SRM-1648.

## Data analysis

Multivariate statistical analysis was made by the well-known technique of Principal Component Analysis (PCA). The data processing was performed using the Statgraphics Plus 5.1 (Manugistics, Inc., Rockville, MD, USA) and Systat 10.2.05 (Systat Software, Inc., Richmond, CA, USA) software packages.

## **Results and discussion**

#### Presentation of the data

The range of PM<sub>10</sub> concentrations measured at Terra Nova Bay during 2000/01 and 2001/02 austral summer are 0.54–1.3  $\mu$ g m<sup>-3</sup> and 0.77–2.95  $\mu$ g m<sup>-3</sup>, respectively. These values are comparable with those found by Mazzera *et al.*<sup>11</sup> at Hut Point (average 3.4  $\mu$ g m<sup>-3</sup>, highest: 10.4  $\mu$ g m<sup>-3</sup>) and at Radar Sat dome (average: 4.1  $\mu$ g m<sup>-3</sup>, highest: 16.6  $\mu$ g m<sup>-3</sup>) located near to Mc Murdo. An average total mass lower than 180 ng m<sup>-3</sup> is reported by Maenhaut *et al.*<sup>12</sup> at the sampling location 5 km from the Amundsen–Scott South Pole station.

The median, maximum and minimum of element concentrations obtained in this study are summarized in Table 3. The concentrations found are extremely low for most metals, confirming the high purity of Antarctic aerosol. Measured concentrations are found to differ by several orders of magnitude from one metal to another. The highest concentrations, falling in the ng m<sup>-3</sup> range, are observed for Al and Fe which are major constituents of crustal material<sup>17</sup> whereas the lowest concentrations, falling in the sub-pg m<sup>-3</sup> range, are observed for elements such as Tl, Cs, Bi, U, which are present at very low concentrations in crustal material.<sup>17</sup>

Comparison with the few data previously published show that our results are higher than the Geographic South Pole results,<sup>12</sup> but lower than those reported by Mazzera *et al.*<sup>11</sup> for Radard Sat which attributes the high values to local emissions from Mc Murdo station. From this comparison and because of the relatively short distance of the sampling site from the

Table 3 Median, maximum and minimum of element concentrations (pg m $^{-3}$ ), measured at Terra Nova Bay during 2000/01 and 2001/02 austral summer<sup>*a*</sup>

Austral summer 2000/01			Austral summer 2001/02			
Element	Median	Maximum	Minimum	Median	Maximum	Minimum
Li	3.95	12.99	2.03	10.17	18.83	7.74
Pb	16.7	38.7	9.7	15.0	48.7	6.80
U	0.135	0.442	bdl	0.881	1.204	0.400
Ва	30.0	65.5	bdl	60.9	109.1	23.7
Bi	0.09	0.16	bdl	0.20	0.73	bdl
Cs	0.23	1.27	0.15	1.47	2.22	0.59
Rb	7.4	24.1	5.4	20.1	29.4	11.3
Tl	0.12	0.17	0.10	0.17	0.25	0.04
Sr	91	204	50	201	290	94
Al	$2.08 \times 10^{3}$	$9.13 \times 10^{3}$	$1.62 \times 10^{3}$	$7.75 \times 10^{3}$	$13.58 \times 10^{3}$	$2.84 \times 10^{3}$
V	3.9	20.2	3.0	22	38	7.1
Fe	$2.31 \times 10^{3}$	$7.81 \times 10^{3}$	$1.58 \times 10^{3}$	$6.58 \times 10^{3}$	$10.99 \times 10^{3}$	$2.74 \times 10^{3}$
Cu	422	641	86	394	110	121
Mn	55	139	30	147	224	45
Zn	81	195	19	109	216	28
Со	1.33	4.03	1.04	5.09	6.28	1.37
Cr	43.0	75.3	19.7	59.0	240.3	17.6
<sup><i>a</i></sup> $bdl = below$	w detection limit.					

Italian station, we can suppose that the human activities at the "Terra Nova Bay" Italian base affects the trace metal concentration. An environmental monitoring programme for "Terra Nova Bay" at the Italian base was implemented from the first year of operation to monitor and keep under control any negative impact on the Antarctic environment due to scientific and logistical activities. A sewage treatment plant, an incinerator and electrical generators are present at the base and they can be considered as contamination point sources. During monitoring of the atmosphere, the concentration levels of heavy metals in the particulate matter was determined and the results suggested that the human activities in the Italian Base are at such a level as to potentially alter only very slightly their concentrations in air (in atmospheric particulate), and only over a very small area and for a short period of time.<sup>18</sup> A partial contribution could derive from the incinerator, which is in operation on average three times a week and affects only a limited area around the station. A larger contribution could be expected from the two electrical power generators that operate during the whole campaign. Chiavarini et al. 19 report that the most representative elements present in the incinerator emissions were V, Cr, Cu, Zn, Cd, Sb with daily average concentrations of about < 0.001, 0.010  $\pm$  0.001, 0.067  $\pm$  0.010, 0.89  $\pm$  $0.10, 0.003 \pm 0.001, 0.030 \pm 0.003 \text{ mg m}^{-3}$ , respectively. The Environmental Monitoring report<sup>18</sup> showed that the average values in the atmospheric particulate (PM<sub>10</sub>) in the area of the Base for Pb, Cd, Cr, Zn, Ni, V and Cu are, respectively 0.8,  $0.06, 1.7, 9, 0.5, 0.40, 16 \text{ ng m}^{-3}$ , which are higher than the levels reported in this study.

In Fig. 2 are reported, as examples, the temporal evolution of the concentration of some elements. Pb, Cu, Cr, Zn, Tl and Sr show a similar trend with wide variation during sampling and about the same concentration levels during the 2000/01 and 2001/02 austral summers. Al, Fe, Cs, U, Ba, Mn, Co, Li, V and Rb instead show similar trends with higher concentration values to the end of the 2000/2001 campaign and at the start of the 2001/2002 campaign. For these elements the mean concentrations obtained during 2001/02 were higher than those obtained for 2000/01. In general no clear temporal evolution of the concentration during the sampling campaign is observed for these elements. This could be due to variations in the direction of the prevalent wind during the sampling or more probably it is due to local emissions.

### Principal component analysis

The trace metal data matrix was analysed by PCA using the element concentrations as variables and the samplings as objects in order to represent the data structure in a smaller number of dimensions (usually two or three); this permits us to observe the object groupings. The two sampling years have been considered simultaneously and each variable was standardized (mean centring and dividing by its standard deviation).

The variance explained by the first three principal components is 91.9% (71.5%, 15.2%, 5.2%, respectively). The plot of component weights on the first three PC's is reported in Fig. 3 and shows that the Pb, Zn, Cr, Cu and Bi variables and Li, U, Ba, Cs, Rb, V, Fe, Mn, Co variables form two distinct groups. This is indicative of the fact that the variables inside the two groups are well correlated with similar trends. Sr and Tl show a poor correlation with all variables.

The component weights of the first PC are similar ranging from 0.117 (Pb) to 0.281 (Ba); the second component is linked particularly to Co, Cr, Cu and Pb with weights of 0.314, 0.435, 0.338 and 0.541, respectively; the third component is linked particularly to Sr and Tl with weights of 0.663 and -0.512, respectively.

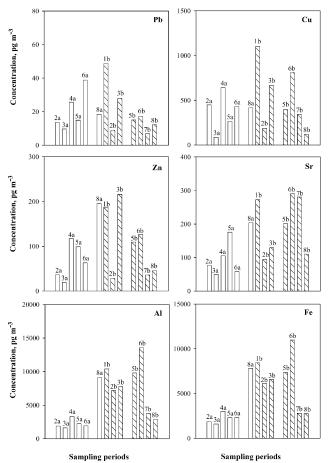


Fig. 2 Pb, Zn, Al, Cu, Sr and Fe concentrations during the 2000/01 and 2001/02 austral summer.

The scatterplot obtained from the first three PC's is reported in Fig. 4. It can be observed that in the left part the samples of the 2000–2001 campaign are prevalent, whereas in the right part those of the 2001–2002 campaign are prevalent. As the weights of the first PC are similar, the first PC seems linked to the total concentrations of the sample, which are generally lower in the 2000–2001 campaign; so for example sample 3a has the lowest value for the total concentration (3.45 ng m<sup>-3</sup>), sample 1b has the highest value and samples 8a and 5b have similar values (1.81 and 2.10 ng m<sup>-3</sup>). The pattern on the second PC is linked to the four elements, that have the greatest weights; so sample 1b has the highest concentration values for Bi, Cu, Cr and Pb. Sample 7b has the lowest Tl concentration; this affects its score (the highest) on the third component and its location on the graph obtained from the first three PC's.

The three dominant sources of atmospheric particulate material in remote areas are human activities (local and from other continents), crustal weathering and the ocean. Generally

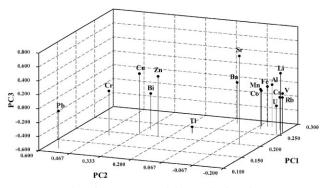


Fig. 3 Plot of component weights on the first three PC's.

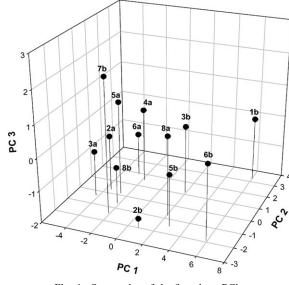


Fig. 4 Scatterplot of the first three PC's.

to identify elements associated with each source some marker elements such as Al, Fe, Na are chosen.<sup>12,20</sup> These observations and the results obtained with principal components analysis show that the elements Li, U, Ba, Cs, Rb, V, Mn, Co are correlated with Al and Fe indicating that crustal material is a significant source. Elements such as Pb, Cr, Cu, Zn, Bi are correlated among themselves, but not with the Al and Fe group, indicating the presence of another origin such as anthropogenic sources. Finally Sr seems to have a different origin from those with anthropogenic and crustal origins, which could be a marine origin, whereas for Tl contemporary but not dominant anthropogenic and crustal sources could be present.

#### Crustal enrichment factor

Crustal influences on aerosol element concentrations can be assessed by crustal enrichment factors ( $EF_c$ ). For this, Al is normally used as the crustal marker element and  $EF_c$  are calculated according to following equation:

$$EF_c = (E/Al)_{air}/(E/Al)_{crust}$$

where  $(E/Al)_{air}$  is the concentration ratio of an element (E) to Al in the aerosol and  $(E/Al)_{crust}$  is their mean concentration ratio in upper crustal rocks.<sup>17</sup>

Mean crustal ratios are only an approximation of the relative composition of crustal material aerosols, due to differing types of crustal material and soils in various source areas and uncertainties concerning fractionation during weathering processes; therefore they must be used with caution to assess atmospheric trace metal sources. Thus  $EF_c$  values from 1 to 10 may still indicate a crustal material source for the elements.<sup>8,12,21</sup>

Ranges and averages of EF values for samples collected during 2000/01 and 2001/02 austral summers are reported in Table 4. It can be seen that for some of the elements, namely Li, U, Ba, Cs, Rb, Tl, Sr, V, Fe, Mn, Co, EF<sub>c</sub> between ~1 and 10 are observed. It is therefore likely that rock and soil dust are significant sources for these elements in the aerosol samples. Conversely, EF<sub>c</sub>'s larger than 10 are observed for Cu, Zn, Cr, Pb, Bi, indicating that the rock and soil dust contribution was minor for these metals, and that they mainly originated from other sources. To our knowledge a few other EF<sub>c</sub>'s are reported in the literature for Antarctic aerosol. Maenhaut *et al.*<sup>12</sup> measured EF<sub>c</sub>'s greater than 10 at the geographic South Pole for Zn, Cu, In, W, Sb, PB, Au, As, Cl, Ag, Se, S, Br and I showing that these elements have other origins (human activ-

Table 4 Crustal enrichment factor  $(EF_c)$  for 2000/01 and 2001/02 austral summers

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Element	2000/01	2001/02	Average
Li	6.0	5.8	5.9
Pb	38	12	25
U	1.7	3.4	2.5
Ва	1.2	0.92	1.1
Bi	17	23	20
Cs	1.4	2.4	1.9
Rb	2.2	1.9	2.0
T1	5.2	2.5	3.9
Sr	9.6	7.4	8.5
Al	1.0	1.0	1.0
V	3.0	3.8	3.4
Fe	2.5	2.1	2.3
Cu	$7.9 \times 10^2$	$3.5 \times 10^{2}$	$5.7 \times 10$
Mn	3.3	2.4	2.9
Zn	41	20	30
Co	3.9	3.6	3.8
Cr	38	18	28

ities, oceanic) than crustal origins. Other elements such as Sc, V, Fe, Co, Mn, Th, Ti, La, Sm, Ce, Co, Cs, Rb, Mg, K, Ba, Cr with EF<sub>c</sub>'s near unity are believed to originate predominantly from the earth's crust. It is also useful to compare our results with EF<sub>c</sub>'s evaluated for dated snow samples. Planchon et al.<sup>10</sup> observed at Coats Land a significant increase in EF<sub>c</sub> values for Cu, Zn, Cr, Ag, Pb, Bi and U in recent snow and consequently in aerosol and attribute those results to emissions to the atmosphere from anthropogenic activities in the South Hemisphere (principally metal production activities). Increases in Pb and Cu concentrations have been well evidenced by Wolff and co-workers<sup>9,22</sup> in snow samples from the 20th century at Coats Land. Therefore the high EF<sub>c</sub> values we have found, could be attributed to emissions from human activities in the other continents of the Southern Hemisphere and their successive transport to Antarctica. Contributions from local emissions such as nearby the Italian station and inputs of metals, especially of Bi, from volcanic activities<sup>23</sup> (such as Erebus and Terror volcanoes on Ross Island) cannot be excluded.

## Conclusions

PM10 samples were collected and chemically characterized at a coastal site of west Antarctica during the austral summers of 2000/01 and 2001/02. Principal Component Analysis and crustal enrichment factors with respect to Al are used for the identification of the principal sources of Antarctic aerosol. From the obtained data we can conclude that: the mean value of PM<sub>10</sub> mass concentrations are in general agreement with the mean values found at higher southern latitudes; however the element concentrations are lower than those reported at McMurdo and higher than those at the Geographic South Pole. For Li, U, Ba, Cs, Rb, V, Fe, Mn a crustal material source has been observed whereas for Cu, Zn, Cr, Pb, Bi anthropogenic sources due to human activities in Terra Nova Bay Italian station or emissions from the other continents of the Southern Hemisphere and successive transport to Antarctica can be hypothesized. With these investigations we have contributed some new information to the study of aerosol in Antarctica but for the future new investigations should be carried out on the role of aerosol in chemical contamination and on the effects of airborne pollutants on Antarctic ecosystems.

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