



## Trace elements in winter snow of the Dolomites (Italy): A statistical study of natural and anthropogenic contributions

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### ABSTRACT

Knowledge of the occurrence of trace elements deposited in fresh alpine snow is very limited. Although current sources of major ionic inorganic species have been well established, this is not the case for many trace elements. This manuscript attempts to reconstruct the origin of Ag, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mo, Mn, Pb, Sb, Ti, U, V and Zn in winter surface snow, extensively collected in the Dolomites region (Eastern Alps, Italy). Sampling of surface snow was conducted weekly during the winter 1998 at 21 sites at altitudes ranging from ~1000 to ~3000 m. This led to a remarkable dataset of trace element concentrations in surface snow from low latitudes. Here we show a preliminary statistical investigation conducted on the 366 samples collected. It was found that V, Sb, Zn, Cd, Mo and Pb have a predominantly anthropogenic origin, linked to the road traffic in the alpine valleys and the nearby heavily industrialised area of the Po Valley. In addition, the occasionally strong Fe and Cr input may reflect the mechanical abrasion of ferrous components of the vehicles. However, much of the Fe along with Mn, U and Ti originates primarily from the geological background of the Dolomites. A marine contribution was found to be negligible for all the trace elements. The origin of other trace elements is less clear: Ag can be possibly attributed to a predominantly anthropogenic origin while Cr, Co, Cu and Ba are usually from crustal rocks but different than the Dolomites.

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### 1. Introduction

Recently the interest in trace element geochemistry of snow and ice has extended from the remote polar sites of Antarctica (Gabrielli et al., 2005a), Greenland (Barbante et al., 2003) and the Arctic (Shotyk et al., 2005) to cover the high altitude zones at lower latitudes. These sites are relatively remote such as those in the Andes (Correia et al., 2003) or next to heavily populated areas such as those in the European Alps (Van de Velde et al., 2000; Schwikowski et al., 2004).

Snow deposited on the Alps documents the effects of anthropogenic emissions in Europe (Schwikowski, 2003). Recent efforts on alpine glaciers have been devoted mainly to the reconstruction of the history of trace element pollution over the last few centuries (Barbante et al., 2004; Schwikowski et al., 2004). However, studies looking at the source attribution of trace elements (TE) entrapped in recent alpine snow are extremely rare (Veyseyre et al., 2001;

Dossi et al., 2007). Such studies are very valuable as they allow policy makers to reduce anthropogenic emissions of specifically targeted heavy metals that are potentially toxic. The goal is to preserve terrestrial and aquatic ecosystems and to protect human health. In addition, source discrimination of naturally occurring TE contributes improved understanding of important biogeochemical cycles.

The Alps are a valuable observation point for anthropogenic emissions as it is located in one of the most industrialised regions in the world. These mountains are heavily influenced by the presence of international and regional highways, industries, refuse incineration plants and the highest density of winter sport infrastructures for any mountain area. Due to the typically lower atmospheric mixing heights during the winter, atmospheric pollutants are frequently trapped in the stable alpine boundary layer, which extends to 3000 m in the Eastern Alps and thus inhibits mixing between the upper and lower levels. Thus we can expect the winter snow collected up to 3000 m in the Dolomites region to be indicative of the tropospheric chemical content in the lower Alps and adjacent regions.

We collected surface snow samples each week from 21 stations in the Dolomites region (Eastern Alps, Italy) over one entire winter

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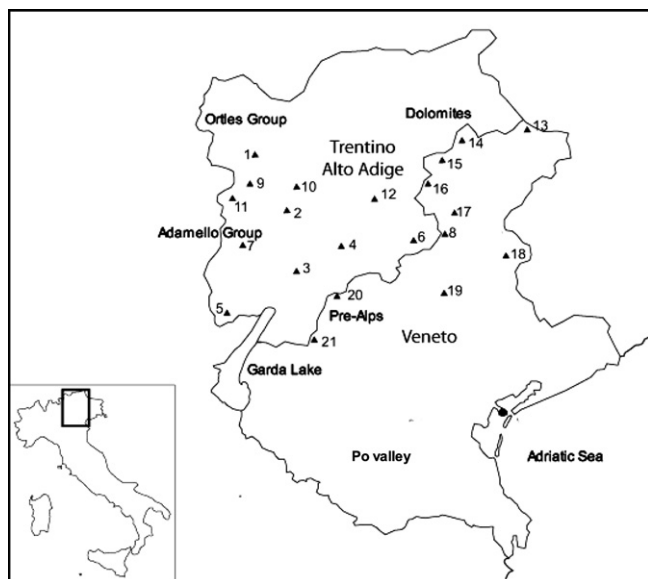
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season (1998). We quantified Ag, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mo, Mn, Pb, Sb, Ti, U, V and Zn in 366 samples. To our knowledge, this is the first extensive study conducted at mid latitudes focusing on TE in surface snow over one complete season. We use Principal Component Analysis (PCA) to highlight the most remarkable features of the data set, with emphasis on the reconstruction of TE sources. This approach attempts to provide to local administrators preliminary information about the origin and the source of TE dispersed in the troposphere of this region during the winter, the most critical period for air quality in the alpine valleys. We will report in detail in another manuscript the TE snow content and fluxes for each location considered in this work.

## 2. Experimental

### 2.1. Area description

Surface snow samples were collected weekly from December 1997 to April 1998 at 21 sampling sites located in the Dolomites region in Northeastern Italy (Fig. 1). This area is very large (~15 000 km<sup>2</sup>), it is approximately 100 km from the Adriatic Sea and has a maximum elevation of 3905 m (Mount Ortles). It is located on the southern slope of the Eastern Alps, which is crossed by the highway connecting Northern Europe with the south through Brenner Pass in the Southern Tyrol. This territory is roughly divided into two main geological domains, the eastern part (the mountain group of the Dolomites), which is characterised by carbonates (dolomite), and the western part (Mount Adamello and Mount Ortles groups) that is characterized mostly by silicate (granites and metamorphic rocks) with only a minor presence of carbonates and dolomite (Brenta group). During winter this area



**Fig. 1.** Sampling sites in the Dolomite regions of Trentino-Alto Adige and Veneto (Italy). (1) Mount Vioz, Tarlenta, 2030 m; (2) Brenta, Prarodont, 1530 m; (3) Bondone, Viote, 1500 m; (4) Lagorai, Panarotta, 1875 m; (5) Ledro, Tremalzo, 1550 m; (6) Lagorai, Brocon Pass, 1550 m; (7) Adamello, Malga Bissina, 1780 m; (8) Primiero, Noana valley, 1025 m; (9) Adamello/Presanella, Tonale Pass, 1880 m; (10) Presanella, Folgarida, 1910 m; (11) Adamello/Presanella, Mount Presena, 3040 m; (12) Latemar, Pampeago, 1900 m; (13) Comelico, Mount Croce Pass, 1960 m; (14) Tofane, Ravales, 2615 m; (15) Dolomites, Mounts of Ornella, 2250 m; (16) Dolomites, Mount Pradazzo, 2200 m; (17) Agner, Gosaldo, 1350 m; (18) Pre-Alps, Favergera, 1605 m; (19) Pre-Alps, Mount Grappa, 1540 m; (20) Folgaria-Asiago, Campomolon, 1735 m; (21) Lessini, Mount Tomba, 1620 m. Further information about the sampling sites can be found on the Internet at [www.meteotrentino.it/AspWeb/Monitoraggi/stations/yeti/Campi\\_neve/mappa/mappa\\_neve.asp](http://www.meteotrentino.it/AspWeb/Monitoraggi/stations/yeti/Campi_neve/mappa/mappa_neve.asp) and [www.arpa.veneto.it/csvdi/nivo.htm#ubicazione](http://www.arpa.veneto.it/csvdi/nivo.htm#ubicazione).

is characterized by an anti-cyclonic high pressure field, whose influence alternates with the advection of humid air masses from the Atlantic, producing snowfalls associated with southerly winds.

The 21 sampling sites were chosen mainly in remote areas to avoid contamination from nearby emissions from roads, villages, tourist stations, alpine huts and artificial snow cannons. However, most of the sampling sites were close to ski areas at an average altitude of ~1800 m. The lowest site was located at 1040 m (8, Noana valley) and the highest at 3040 m (11, Mount Presena).

### 2.2. Sampling and materials

During the winter of 1998, shallow snow was collected weekly at all sites, resulting in a total of 366 samples. Frequent snowfalls affected the entire territory from December until the first part of January and then again in April. In contrast, from the end of January until the end of March, stable weather conditions resulted in a general lack of snowfall. Thus, wet deposition occurred mainly in the first and the last period of the sampling campaign whereas dry deposition dominated in the interim.

At the sampling sites, the specific location for the collection of the snow samples was chosen weekly according to the snow surface conditions. Inhomogeneities such as the presence of sastrugi and animal footprints were carefully avoided. The 30 operators involved in this project were specifically trained in clean procedures and wore special clean-room clothing and polyethylene gloves during sampling. Sampling was conducted by plunging low-density polyethylene (LDPE) ultra cleaned wide mouth bottles (500 ml) directly into the snow, upwind of the operators. Typically, the first 2 cm of snow were collected along several short horizontal transects of about 50 cm. The volume of snow sampled corresponded to 100–150 g of water. The containers were capped, sealed in double polyethylene bags and stored frozen until analysis.

LDPE sampling bottles were previously acid cleaned inside a class 100 clean bench. The ultra pure water was obtained by coupling a reverse osmosis system (Milli-RO) with a four-column ion exchange system Milli-Q (Millipore, Bedford, MA). The acids used were Merck "Suprapur" grade HNO<sub>3</sub> (Merck, Darmstadt, Germany) and HNO<sub>3</sub> (70%) doubly distilled at the National Institute of Standards and Technology (NIST, Gaithersburg, MD).

### 2.3. Analytical methods

Samples were treated and melted in a class 100 laminar flow clean bench. A 5 ml aliquot was transferred in a 10 ml ultra clean LDPE vial and acidified with ultra pure HNO<sub>3</sub> (NIST) (2% v/v) for the quantification of Ag, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mo, Mn, Pb, Sb, Ti, U, V and Zn by Inductively Coupled Plasma Sector Field Mass Spectrometry (Finnigan MAT Element, Thermo, Bremen, Germany) following the procedure developed for ultra trace quantification described in detail elsewhere (Barbante et al., 1999).

Solid particles transported to high altitudes in the Alps ranges from a few micrometre to 10–20 µm in diameter and have a mode of 2–5 µm (Delmonte, B., Personal communication). Occasionally, few considerably larger particles (<1 mm) were observed in our samples. It has been calculated that particles <10 µm in diameter are atomised in the first 15–20 mm of the plasma discharge (Barnes and Schleicher, 1974) and therefore most of the insoluble particles are ionized in the hot plasma (~7000 K).

However, this does not always hold true for silicate particles, where some TE are strongly bound to minerals. The total TE content was recently determined in some ice samples, after digestion with ultrapure HNO<sub>3</sub> and HF, with microwave irradiation. The results show that different TE has a different behavior. As an example, the fraction of Mn determined after acidification with HNO<sub>3</sub>

corresponds to the total element content, while only from ~50% to ~65% of Ba is determined (Gabrielli et al., 2005b). We note that, as the concentration obtained is proportional to the total content, linear relationships among the TE are not altered.

Finally, 30 ml aliquots were taken in 100 ml ultra clean LDPE bottles for the determination of major ions taken as ancillary parameters, such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  by Ion Chromatography (IC) (Gragnani et al., 1998).

### 3. Results and discussion

#### 3.1. Ranges of concentration

The aim of this paper is to extract the overall features of the large data set obtained (~8000 concentration data). A subsequent manuscript will provide an exhaustive description of the spatial and temporal variability of the concentrations and fluxes to each location. However, the main statistics of the chemical data set are given in Table S1 (Supplementary material) while the average concentrations at each station and the entire data set are illustrated in Tables S2 and S3 (Supplementary material).

Low average concentrations were found for TE, ranging from  $8.6 \text{ pg g}^{-1}$  of U up to  $27 \text{ ng g}^{-1}$  of Fe. Higher mean values were determined for the ancillary major ions ranging between  $\sim 100 \text{ ng g}^{-1}$  for  $\text{Mg}^{2+}$  and  $\sim 900 \text{ ng g}^{-1}$  for  $\text{NO}_3^-$ . The snow TE concentrations from the Dolomites region are consistent with those determined in relatively recent (after 1970) summer firn and ice, drilled at Colle Gnifetti (4450 m) (Mount Rosa, Swiss-Italian Western Alps) (Barbante et al., 2004). For instance, mean Zn and Cd concentrations were found to be  $3176 \text{ pg g}^{-1}$  and  $58 \text{ pg g}^{-1}$  on Colle Gnifetti, whereas in the Dolomites region, mean winter values of  $3450 \text{ pg g}^{-1}$  and  $60 \text{ pg g}^{-1}$  were determined.

An indication of the spatial heterogeneity of the concentrations can be obtained by comparing the mean values of the different sampling sites (Table S2, Supplementary material). As expected, this is very high, due to the different altitudes, geographic positions and distances from anthropogenic sources of emissions. For the scope of this paper it is sufficient to state that the lowest concentrations are found in snow collected above ~2000 m of altitude, whereas higher concentrations occur in snow taken at lower altitudes, especially in the Pre-Alps. Our results are in agreement with other studies performed in alpine mosses where the highest TE concentrations were observed at mid altitudes (1400–1800 m) (Gerdol and Bragazza, 2006).

#### 3.2. Statistical method of analysis

To provide regional administrators with a general characterization of the sources and origin of the TE in the snow of the Dolomites region, PCA was used. Before applying the PCA, the non-normal distribution of the variables (see skewness and kurtosis in Table S1, Supplementary material), led us to perform a data set transformation by substituting the concentration with its rank position (Baxter, 1995; Molinaroli et al., 1999). This procedure is based on a robust descriptive statistic (Swan and Sandilands, 1995). Ranked data allow the application of methods with fewer assumptions about the underlying distribution (Lebart et al., 1984; Korhonen and Siljamaki, 1998).

This particular approach has several advantages: (i) concentration values below the limit of detection are taken into account; (ii) the data are not constrained by the units of measurement that could produce a virtual variability; (iii) PCA is more robust for outliers (Baxter, 1995); (iv) a limited pool of data with strong variations cannot dominate the entire variability; (v) a single chemical variable cannot dominate the total variance and (vi) the essential

variability is taken into account by ignoring the background noise (Molinaroli et al., 1999). This approach may have some minor drawbacks as ranking conceals the existence of the outliers and this is not necessarily desirable (Baxter, 1995).

We applied a cluster analysis on the score matrix of the significant principal components (PCs) extracted (Table S4, Supplementary material), by adopting the Euclidean distance and the Ward method for group aggregation (Swan and Sandilands, 1995) (Fig. 2 and Figs. S1–S3, Supplementary material). This emphasizes the associations among the chemical variables highlighted by the PCs scores and allows an improved evaluation of several weaker links.

#### 3.3. PCA applied to the entire data set

The PCA applied to the entire chemical data set (PCA1) resulted in three PCs reporting 61%, 10% and 6% of the total variance of 22 chemical variables (Tables S4 and S5, Supplementary material).  $\text{K}^+$  was found to be insignificant, as there were too many values below the detection limit.

Ag, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mo, Mn, Pb, Sb, Ti, U, V and Zn obtained high scores on PC1;  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  on PC2;  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  on PC3. We interpret the large aggregation of all the TE as reflecting the fact that sampling sites with heavy (or low) anthropogenic input were quite often also influenced by heavy (or low) crustal fallout (see below). However, some TE such as Ti, U, Mn, Fe, Ba and to a lesser extent Cu, Co and Cr scored rather high on PC3 that is governed by  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (Table S4, Supplementary material). In contrast, another group of metals, composed of V, Sb, Zn, Cd, Mo and Pb, obtained high scores on PC2 governed by  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ,  $\text{Na}^+$ . This is visually emphasized by cluster analysis (Fig. 2) where TE are indeed divided into two sub-groups composed of Ti, U, Mn, Fe, Ba, Cu, Co, Cr and V, Sb, Zn, Cd, Mo, Pb, Ag, Bi. In addition, cluster analysis separates PC2 in two sub-groups composed of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Na}^+$ ,  $\text{Cl}^-$ .

The data set was disaggregated and nine additional PCA were performed (see Figs. S1–S3, Supplementary material). Interestingly, we observe that these show similar relationships. We interpret this as evidence for a common regional atmospheric signature influenced by similar sources for TE and ionic species. In the following paragraphs we explain the linkages that emerged from the statistical analysis.

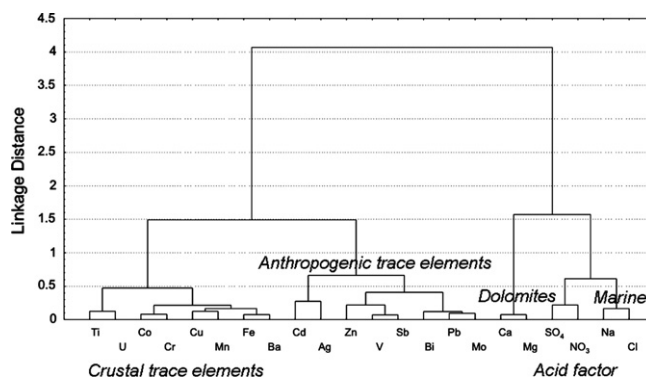


Fig. 2. Cluster analysis calculated from the principal components score matrix extracted from the entire data set. Trace elements on PC1 are divided into two sub-groups composed of Ti, U, Mn, Fe, Ba, Cu, Co, Cr (crustal elements) and V, Sb, Zn, Cd, Mo, Pb, Ag, Bi (anthropogenic elements). Cluster analysis separates PC2 in two sub-groups composed of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  (anthropogenic acid factor) and  $\text{Na}^+$  and  $\text{Cl}^-$  (marine component).



### 3.4. The crustal contribution

The division of TE into two distinct groups can be explained by comparing concentrations determined in the snow with the average concentrations in the carbonate rocks (Taylor and McLennan, 1985). The  $\text{Ca}^{2+}$  contribution from remote crustal sources is considered negligible as no significant transport of Saharan dust to the Alps occurred during the winter of 1998 (Guerzoni, S., Personal communication). In general,  $\text{Ca}^{2+}$  (as well as  $\text{Mg}^{2+}$ ) can be considered as the most characteristic crustal species over this region. This is supported by the strong link between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and by the fact that, in areas where carbonates dominate, average  $\text{Ca}^{2+}$  concentrations range between 300 and 600  $\text{ng g}^{-1}$  (Table S2, Supplementary material). However, where a granitic and/or metamorphic background exists, average  $\text{Ca}^{2+}$  concentrations such as those at (7) Malga Bissina (226  $\text{ng g}^{-1}$ ), (11) Mount Presena (88  $\text{ng g}^{-1}$ ) and (1) Tarlenta (149  $\text{ng g}^{-1}$ ) are lower, consistently with the weaker linkage strength between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Fig. S2a, Supplementary material).

For a given TE, (e.g. Mn), the percentage of the carbonate's contribution can be calculated as

$$\text{Mn}\% = \left[ \frac{((\text{Mn})_r / (\text{Ca}^{2+})_r)}{(\text{Mn})_s / (\text{Ca}^{2+})_s} \right] \times 100 \quad (1)$$

where  $(\text{Mn})_s$  and  $(\text{Ca}^{2+})_s$  represent the concentration in the snow and  $(\text{Mn})_r$  and  $(\text{Ca}^{2+})_r$  the average concentration in the carbonate rocks (Taylor and McLennan, 1985). The carbonate's average contribution was high for Mn (100%), U (91%), Ti (65%), Fe (50%), Cr (32%) and V (24%), whereas it was less than 3% for Ag, Cd, Co, Sb, Mo, Cu, Pb, Ba and Zn. We can conclude that Mn, Ti, Fe and U scored high on PC3 of PCA1 governed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  because they originate from the geological background of the Dolomites. Mn, Ti and U, as shown later, are always independent from those TE of predominantly anthropogenic origin even at rural sites (Fig. S3b, Supplementary material). In contrast, Fe and Cr may be linked to a predominant anthropogenic TE fallout when the snow is likely affected by road traffic emissions as evidenced by their link illustrated in Fig. S3b (Supplementary material). This may reflect the emissions of Fe and Cr caused by the mechanical abrasion of ferrous components of the vehicles as Cr is abundant in stainless steel for instance.

A rock and soil dust contribution for Mn, Ti, Fe and U was also observed in ice and snow from the Western Alps (Van de Velde et al., 1998; Veysseyre et al., 2001). Interestingly, U in the Dolomite region did not show an excess above the crustal contribution, in contrast with U enrichment found in Mont Blanc (Western Alps) snow and ice, which was attributed to extensive mining activity in Germany (Barbante et al., 2001).

Finally, we note that a crustal contribution from a different geological background than the Dolomites is likely for Cr, Co, Cu and Ba as they show a crustal behavior linked to their association with Ti, U, Mn and Fe even though they obtain low carbonate contributions.

### 3.5. The marine contribution

Given that  $\text{Na}^+$  provides a proxy for marine aerosols, the calculated marine contribution, (based on  $\text{Na}^+$  concentration in the snow and the TE/ $\text{Na}^+$  mass ratio in the sea), to the budget of TE is always negligible. The excellent linkage between  $\text{Na}^+$  and  $\text{Cl}^-$ , concurrently with the mean mass ratio for  $\text{Cl}^-/\text{Na}^+$  of 2.5 (the marine ratio is 1.8) supports a prevalent marine input for these two major ions. The  $\text{Cl}^-$  excess in snow samples from the Alps could be attributed to a minor anthropogenic contribution of HCl, probably originating from coal combustion and waste incineration (Lightowlers and Cape, 1988). However, the prevalent marine input is most likely due to the close proximity of the Mediterranean

Sea. There is an apparent spatial concentration gradient between the sampling sites more exposed to the sea such as the Pre-Alps (for  $\text{Na}^+$ , (21) Mount Tomba (170  $\text{ng g}^{-1}$ ), (19) Mount Grappa (330  $\text{ng g}^{-1}$ ), (18) Faverghera (138  $\text{ng g}^{-1}$ ) and the more interior snow fields in the north western part of the Trento Province (for  $\text{Na}^+$ , (11) Mount Presena (47  $\text{ng g}^{-1}$ ), (1) Tarlenta (43  $\text{ng g}^{-1}$ ), (7) Malga Bissina (53  $\text{ng g}^{-1}$ )). A marine origin for  $\text{Na}^+$  and  $\text{Cl}^-$  is finally supported by air mass trajectories impacting the Dolomite region during the winter 1998 that often originated from the Mediterranean Sea (Fig. 3).

### 3.6. The anthropogenic contribution

The frequent linkage of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , suggests a predominantly anthropogenic origin for these two major ions. This well known anthropogenic acid factor ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) has been previously demonstrated (Preunkert et al., 2001). The anthropogenic precursors ( $\text{NO}_x$  and  $\text{SO}_2$ ) dominate the corresponding natural sources. Average  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations in snow were found to be higher in the Pre-Alps, which are in close proximity to the heavily industrialized Po Valley. For example  $\text{NO}_3^-$  in (18) Faverghera (1288  $\text{ng g}^{-1}$ ), (19) Mount Grappa (1371  $\text{ng g}^{-1}$ ) and (21) Mount Tomba (1047  $\text{ng g}^{-1}$ ), is higher relative to that in the less exposed internal sites ( $\text{NO}_3^-$  on (1) Tarlenta (743  $\text{ng g}^{-1}$ ), (2) Prarodont (752  $\text{ng g}^{-1}$ ) and (3) Viote (888  $\text{ng g}^{-1}$ )). Similar North-South spatial gradients for  $\text{SO}_4^{2-}$  were previously reported (Nickus et al., 1998). Although  $\text{SO}_4^{2-}$  shows a frequent linkage with  $\text{Na}^+$  and  $\text{Cl}^-$ , a marine origin for  $\text{SO}_4^{2-}$  can be eliminated because the non-sea salt-sulphate average contribution (based on  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  concentrations in the snow and the  $\text{SO}_4^{2-}/\text{Na}^+$  mass ratio in the sea) is  $\sim 90\%$ .

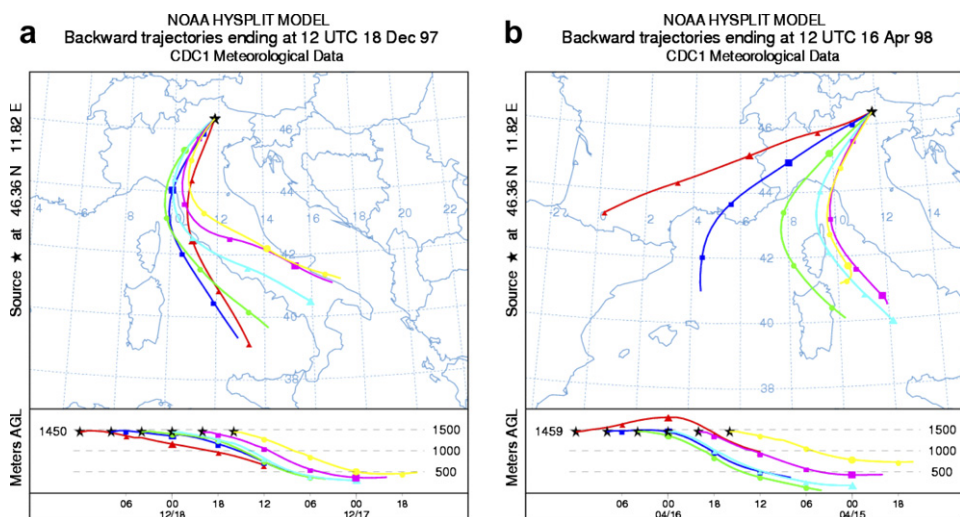
As observed, V, Sb, Zn, Cd, Mo, Pb, Ag and Bi cannot be linked to the dolomite-carbonate background as they have a low carbonate contribution along with very low scores on the PC governed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Nevertheless, with the exception of Ag and Bi, this group of trace metals often shows a relationship with the anthropogenic acid factor ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) (see text, Supplementary material) supporting a significant anthropogenic contribution for V, Sb, Zn, Cd, Mo and Pb.

In particular, we suggest that Pb, V and Sb indicate a contribution from road traffic emissions as they are strongly linked in snow samples likely affected by this source (Fig. S3b, Supplementary material). Moreover V is known to be a characteristic trace component of oil (especially that from Venezuela) while traffic emissions of Sb likely originate from brake wear (Sternbeck et al., 2002). Finally intensive automobile and heavy goods traffic in the alpine valleys is documented as source of Pb in the region. In 1995, in Trento Province, this source was responsible for the emission of  $\sim 40 \text{ t y}^{-1}$  of Pb (Trento Province data, from [www.appa-agf.net/article/articleview/30/1/20/](http://www.appa-agf.net/article/articleview/30/1/20/)).

Mo, Zn, Ag and Cd may originate from the different activities in parentheses: Mo (coal and oil combustion in power plants), Ag (waste incineration plants) and Zn (refuse incineration, nonferrous metal and steel production). In 1992 in Italy, Cd was emitted by electric power plants ( $\sim 20 \text{ t y}^{-1}$ ), industrial activities ( $\sim 15 \text{ t y}^{-1}$ ) and road transport traffic ( $\sim 15 \text{ t y}^{-1}$ ).

Preliminary estimates of Pb and Cd dry fallouts to our four most remote stations (11, 14, 15 and 16) indicate values of 4.2 and 0.09  $\text{g ha}^{-1} \text{ y}^{-1}$  ( $1 \text{ g ha}^{-1} \text{ y}^{-1} = 10^{-4} \text{ g m}^{-2} \text{ y}^{-1}$ ), respectively. When compared to critical loads for these ecosystems (Hettelingh et al., 2005) we note that Cd is significantly below its critical load ( $1 \text{ g ha}^{-1} \text{ y}^{-1}$ ) while Pb is of equal magnitude ( $10 \text{ g ha}^{-1} \text{ y}^{-1}$ ), indicating that this latter needs to be carefully monitored.

The relationship between the anthropogenic acid factor, the anthropogenic TE contribution (V, Sb, Zn, Cd, Mo, Pb) and, unexpectedly, with the marine component can be explained by a com-



**Fig. 3.** 24 h back trajectories calculated from (16) Mount Pradazzo during two snowfall events that occurred in December 1997 (a) and in April 1998 (b). In both cases a low-pressure field developed in the Mediterranean Sea allowing the advection of southern humid air masses. Before meeting the Alps, these air masses passed over the sea and above the polluted Po Valley. These trajectories are consistent with the input of predominantly anthropogenic trace elements from the Po Valley and with the marine contribution to the surface alpine snow that is suggested by the PCA.

mon transport trajectory that brought the air masses from the Mediterranean Sea to the alpine sites through the Po Valley (Seibert et al., 1998) as evidenced by several back trajectories (Fig. 3). These air masses might have had a predominantly marine signature but as they passed through the Po Valley, they became polluted with predominantly anthropogenic contaminants such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , V, Sb, Zn, Cd, Mo, and Pb. This explanation is supported by the high occurrence of southerly winds observed during the winter of 1998 (40 days). Thus the PC2 extracted by PCA1 might reflect a southern provenance of the snow contaminants.

#### 4. Conclusions

A remarkable carbonate contribution to TE and the good linkage with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , indicates that the bedrock of the Dolomites highly influence the budget of Ti, U, Mn and Fe. In contrast, the marine contribution is negligible.

V, Sb, Pb, Cd, Zn and Mo are linked with the anthropogenic acid factor ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) and are highly enriched with respect to the crustal contribution. This suggests a predominantly anthropogenic origin for these TE. In particular the linkage among Pb, V and Sb suggests a prevalent contribution from road traffic emissions, while the occasional link between Fe and Cr may reflect the mechanical abrasion of ferrous components of the vehicles. The relationship between the anthropogenic ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , V, Sb, Zn, Cd, Mo, Pb) and the marine ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) components of the aerosol may arise from a common transport trajectory as the air masses from the Mediterranean Sea to the alpine sites pass through the heavily industrialised area of the Po Valley. The origin of other TE is less clear. Although Ag does not show a link with the anthropogenic acid factor, it can possibly be ascribed to a predominantly anthropogenic origin because of its negligible crustal contribution. Other TE such as Cr, Co, Cu and Ba could be usually attributed to a crustal origin although from a different geological background than the Dolomites.

In conclusion our observations expand significantly the knowledge of the source and origin of several TE in the Italian alpine environment. This study facilitated a prompt response to the local administrators responsible for setting the priorities for monitoring water and air pollution impacted by heavy metals. This work will constitute the first comparison of future studies that will be conducted in the same region.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.04.076.

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