

## Source and origin of atmospheric trace elements entrapped in winter snow of the Italian Eastern Alps

P. Gabrielli, G. Cozzi, S. Torcini, P. Cescon, C. Barbante

### ▶ To cite this version:

P. Gabrielli, G. Cozzi, S. Torcini, P. Cescon, C. Barbante. Source and origin of atmospheric trace elements entrapped in winter snow of the Italian Eastern Alps. Atmospheric Chemistry and Physics Discussions, 2006, 6 (5), pp.8781-8815. hal-00302116

## HAL Id: hal-00302116 https://hal.science/hal-00302116

Submitted on 18 Jun 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Atmos. Chem. Phys. Discuss., 6, 8781–8815, 2006 www.atmos-chem-phys-discuss.net/6/8781/2006/ © Author(s) 2006. This work is licensed under a Creative Commons License.



**ACPD** 

6, 8781-8815, 2006

Atmospheric trace elements in Alpine snow

P. Gabrielli et al.

### **Title Page** Introduction Abstract Conclusions References Tables **Figures** ►T. Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

# Source and origin of atmospheric trace elements entrapped in winter snow of the Italian Eastern Alps

P. Gabrielli<sup>1</sup>, G. Cozzi<sup>2</sup>, S. Torcini<sup>3</sup>, P. Cescon<sup>1,2</sup>, and C. Barbante<sup>1,2</sup>

<sup>1</sup>Institute for the Dynamics of Environmental Processes-CNR, 30123 Venice, Italy <sup>2</sup>Department of Environmental Sciences, University of Venice, Ca' Foscari, 30123 Venice, Italy <sup>3</sup>ENEA, Casaccia, Roma, Via Anguillarese, 301 00060 S.Maria di Galeria, Roma, Italy

Received: 14 June 2006 - Accepted: 13 July 2006 - Published: 19 September 2006

Correspondence to: C. Barbante (barbante@unive.it)

#### Abstract

wind.

Trace elements concentrations were determined in shallow snow samples from 21 sites in the Italian Eastern Alps in order to identify the sources of the contaminants present in the tropospheric winter boundary layer. The collection of superficial snow layers was carried out weekly at altitudes between 1000 and 3000 m next to meteorological 5 stations, far away from villages, roads and ski slopes. Ultra clean procedures were adopted in order to avoid contamination of the snow during the different experimental phases. Trace elements (Ag, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mo, Mn, Pb, Sb, Ti, U, V and Zn) were determined by Inductively Coupled Plasma Sector Field Mass Spectrometer (ICP-SFMS). Ancillary parameters such as major ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, 10 Na<sup>+</sup>, Cl<sup>-</sup>) were measured by Ion Chromatography (IC) and were useful in identifying the trace elements sources. The structure of the data was studied by using Principal Component Analysis (PCA) applied on the ranked data set matrix in order to minimize the weight of the outliers. Although concentrations were low at high altitudes in the heart of the Alps, and higher at lower altitudes (Pre-Alps), the structure of the chemical 15 content deposited by wet/dry mechanisms, resulted as rather uniform over the territory studied during the time considered. PCA shows that the chemical content of the snow is characterised by an anthropogenic component (V, Sb, Zn, Cd, Mo, Pb, Ag, Bi,  $SO_4^{2-}$ , NO<sub>3</sub>), mainly originating from the traffic in the adjacent Alpine valleys and the nearby heavily industrialised area of the Po Valley, a crustal component (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Mn, U, Ti,

heavily industrialised area of the Po Valley, a crustal component (Ca<sup>-+</sup>, Mg<sup>-+</sup>, Mn, U, Ti, Fe, Cr, Co, Cu and Ba) mainly from the geological carbonate background (Dolomites) of the Eastern Alps, and a marine component (Na<sup>+</sup>, Cl<sup>-</sup>) from the Mediterranean Sea. It is likely that transport and mixing of trace elements in the winter boundary layer occurred at a local (~10 km) and regional (~100 km) scale, and was due not only to the weak convection within the winter boundary layer but also to orographically induced winds and turbulences arising in the Alpine valleys due to the action of the synoptic

## ACPD 6,8781-8815,2006 Atmospheric trace elements in Alpine snow P. Gabrielli et al. **Title Page** Introduction Abstract Conclusions References **Figures** ►T. Back Full Screen / Esc **Printer-friendly Version** Interactive Discussion

#### 1 Introduction

Snow deposited on the Alps has the potential to provide valuable information on the atmospheric concentrations of short-living species, such as aerosol particles, and to document the effects of anthropogenic emissions on air in Europe (Schwikowski, 2003).

- In fact, since snow crystals form in the clouds, they entrap aerosol particles called ice nuclei (Fuzzi, 1994). In addition, atmospheric water drops, containing condensation nuclei, can freeze on the surface of a snowflake (riming process) and, during their precipitation, can scavenge other particles below the clouds (aerosol scavenging) (Davidson, 1989). These mechanisms are widely known as wet deposition processes. Alter-
- natively, aerosol particles are transported by wind turbulences and directly deposited onto the snow at the soil level (dry deposition process) (Cadle, 1991). This is the reason why the snow is characteristically marked by the chemical content both of the cloud generating air masses and by the aerosol particles contained in the troposphere during and after a precipitation event. In this context, snow concentrations reflect better
- the atmospheric concentration in the case of wet deposition, whereas fluxes are better suited to describing atmospheric concentrations in the case of predominantly dry deposition (Alley et al., 1995).

Since the last decade the interest in the snow and ice contaminants has extended from studies conducted in the extremely remote polar site of Antarctica (Wolff Suttie, 1994; Gabrielli et al., 2005; Gaspari et al., 2006), Greenland (Hong et al., 1996; Barbante et al., 2003; Gabrielli et al., 2004) and the Arctic (Gauchard et al., 2004; Krachler et al., 2005; Shotyk et al., 2005) to cover the high altitude zones of different mountainous areas in the world such as remote sites in the Andes (Ferrari et al., 2001; Correia et al., 2003; Hong et al., 2004) and also those next to heavily populated areas such as the

European Alps (Van de Velde et al., 1998, 1999, 2000; Barbante et al., 2001a, 2002, 2004; Veysseyre et al., 2001). Although many studies, aiming at understanding the evolution of atmospheric contaminants in Europe during the past few centuries have been conducted on Alpine ice archives, studies regarding the present trace elements

## ACPD 6,8781-8815,2006 Atmospheric trace elements in Alpine snow P. Gabrielli et al. **Title Page** Introduction Abstract Conclusions References **Figures** ►T. Back Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

content of the Alpine snow are rare (Veysseyre et al., 2001). These kind of studies are extremely valuable because some contaminants can provide not only a better understanding of important global biogeochemical cycles but also because some are potentially very toxic to humans and to other organisms even at low concentrations.

- <sup>5</sup> Polar studies provide information about the presence of natural contaminants and pollutants in the global atmosphere (Barbante et al., 2001b; Planchon et al., 2002; Shotyk et al., 2005) and efforts on European Alpine Glaciers have been mainly devoted to the reconstruction of the history of trace elements pollution over the last few centuries (Barbante et al., 2004; Schwikowski et al., 2004). However, this study aims at
- identifying these contaminants by focusing on a regional scale and offering a picture of the recent situation in the delicate and complex environment of the Alps. This mountain chain is a valuable observation point since it is located in the centre of Europe, one of the most densely populated and industrialised regions in the world. In addition, Alps are themselves very heavily influenced by man, especially by the international and regional highwave, industrials, refuse incineration plants and also by the highest density.
- <sup>15</sup> gional highways, industries, refuse incineration plants and also by the highest density of winter sport infrastructures for a mountain area in the world.

Due to the typically lower mixing heights during the winter, pollutants remain entrapped in the rather stable Alpine boundary layer, which extends its influence up to an altitude of 3000 m in the Eastern Alps (Kappeberger and Kerkmann, 1997) and does not allow an easy exchange between upper and lower levels. Thus we can expect the

not allow an easy exchange between upper and lower levels. Thus we can expect the winter snow collected at an intermediate altitude in the Eastern Alps (up to 3000 m) to be representative of the atmospheric chemical content of the lower Alpine troposphere and of the adjacent regions.

We collected shallow snow samples in the Italian Eastern Alps and we determined trace elements (Ag, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mo, Mn, Pb, Sb, Ti, U, V and Zn) and major ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>) in order to study directly the chemical composition of the snow and indirectly the structure and the sources of the contaminants present in the low Alpine troposphere. To have more specific information on the atmospheric path taken by the contaminants to reach the Alpine snowfield,



8785

particular attention was paid to the relationship between the snow chemical content and the meteorological conditions.

#### 2 Experimental

- 2.1 Sampling sites
- Shallow snow samples were collected weekly from December 1997 to April 1998 in 21 sampling sites located in the North-East of Italy (see Fig. 1 and Table 1). This area has a surface of ~15 000 km<sup>2</sup>. The mean sampling site density was 1.4×100 km<sup>2</sup>, which constitutes a high level of detail for this kind of study. This mountain area is approximately 100 km from the Gulf of Venice, and has a maximum elevation of 3905 m (Mount Ortles). It is located on the southern slope of the Italian Eastern Alps, which is crossed
- by the important highway connecting Northern Europe with the south through the Brenner Pass in the Southern Tyrol. This territory is roughly divided into two main geological domains, the eastern part (the Dolomites) is characterised by carbonates (dolomite), whereas the western part (Mount Adamello and Mount Ortles groups) is mostly silicate
- (granites and metamorphic rocks). During winter this area is normally characterized by an anti-cyclonic pressure field, whose influence is alternated with an Atlantic meteorological regime that conveys humid air masses to the southern Alpine slopes, producing snowfall events that often run concurrently with strong southern winds (Latini, 1987).

The 21 sampling sites were chosen mainly in rural/remote areas in order to avoid contamination from nearby sources of emissions such as roads, villages, tourist stations, Alpine huts and artificial snow guns. 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 (Noana valley) and the highest at 3040 m (Mount Presena).

Each sampling site was chosen by proximity to manual and/or automatic meteorological stations, which recorded local meteorological parameters such as maximum, minimum and average temperature, average and maximum wind intensity, typology



start/end time of snowfall/rain, depth of snow, quantity of rain and presence/absence of superficial rime. These data were ancillary to our data set and allowed us to have precise information, especially concerning precipitation and snow conditions. The territorial meteorological offices provided daily data, which were significant for the entire sampling area, such as the wind velocity/intensity, the wind flow in the free troposphere (estimated from the on line station of Mount Pradazzo (Dolomites)), the vertical profile of temperature (at soil level, 1000, 2000, 3000 m) and the altitude of the 0°C isotherm (from the radiosonde vertical profile in Udine).

2.2 Sampling and materials

<sup>10</sup> Snow collection was carried out by adopting the stringent contamination free procedures used to sample the snow in Antarctica (Planchon et al., 2001). During the winter of 1998, shallow snow was collected weekly at all sites, obtaining a total amount of 366 samples. Operators wore special clean-room clothing and polyethylene gloves. Sampling was conducted by plunging low-density polyethylene (LDPE) ultra cleaned <sup>15</sup> wide mouth bottles (500 ml) directly into the snow, downwind of the technicians. The containers were then capped, sealed in double polyethylene bags and stored frozen until analysis (Barbante et al., 1997; Planchon et al., 2001).

LDPE sampling bottles were previously acid cleaned inside a class 100 clean bench installed inside a class 10 000 clean room. For the acid cleaning we adopted a 5-20 step procedure (Barbante et al., 1997) using ultra pure water, obtained by coupling a reverse osmosis system (Milli-RO) with a four-column ion exchange system Milli-Q (Millipore, Bedford, MA), Merck "Suprapur" HNO<sub>3</sub> (Merk, Darmstadt, Germany) and HNO<sub>3</sub> (70%) doubly distilled at the National Institute of Standards and Technology (NIST, Gaithersburg, MD) were used for the acid cleaning stages. At the end of the 25 cleaning steps the LDPE bottles were rinsed three times and filled with ultra pure water for storage, the water was discarded just before snow collection at the sampling site.



#### 2.3 Analytical methods

Samples were treated and melted in LDPE sampling bottles in a class 100 laminar flow clean bench inside a clean laboratory (Boutron, 1990). A 5 ml aliquot was transferred in a 10 ml ultra clean LDPE vial and acidified (2%) with ultra pure concentrated
<sup>5</sup> HNO<sub>3</sub>(NIST) 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 (ICP-SFMS) (Finnigan MAT Element, Thermo, Bremen, Germany) according to the procedure described by Barbante and co-workers (Barbante et al., 1999). The relative standard deviation ranged from 12% to 46% depending upon the metals and the
<sup>10</sup> concentration levels. Accuracy was verified by adopting the standard reference material SLRS-3 Riverine Water from the National Research Council of Canada. Working analytical conditions, blanks, accuracy and precision are described in detail elsewhere (Barbante et al., 1999).

30 ml aliquots were also taken in a 100 ml ultraclean LDPE bottle for the determination of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup> by Ion Chromatography (IC), according to the procedure described in detail elsewhere (Gragnani et al., 1998), using a DIONEX AS5 column and NaOH (Baker) as eluant for anion determination and a DIONEX CS12 column with Methane sulphonic acid (MSA) as an eluant for the determination of cations. In addition a Cation Self Regenerating Suppressor (CSRSDIONEX) and an Anion Self Regenerating Suppressor (ASRS-DIONEX) were applied at the end of the columns. The relative standard deviation ranged from 0.5% to 9.2% depending upon the different species and ion concentration. Other analytical aspects are given in detail elsewhere (Gragnani et al., 1998).

### ACPD 6,8781-8815,2006 Atmospheric trace elements in Alpine snow P. Gabrielli et al. **Title Page** Introduction Abstract Conclusions References Tables **Figures** ►T. Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

#### 3 Results and discussion

#### 3.1 Main characteristics of the data set

The main statistics of the chemical data set are given in Table 2. As expected, low average concentrations were found for trace elements, ranging from 8.6 ppt of U  $_{5}$  (1 ppt=1 pg g<sup>-1</sup>=10<sup>-12</sup> g g<sup>-1</sup>) up to 27 ppb of Fe (1 ppb=1 ng g<sup>-1</sup>=10<sup>-9</sup> g g<sup>-1</sup>), whereas higher mean values were determined for the major ions ranging between ~900 ppb of NO<sub>3</sub><sup>-</sup> and ~100 ppb for Mg<sup>2+</sup>.

In some cases, concentrations of some major ions were found to be below the detection limit. This mainly occurred for K<sup>+</sup>, which was determined only in 153 of the 366 samples. Looking at the distributions, median values represent in average 47% of the arithmetic mean; the mean skewness (positive asymmetry of the distribution) value is 7 and the mean kurtosis (indicating the distribution around a central value) is 70. The chemical data set is therefore characterised by log normal like distributions.

- In general, mean trace elements concentrations found on the Eastern Alps are higher than those obtained by Veisseyre and co-workers (Veysseyre et al., 2001) in shallow snow samples taken in the French western Alps (1150–3532 m) at comparable altitudes. This is essentially due to the fact that in the Veyssyre's study, only fresh snow samples, representative of wet deposition, were considered. If we take the lowest Eastern Alps concentration values, which were determined in fresh snow samples as
- well, then concentrations found in the two studies are in good agreement. For example Pb shows a minimum concentration of 23 ppt in a sample collected during the snow event recorded on 3 December 1997 at Mount Presena (3020 m) whereas minimum Pb concentration reported by Veisseyre and and co-workers was 65 ppt at 3080 m in the Vallée Blanche (Mount Blanc, France). As previously observed (Veysseyre et al.,
- 25 2001), trace elements concentrations in Alpine fresh snow collected at medium altitudes can be comparable to values determined in remote Greenland snow samples (Barbante et al., 2003). In the Eastern Alps, for instance, a minimum U concentration of 0.1 ppt was found on 3 December on Mount Presena whereas in Greenland, the



minimum U concentration found in samples from a snow pit was 0.2 ppt (Barbante et al., 2003).

In general, the Eastern Alps trace elements data set is more directly comparable with concentrations determined in relatively recent (after 1970) summer firn and ice, such

as those drilled at Colle Gnifetti (4450 m) (Mount Rosa, Swiss-Italian Western Alps), a particular Alpine site where summer snow accumulation is dominant (Barbante et al., 2004). For instance, mean Zn and Cd concentration were found to be 3176 ppt and 58 ppt on Colle Gnifetti, whereas at the lower altitudes of the Eastern Alps sampling sites, mean winter values of ~3450 ppt and ~60 ppt were determined. This similarity is
 likely due to the fact that the trace elements content of summer snow taken on the high altitude Alpine glaciers and trace elements deposited on and within the winter snow layers of the lower Eastern Alps snow fields, originate from areas characterized by the

same categories of emissions.
 A strong vertical air mixing occurs in fact in the Alpine region especially during summer, that transports anthropogenic contaminants from cities, roads and industrialized areas, such as the Po valley for instance, upwards to ~4000 m of altitude. In contrast during winter, the occurrence of a rather low altitude stable boundary layer, does not allow contaminants to reach the highest Alpine glaciers and confines them in this portion of troposphere. For example, winter firn/ice drilled above the winter boundary

- <sup>20</sup> layer, such those drilled at Dome du Gouter (4304 m, Mont Blanc, French-Italian western Alps), show much lower values (Van de Velde et al., 1998) than in summer. In this latter case, since winter snow concentrations are minimally influenced by regional emissions, they can represent a larger scale atmospheric trace element background. In contrast, summer Alpine snow at whatever altitude and Alpine winter snow within
- the winter boundary layer (this study) are more likely to be representative of a regional (~10–100 km) tropospheric background.

## ACPD 6,8781-8815,2006 Atmospheric trace elements in Alpine snow P. Gabrielli et al. **Title Page** Introduction Abstract Conclusions References **Tables Figures** 14 ►T. Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

#### 3.2 Temporal variability and fluxes

Snowfalls affected the entire territory from December until the first half of January and then again in April. In contrast, from the second half of January until the end of March, stable weather conditions were observed with a general lack of snowfall. Thus, wet de-

<sup>5</sup> position occurred mainly in the first and in the last part of the sampling period whereas dry deposition dominated in-between. In general, for all trace elements and at all sampling sites, maximum concentrations were observed in periods characterized by dry deposition, whereas minimum concentrations coincided with wet deposition.

For instance, Ba concentrations determined in fresh and old (several weeks old) snow samples, taken in Malga Bissina (1780 m), varied by 2–3 orders of magnitude from 0.05 up to 13 ppt (see Fig. 2). Fe varied in a similar way at Folgarida (1910 m) from 0.1 up to 79 ppb. In general, trace elements temporal profiles were found to be redundant and concentrations varied by about 2–3 orders of magnitude depending only on whether snow samples were collected during or just after wet deposition events, or

after a period of dry deposition. The Ba profile reported in Fig. 2 is quite representative of the relative temporal variation of most of the trace elements in the whole territory considered. The only clear exception is Cd, which generally varied by less than one order of magnitude during the sampling period as can be shown, for instance, from snow samples collected on the Mounts of Ornella (2250 m) where Cd concentration
 values varied only from 0.02 ppb up to 0.07 ppb during the field season.

The long dry deposition period during February and March, which was broken only by two minor snow events on 23 February and on 23 March, offers the possibility of estimating the dry fluxes of trace elements and species to the Eastern Alps. For this investigation, concentration data from the four highest sampling sites were selected.

This minimized the influence of local contamination and ruled out the possibility of percolation of molten snow that would have modified the original analyte concentrations (Davis, 1991). Data from Mount Presena (3040 m), Ravales (2615 m), Mounts of Ornella (2250 m) and Mount Pradazzo (2200 m) were thus selected specifically dur-

## ACPD 6,8781-8815,2006 Atmospheric trace elements in Alpine snow P. Gabrielli et al. **Title Page** Introduction Abstract Conclusions References **Figures** ►T. Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

ing two time periods when the maximum temperature was continuously below  $0^{\circ}C$  (19 January–4 February ; 24 February–11 March. The flux (F) was obtained as:

 $F = \{(\Delta C / \Delta t)_m\} \times \rho \times h$ 

where  $(\Delta C/\Delta t)_m$  is the mean difference of concentration of samples collected in successive week,  $\rho$  is the mean snow density (~300 kg m<sup>-3</sup>) and h the height of the snow layer sampled (~2 cm).

Fluxes obtained for each trace element and ions are reported in Table 3. It should be noted that the fluxes calculated over the two different periods show on average a deviation of only ~24%, which can be considered for most of the trace elements and ions within the range experimental error. It is also interesting to compare the fluxes found for trace elements and major ions with the critical loads that are available for these ecosystems in the literature (Posch et al., 2005). Critical loads of Pb and Cd for forests and soils are 10 and 1 g ha<sup>-1</sup>y<sup>-1</sup> whereas Pb and Cd fluxes to the Eastern Alps are estimated to be 4.2 and 0.09 g ha<sup>-1</sup> y<sup>-1</sup>, respectively. For S and N the critical loads
<sup>15</sup> in alpine and sub-alpine grassland are 39 and 42 kg ha<sup>-1</sup> y<sup>-1</sup> whereas S and N fluxes (estimated from the fallout of sulphate and nitrate only) are 0.44 and 0.63 kg ha<sup>-1</sup> y<sup>-1</sup>. It can be observed that trace elements and major ions fluxes are significantly below the critical loads, with the exception of Pb, indicating that it needs to be more carefully monitored in the future.

20 3.3 Spatial variability

25

The spatial variability of the average concentrations is illustrated in Table 4. This is very high, reflecting the heterogeneity of the sampling sites due to their different altitudes, geographic positions and distances from anthropogenic sources of emission. In general the lowest concentrations are found in snow collected at more than 2000 m of altitude, whereas higher concentrations are determined in snow taken at low-medium altitudes and especially in the Pre-Alps. For instance, mean V concentrations on Mount Pradazzo (2200 m) were 0.08 ppb, on Mount Vioz (2030 m) 0.09 ppb, on

6, 8781-8815, 2006

(1)

Atmospheric trace elements in Alpine snow

ACPD

P. Gabrielli et al.



Mounts Ornella (2250 m) 0.1 ppb and on Presena Summit (3040 m) 0.1 ppb whereas at Viote (1500 m) it was 0.23 ppb, on Mount Grappa (1540 m) 0.4 ppb and in Faverghera (1605 m) 0.5 ppb.

- Our results are in contrast with other studies performed by determining heavy metal concentrations in mosses sampled on the Alps. They observed in fact the highest concentrations at mid altitudes (1400–1800 m) (Gerdol, Bragazza, 2006) or reported a remarkable increase in heavy metals concentrations with rising altitude (Zechmeister, 1995) (these two studies both occurred in late summer). The decrease of concentrations values concomitant to the increasing altitude observed in our study can be explained by first considering that the higher Alpine sites are less influenced by the
- anthropogenic emissions originating that the higher Alpine sites are less initiative by the anthropogenic emissions originating from the adjacent Alpine valleys (Veysseyre et al., 2001) and secondly that snow accumulation at higher altitudes is likely to be higher than at lower altitudes, causing a dilution effect. Very high concentrations on the Pre-Alps can be explained by taking into account the proximity of the Pre Alpine sites to the
- <sup>15</sup> Po valley, the most extended industrialised area of Italy, that probably heavily contaminates the closest sub Alpine areas.

High concentrations are observed sometimes also at rather elevated Alpine sites but in these few cases this observation is explained by the presence of local intense anthropogenic sources, which strongly influenced the chemical composition of the snow, es-

- <sup>20</sup> pecially during the dry deposition periods. This is the case of the Tonale Pass (1860 m) snow samples that were certainly influenced by the emissions from the intense traffic of the adjacent (~1 km) tourist station. This is also the case for the snowfield of Ravales in the Dolomites. This station is at 2615 m of altitude and is exactly above the very important tourist station of Cortina d'Ampezzo (1200 m). In Ravales, average
- <sup>25</sup> concentrations of 3.3 ppb of Zn, 3.8 ppb of Ti, 0.052 ppb of Sb and 0.30 ppb of Cu were found. In comparison, at the heavily anthropized Tonale Pass, average concentrations of 7.4 ppb of Zn, 9.3 ppb of Ti, 0.56 ppb of Sb and 3.13 ppb of Cu were found, whereas at the remote site of Val Noana (1025 m) 0.6 ppb of Zn, 1.3 ppb of Ti, 0.027 ppb of Sb and 0.17 ppb of Cu were observed.



3.4 Sources assessment of the contaminants

#### 3.4.1 The statistical method

To evaluate the origin of the trace elements determined in the snow of the Eastern Alps, a principal component analysis (PCA) (Stanimirova et al., 2005) was carried out 5 in order to reveal linear relations existing in the chemical data set.

The large range covered by the concentrations values (~6 orders of magnitude), the lognormal like distributions of the chemical variables and the frequent occurrence of several outliers, highlighted the need to adopt a data set transformation before applying the PCA. This consisted of the substitution of the chemical concentration with its rank position (Baxter, 1995). This yielded several advantages: firstly, ranking avoids the data set being constrained by the unity of measure that could produce a virtual variability, secondly a PCA based on ranks can be expected to be more robust to outliers (Baxter, 1995) and thirdly this transformation accentuates the essential variability of the data set, by ignoring the secondary variability (background noise) (Molinaroli et al., 1999).

<sup>15</sup> Coherent with the ranking, is the substitution (before the rank transformation) of missing data with the median, a robust parameter depending only on the rank position (Thomson, 1993). PCA was adopted by applying the varimax rotation. In order to represent at least one variable, the minimum acceptable variance (eigenvalue) of the principal components selected for the following discussion was 1. In addition, a variable
 <sup>20</sup> was considered significant and representative for this statistical description when the fraction of its explained variance (communality) obtained at least the value of 0.50.

#### 3.4.2 Results of the PCA

PCA applied on the entire chemical data set put in evidence three principal components, summarising the information contained in 22 chemical variables on the 23 available.  $K^+$  resulted in fact as not significant when compared to the above fixed criteria. Variance distribution of the first three principal components and the scores of the chem-

ACPD								
6, 8781–8815, 2006								
Atmospheric trace elements in Alpine snow P. Gabrielli et al.								
Title Page								
Abstract Introduction								
Conclusions References								
Tables	Figures							
I	►I							
•	•							
Back	Close							
Full Scre	een / Esc							
Printer-frier	ndly Version							
Interactive	Discussion							
FC	NU							

ical variables are reported in Tables 5 and 6 respectively. It is remarkable to mention that the application of PCA to sub groups of selected samples such as those coming from high/low altitude sampling sites, fresh/old snow samples, remote/rural sampling sites did not produce substantially different results from those reported below for the PCA applied to the entire data chemical set (Gabrielli, 1998).

Trace elements (Ag, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mo, Mn, Pb, Sb, Ti, U, V and Zn) obtained high scores on the first principal component, Cl<sup>-</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> on the second, Mg<sup>2+</sup> and Ca<sup>2+</sup> on the third. It should be noted that some trace elements such as Ti, U, Mn, Fe, Ba and to a lesser extent Cu, Co and Cr obtained rather high scores also on the third principal component governed by Mg<sup>2+</sup> and Ca<sup>2+</sup>. On the other hand, another group of metals, composed of V, Sb, Zn, Cd, Mo, Pb obtained significant scores also on the second principal component governed by SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> Cl<sup>-</sup>, Na<sup>+</sup>. This is visually emphasized, by applying a cluster analysis on the principal component score matrix (Fig. 3), adopting the Euclidean distance and the Ward method for group aggregation (Swan Sandilands, 1995). Trace elements are into two sub-groups composed of Ti, U, Mn, Fe, Ba, Cu, Co, Cr on one side and V, Sb, Zn, Cd, Mo, Pb, Ag and Bi on the other. In addition, the cluster analysis disaggregates distinctly also the second principal component in two sub-groups composed of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> on one

side and Na<sup>+</sup> and Cl<sup>-</sup>on the other.

20 3.4.3 Sources analysis

5

25

#### The crustal contribution

An explanation of the trace elements disaggregation into two distinct clusters can be obtained by comparing the trace elements concentrations in the snow with the average trace element concentration determined in the carbonates (Taylor McLennan, 1985), that constitute the geological background of the Dolomites. The Ca<sup>2+</sup> contribution from remote crustal sources can be considered negligible since no significant



transport of Saharan dust to the Alps occurred during the winter of 1998. This type of transport is in fact usually not occurring in the Alps during the cold season (De Angelis Gaudichet, 1991). Ca<sup>2+</sup> can thus be adopted as the most characteristic crustal species over the examined territory. The prevalent regional origin of Ca<sup>2+</sup> (but also of Mg<sup>2+</sup>) is confirmed considering that its average concentrations in the sampling sites, mostly characterised by a granitic and metamorphic background such as Malga Bissina (226 ppb), Presena Summit (88 ppb) and Mount Vioz (149 ppb), are mainly lower than elsewhere (~300–600 ppb), where, in contrast, carbonates dominate.

For a given trace element, Mn for instance, the percentage of the carbonates contri-10 bution to its budget can be calculated as

 $[((Mn)_r/(Ca^{2+})_r)/(Mn)_s/(Ca^{2+})_s)] \times 100$ 

where, (Mn)<sub>s</sub> and (Ca<sup>2+</sup>)<sub>s</sub> represent the concentration in the snow sample and (Mn)<sub>r</sub> and (Ca<sup>2+</sup>)<sub>r</sub> the average concentration in the carbonates (Taylor McLennan, 1985). The carbonates average contribution resulted as high for Mn (100%), U (91%), Ti (65%), Fe (50%), Cr (32%), V (24%), whereas for Ag, Cd, Co, Sb, Mo, Cu, Pb, Ba and Zn it was less than 3%. Thus we can conclude that trace elements such as Ti, U, Mn and Fe obtained rather high scores on the third principal component governed by Ca<sup>2+</sup> and Mg<sup>2+</sup> because they were most likely originating from the Alpine geological background and in particular from the Dolomites. However, a concurrent secondary crustal contribution from different geological backgrounds, such as granitic and metamorphic rocks, which are particularly diffuse in the western part of the examined territory (and more in general in the entire Alpine chain), is likely not only for Ti, U, Mn, Fe but especially for Cr, Co, Cu and Ba. These latter elements showed in fact a crustal

behaviour linked to their association with Ti, U, Mn, Fe but had rather low or negligible carbonate contributions.

An important rock and soil dust contribution for Cu, Mn, Ti, Fe, Ba, Co and U was found in Alpine ice and snow also from Van de Velde and Veysseire and co-workers (Van de Velde et al., 1998; Veysseyre et al., 2001). Interestingly, U on the Eastern



(2)

Alps was not found to show an excess above the crustal contribution, in contrast with the excesses recently reported for U determined in Mont Blanc snow and ice, which was attributed to extensive mining activity in former Eastern Germany (GDR) during the '80s (Barbante et al., 2001a).

#### The marine contribution

5

The excellent linkage between Na<sup>+</sup> and Cl<sup>-</sup>, concurrently with the mean mass concentration ratio Cl<sup>-</sup>/Na<sup>+</sup> of 2.5 (not far from the marine ratio of 1.8; the slight Cl<sup>-</sup>
excess in our samples could be attributed to a minor anthropogenic contribution of HCl; Puxbaum, 1991; Nickus et al., 1997; Winiwarter et al., 1998), clearly shows a prevalent marine input for these two major ions. This is likely due to the close proximity of the Mediterranean sea and the Adriatic sea in particular, since there is an apparent spatial concentration gradient (also shown previously by Della Lucia and co-workers;
Della Lucia et al., 1996) amongst the more sea exposed sampling sites in the Pre-Alps (for Na<sup>+</sup>, Mount Tomba (170 ppb), Mount Grappa (330 ppb), Faverghera (138 ppb))

and the more internal snow fields in the north western part of Trentino (for Na<sup>+</sup>, Mount Presena (47 ppb), Mount Vioz (43 ppb), Malga Bissina (53 ppb)).

A prevalent marine origin for  $SO_4^{2-}$  can be ruled out because the non sea saltsulphate average contribution is ~90%. This calculation was carried out by considering the nss-sulphate concentration as

$$(SO_4^{2-})_{nss} = (SO_4^{2-})_s - (CI^{-})_s (SO_4^{2-})_m / (CI^{-})_m,$$

where  $CI^-$  is considered as the marine reference (the calculation performed with Na<sup>+</sup> gives essentially the same result),  $(SO_4^{2-})_s$  and  $(CI^-)_s$  are concentrations in the snow and  $(SO_4^{2-})_m/(CI^-)_m$  is the mean concentration ratio in the sea. The marine contribution to the budget of trace elements determined in the Eastern Alps snow was found also always negligible.

## ACPD 6,8781-8815,2006 Atmospheric trace elements in Alpine snow P. Gabrielli et al. **Title Page** Introduction Abstract Conclusions References **Figures** Back Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

(3)

The linkage between  $SO_4^{2-}$  and  $NO_3^{-}$  suggests an anthropogenic origin for these two major ions and this study also demonstrates this well known anthropogenic acid <sup>5</sup> factor (SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>) (Maupetit et al., 1995; Schwikowski et al., 1999; Preunkert et al., 2001). The emissions of their original compounds (NO<sub>x</sub> and SO<sub>2</sub>) are in fact greatly predominant when compared to their corresponding natural sources.  $SO_4^{2-}$  and  $NO_3^{-}$ average concentrations in snow were found generally higher in the Pre-Alpine sites, which are next to the heavily anthropized Po Valley (NO<sub>3</sub><sup>-</sup> in Faverghera (1288 ppb), Mount Grappa (1371 ppb) and Mount Tomba (1047 ppb)), when compared to other less exposed internal sites (NO<sub>3</sub><sup>-</sup> on Mount Vioz (743 ppb), Prarodont (752 ppb) and Viote (888 ppb)) in the western part of the territory examined. Similar north-south spatial gradients were previously reported by Nickus and co-workers for  $SO_4^{2-}$  (Nickus et al., 1998) and from Balestrini and co-workers (Balestrini et al., 2000). Interestingly, the  $NO_3^2/SO_4^{2-}$  ratio is very often higher than 1, as already previously reported in 15 the Eastern Alps (Nickus et al., 1997). This can be ascribed to the fact that air masses coming from the Po Valley contain higher concentrations of NO<sub>2</sub> compared to SO<sub>2</sub> because of the large use of methane in domestic heating, which enriches the air in NO<sub>2</sub> (Camuffo et al., 1991). In addition, in Trentino, emissions of NO<sub>x</sub>  $(15000 \text{ kg y}^{-1})$  mainly due to road transport are much higher than emissions of SO<sub>x</sub> 20  $(1000 \text{ kg y}^{-1})$  that are mainly due to agriculture and industry (Provincia di Trento, 1998).

#### The trace element anthropogenic contribution

V, Sb, Zn, Cd, Mo, Pb, Ag and Bi cannot be linked to a regional geological background because they have a low or negligible carbonate contribution and very low scores on the third principal component, governed by the crustal variables. With the exception of Ag and Bi, this group of trace metals obtains rather significant scores on the second principal component, showing a relationship with its governing variables,

represented by the anthropogenic acid factor ( $SO_4^{2-}$  and  $NO_3^{-}$ ) (Maupetit et al., 1995; Schwikowski et al., 1999; Preunkert et al., 2001) and the marine component (Na<sup>+</sup> and Cl<sup>-</sup>).

Among these trace elements, Pb and Cd can be associated to anthropogenic emis-<sup>5</sup> sions, as concluded from other Alpine snow and ice studies (Van de Velde et al., 1998; Barbante et al., 2004; Schwikowski et al., 2004), because their contribution from anthropogenic sources is greatly prevalent over natural sources (Nriagu Pacyna, 1988; Pacyna, 2001). Just to give an example, in Italy in 1992, Pb was emitted mostly by road transport traffic ( $\sim 2000 \text{ ty}^{-1}$ ) and industrial activities ( $\sim 1000 \text{ ty}^{-1}$ ), and Cd by refuse incineration/electric power plants ( $\sim 20 \text{ ty}^{-1}$ ), industrial activities ( $\sim 15 \text{ ty}^{-1}$ ) and 10 road transport traffic ( $\sim 15 \text{ ty}^{-1}$ ), whereas natural emissions where negligible; Techne, 1998). In particular the intensive automobile and truck traffic in the alpine vallevs was likely responsible for the emission of Pb and Cd in the considered territory. For instance in Trentino, these sources were responsible in 1995 of the emission of remarkable guantities of Cd ( $\sim 0.25 \text{ ty}^{-1}$ ) and Pb ( $\sim 40 \text{ ty}^{-1}$ ) (Provincia di Trento, 1998). In 15 addition, significant contributions of Pb and Cd could have originated from the electrometallurgical and electrochemical industries present in the Po Valley.

The linkage with two typically anthropogenic trace elements such as Pb and Cd together with the association with the anthropogenic acid factor ( $SO_4^{2-}$  and  $NO_3^{-}$ ) and the

- negligible carbonate contribution, leads us to consider as anthropogenic other trace element determined in our snow samples and emitted by different activities (in parentheses) such as Mo and Sb (coal and oil combustion in power plants), Ag (waste incineration plants), Zn (refuse incineration, nonferrous metal and steel production) and V (thermal power plants and industrial, commercial and residential use of fuel).
- <sup>25</sup> The significant relationship evidenced by the second principal component (see Table 6) between the anthropogenic acid factor (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>) (Maupetit et al., 1995), and the anthropogenic trace element contribution (V, Sb, Zn, Cd, Mo, Pb) but also, unexpectedly, with the marine component (Na<sup>+</sup>, Cl<sup>-</sup>) can be tentatively explained with a common transport trajectory that was taken by the air masses from the Adriatic basin



to the Alpine sites through the Po Valley (Seibert et al., 1998). These air masses probably had an initially prevalent marine signature and, due to their passage above the Po Valley, they became polluted by anthropogenic contaminants such as  $SO_4^{2-}$ ,  $NO_3^-$ , V, Sb, Zn, Cd, Mo, and Pb. This tentative explanation is supported by the high occurrence of southern winds observed during the winter of 1998. In general the second principal component might thus show a southern provenance for ionic species such as Na<sup>+</sup>, Cl<sup>-</sup>,  $SO_4^{2-}$ , NO<sub>3</sub> and the anthropogenic trace elements.

#### 3.5 Meteorological data and transport processes

Chemical data, determined from our samples with the frequency of a week, were cou-<sup>10</sup> pled to the continuous meteorological data set, by calculating for every meteorological data point a mean time period from the snowfall day until the sampling day. The PCA applied to the entire chemical and meteorological data set evidenced a clear separation between chemical and meteorological parameters. This could be due to the fact that strictly local meteorological parameters are independent from wet and dry depo-<sup>15</sup> sition phenomena characterized by a larger spatial scale. This could also mean that the descriptive linear statistics used (PCA) and/or the frequency of sampling was not

suitable to evidence possible non-linear relationships between the meteorological and wet/dry deposition phenomena.

However, the evidenced independence of the chemical variables from large-scale
 transport parameters, such as the wind direction in the free troposphere, is also consistent with the kind of transport characterized by convective turbulences that diffuse local and regional contaminants within the boundary layer. During the winter of 1998, particularly high temperatures were recorded at soil level and in the free troposphere (isotherm of 0°C at 3000 m during the first half of February, for instance). This may
 have produced a frequent enhancement of the upper limit of the winter boundary layer.

Eastern Alps sampling sites, located between 1000 m and 3000 m, were therefore probably within the boundary layer and were often exposed to the deposition of local and regional contaminants.



In any case, it seems unlikely that the weak convection originating from the low temperature gradient was the unique cause of the transport of contaminated air masses from the lower to the upper tropospheric levels. During the sampling period, the Alpine troposphere had very often conditions of neutral stability up to 3000 m (with a gradient of 6°C/km in average). Orographic induced vertical transport, originating from the action of the synoptic wind, was probably responsible for a more efficient vertical air

- mixing. Air masses impacting frequently on the southern slope of the Alps might have in fact transported contaminants from the Po Valley to the more exposed slopes of the Pre-Alps. In addition, turbulences generated by the synoptic wind within the more inter-
- nal Alpine valleys, might have assisted in mixing contaminants at different levels. This interpretation is coherent with the suggestions of Seibert and co-workers that defined as "sub-grid vertical transport" these modalities of advection not included in their model (Seibert et al., 1998).

#### 4 Conclusions

- We found that trace element content and structure of the winter snow of the Eastern Alps is complex because of the superimposition of several contributions from different sources. The crustal component is represented mainly by Ca<sup>2+</sup> and Mg<sup>2+</sup> originating from the carbonates background of the Eastern Alps (Dolomites) and from trace elements such as Mn, U, Ti, Fe and to a lesser extent Cr, Co, Cu and Ba. The marine
  component as represented by Na<sup>+</sup> and Cl<sup>-</sup>, probably originated from the nearby Adriatic basin. The anthropogenic contribution is represented by trace metals such as V, Sb, Zn, Cd, Mo, Pb, Ag, Bi and by the major ions SO<sup>2-</sup><sub>4</sub> and NO<sup>-</sup><sub>3</sub> representing the anthropogenic contaminants entrapped within the boundary layer, have probably
- a local and a regional origin. Our data suggests that the very industrialised Po Valley can affect especially the more exposed Southern Pre-Alpine slopes. The influence on the chemical snow composition of other very diffuse sources of emission (roads, tourist



stations, villages) in the internal alpine valleys is also very likely. The mechanism of transport of contaminants from low altitude to the snow of the Alpine fields could be due, in addition to the weak convective turbulence inside the winter boundary layer, as well as the vertical transport and turbulences generated by the synoptic wind.

- Acknowledgements. This project was carried out in collaboration with the Snow Avalanches and Meteorology Office of the Trento Province, the Environmental Protection Agency of the Trento Province, the Experimental Centre For Avalanches and Idrogeology Defence of the Environmental Protection Agency of Veneto Region. The authors are thankful for the technical and scientific support in particular from G. Tecilla, M. Mazzola, G. Tognoni, P. Cestari and M. Tava (Trente Prevince) A Luchette M. Volt T. Cerese and A. Cegneti (Venete Pagier) and for the pre-
- (Trento Province), A. Luchetta, M. Valt, T. Corso and A. Cagnati (Veneto Region) and for the precious help in data elaboration with G. Rampazzo (University Ca'Foscari of Venice). W. Cairns (IDPA) is acknowledged for useful discussions. The financial support of Istituto Nazionale della Montagna (IMONT) is kindly acknowledged.

#### References

20

<sup>15</sup> Alley, R. B., Finkel, R. C., Nishiizumi, K., Anandakrishnan, S., Shuman, C. A., Mershon, G., Zielinski, G. A., and Mayewski, P. A.: Changes in continental and sea-salt atmospheric loadings in central Greenland during the most recent deglaciation: model-based estimates, J. Glaciol., 41, 503–514, 1995

Balestrini, R., Galli, L., and Tartari, G.: Wet and dry atmospheric deposition at prealpine and alpine sites in northern Italy, Atmos. Environ., 34, 1455–1470, 2000

- Barbante, C., Bellomi, T., Mezzadri, G., Cescon, P., Scarponi, G., Morel, C., Jay, S., Van de Velde, K., Ferrari, C., and Boutron, C. F.: Direct determination of heavy metals at pico gram per gram level in Greenland and Antarctic snow by Double Focusing Inductively Coupled Plasma Mass Spectrometry, J. Anal. At. Spectrom., 12, 925–931, 1997
- <sup>25</sup> Barbante, C., Boutron, C. F., Moreau, A. L., Ferrari, C., Van de Velde, K., Cozzi, G., Turetta, C., and Cescon, P.: Sasonal variations in nickel and vanadium in Mont Blanc snow and ice dated from the 1960 and 1990s, J. Environ. Monit., 4, 960–966, 2002

Barbante, C., Boutron, C. F., Morel, C., Ferrari, C., Jaffrezo, J. L., Cozzi, G., Gaspari, V., and



EGU

Cescon, P.: Seasonal variations of heavy metals in central Greenland snow deposited from 1991 to 1995, J. Environ. Monit., 5, 328–335, 2003

- Barbante, C., Cozzi, G., Capodaglio, G., Van de Velde, K., Ferrari, C., Boutron, C. F., and Cescon, P.: Trace element determination in alpine snow and ice by double focusing induc-
- tively coupled plasma mass spectrometry with microcentric nebulization, J. Anal. At. Spectrom., 14, 1433–1438, 1999.
  - Barbante, C., Schwikowski, M., Doring, T., Gaggeler, H. W., Shottered, U., Tobler, L., Van de Velde, K., Ferrari, C., Cozzi, G., Turetta, A., Rosman, K., Bolshov, M. A., Capodaglio, G., Cescon, P., and Boutron, C. F.: Historical Record of European Emission of Heavy Metals
- to the Atmosphere Since the 1650s from Alpine Snow/Ice cores Drilled near Monte Rosa, Environ. Sci. Technol., 38, 4085–4090, 2004
  - Barbante, C., Van de Velde, K., Cozzi, G., Capodaglio, G., Planchon, F., Hong, S., Ferrari, C., and Boutron, C. F.: Post-World War II Uranium Changes in Dated Mont Blanc Ice and Snow, Environ. Sci. Technol., 35, 4026–4030, 2001a
- <sup>15</sup> Barbante, C., Veysseyre, A., Ferrari, C., Van de Velde, K., Morel, C., Capodaglio, G., Cescon, P., Scarponi, G., and Boutron, C. F.: Greenland snow evidence of large scale atmospheric contamination from platinum, palladium and rhodium, Environ. Sci. Technol., 35, 835–839, 2001b

Baxter, M. J.: Standardization and Trasformation in Principal Component Analysis, with Appli-

- cations to Archaeometry, App. Stat., 44, 513–527, 1995
   Boutron, C. F.: A clean laboratory for ultralow concentration heavy metal analysis, Fresenius J.
  - Anal. Chem., 337, 482–491, 1990
    Cadle, S. H.: Dry deposition to snowpack. Seasonal snowpacks, in: series, edited by: Davis, T. D., Tranter, M., Jones, H. G., NATO ASI series, 28, Springer Verlag, Berlin, 1991.
- <sup>25</sup> Camuffo, D., Bernardi, A., and Bacci, P.: Transboundary transport of atmospheric pollutants through the eastern alps, Atmos. Environ., 25, 2863–2871, 1991
  - Correia, A., Freydier, R., Delmas, R. F., Simoes, J. C., Taupin, J. D., Dupré, B., and Artaxo, P.: Trace elements in South America aerosol during 20th century inferred from a Nevado Illimani ice core, Eastern Bolivian Andes (6350 m a.s.l.), Atmos. Chem. Phys., 3, 1337–1352, 2003
- <sup>30</sup> Davidson, C. I.: Mechanism of wet and dry deposition of atmsopheric contaminants to snow surfaces, in: The environmental record in glacier and ice sheets, edited by: Wiley, J., New York, 1989.

Davis, R. E.: Links between snowpack physics and snowpack chemistry, in: Processes of

AC	ACPD									
6, 8781–8	6, 8781–8815, 2006									
Atmospheric trace elements in Alpine snow P. Gabrielli et al.										
Title	Page									
Abstract	Introduction									
Conclusions	References									
Tables	Figures									
14	▶									
•	•									
Back	Close									
Full Scr	een / Esc									
Printer-frie	ndly Version									
Interactive	Discussion									

Chemical Change in Snowpacks, Springer-Verlag, edited by: Davies, T. D., Tranter, M., and Jones, H. G., Berlin, 115–139, 1991.

- De Angelis, M. and Gaudichet, A.: Saharan dust deposition over Mont Blanc (French Alps) during the last 30 years, Tellus, 34B, 61–75, 1991
- <sup>5</sup> Della Lucia, M., Marchetto, A., Mosello, R., and Tartari, G.: Studies on a chemical gradient of atmospheric deposition from the Po Valley to the Alps, Water Air Soil Pollut., 87, 171–187, 1996
  - Ferrari, C. P., Clotteau, T., Thompson, L. G., Barbante, C., Cozzi, G., Cescon, P., Hong, S., Maurice-Bourgoin, L., Francou, B., and Boutron, C. F.: Heavy metals in ancient tropical ice: initial results, Atmos. Environ., 35, 5809, 2001
  - Fuzzi, S.: Clouds in the troposphere, in: Topics in atmospheric and interstellar physics and chemistry, edited by: Boutron, C. F., Les Editions de physique, Les Ulis, 1994.
  - Gabrielli, P.: Elementi in traccia nelle precipitazioni nevose delle Alpi Orientali: origine, evoluzione stagionale e relazione con le condizioni meteorologiche, Tesi di laurea, University of Venice, 1998.

10

Gabrielli, P., Barbante, C., Boutron, C. F., Cozzi, G., Gaspari, V., Planchon, F., Ferrari, C., and Cescon, P.: Variations in atmospheric trace elements in Dome C (East Antarctica) ice over the last two climatic cycles, Atmos. Environ., 39, 6420–6429, 2005.

Gabrielli, P., Barbante, C., Plane, J. M. C., Varga, A., Hong, S., Cozzi, G., Gaspari, V., Planchon,

- F., Cairns, W., Ferrari, C., Crutzen, P., Cescon, P., and Boutron, C. F.: Meteoric smoke fallout over the Holocene epoch revealed by iridium and platinum in Greenland ice, Nature, 432, 1011–1014, 2004.
  - Gaspari, V., Barbante, C., Cozzi, G., Cescon, P., Boutron, C. F., Gabrielli, P., Capodaglio, G., Ferrari, C., Petit, J. R., and Delmonte, B.: Atmospheric iron over the last deglaciation:
- <sup>25</sup> Climatic implications, Geophys. Res. Lett., 33, L03704, doi:10.1029/2005GL024352, 2006.
   Gauchard, P. A., Aspmo, K., Temme, C., Steffen, A., Ferrari, C., Berg, T., Planchon, F., Dommergue, A., Bahlmann, E., Magand, O., Ebinghaus, R., Banic, C., Storm, J., Barbante, C., Boutron, C. F., and Baussand, P.: An international study of Mercury, Ny-Ålesund spring 2003: Characterizing atmospheric mercury depletion events, Atmos. Environ., 39, 7620–7632, 2004.
  - Gerdol, R. and Bragazza, L.: Effects of altitude on element accumulation in alpine moss, Chemosphere, 64, 810–816, 2006.

Gragnani, R., Smiraglia, C., Stenni, B., and Torcini, S.: Chemical and isotopic profiles from

ACPD									
6, 8781–8815, 2006									
Atmospheric trace elements in Alpine snow									
Title Page									
Abstract Introduction									
Conclusions	References								
Tables	Figures								
I٩	►I.								
•	•								
Back	Close								
Full Scr	een / Esc								
Printer-frie	ndly Version								
Interactive	Discussion								
F	30								

<sup>15</sup> 

snow pits and shallow firn cores on Campbell Glacier (Northern Victoria Land, Antarctica, Ann. Glaciol., 27, 679–684, 1998.

- Hong, S., Barbante, C., Boutron, C. F., Gabrielli, P., Gaspari, V., Cescon, P., Thomson, D. S., Ferrari, C., Francou, B., and Bourgoin, M.: Atmospheric heavy metals in tropical South
- 5 America during the past 22 000 years recorded in a high altitude ice core from Sajama, Bolivia, Jour. Env. Monitor., 6, 222–226, 2004.
  - Hong, S., Candelone, J. P., Patterson, C. C., and Boutron, C. F.: History of ancient copper smelting pollution during Roman and medieval times recorded in Greenland ice, Science, 272, 246–249, 1996.
- <sup>10</sup> Kappeberger, G. and Kerkmann, J., II tempo in montagna, manuale di meteorologia alpina, Zanichelli, Milano, 1997.
  - Krachler, M., Zheng, J., Koerner, R. M., Zdanowicz, C., Fisher, D. A., and Shotyk, W.: Increasing atmospheric antimony contamination in the northern hemisphere: snow and ice evidence from Devon Island, Arctic Canada, J. Environ. Monit., 7, 2005.
- Latini, A.: Analisi della distribuzione delle precipitazioni nevose sulle Alpi italiane in relazione ai tipi di tempo e alle correnti in quota, Rivista di meteorologia areonautica, 47, 198, 1987.
   Maupetit, F., Wagenbach, D., Weddeling, P., and Delmas, R. F.: Seasonal fluxes of major ions to high altitude cold alpine glacier, Atmos. Environ., 29, 1–9, 1995

Molinaroli, E., Pistolato, M., Rampazzo, G., and Guerzoni, S.: Geochemistry of natural and anthropogenic fallout (aerosol and precipitation) collected from the NW Mediterranean: two different multivariate statistical approaches, App. Geochem., 14, 423–432, 1999.

20

30

- Nickus, U., Kuhn, M., Baltensperger, U., Delmas, R. F., Gaeggeler, H. W., Kasper, A., Kromp-Kolb, H., Maupetit, F., Novo, A., Pichlmayer, F., Preunkert, S., Puxbaum, H., Rossi, G. C., Schoner, W., Schwikowski, M., Seibert, P., Staudinger, M., Trockner, V., Wagenbach, D., and
- <sup>25</sup> Winiwarter, W.: SNOSP: Ion deposition and concentration in high alpine snow packs, Tellus, 49B, 56–71, 1997.
  - Nickus, U., Kuhn, M., Novo, A., and Rossi, G. C.: Major element chemistry in Alpine snow along a North-South transect in the Eastern Alps, Atmos. Environ., 32, 4053–4060, 1998
    Nriagu, J. O. and Pacyna, J. M.: Quantitative assessment of world-wide contamination of air, water and soils by trace metals, Nature, 333, 134–139, 1988.
  - Pacyna, J. M. and Pacyna, E. G.: An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources world-wide, Environ. Rev., 9, 269–298, 2001.

Printer-friendly Version

Interactive Discussion

EGU

Planchon, F., Boutron, C. F., Barbante, C., Cozzi, G., Gaspari, V., Wolff, E. W., Ferrari, C., and Cescon, P.: Changes in heavy metals in Antarctic snow from Coats Land since the mid-19th to the late-20th century, Earth Planet. Sci. Lett., 200, 207–222, 2002.

Planchon, F., Boutron, C. F., Barbante, C., Wolff, E. W., Cozzi, G., Gaspari, V., Ferrari, C.,

<sup>5</sup> and Cescon, P.: Ultrasensitive determination of heavy metals at the sub-picogram per gram level in ultraclean Antarctic snow samples by inductively coupled plasma sector field mass spectrometry, Anal. Chim. Acta, 450, 193–205, 2001.

Posch, M., Slootweg, J., and Hettelingh, J. P.: European Critical loads and Dynamic modelling: CCE Status Report 2005, 2005.

Preunkert, S., Legrand, M., and Wagenbach, D.: Sulfate trends in a Col du Dome (French Alps) ice core: A record of anthropogenic sulfate levels in the European midtroposphere over the twentieth century, J. Geophys. Res., 106, 31 991–32 004, 2001.

Provincia di Trento, Piano provinciale di risanamento e tutela della qualità dell'aria, in: APPA, (Ed), Provincia di Trento, 1998.

<sup>15</sup> Puxbaum, H.: Chemical composition and fluxes of wet deposition at elevated sites (700– 3195 m a.s.l.) in the Eastern Alps (Austria), in: Seasonal Snowpacks Processes of Compositional Change 28, edited by: Davies, T. D., Tranter, M., and Jones, H. G., Springer-Verlag, Berlin, p. 471, 1991.

Schwikowski, M.: Reconstruction of European air pollution from Alpine ice cores, in: Earth

- paleoenvironments: Records preserved in Mid and Iow Latitude Glaciers, edited by: Cecil, L. D., Thompson, L. G., Steig, E. J., and Green, J. R., ,Kluwer Academic/Plenum Publishers, 2003.
  - Schwikowski, M., Barbante, C., Doering, T., Gaeggeler, H. W., Boutron, C. F., Schotterer, U., Tobler, L., Van de Velde, K., Ferrari, C., Cozzi, G., Rosman, K., and Cescon, P.: Post-17-
- <sup>25</sup> Century Changes of European Lead Emissions Recorded in High-Altitude Alpine snow and Ice, Environ. Sci. Technol., 38, 957–964, 2004
  - Schwikowski, M., Doscher, A., Gaeggeler, H. W., and Shottered, U.: Anthropogenic versus natural sources of atmospheric sulphate from an Alpine ice core, Tellus, 51B, 938–951, 1999 Seibert, P., Kromp-Kolb, H., Kasper, A., Kalina, M., Puxbaum, H., Jost, D. T., Schwikowski,
- <sup>30</sup> M., and Baltensperger, U.: Transport of polluted boundary layer air from the Po Valley to high-Alpine sites, Atmos. Environ., 32, 3953–3965, 1998
  - Shotyk, W., Zheng, J., Krachler, M., Zdanowicz, C., Koerner, R. M., and Fischer, D.: Predominance of industrial Pb in recent snow (1994–2004) and ice (1842–1996) from Devon Island,

AC	ACPD								
6, 8781–8815, 2006									
Atmospheric trace elements in Alpine snow P. Gabrielli et al.									
Title	Title Page								
Abstract	Abstract Introduction								
Conclusions	References								
Tables	Figures								
I	۶I								
•	•								
Back	Close								
Full Scre	een / Esc								
Printer-frier	ndly Version								
Interactive	Discussion								
50									

Arctic Canada, Geophys. Res. Lett., 32, L21814, doi:10.1029/GL023860, 2005.

- Stanimirova, I., Daszykowski, M., Massart, D. L., Questier, F., Simeonov, V., and Puxbaum, H.: Chemometrical exploration of the wet precipitation chemistry from the Austrian Monitoring Network (1988–1999), Jour. Env. Manag., 74, 349–363, 2005.
- <sup>5</sup> Swan, A. and Sandilands, M. H.: Introduction to Geological Data analysis, Blackwell Science Ltd., Oxford, 1995.

Taylor S. R. and McLennan, S. M.: The continental crust: its composition and evolution, Blackwell Scientific publications, 1985.

Techne, Statistiche di emissioni, Roma, 1998.

- <sup>10</sup> Thomson, M.: Efficacy of robust analysis of variance for the interpretation of data from collaborative trials, Analyst, 118, 235–240, 1993
  - Van de Velde, K., Boutron, C. F., Ferrari, C., Bellomi, T., Barbante, C., Rudnev, S., and Bolshov, M. A.: Seasonal variation of heavy metals in the 1960s Alpine ice: sources versus meteorological factors, Earth Planet. Sci. Lett., 164, 521–533, 1998
- <sup>15</sup> Van de Velde, K., Boutron, C. F., Ferrari, C., Moreau, A. L., Delmas, R. F., Barbante, C., Bellomi, T., Capodaglio, G., and Cescon, P.: A two hundred years record of atmospheric Cadmium, Copper and Zinc concentrations in high altitude snow and ice from the French-Italian Alps, Geophys. Res. Lett., 27, 249–252, 2000

Van de Velde, K., Ferrari, C., Barbante, C., Moret, I., Bellomi, T., Hong, S., and Boutron, C.

- F.: A 200 Year Record of Atmospheric Cobalt, Molybdenum, and Antimony in High Altitude Alpine Firn and Ice, Environ. Sci. Technol., 33, 3495–3501, 1999
  - Veysseyre, A., Moutard, K., Ferrari, C., Van de Velde, K., Barbante, C., Cozzi, G., Capodaglio, G., and Boutron, C. F.: Heavy metals in fresh snow collected at different altitudes in the Chamonix and Maurienne valleys, French Alps: initial results, Atmos. Environ., 35, 415–425, 2001
  - Winiwarter, W., Puxbaum, H., Schoner, W., Bohm, R., Werner, A., Vitovec, W., and Kasper, A.: Concentration of ionic compounds in the wintertime deposition: results and trends from the Austrian Alps over 11 years (1983–1993), Atmos. Environ., 32, 4031–4040, 1998

Wolff, E. W. and Suttie, E. D.: Antarctic snow record of Southern Hemisphere lead pollution,

<sup>30</sup> Geophys. Res. Lett., 21, 781–784, 1994

25

Zechmeister, H. G.: Correlation between altitude and heavy metals deposition in the Alps, Environ. Pollut., 89, 73–80, 1995

#### Atmospheric trace elements in Alpine snow

ACPD

P. Gabrielli et al.



**Table 1.** Sampling sites in Trentino (TN) and in Veneto (Province of Belluno (BL), Province of Vicenza (VI) and Province of Verona (VR)) in the Italian Eastern Alps. Further information can be found in Internet on http://www.meteotrentino.it/AspWeb/Monitoraggi/stations/yeti/Campi\_neve/mappa/mappa\_neve.asp and http://www.arpa.veneto.it/csvdi/nivo.htm\#ubicazione.

N°	Area	Locality	Altitude (m)
1	Mount Vioz	Tarlenta (TN)	2030
2	Brenta	Prarodont (TN)	1530
3	Bondone	Viote (TN)	1500
4	Lagorai	Panarotta (TN)	1875
5	Ledro	Tremalzo (TN)	1550
6	Lagorai	Brocon Pass (TN)	1550
7	Adamello	Malga Bissina (TN)	1780
8	Primiero	Noana valley (TN)	1025
9	Adamello/Presanella	Tonale Pass (TN)	1880
10	Presanella	Folgarida (TN)	1910
11	Adamello/Presanella	Mount Presena (TN)	3040
12	Latemar	Pampeago (TN)	1900
13	Comelico	Mount Croce Pass (BL)	1960
14	Tofane	Ravales (BL)	2615
15	Dolomites	Mounts of Ornella (BL)	2250
16	Dolomites	Mount Pradazzo (BL)	2200
17	Agner	Gosaldo (BL)	1350
18	Pre – Alps	Faverghera (BL)	1605
19	Pre – Alps	Mount Grappa (VI)	1540
20	Folgaria-Asiago	Campomolon (VI)	1735
21	Lessini	Mount Tomba (VR)	1620

### **ACPD**

6, 8781-8815, 2006

Atmospheric trace elements in Alpine snow

P. Gabrielli et al.



#### Table 2. Summary of statistics.

Α	С	Ρ	D

6, 8781–8815, 2006

	N°	Mean (ppb)	SD (ppb)	Median (ppb)	Minimum (ppb)	Maximum (ppb)	Max/Min	Skewness	Kurtosis	Atmospheric tr elements in Alg	ace bine
Ag	366	0.005	0.007	0.003	0.001	0.11	107	9.4	117.3	snow .	
Ba	366	1.3	2.7	0.5	0.009	36.5	365	7.7	85.7		
Bi	366	0.006	0.011	0.003	0.0001	0.12	116	5.9	47.5	P. Gabrielli et a	al.
Cd	366	0.061	0.033	0.052	0.016	0.22	14	1.7	3.5		
Co	366	0.048	0.084	0.025	0.002	0.97	487	6.1	50.9		
Cr	366	0.10	0.21	0.045	0.003	3.0	995	8.5	97.9		
Cu	366	0.72	1.86	0.28	0.008	29.1	2911	11.2	157.4	Title Page	
Fe	366	27.3	74.6	10.1	0.067	1.1×10 <sup>3</sup>	10577	9.4	112.3		
Mn	366	4.3	14.0	1.2	0.001	173	1731	9.1	97.3	Abstract Introd	uction
Мо	366	0.052	0.054	0.040	0.011	0.72	66	6.4	66.5		
Pb	366	1.8	2.9	0.87	0.023	33.7	337	5.2	44.7	Conclusions Refere	ences
Sb	366	0.076	0.362	0.031	0.0017	6.2	3087	14.7	233.8		
Ti	366	2.6	6.7	0.9	0.008	106	1063	10.9	158.4	Tables Figu	ures
U	366	0.0086	0.0228	0.0025	0.0001	0.27	2654	7.8	73.6		
V	366	0.22	0.37	0.13	0.003	4.6	460	6.2	58.3	14	-
Zn	366	3.5	6.2	1.7	0.002	63.1	631	5.4	38.4		-
0.		0	0	0		0					•
Ca <sup>2+</sup>	332	$0.51 \times 10^{3}$	$0.84 \times 10^{3}$	$0.23 \times 10^{3}$	4	$7.4 \times 10^{3}$	1862	4.3	24.5		
CI_	365	162	0.33×10 <sup>3</sup>	70	5	4.0×10 <sup>3</sup>	800	6.5	58.0	Back Clo	ose
$K^+$	153	114	0.29×10 <sup>3</sup>	32	1	2.7×10 <sup>3</sup>	2700	5.9	43.3		
Mg <sup>2+</sup>	302	102	133	63	4	1.1×10 <sup>3</sup>	282	4.0	23.4	Full Screen / Esc	>
Na <sup>+</sup>	325	112	$0.24 \times 10^{3}$	37	1	$2.7 \times 10^{3}$	2729	6.1	52.6		
NO <sup>-</sup>	366	$0.90 \times 10^{3}$	$0.81 \times 10^3$	$0.64 \times 10^3$	27	$5.4 \times 10^3$	198	21	62	Database (strength a) (strength	•
SO <sup>2-</sup>	362	$0.53 \times 10^3$	$1.3 \times 10^3$	$0.31 \times 10^3$	15	$22.4 \times 10^{3}$	1/88	13.0	230 3	Printer-triendly Vers	sion
- 30 <sub>4</sub>	502	0.55×10	1.5×10	0.51 × 10	15	22.5×10	1400	10.9	200.0	Internativa Discussi	ion

EGU

cussion

**Table 3.** Mean trace elements and major ions fluxes to the snow and the deviation of the two mean fluxes averaged for each of the two selected periods of dry deposition (data from 19 January–4 February; 24 February–11 March on sites N° 11 Mount Presena (3040 m) in Trentino, N° 14 Ravales (2615 m), N° 15 Mounts of Ornella (2250 m) and N° 16 Mount Pradazzo (2200 m) in Veneto).

Flux g ha <sup>-1</sup> yr <sup>-1</sup>	Deviation g ha <sup>-1</sup> yr <sup>-1</sup>		Flux g ha <sup>-1</sup> yr <sup>-1</sup>	Deviation g ha <sup>-1</sup> yr <sup>-1</sup>
0.011	0.003	Ti	9	2
0.017	0.003	Mn	9	2
0.02	0.01	Zn	19	2
0.12	0.05	K+	34	11
0.09	0.03	Fe	68	25
0.14	0.03			
0.19	0.05	Na <sup>+</sup>	243	122
0.5	0.3	Mg <sup>2+</sup>	254	58
0.27	0.03	CI <sup>–</sup>	240	7
1.4	0.4	$SO_4^{2-}$	1314	289
2	1	Ca <sup>2+</sup>	1454	363
4.2	0.3	$NO_3^-$	2797	280
	Flux gha <sup>-1</sup> yr <sup>-1</sup> 0.011 0.017 0.02 0.12 0.09 0.14 0.19 0.5 0.27 1.4 2 4.2	FluxDeviation $gha^{-1}yr^{-1}$ $gha^{-1}yr^{-1}$ 0.0110.0030.0170.0030.020.010.120.050.090.030.140.030.190.050.50.30.270.031.40.4214.20.3	$\begin{array}{c cccc} Flux & Deviation \\ g ha^{-1} yr^{-1} & g ha^{-1} yr^{-1} \\ \hline 0.011 & 0.003 & Ti \\ 0.017 & 0.003 & Mn \\ 0.02 & 0.01 & Zn \\ 0.12 & 0.05 & K+ \\ 0.09 & 0.03 & Fe \\ 0.14 & 0.03 & \\ 0.19 & 0.05 & Na^+ \\ 0.5 & 0.3 & Mg^{2+} \\ 0.27 & 0.03 & Cl^- \\ 1.4 & 0.4 & SO_4^{2-} \\ 2 & 1 & Ca^{2+} \\ 4.2 & 0.3 & NO_3^- \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

### **ACPD**

6, 8781-8815, 2006

#### Atmospheric trace elements in Alpine snow

P. Gabrielli et al.



### ACPD

6, 8781–8815, 2006

#### Atmospheric trace elements in Alpine snow

P. Gabrielli et al.

Title Page								
Abstract	Introduction							
Conclusions	References							
Tables	Figures							
	► I							
•	•							
▲ Back	► Close							

Printer-friendly Version

Interactive Discussion

EGU

Table 4.	Mean	concen	trations	(ppb) c	of trace	metals	and ma	ajor ions	at the s	sampling	g sites in	the
Eastern A	Alps.											

	1 Tarlenta	2 Prarodont	3 Viote	4 Panarotta	5 Tremalzo	6 Brocon Pass	7 Malga Bissina	8 Noana valley	9 Tonale Pass	10 Folgarida	11 Mount Presena	12 Pampeago	13 Mount. Croce Pasi	14 Ravales	15 Mounts of Ornella	16 Mount Pradazzo	17 Gosaldo	18 Faverghera	19 Mount Grappa	20 Campomolon	21 Mount Tomba
Aα	0.005	0.005	0.007	0.003	0.002	0.003	0.007	0.003	0.011	0.003	0.005	0.004	0.004	0.004	0.002	0.002	0.002	0.007	0.005	0.004	0.004
Ba	0.6	1.7	1.7	1.4	0.9	0.6	2.7	0.7	3.9	2.4	0.4	0.8	2.0	0.5	0.5	0.4	0.6	1.5	1.2	0.8	0.5
Bi	0.002	0.007	0.004	0.009	0.003	0.004	0.015	0.004	0.013	0.005	0.003	0.004	0.004	0.004	0.002	0.002	0.003	0.010	0.009	0.006	0.004
Cd	0.046	0.071	0.050	0.079	0.068	0.070	0.070	0.053	0.088	0.077	0.054	0.051	0.063	0.064	0.044	0.042	0.048	0.067	0.054	0.056	0.046
Co	0.052	0.039	0.052	0.026	0.037	0.030	0.069	0.036	0.216	0.048	0.045	0.045	0.022	0.043	0.025	0.019	0.021	0.046	0.036	0.032	0.030
Cr	0.050	0.084	0.116	0.083	0.061	0.060	0.154	0.031	0.398	0.067	0.065	0.072	0.047	0.077	0.071	0.052	0.080	0.186	0.116	0.090	0.053
Cu	0.42	0.89	0.57	0.72	0.43	0.31	1.04	0.17	3.13	1.05	0.25	0.64	0.48	0.30	0.27	0.25	0.38	0.92	0.86	0.91	0.44
Fe	18.7	26.0	46.3	14.1	17.1	13.4	59.7	15.5	113.7	23.2	12.7	26.3	13.0	14.5	15.6	11.2	10.7	36.8	27.0	15.2	11.4
Mn	3.0	8.9	1.3	5.4	1.0	1.7	4.5	3.1	8.9	28.0	1.4	2.5	1.7	1.7	2.0	1.6	2.8	3.7	2.1	2.1	1.5
IVIO Dh	0.044	0.049	1.001	1.5	0.047	0.038	0.066	0.039	0.130	0.061	0.039	0.047	0.047	0.052	0.031	0.028	0.030	0.060	0.057	0.053	0.042
PD Sh	0.7	2.7	0.065	0.041	0.029	0.024	0.076	0.027	4.7	2.9	0.0	0.045	0.042	0.052	0.7	0.022	0.9	0.092	2.5	0.057	0.045
Ti	0.022	1.8	4.1	0.041	3.7	1.0	3.0	13	0.302	2.3	0.020	2.5	23	3.8	1.3	1 /	3.1	4.0	23	1.5	0.045
ü	0.0064	0.0084	0.0147	0.0030	0.0073	0.0038	0.0293	0.0041	0.0226	0.0087	0.0038	0.0066	0.0069	0.0058	0.0042	0.0025	0.0030	0.0128	0.0085	0.0057	0.0034
v	0.09	0.18	0.23	0.18	0.18	0.12	0.28	0.07	0.74	0.20	0.10	0.13	0.13	0.21	0.10	0.09	0.15	0.48	0.38	0.26	0.23
Zn	1.9	4.2	2.5	3.5	2.4	1.5	9.5	0.6	7.4	5.8	3.7	2.1	2.8	3.3	1.9	2.0	1.6	3.6	3.2	3.7	2.3
Ca 2+	149	214	772	177	1713	425	226	721	848	297	88	439	670	527	430	478	885	618	494	301	437
CI	66	81	349	87	402	140	93	45	219	160	65	133	122	82	74	71	73	247	448	101	286
K <sup>*</sup>	43	115	27	224	42	198	22	126	119	501	20	45	56	20	17	31	31	129	47	22	33
Mg 2+	59	53	164	58	72	79	46	137	101	80	29	160	137	100	104	87	130	161	168	88	74
Na	43	54	202	40	298	96	53	17	155	81	47	92	126	47	41	127	42	138	330	62	170
NO <sub>3</sub>	743	752	888	786	947	904	858	261	1132	1054	609	858	961	728	946	1017	760	1288	1371	795	1047
SO4-	282	316	395	392	675	295	383	154	615	396	384	630	1157	382	320	404	295	1774	596	451	703

### ACPD

6, 8781–8815, 2006

Atmospheric trace elements in Alpine snow

P. Gabrielli et al.

Title Page									
Abstract	Introduction								
Conclusions	References								
Tables	Figures								
	▶1								
•	•								
Back	Close								
Full Scre	en / Esc								
Printer-frier	dly Version								
Interactive	Discussion								
EGU									

**Table 5.** Variance distribution of the first three extracted principal components.

Component	Variance	Variance %	Cumulative variance	Cumulative variance %
1	13,48	61	13,48	61
2	2,15	10	15,63	71
3	1,29	6	16,93	77

### ACPD

6, 8781–8815, 2006

	P1	P2	P3	Com.
Ag	0.74	0.02	-0.15	0.57
Ba	0.84	0.12	0.39	0.88
Bi	0.87	0.11	0.13	0.78
Cd	0.67	0.27	-0.07	0.52
Со	0.79	0.09	0.29	0.71
Cr	0.82	0.16	0.26	0.77
Cu	0.84	0.21	0.34	0.87
Fe	0.86	0.05	0.42	0.92
Mn	0.76	0.18	0.43	0.79
Мо	0.84	0.22	0.13	0.76
Pb	0.91	0.20	0.18	0.91
Sb	0.86	0.36	0.11	0.88
Ti	0.69	0.05	0.59	0.82
U	0.79	0.08	0.53	0.91
V	0.79	0.38	0.13	0.78
Zn	0.76	0.35	0.29	0.78
Ca <sup>2+</sup>	0.37	0.26	0.75	0.76
CI⁻	0.30	0.71	0.42	0.76
Ma <sup>2+</sup>	0.30	0.26	0.72	0.67
Na <sup>+</sup>	0.13	0.68	0.42	0.66
NOT	0.16	0.80	0.15	0.69
SO <sup>2-</sup>	0.18	0.83	_0.06	0.73
$50_4$	0.10	0.00	-0.00	0.70

Atmospheric trace elements in Alpine snow						
P. Gabrielli et al.						
Title Page						
Abstract	Introduction					
Conclusions	References					
Tables	Figures					
I	►I					
•	Þ					
Back	Close					
Full Screen / Esc						
Printer-friendly Version						
Interactive Discussion						
EGU						

**Table 6.** Scores of the first three factors and cumulative communality of each chemical variable.















**Fig. 3.** Cluster analysis calculated from the principal component score matrix of the entire data set. The method for grouping is the Ward and distances are Euclidean.

