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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source and origin of atmospheric trace elements entrapped in winter snow of the Italian Eastern Alps" *by* P. Gabrielli et al.

P. Gabrielli et al.

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Response to the comments of the referees on "Source and origin of atmospheric trace elements entrapped in winter snow of the Italian Eastern Alps" by P. Gabrielli et al.

Anonymous Referee #1

We thank Referee #1 for the helpful and constructive review. Here is a point-by-point answer.

Point 1: Experiment design "Although the treatment and analysis of the samples using stringent contamination-free procedures is described in detail, the actual snow sampling method is not at all discussed. From the flux calculation on page 8792, I assume

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that a 2 cm snow layer was collected every week, independent on the actual amount of snowfall. This might be an acceptable method to study dry deposition (or sublimation, see below), but the wet deposition flux cannot be determined. A snow pit, collected at the end of the studied period, would have been a more suitable experiment".

We believe that the main objective of this research was not sufficiently explained. This is the first large study conducted at mid latitudes focusing on atmospheric trace elements entrapped in superficial snow on a relatively large spatial scale during one whole season. This research should be considered as an extensive but preliminary and explorative study primarily intended to reconstruct the source and the origin of trace elements entrapped in winter snow in the Italian Eastern Alps, as clearly stated in the title and in the abstract. This is now emphasized in the introduction. The experimental design was not conceived to determine total fluxes (dry plus wet deposition). The experimental design aimed at obtaining the most significant pool of snow samples in order to allow a statistically robust reconstruction of the source/origin of atmospheric trace elements in the Italian Eastern Alps. This is now emphasized in the text, illustrating that the experiment design was suitable to fulfill the main goal and that consequently the adopted sampling methodology does not affect the results and the interpretation presented in the paper. In addition, the sampling method is now discussed in detail in the text and in the conclusions, it is also mentioned that the next step of this program of research will be to determine both dry and wet fluxes of trace elements by sampling several Alpine snow pits at the end of a future winter season.

Point 2: Deposition fluxes: "I don't understand how the deposition fluxes in g ha-1 yr-1 were calculated from two 14-day periods of observation. Although the concentrations in fresh snow were much lower, the wet deposition might be significant simply because of the amount of snow and should therefore be considered. In addition to dry deposition, sublimation of snow might have occurred, a process which has been observed on glaciers during long dry periods (see e.g. Schotterer et al., The influence of postdepositional effects on ice core studies: examples from the Alps, Andes, and the Altai, in:

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Earth Paleoenvironments: Records preserved in Mid- and Low-Latitude Glaciers, Eds. L.D. Cecil, J.R. Green, and L.G. Thompson, Kluwer Academic Publishers, and references therein). Sublimation results in an enrichment of irreversibly deposited trace species in the upper snow layer, but would not increase the flux - in contrast to dry deposition.

The two 14 day- periods of observation were selected because they were representative of dry deposition conditions. In fact, during these two periods, only very minor snow events were observed and so wet fluxes could be neglected. Since our experimental design is suitable to determine only dry fluxes, we only tried to determine preliminary estimates of dry fluxes according to the equation reported in the text. Although sublimation might play a role in modifying the trace elements concentration in tropical superficial snow, this variation was probably negligible in the Alpine snow fields (also the reference suggested does not stress the role of snow sublimation in the Alps) especially when compared to the instrumental uncertainty of trace elements concentrations determined by ICP SFMS (12-48%). Most importantly, sublimation could not in any case perturb the internal structure of trace elements and ions in the snow samples (reciprocal mass ratios). As such is would not affect our conclusions based on linear statistics such as the Principal Component Analysis. This discussion is now reported in the text.

Point 3: Principal Component Analysis. “The interpretation is rather descriptive and weak. The results seem to be interpreted in the light of assumptions to find the crustal, marine and anthropogenic source. Only the second and third principal components are discussed although they represent together just 16% of the variability. The finding that all the trace elements show high scores in P1, whereas the major ions don’t, is not further investigated. Probably the concentration data were influenced mainly by the different processes wet and dry deposition (or sublimation), rather than by different emission sources and accordingly P1 could reflect the enrichment behaviour of the trace elements. Maybe a classification of the data set in a wet and dry period before

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the PCA could give a clearer picture."

Principal Component Analysis (PCA) is a multivariate statistical technique that aims at describing qualitatively the data set by summarizing the main features. Thus the descriptive character of our analysis is implicit in the technique used. However, the classification of the principal components in anthropogenic, marine and crustal is quantitatively corroborated by several cross evidences based on geochemical tools such as the crustal contribution calculation, the marine ratios comparison and typical anthropogenic mass ratios. The research for particular sources in the data set such as the crustal, marine and anthropogenic was based on what is widely suggested by the current state of art reported in the literature. P1 is likely indicating the total load of trace elements in the snow. This is quite to be expected and might have been put in evidence also with a simple matrix of correlation. That is why a major emphasis is given to P2 and P3 that represent the real net benefit given by the PCA. However, we agree that it is puzzling that, in contrast with the trace elements, that the major elements do not show high scores on P1. In any case, this cannot be due to sublimation (that does not modify reciprocal mass ratios) nor to the fact that the concentrations could have been influenced by different processes other than wet and dry deposition. In fact PCA conducted on two different data sets obtained by separating wet and dry deposition periods, did not produce any significant variations from the structure described by the general PCA. Now this discussion is also reported in the text.

Point 4 "Chapter 3.5 about meteorological data is weak and not supported by any data or figure"

The study of sources and origins of trace elements necessarily implies that once these have been determined, some hypothesis of transport from the source to the sink should be advanced in order to show that the conclusions reached are plausible. This chapter has exactly this function: to suggest a plausible scenario. Now these hypotheses are supported with supplementary synoptic data referring to the whole territory and with meteorological data obtained during the winter season 1998 by local weather me-

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teorological stations. In addition, the structure of the paragraph has been completely modified and the link between both meteorological and chemical data with the transport processes suggested has been reported in a cause-effect sequence.

Specific suggestions have been addressed and changes have been made accordingly in most cases. In particular:

I suggest English editing An English native speaker has performed a careful review of English editing.

Page 8786: “sampling downwind of the technicians”: I assume this was done upwind As the referee assumed, we report now that the sampling was performed upwind.

Page 8788, Table 2: Concentrations below detection limit are measured values and cannot simply be ignored for the calculation of averages. A normal practice is to use the detection limit divided by two. In our opinion the meaning of the statistics reported in the table is clear since the number of samples above the detection limit is given. Now the fact that N is referring to the number of samples above the detection limit is remarked also in the table.

Page 8789: The last paragraph belongs to the introduction Accordingly, we have moved the last paragraph of page 8879 to the introduction.

Page 8791: Define the concept of critical loads. The concept of critical loads has now been defined in the text and explained in this context

Page 8795: The statement that Saharan dust transports usually don’t occur in the cold season is wrong. Highest frequency is from March to July (see e.g. Collaud Coen et al., Atmos. Chem. Phys., 4, 2465-2480, 2004). We have now clarified that advection of Saharan dust does not occur often during winter and not generally during the cold season as reported (from a meteorological point of view the winter is considered to start at the beginning of December and to finish at the end of February).

Page 8797: SO42- and NO3- are most probably not deposited as acids, but mostly

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neutralized by NH3. NOx and SO2 are precursors and not original compounds. To my knowledge agriculture is not a source of SO2. It is not so straightforward that SO42- and NO3- are not deposited as acids, but are mostly neutralized by NH3. In fact concentrations of NH4+ found in the snow collected in the same area in winter 2005 were extremely low when compared to the concentrations of SO42- and NO3- and a pH of around 4.5 was found (Jacopo Gabrieli, Università di Padova, Tesi di Laurea). The facts that NOx and SO2 are precursors has now been inserted in the text. The word “Agriculture” was erroneously inserted: it is replaced now with “tertiary activities”.

Table 4: Font size is too small Font sizes have been enlarged.

Technical corrections: Page 8784 and references: correct: Kappenberger Corrected

Anonymous Referee #2

We thank Referee #2 for helpful and constructive review. Here is reported a point-by-point answer.

Point 1: “it does not seem that the conclusions are at the level of this investment. Particularly, there are no investigations on the spatial character of the data set, on the variability of the results in term of specific location of the sampling area and associated meteorological situation”.

We remark that the main objective of this paper was to reconstruct the overall sources and origins of trace elements in winter snow in the Italian Eastern Alps. Unfortunately, because of the heterogeneity of the sampling sites chosen we could not extrapolate from our data set a consistent distribution of concentrations and/or fluxes. To do this would have required much more similar sampling points (at approximately the same altitude above the limits of the forests). However, although the aim of the paper was not to focus the attention on the characteristics found at a specific location, some interesting case studies have been mentioned in paragraph “3.3 Spatial variability”. We agree with the referee that it was possible to reach our conclusions concerning origin

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and sources of trace elements adopting fewer sampling sites. However this was not obvious before this research and this is a remarkable conclusion of this explorative study that will be useful in the planning of other similar studies in the future. This discussion and clarification is now reported in the text.

Point 2: “A large fraction of the conclusion is dealing with atmospheric transport processes that are not really demonstrated in the course of the discussion”

The study of the sources and origins of the trace elements implies that these have been determined; some hypotheses of transport from the source to the sink should be made in order to show that the conclusions reached are plausible. This chapter has exactly this function: to suggest a plausible scenario. Now these hypotheses are supported with supplementary synoptic data that refers to the whole territory and by meteorological data obtained during the winter season 1998 by local weather meteorological stations. In addition, the structure of the paragraph has been completely modified and the link between both meteorological and chemical data with the transport processes suggested has been reported in a cause-effect sequence.

Point 3: “Finally, the level of English does not preclude proper understanding of the ideas, but could be well improved in many places”

An English native speaker has performed a careful review of English editing

Specific comments:

“Introduction, second paragraph: all of the references are mainly dealing with metals, while it states “contaminants”

The text has been changed accordingly to this comment.

“Introduction, last paragraph: you do not mention the motivation for such a large spatial coverage”

The experimental design aimed at obtaining the most significant pool of snow samples

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in order to allow a statistically robust reconstruction of the source/origin of atmospheric trace elements in the Italian Eastern Alps. This is now mentioned in the introduction.

Section 2.1, 3rd paragraph: you have to describe precisely the meteorological data set that was gathered during the program. This will help understanding the section 3.5 (pages 8799-8800), where it is currently not possible to figure out the data set used for the second PCA including both chemical and meteorological data (see below).

Now a new Table (2) gives a list of the meteorological parameters used for the PCA

Section 2.2, first paragraph: you do not mention the depth of the layers that were collected, if it represented an overall snowfall event or if it was always the same. You should discuss about this sampling strategy versus the heterogeneity of concentrations during a snowfall event, the evolution of surface concentration during dry periods, and the remobilization of snow surface by the wind

Sampling was conducted always by collecting approximately the first 2 cm of snow independent of whether it was fresh or old snow. The sampling method is now described in detail in the text. The discussion about the sampling strategy versus the heterogeneity of concentrations during a snowfall event and the study of the influence of the remobilization of snow surface by the wind is beyond the scope of the paper. The evolution of surface concentrations during two particular dry periods of about a half month duration each is discussed in paragraph 3.2 when considering dry fluxes.

Section 3.1, second paragraph, and Table 2: this table should include the DL for all species. Also, the values of skewness and kurtosis should be discussed

Now the DL for all the species have been inserted in Table 2 and skewness and kurtosis are discussed in the paragraph 3.4.1.

Section 3.1, 4th and 5th paragraphs: this idea of similar source regions for contaminants at winter-period-low-altitude sites and summer-period-higher-altitude sites is not well substantiated. First, you should show that the comparison is valid for more than 2

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chemical species. Second, you should prove that the data series are statistically identical (taken into account the very large variability in your series). Further, the fact that the origins of the species are the same would not necessary lead to similar concentrations. Finally, several previous studies indicate that the source regions of summer precipitations at high altitude sites in the Alps are much more continental than regional (refe).

A PCA was performed on a similar data set of trace elements determined in ice core samples extracted at Colle Gnifetti (Andrea Turetta, Tesi di Laurea, University of Venice) in the group of Monte Rosa. These samples are mainly representative of summer depositions because winter snow is mostly blown away from this site. The structure of the PCA obtained with Colle Gnifetti "summer samples" is nearly identical to the structure obtained with Eastern Alps "winter samples". This analysis substantiates our hypothesis that atmospheric trace elements originated from the same kind of regional/local sources. Now this discussion is reported in the text.

Section 3.2, last paragraph: how do you evaluate "the range of experimental error"? Is it valid to perform a comparison of fluxes at relatively high altitude sites and critical loads for forests?

The range of experimental error is evaluated according to the instrumental standard deviation of every trace element analyzed by ICP -SFMS. This is now mentioned in the text. Comparison of dry fluxes at relatively high altitude and critical loads for alpine ecosystems (not just for forests as reported by the referee but for an alpine ecosystem at medium-high altitudes) is purely indicative in the sense that dry fluxes could be considered as lower limits of total fluxes (wet plus dry deposition). Now this is reported also in the text.

Table 4: the table is too small. Also, taking into account the variability of the data set, it is not really informative to present an arithmetic mean only.

The font size of the Table has been enlarged. As it is impossible to present in the paper

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the whole data set (about 8500 data points) we believe that this table is helpful to the scientific community to have an idea of the large range of concentrations observed in sites with different geographic characteristics. However, the whole data set is reported now as Supplementary Information.

Section 3.3: It is very surprising that the data set was not explored more in depth to get more information on the spatial variability. The comments presented in this section are rather minor and ballpark examination, considering the very huge amount of work that was needed to gather the samples and obtain the results. Any attempt for statistical analysis in this direction? Also, there is not attempt to reconciliate the observation of this study with that from the moss study.

A deep analysis of the spatial variability is beyond the main scope of this paper and in any case, because of the geographic heterogeneity of the sampling sites, we cannot extrapolate from our data set a map of the distribution of concentrations or fluxes as the sampling sites are too different. Just to give an example: the sampling stations of Tonale Pass and Presena are very close (a few km) but they there is an enormous concentration gradient between them because the first site is located not far from a tourist station at 1800 m whereas the second is on a nearby summit at 3000 m. This would result in a misleading representation of the concentrations or fluxes distribution in that sector of the analyzed territory. Concerning the moss studies, we believe that a possibility for the observed opposite vertical gradient in concentration is that a higher snow accumulation rate, that is characteristics of the highest alpine sites, might have diluted the trace elements. In other words, a careful study of wet deposition fluxes might reconcile the two observations. This discussion is now reported in the text.

Section 3.4.1., second paragraph: if the data series are log-normally distributed, why don't you use geometric means and standard deviations in table 2? What are these "outliers"? You have to better explain that notion of "rank position" and how you apply it. What kind of information do you loose in doing so? What are the drawbacks of replacing missing data with the median?

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In the table we use the median instead of the geometric means as an alternative robust descriptive parameter of the data set. In addition, the median is based on a ranking technique that was adopted for the data set transformation before the application of the PCA. The notion of outliers and ranking are most likely widely known and the readers should have no problems in understanding these concepts. It is correct that ranking implies a certain degree of loss of information. What we lose are essentially eventual non-linear characteristics of the data set that might become recognized as linear. This is a general problem for the PCA but by applying the ranking, this could be even more emphasized. This is now reported in the text. The use of the median to replace missing data, limits as much as possible the distortion of the results obtained with the PCA applied on a ranked data set. There are no drawbacks, because the alternative is to eliminate the sample or to replace the missing data with the non-robust arithmetic mean, implying a major loss or distortion of the information produced. This discussion is now reported also in the text.

Section 3.4.2., 1st paragraph: any idea on why K+ is not included in any significant result of your statistical analysis? What are the reasons of the robust character of the results independently of the data subset? How do you explain that the trace elements are all gathered on the first component, irrespective of their individual origin / source (as determined in the later sections)?

K+ resulted not significant because there were too many K+ values below the detection limit that were all substituted by the same median value. Therefore K+ shows an inevitably distorted behavior that makes it insignificant (low communality on the first 3 extracted principal components). We interpret the robust character of the results obtained (independently from the data set used for the PCA (fresh/old snow samples; remote/rural samples) as a consequence of the common regional source for all the trace elements determined in these different pools of samples. This is now much more emphasized in the text. The first component represents the total charge of crustal and anthropogenic trace elements. All trace elements obtain high scores on the first

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principal component because most often sampling sites that are under strong anthropogenic influence were also under a strong crustal influence: that is why most of the samples were characterized by high or low concentrations for all the trace elements independently from their origin. This comment is now reported in the text.

Page 8796, line 9-10: an excess of Cl- of 39% cannot be seen as “a slight excess” and the associated contribution as a “minor contribution”. It is therefore surprising that Cl- is used as a marine tracer.

We recognize that this excess is not slight and we have eliminated this word from the text. However, as reported in lines 23-24, this does not preclude its use as marine tracer because the marine contribution calculated by using Na+ gives nearly identical results despite the fact that Na+ might be also affected by a not negligible (but hardly determinable) crustal contribution. However, nearly identical results obtained both with Na+ and Cl- gives us confidence that calculation of marine contributions is reasonable and that anthropogenic (for Cl-) and crustal (for Na+) contribution negligibly affect this calculation. This discussion is now reported in the text.

Page 8797, lines 14-21: the ratio of NO3- / SO42- in aged snow is governed by far more processes than just the initial concentrations of NOx and SO2 in air. Presenting a very general fact (concentrations of precursors in one of the potential sources regions) as the sole reason of concentration ratios observed in snow is really dubious.

We agree with this comment by the referee and we now report this in the text, and we leave some open questions concerning the meaning of the ratio NO3- / SO42 determined in snow samples.

Section 3.5 (pages 8799-8800): All this section should be more carefully explained and presented. What is the rationale for the calculation of a time period between “the snowfall day until the sampling day”? What are the meteorological data that were included in this second PCA? Does this mix both local meteorological data and large scale ones? Were these data also ranked? If not, cannot it be a reason for “the clear

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separation between chemical and meteorological parameters"? Why do you state that wet and dry depositions are only dependent of large scale processes?

All this section was carefully restructured and integrated with more detailed explanations. Now the hypothesis about transport is supported by additional synoptic data and meteorological data obtained during the winter season 1998 by local weather meteorological stations. Before applying the PCA to the whole data set of chemical and meteorological data, we had to associate a given concentration series of one sample (representative of one week) to a given meteorological value (these data were recorded daily). So we decided to associate to the concentration values of a given sample an average meteorological value calculated over the entire period in which the snow sampled was standing at ground level: from the day of the snow event until the sampling day. This is now explained in the text. Meteorological data included in the PCA are now given in Table 2. These were ranked exactly as the concentrations values before the application of the PCA. During the winter season, wet deposition processes are linked to humid air masses that are transported mainly from the Atlantic and the Mediterranean sea whereas dry deposition processes are mainly influenced by stable weather conditions governed by large scale high pressure fields. In this sense these phenomena are linked to large-scale processes. This is now added to the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 8781, 2006.