Atmos. Chem. Phys. Discuss., 11, C6568–C6581, 2011
www.atmos-chem-phys-discuss.net/11/C6568/2011/

Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Seasonal impact of natural and anthropogenic emissions on the highest glacier of the Eastern European Alps" *by* J. Gabrieli et al.

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Received and published: 18 July 2011

"Trace element concentrations in Alpine snow and ice have been investigated in many studies, covering in most cases much longer time periods. The findings which elements and ions are of anthropogenic origin are not new".

REPLAY: Although several studies have been published regarding trace elements and ionic compound concentrations in snow and ice in the Western European Alps and anthropogenic and natural sources of trace species have been discussed in the literature, no similar investigations have been carried out on high-altitude glaciers in the Eastern Alps. The finding that trace element data from the Alto dell'Ortles are compa-

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rable with those obtained from high-altitude glaciers over the Western Alps indicates similar sources and transport processes in the two sites. This correspondence has been previously never demonstrated, and especially not at seasonal time scales and represents a first, not trivial, result of this study. This point has been emphasized both in the abstract and in the manuscript.

"The discussion of possible anthropogenic sources of trace elements is purely based on literature and not related to the results of this study".

REPLAY: In the revised version of the manuscript we have identified direct links between the literature and our data. First we have studied the national emission inventories of As, Cd, Cr, Cu, Ni, Pb, Zn NOx, SOx, NH3 and dust, created by applying the CORINAIR (CORe INventory AIR emissions) method developed by the European Monitoring and Evaluation Program (EMEP) by local administrative scale (province), and divided into different emission sources (industrial combustion, non-industrial combustion, transport, etc.). Second, we used 2001 population census data from the Italian National Statistics Institute (ISTAT) to investigate the population distribution, employment classes (agriculture, industry, mining, tourism, trade, etc.), motor vehicle number (cars, tracks), numbers of hotels number and numbers of equivalent inhabitants. Table 1 demonstrates the ratios of trace species and elements in emissions from the Pò Valley and local areas (radius of $\sim$50 km from Ortles). These emission ratios are compared with those in Alto dell'Ortles snow (median data) and firn layers in the Colle Gnifetti ice core (1980-93). We report relevant seasonal differences in trace species ratios in the Alto dell'Ortles snow. Trace species ratios in snow layers formed during warm periods correlate well with the emission ratios of the Pò Valley ($R2=0.83$, $p<0.001$), while the influence of local emissions sources appears to be minor. This is an important new result that suggests the predominance of the regional over the local pollution of trace metals and species at the highest elevations of the Eastern European Alps during summer. The trace species ratios in snow layers formed during cold periods correlate well with the corresponding Pò Valley emissions ($R2=0.56$, $p=0.024$)

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while cold period ratios in Ortles snow differ significantly from local sources ($R2=0.21$, $p=0.23$). The lower correlation coefficients during cold periods indicate a stronger influence of long-range transport. The different summer and winter sources are consistent with the back-trajectories and meteorological data. During summer, about 80% of back-trajectories are from W and SW of Alto dell'Ortles, with strong convective movements associated to unstable meteorological conditions (such unstable conditions occur between 50% to 70% of the total days between May to September). These conditions result in a more efficient transport of pollutants from the Pò Valley and, in particular, from the Milan district, which is the most populated and industrialized district in Italy and one of the most heavily industrialized areas of Europe (Fig. 1). Table 1 demonstrates that the influence of local sources (calculated as a 50 km radius from Alto dell'Ortles) appears to be negligible when compared with Pò Valley sources. The area around Ortles is mainly rural and/or mountainous, with a low population density and low levels of manufacturing production (Fig. 1). The principal economic activities are linked with tourism, agriculture, and farming, all of which are often conducted as family business. Quantitatively, the local source contributions to the total emissions of the Pò Valley and surroundings ranges from 1.7% (As) to 7.1% (Zn) and 7.4% (Ni). The ratios between the Pò Valley and local emissions, normalized for surface area, decrease in this order: As (31), SOx (20), Cr (13), Zn (9), Cd (5), Cu, NOx and NH3 (4), Ni (2). Figure 1 demonstrates a more uniform pollutant emissions distribution in the Pò Valley (at district administrative levels) for Cu (0.62 ± 0.57 kg/km2), Cr (0.43 ± 0.36 kg/km2), Cd (0.057 ± 0.051 kg/km2), NOx (7.2 ± 5.8 ton/km2) and NH3 (3.4 ± 2.6 ton/km2) respect to Zn (6 ± 11 kg/km2), Ni (1.0 ± 1.9 kg/km2), Pb (1.7 ± 2.5 kg/km2) and SOx (1.9 ± 2.4 ton/ km2). The Bergamo/Brescia region has particularly high Zn and Pb emissions while Milano/Brescia is a hot-spot of Ni emissions. These regions are S and SW from Mt. Ortles, respectively. Ratios of trace species and elements in Alto dell'Ortles and Colle Gnifetti snow/ice are comparable, indicating a general consistency of the Pò Valley contaminants deposition over high-altitude Alpine glaciers. This agreement holds except for the Cr/Cd, Zn/Cu and Pb ratios. The differences in Pb concentrations are

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likely due to the higher Pb emissions in the period 1980-93 than during recent years. This change in Pb concentrations results in higher Pb/Trace element ratios for Colle Gnifetti. The differences in Cr/Cd and Zn/Cu ratios between Alto dell'Ortles and Colle Gnifetti may be explained by different mobilization of these metals along an altitudinal transect, due to a different size distribution in aerosol particles (Allen et al., 2001). Although pollutant transport inside the Pò Valley is very efficient (Deserti et al. 2006), the presence of hot-spot emissions may affect pollutant deposition over the Alps.

"Also the strong seasonality of aerosol-related parameters due to changing vertical stability of the atmosphere especially in mountain regions is well known".

REPLAY: This strong seasonality is well known in the Western Alps but was never verified for the Eastern Alps. Moreover, we quantitatively characterized the sampling site in terms of air mass pathways, boundary layer depths, and atmospheric stability, by applying specific modelling schemes.

"The data set covers only two years which is too short for sound statements about spatial or temporal trends, considering the strong variability due to changing meteorological conditions. Trace element and major ion concentrations in Alpine snow and ice generally show high variability and most of them have strong temporal trends. This high variability was also detected in the snow pit from Alto dell'Ortles (Table 1, e.g. Al mean: 3440 pg g-1 SD 4290 pg g-1). Considering the high variability at individual sites (t-test) and the different time periods compared (apples and oranges) I doubt that the two years data are sufficient to deduce significant spatial or temporal trends between Eastern and Western Alps".

REPLAY: We agree with the referee and we deeply revised this section of the manuscript. In particular, we removed completely the temporal comparison with the other sites in the Western and Eastern Alps. Despite the large spatial variability, we, underline in the revises manuscript the limitation of this analysis.

"A related paper was published in 2010 (Gabrielli et al., J. Glaciology), where parts of the results of the snow pit study are already presented".

REPLAY: In Gabrielli et al. 2010 (Journal of Glaciology) the first glaciological data from Alto dell'Ortles were reported, with the aim of investigating whether this site is suitable for extracting a long-term environmental record from an ice core drilled to bedrock. Gabrielli et al., (2010) estimates glacier thickness using a geo-radar survey, air-temperature and mass-balance reconstructions, and investigates the preservation of climatic and environmental signal in a shallow firn core. In Gabrielli et al., 2010 we compared the records of a few trace species (Ca2+, NO3-) and trace elements (Cu, Cd, Al) of the snowpit with the chemical records and physical observations of the shallow core to evaluate seasonal signal preservation. Gabrielli et al. does not discuss anthropogenic sources and deposition mechanisms and only use this data to support the firn core dating. For these reasons, and considering the very limited data overlap (5 elements presented in Gabrielli et al., out of the 33 elements and species presented here), we argue that our results are novel and augment the geophysical observations provided by Gabrielli et al.

"Overall the authors should point out more clearly what was the motivation of this study, what is the added value and what is not already known from previous studies".

REPLAY: We present the first comprehensive dataset of a large suite of trace elements and ionic compounds in snow and firn sampled from a 4.5m snow-pit at 3830m a.s.l. in the Eastern Alps. Although several chemical species data and trace elements deposition records are available in the Western Alps (Colle Gnifetti, Grenzgletscher, Col du Dome, Dome du Goutier) there are few reliable data from Eastern Alpine glaciers. Our work starts to fill this gap in existing data, and therefore is a significant result. Alto dell'Ortles is the highest glacier in the Eastern Alps, yet only now are studies (this paper and Gabrielli et all., 2010) investigating the glaciology and geochemistry. We discuss the chemical data in the light of the available meteorological and atmospheric circulation data including the boundary layer depth, atmospheric stability and calculated back-trajectories. We connected the chemical profiles with the snowpack

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stratigraphy and, for the first time, we successfully applied this combined approach to evaluate the seasonal variations in trace species deposition. In the revised manuscript, we have highlighted the climatic differences between Eastern and Western Alps and the related consequences of the transport mechanisms from anthropogenic areas to the glaciers. In fact, the climatic conditions of Tyrol (the Italian-Austrian border region) differ significantly from other well characterized glacial areas of the Western Alps, especially for the amount and seasonality of precipitation. Brunetti et al. (2006) identifies the Italian Alps as one single homogenous air temperature region (Italian Alpine region, Liguria and Piedmont), but identifies two precipitation sub-regions: Northwestern Italy and the northern part of Northeastern Italy. Schwarb (2000) extrapolated high-altitude rain gauge datasets, calculating the mean annual precipitation in the Mt. Ortles area as 800-1000 mm/yr, while Monte Rosa and Mont Blanc receive about 1600-2000 mm/yr. Frei and Schär interpolated valley floor rain gauge datasets and estimated the mean annual precipitation in Ortles as about 750-850 mm/yr while Monte Rosa and Mont Blanc receive 1100-1300 mm/yr. Monte Rosa and Mont Blanc are characterized by equinoctial precipitation maximum regimes and a winter minimum, while on Mt. Ortles the maximum in precipitation occurs during summer. The percentage of winter precipitation is extraordinarily low in some Southern Central Alpine areas such as the Venosta Valley and Ortles. This precipitation pattern can be explained as consequence of a lack of convectional precipitation during winter, while during summer the prevailing westerly cyclonic winds provides significant precipitation only to the northern edge of the Alps. Moreover, the north-western Alps contained a positive trend, (1901-1990) during the winter season while no significant tendencies are reported for the Mt. Ortles region (Schmidli et al. 2002). This evidence highlights a remarkable climatic difference between the Western and the Eastern Alps that further justifies the novelty of this study.

“In addition, it is not clear how much the trace element and ion concentrations at Alto dell’Ortles are influenced by melt water percolation and ablation. The same limitations apply for the flux comparison. Fluxes are even more complex, since secondary processes such as wind erosion and ablation by summer melt/evaporation play a role. Net

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accumulation rates are regionally extremely different, depending on local topography and meteorology and can not easily be interpreted in terms of precipitation to calculate fluxes. Is there anything known about wind erosion or summer ablation at Alto dell'Ortles?"

REPLAY: We agree with the referee that secondary processes such as wind erosion, ablation and other post-depositional processes are likely to have played a role which could have partially biased the flux calculation. However, this is actually the case for all the European Alpine drilling sites. We have now better explained in the manuscript the possible limitations of the flux comparisons due to these secondary processes. Hereafter we discuss these possible post depositional processes. In Gabrielli et al. 2010 we show that annual mean melt estimates on Mt. Ortles are 400 mm/year, ranging from 250 to 600 mm/year over the 2002-2009 period. The estimated total annual precipitation in the same period is 1,200 mm/year, and the net annual mass balance is 800 mm/year (Gabrielli et al., 2010). Despite such considerable melting, the strong seasonal variability, as inferred from the snow pit chemical and isotopic profiles, confirmed the limited influence of ablation and water percolation on the chemical content of the surface snow layers. Snow pit density measurements and visible stratigraphy suggest that percolation within the upper snow pack is limited. In any event, the presence of a thick melt-freeze crust at 60-65 cm and the smoothing of stable oxygen isotopes during the 2007 and 2008 summers (Gabrielli et al. 2010) suggests that percolation within the snow pack and firn layers does have occurred. No direct measurements of wind erosion are available from Mt. Ortles. Data from automatic weather stations (AWS) located in a similar nearby wind-exposed environment (La Mare glacier, Cevedale massif; Luca Carturan, unpublished data) indicate that the snow accumulation from November to April is significantly reduced or completely removed by wind due to dry conditions, low temperatures and high wind speed (Suter et al. 2004). Nevertheless, the clear presence of thick winter layers in the 2009 Alto dell'Ortles snow pit (about 190 cm for the 2008/08 winter layer) suggest that this erosion process was less important at this site.

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“Geogenic tracers in Alpine snow are strongly influenced by Saharan dust deposition which has a sporadic nature and induces even larger inter-annual variability”

REPLAY: The contribution of Saharan dust to Eastern Alpine glacier surfaces is currently unknown, but this deposition is likely to influence the measured geogenic tracers in the Eastern Alps due to their proximity to both the Western Alps and the Sahara. However, our results demonstrate a primarily local crustal dust contribution during the two years represented by the snow pit samples. This point has been discussed in the revised version of the manuscript. The different precipitation regime on Mt. Ortles with respect to the Western Alps where the maximum precipitation occurs in summer and spring, respectively, may influence the Saharan dust inputs. Indeed Saharan advection occurs mostly during the springtime but is rare during summer.

“The positive relation between accumulation and ionic fluxes (page 6504 and 6505) is trivial since the flux is calculated as product of concentration and accumulation. This does not indicate anything about the scavenging process”.

REPLAY: We fully agree with the referee and have revised this section. In particular, we have removed the sentence: “This positive relationship between accumulation and ionic fluxes indicates that wet-deposition likely represents the most efficient scavenging process of SO42- in high-altitude mountainous areas”.

“The first component of the PCA (PC1) accounts for 57% of the total variance, but it is not explained at all why it has loadings in every trace element and major ion. Since the concentration levels of the trace species differ by more than an order of magnitude, concentrations should be normalized (probably using the logarithmic data, depending on the distributions) before conducting the PCA. Again, considering the short time period of two years the data set is probably over-interpreted by conducting a PCA”.

REPLAY: Before conducting the PCA, we standardized the data set by using the mean and the standard deviation, in order to eliminate the influence of the absolute magnitude linked to the variables. In this way, all the variables have the same weight. As for almost all the variables the data distribution is not normal but asymmetric, a log-normal distribution represents a better fitting. For this reason, as suggested by the referee, we have run a new PCA using the logarithm of the concentrations. In this case, the first principal component (PC1) explains, the main features of the data set. In PC1, almost all the variables have a relevant weight while in PC2 and PC3, which explain smaller variance, there are only few significant variables characterized by high weights. These components, when compared with PC1, normally evidence different detailed characteristics of the data set. PC1 accounts for 63% of the total variance, with comparable negative loadings for all the variables, except for TOC and δ18O. This indicates a quite homogeneous chemical matrix. PC1 discriminates samples on the basis of the aerosol and trace species content. In particular, samples characterized by high concentrations (warm periods) show very negative loadings (PC1 sectors A, B in Figure 2, panel a) while diluted samples (cold periods) show positive loadings (PC1 sectors E, F, G in Figure 2, panel c). This behavior is thus clearly linked with the seasonality since snow deposited during warm periods is characterized by higher concentrations of trace elements and ionic compounds with respect to the cold seasons. Samples characterized by smaller loadings on PC1 show intermediate concentration levels of trace species (PC1 sectors D, E in Figure 2). These snow layers could have been formed in intermediate atmospheric conditions, for example during spring and autumn or from the mixing of different layers, due to post-depositional processes, such as wind redistribution and/or melting. The small loadings on PC1, for samples deeper than 300 cm (Figure 2, panel b), may be due to percolation of melting water. Despite the large number of samples which are not clearly discriminated by PC1, taking into account the samples with important negative and positive loading (sectors A, B and E, F, G on Figure 2, respectively), we obtain a good seasonal subdivision which is consistent with the stratigraphic observations and the chemical profiles (Figure 2, panel b). The second PCA component (PC2) accounts for 10% of the total variance and has positive loadings for Mg2+, Ca2+, Li, Rb, Sr, Ba, Al, Ti, Fe, Ga, Mn, Co, U and negative loadings for d18O, TOC, NO3-, SO42-, Cl-, Na+, NH4+, As, Cd, Sb, Pb, Bi, V, Ni, Cu,

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Zn. We interpret PC2 as the component that separates crustal, anthropic and marine variables. Cr, Tl and K+ are not discriminated by PC2 indicating that the sources of these elements may be mixed. Finally, we agree with the referee that, since this study covers only two years, the discussion of the PCA results should be considered preliminary and not conclusive. On the other hand, through the interpretation of this PCA we obtain relevant information regarding the seasonality and the different sources of trace species during the period covered by our investigation. This is now emphasized in the revised manuscript.

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Table 1 Trace species ratios for estimated emissions (2000 AD), Alto dell'Ortles snow and Colle Gnifetti firn (1980 to 1993 AD).

	Emissions		Alto dell'Ortles snow pit			CG core
	Po' Plain	local	median	warm	Cold	1980-93
NO_3^-/NH_4^+	1.7	1.4	1.7	2.0	2.5	2.1
SO_4^{2-}/Cd (*)	27	5.9	30	39	21	18
SO_4^{2-}/Cr (*)	5.9	1.4	5.9	11	4.7	12
SO_4^{2-}/Ni (*)	1.6	0.5	1.1	1.5	0.7	-
Pb/Cd	32	45	15	21	10	44
Pb/Cr	5.1	9.8	2.9	5.6	2.3	31
Pb/Zn	0.21	0.10	0.13	0.18	0.11	0.49
Pb/As	5.4	40	5.1	8.2	3.1	-
Cr/Cd	6.3	2.5	5.1	4.7	4.5	1.4
Zn/Cr	32	49	27	37	29	-
Zn/Cu	8.6	35	5.7	4.4	5.7	16
Zn/SO_4^{2-} (#)	5.1	33	4.8	3.6	4.8	5.1

(*) divided by 1,000
(#) multiplied by 1,000

Fig. 1. TAB_1

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Figure 1 Annual emissions (2005) of some selected pollutants in the Pò Valley (EMEP-CORINAIR data).

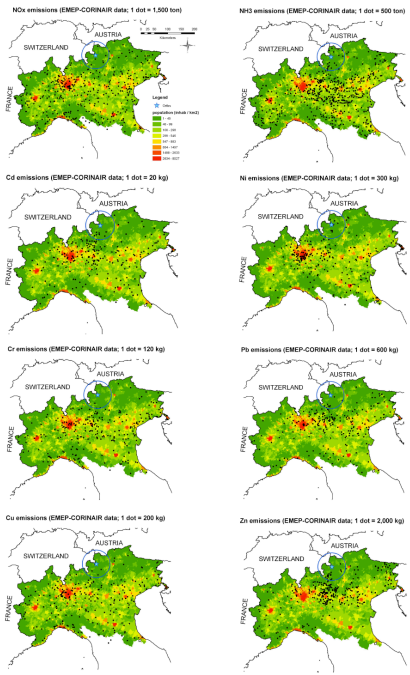

Fig. 2. FIG_1

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Figure 2 Principal Component Analysis (PCA) biplot (panel a) of all the chemical variables and cases on the first two PC which explain 62.5% and 9.9% of the total variance, respectively. The red cases correspond to samples from warm periods while the black ones those from cold periods, as inferred from the stratigraphic observations. In panel b, we show the seasonal distribution as reconstructed from the depth profiles of negative and positive PC1 loadings (sectors A, B and E, F, G, respectively). In panel c, we show the relation between PC1 and the trace element concentration.

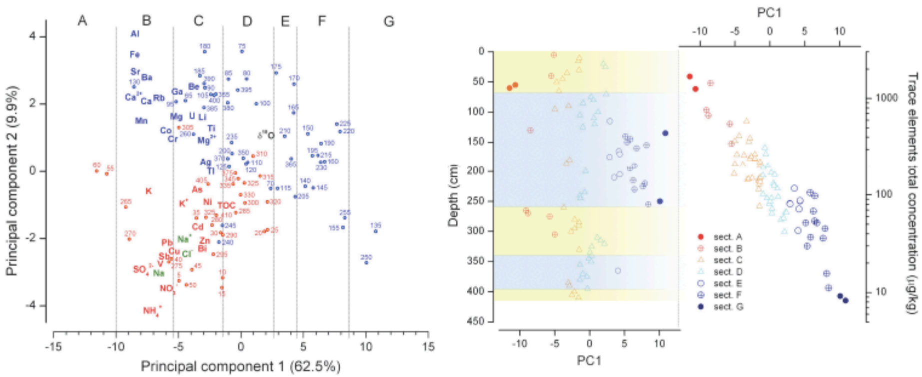

Fig. 3. FIG_2

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