

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Seasonal impact of natural and anthropogenic emissions on the highest glacier of the Eastern European Alps

J. Gabrieli^{1,2}, L. Carturan³, P. Gabrielli⁴, C. Turetta², N. Kehrwald², G. Cozzi², H. Staffler⁵, R. Dinale⁶, R. Seppi⁷, G. dalla Fontana³, L. Thompson⁴, and C. Barbante^{1,2}

¹Institute for the Dynamics of Environmental Processes IDPA-CNR, University of Venice, Dorsoduro 2137, 30123 Venice, Italy

²Department of Environmental Sciences, University Ca' Foscari of Venice, Dorsoduro 2137, 30123 Venice, Italy

³Department of Land, Environment, Agriculture and Forests, Agripolis, University of Padua, Viale dell'Università 16, 35020 Legnaro, Italy

⁴School of Earth Sciences and Byrd Polar Research Center, The Ohio State University, 108 Scott Hall, 1090 Carmack Road, 43210 Columbus, USA

⁵Ripartizione Protezione Antincendi e Civile – Provincia Autonoma di Bolzano, Viale Drusio 116, 39100 Bolzano, Italy

6493

⁶Ripartizione Protezione Antincendi e Civile, Ufficio Idrografico – Provincia Autonoma di Bolzano, Via Mendola 33, 39100 Bolzano, Italy

⁷Earth Science Department, University of Pavia, Via Ferrata 1, 27100 Pavia, Italy

Received: 27 November 2010 – Accepted: 11 February 2011 – Published: 23 February 2011

Correspondence to: J. Gabrieli (gabrieli@unive.it)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

In June 2009, we conducted the first extensive glaciological survey of Alto dell'Ortles, the uppermost glacier of Mt. Ortles which at 3905 meters above sea level (m a.s.l.) is the highest summit of the Eastern European Alps. We analyzed snow samples collected from a 4.5 m snow-pit at 3830 m a.s.l. Here, we present a comprehensive data set including a large suite of trace elements and ionic compounds that comprise the atmospheric depositions over the past few years.

Trace element concentrations measured in snow samples are extremely low with mean concentrations at pg g^{-1} level. Only Al and Fe present median values of 1.8 and 3.3 ng g^{-1} , with maximum concentrations of 21 and 25 ng g^{-1} . The median EFC values for Be, Rb, Sr, Ba, U, Li, Al, Ca, Cr, Mn, Fe, Co, Ga and V are lower than 10 suggesting that these elements originated mainly from soil and mineral aerosol. EFC higher than 100 are reported for Zn (118), Ag (135), Bi (185), Sb (401) and Cd (514), demonstrating the predominance of non-crustal depositions and suggesting an anthropogenic origin.

Our data show that the physical stratigraphy and the chemical signals of several species were well preserved in the uppermost snow of the Alto dell'Ortles glacier. A clear seasonality emerges from the data as the summer snow is more affected by anthropogenic and marine contributions while the winter aerosol flux is dominated by crustal sources. For trace elements, the largest mean EFC seasonal variations are displayed by V (with a factor of 3.8), Sb (3.3), Cu (3.3), Pb (2.9), Bi (2.8), Cd (2.1), Zn (1.9), Ni (1.8), Ag (1.8), As (1.7) and Co (1.6).

The chemical data are also discussed in light of the atmospheric stability and back-trajectories analyses in order to explain the observed seasonal variability and how human activities impact the high altitude environment in the Eastern Alps. The origin and behavior of air masses as inferred from the evaluation of 48-h back-trajectories show significant seasonal differences. However, the large changes in trace elements concentrations seem to be more related to the vertical structure of the troposphere at a regional scale rather than the synoptic weather patterns.

6495

1 Introduction

Impurities trapped in snow and ice provide insight into past atmospheric composition and environmental variations. In particular, the study of trace elements and ionic compounds contribute to the understanding of changes in past atmospheric circulation and to estimating the relative contribution of different sources. Trace element measurements in ice cores from around the globe are suited for the determination of natural background concentrations and anthropogenic pollution (Barbante et al., 2009; Hong et al., 2009; Kaspari et al., 2009; Shotyky et al., 2005). During the past few decades, several reconstructions of trace elements and heavy metals in polar ice-cores, especially from Antarctica (Planchon et al., 2003) and Greenland (McConnell et al., 2002), demonstrate consistent anthropogenic pollution in recent snow samples. The European Alpine glaciers are located near densely populated and industrialized areas and have considerable potential to provide excellent archives for past air pollution. These glaciers may accurately document the environmental impact of anthropogenic emissions over the previous centuries as well as the efficacy of recent air pollution controls (Schwikowski, 2004).

The first heavy metal concentrations in Alpine firn and ice samples were obtained from the analysis of a 140 m snow/ice core drilled on the Col du Gouter, in the Mont Blanc Massif (4304 m a.s.l.). Van de Velde et al. (1999) determined the seasonal variations of several trace elements (Pb, Zn, Cu, Cd, Bi, Mn and Al) from 1960–1968. In addition, two other studies (Van de Velde et al., 1999, 2000) determined the concentrations of Co, Cr, Mo, Sb, Au, Ag, Pt, Pd and Rh, in the same ice core covering the last two centuries. Barbante et al. (2001) report the changes in post-World II uranium concentrations. Concentrations of many heavy metals (Cr, Cd, Zn, Co, Ni, Mo, Rh, Pd, Ag, Cd, Sb, Bi, Pt, Au, U) were also determined in a 109 m ice core drilled in 1982 on Colle Gnifetti, Monte Rosa massif, since 1650 AD (Barbante et al., 2004). Schwikowski et al. (2004) analyzed the same samples for Pb concentration and isotopes. Surprisingly, little attention has been paid to the investigation of heavy metals in fresh snow and

6496

seasonal snow-pack from high altitude European Alpine areas and only few reliable data concerning winter snow have been published (Gabrielli et al., 2008; Veysseyre et al., 2001).

In contrast, ionic compounds have been extensively studied in Alpine snow and ice. The historical records of major ion deposition on high-altitude glaciers from the Western Alps were inferred from the following firn and ice cores: Col du Dome near Mont Blanc (Preunkert et al., 1999), Colle Gnifetti (Sigl, 2009; Bolius, 2006) and Grenzgletscher (Eichler et al., 2004) in the Monte Rosa Group; and Fiescherhorngletscher in the Bernese Alps (Eichler et al., 2004). Major ions were also determined in recent snow from the Eastern Alps: Careser glacier (Novo and Rossi, 1998), Stubai glacier (Kuhn et al., 1998), Sonnblick glacier (Puxbaum and Tschewenka, 1998) and in the snowpack of mid-altitude sites (1500–2650 m a.s.l.) in the Dolomites (Gabrieli et al., 2008, 2010a).

A general prerequisite for the preservation of climatic and environmental information in glaciers is the presence of sufficiently cold firn temperatures and the absence of significant meltwater percolation. Until now, these conditions were expected to occur above 4000 m a.s.l. and 4300 m a.s.l. in the northern and southern sectors of the European Alps, respectively (Schwikowski, 2004). Given this possible limitation, only the Mont Blanc region, the Monte Rosa Massif and a few locations in the Bernese Oberland were previously considered as possible drilling sites.

The highest peak of the Eastern Alps is Mt. Ortles (3905 m a.s.l.) located in the Southern Rhaetian Alps, Italy. This area lies at the boundary between the central and southern European climate regions (Davis et al., 2003) and therefore is subject to a continental precipitation regime with the lowest precipitation amounts of precipitation in the Alps which are lower by a factor of two to three from the Alpine average (Schwarb, 2000). The region near Mt Ortles is often referred to as the inner dry Alpine zone (Frei and Schär, 1998). This low precipitation suggests that although Alto dell'Ortles has a relatively low altitude for obtaining a conserved paleo-glaciological record, the glacier could still contain ice up as old as several millennia. Supporting evidence for old ice

6497

includes the discovery of the prehistoric Otztaler man (5200 BP) from the ablating ice at Similaun (3280 m a.s.l.), just 30 km west of the Alto dell'Ortles glacier (Baroni and Orombelli, 1996).

To evaluate the potential of Alto dell'Ortles glacier as a glacial archive for paleo-environmental studies, we conducted the first extensive glaciological survey in June 2009 (Gabrielli et al., 2010). This survey included various glaciological measurements, a ground penetrating radar (GPR) survey, drilling a 10 m shallow core and sampling a 4.5 m snow-pit. Here, we present a new comprehensive dataset of a large suite of trace elements and ionic compounds in snow sampled from the 4.5 m snow-pit at 3830 m a.s.l., near the summit of Mt. Ortles. The data are discussed in light of the available meteorological and atmospheric circulation data including the boundary layer depth, atmospheric stability and calculated back-trajectories. This compilation provides the first data for the seasonal variability of trace species deposition in the Eastern Alps and the impact of human activities on this high altitude environment.

2 Methods

2.1 Study area

Mt. Ortles (46°30'32" N, 10°32'41" E) is located in the northern Ortles-Cevedale massif in the Southern Rhaetic Alps (Provincia Autonoma di Bolzano, Alto Adige South Tyrol, Italy), and is the highest peak in the Eastern European Alps (3905 m a.s.l.) (Fig. 1). This section of the Ortles-Cevedale massif is composed by sedimentary rocks such as stratified dolomites with interblended laminated and slab-shaped black limestone (Desio, 1967). The northwestern flank of Mt. Ortles is covered by the Alto dell'Ortles glacier. The upper part of the glacier has a slope of 8–9 degrees which then flows to steeper bedrock to form two major tongues. The glacier surface area is 1.04 km² and ranges in elevation from 3905 to 3018 m a.s.l (Gabrielli et al., 2010).

6498

core in the Monte Rosa Group (Gabrieli, 2008; Barbante et al., 2004; Schwikowski et al., 2004). Although the magnitude is comparable, the trace elements concentrations from the Alto dell'Ortles snow pit are generally lower than those determined in the recent Colle Gnifetti firn (1980–1993). For instance, Pb concentrations are 15 times lower in Alto dell'Ortles while Ba, V, Mn, Zn, Fe and Al are about 3–5 times lower. This variation in concentrations can be explained by differences in regional precipitation where the estimated snow accumulation on the Alto dell'Ortles glacier over the last 3 years ranged from 550 to 1050 mm w.e. (Gabrielli et al., 2010) while at Colle Gnifetti accumulation ranged from 210 to 450 mm w.e. (Jenk et al., 2009; Doescher et al., 1995). As the concentrations may be dependent upon accumulation rates it is therefore more representative to calculate deposition fluxes of trace elements (Table 2). The fluxes of Ba, Mn, Fe and Al, which are major constituents of rock and soil, are 50–75% lower at the Alto dell'Ortles with respect to those at Colle Gnifetti during the last 50 years, suggesting a lower crustal dust deposition on Mt. Ortles. The recent deposition of trace elements, such as Cu, Pb, Zn and Cd, on the Alto dell'Ortles is about one order of magnitude higher than at Colle Gnifetti during pre-industrial time (before 1700), but lower than from 1950 to 1993 (the most recent available data). For instance, the Pb flux on the Alto dell'Ortles glacier is about $85 \mu\text{g m}^{-2} \text{yr}^{-1}$, which is double that of Colle Gnifetti before the 18th Century ($43 \mu\text{g m}^{-2} \text{yr}^{-1}$) but about 25 times lower than in the time window from 1950 to 1983. Despite the distance between these two areas (about 200 km), this might be consistent with a continuous decrease of heavy metals in European emissions from anthropogenic sources during the last few decades (Pacyna and Pacyna, 2001). The emission inventories of heavy metals in Italy (available at the website: http://webdab1.umweltbundesamt.at/scaled_country_year.html?cgiproxy_skip=1) demonstrate a general reduction from 1990 to 2006 for Pb (–94%), Cr (–38%), Cd (–17%), Ni (–5%) and Cu (–4%). During this time period, As and Zn increase by 11% and 8%, respectively.

In order to evaluate the relative trace element contributions from rock and soil dust versus other sources such as anthropogenic emissions and sea-salt, we calculated the

6501

crustal enrichment factors (EF_c). EF_c is defined as the concentration ratio of a given metal to that of a conservative element (in this work we use Ti) which derives mainly from rock and soil dust, normalized to the same concentration ratio characteristic of the upper continental crust (Wedepohl, 1995). For instance, the EF_c for Pb is:

$$\text{EF}_{c(\text{Pb})} = ([\text{Pb}]/[\text{Ti}]_{\text{snow}})/([\text{Pb}]/[\text{Ti}]_{\text{upper crust}})$$

The crustal dust is transported to the Alto dell'Ortles glacier from several areas (see Sect. 3.5), and therefore may be characterized by elemental compositions that are significantly different from the upper crustal mean. This mixing leads to a higher uncertainty in the determination of the EF_c. For this reason we assume that only calculated EF_c values that are larger than 10 suggest a pronounced contribution from non-crustal sources. The median EF_c values for Be, Rb, Sr, Ba, U, Li, Al, Ca, Cr, Mn, Fe, Co, Ga and V are lower than 10 suggesting that these elements originated mainly from rock and soil dust. For Ti, Pb, Ni, and Cu, median EF_c values are between 10 to 100, where a few samples contain an EF_c lower than 10. This difference suggests that for these elements the anthropogenic contribution is generally important even if it is not always predominant with respect to natural sources. EF_c higher than 100 are reported for As (107), Zn (118), Ag (135), Bi (185), Sb (401) and Cd (514), demonstrating the predominance of non-crustal depositions and suggesting an anthropogenic origin.

3.1.2 Possible anthropogenic sources of the trace elements

Stationary fossil fuel combustions contribute more than 85% to the total European anthropogenic inputs of As, V, Mn, Ni and Ti while non-ferrous metal production is the major source of Zn (Pacyna and Pacyna, 2001). Potential anthropogenic sources of Sb emission to the atmosphere are numerous and include coal combustion, Pb and Cu smelting, refuse incineration, retardants for plastics and textiles, catalysts in PET production and are a constituent of automobile brake pads (Smichowski, 2008). The combustion of leaded gasoline is the major source of atmospheric Pb emission on the global scale even if its use rapidly decreased starting in the 80s (Schwikowski et al.,

6502

2004). According to the calculated inventories of atmospheric emissions in Italy, in 2006 the automobile source represents less than 2% of total Pb fallout while in 1990 it accounts for 78%. Secondary sources of Pb are non-ferrous production, chemical industry, steel, bullets and batteries making, coal burning, and refuse incineration (Shotyk et al., 2005). At the present time, the major atmospheric Pb sources are industrial combustion processes (80%). Industrial combustion and smelting activities contribute 23% and 72% to the Zn emissions and 38% and 19% to the Cd emissions. The main As sources are industrial combustion (83%) and electricity production (9%). For Ni, 60% of the total emissions are related to combustion processes while maritime activities contribute up to 36%. Bi is emitted by fossil fuel combustion, refuse incineration. Bi compounds are used for manufacturing alloys, solder, metallurgical additives, cosmetics, medicines, and recent new Pb-replacement alloy.

3.1.3 Ionic compounds concentrations and fluxes

The mean concentrations of ionic compounds in snow of Alto dell'Ortles are approximately three orders of magnitude higher than those of the trace elements, with a range in means from 19 ng g^{-1} for K^+ to over 377 ng g^{-1} for NO_3^- (Table 1). The mean concentrations of SO_4^{2-} and NO_3^- , and NH_4^+ are 297 ng g^{-1} , 377 ng g^{-1} and 205 ng g^{-1} , respectively. These compounds are produced by the atmospheric oxidation of their precursor gaseous species, SO_2 , NO_x and NH_3 , primarily emitted by anthropogenic sources and in particular the combustion of fossil fuels, high-temperature combustions and agriculture. In Table 3, the ionic compounds concentrations are compared with those determined in other Alpine sites. The measured mean concentrations for SO_4^{2-} , ($163\text{--}677 \text{ ng g}^{-1}$), NO_3^- ($151\text{--}1297 \text{ ng g}^{-1}$) and NH_4^+ ($41\text{--}259 \text{ ng g}^{-1}$) are within the reported ranges determined in other recent snow and ice samples in the European Alps (Gabrieli et al., 2008, 2010a; Novo and Rossi, 1998; Kuhn et al., 1998; Puxbaum and Tschirwenka, 1998). These recent concentrations are higher by several factors (3–10) than those observed in the Colle Gnifetti core in pre-industrial times (before

6503

1700) (Sigl, 2009). The highest concentrations of ionic compounds are generally observed in snow samples from low-medium altitudes (1000–2500 m a.s.l.) in the Eastern Alps (Dolomites, Sonnblick, and Careser). This can be explained considering that the Dolomites and Careser represent the first geomorphologic barrier that may block the pollutants originating from the heavily populated and industrialized Pò Valley (Weiss et al., 1999). In addition, these relatively low mountain areas are also affected by the convective transport of local pollutants from the bottom of the valleys.

The high correlation between Cl^- and Na^+ ($R^2 = 0.90$, 95% confidence) and their mean mass ratio (1.43 ± 0.21) is close to the marine ratio of 1.8, demonstrating a prevalent marine origin of these two ions. The slight Na^+ excess could be attributed to a minor contribution from crustal sources such as gypsum which is present in regional closed-basin lakes. This correlation is in accordance with results from other glaciological records in the Western Alps (Eichler et al., 2000; Schwikowski et al., 1999; Maupetit and Delmas, 1994) but not consistent with data from winter snow collected in the Eastern Alps at low-medium elevation (Gabrielli et al., 2008). In the Eastern Alps a slight Cl^- excess is attributed to a minor anthropogenic HCl contribution. As this excess and range (5 to 291 ng g^{-1}) is greater than ratios related to sea-salt deposition (Gabrielli et al., 2008). Using Cl^- as the marine reference, we calculated the non sea sulfate (NSS) contribution to the total SO_4^{2-} budget as:

$$[\text{SO}_4^{2-}]_{\text{NSS}} = [\text{SO}_4^{2-}]_{\text{snow}} - [\text{Cl}^-]_{\text{snow}} \cdot ([\text{SO}_4^{2-}]_{\text{marine}} / [\text{Cl}^-]_{\text{marine}})$$

The marine contribution of SO_4^{2-} is almost negligible, and accounts on average for 6% of total.

The ionic fluxes on Ortles are similar to those observed at Colle Gnifetti, Careser and Stubai ($330\text{--}1250 \text{ mm w.e. yr}^{-1}$) but much lower than at Col du Dome, Fiescherhorn gletscher and Grenz gletscher, where the accumulation is higher (~ 1400 to $\sim 2700 \text{ mm w.e. yr}^{-1}$). For example, SO_4^{2-} fluxes range from 220 to $360 \text{ mg m}^{-2} \text{ yr}^{-1}$ in sites with accumulation lower than $1250 \text{ mm w.e. yr}^{-1}$ and from 510 to $1040 \text{ mg m}^{-2} \text{ yr}^{-1}$ in others where the accumulation is higher than $1400 \text{ mm w.e. yr}^{-1}$

6504

(Table 3). This positive relationship between accumulation and ionic fluxes indicates that wet-deposition likely represents the most efficient scavenging process of SO_4^{2-} in high-altitude mountainous areas. The comparison between deposition on Mt. Ortles and Careser is of particular interest because these two glaciers are only ~ 15 km apart from each other and, for this reason, are likely to be comparable. The fluxes of NO_3^- (300 to $430 \text{ mg m}^{-2} \text{ yr}^{-1}$) and SO_4^{2-} (240 to $360 \text{ mg m}^{-2} \text{ yr}^{-1}$) are up to $\sim 50\%$ greater at Careser, and for Cl^- are up to 6 times greater ranging between 48 to $270 \text{ mg m}^{-2} \text{ yr}^{-1}$. This evidence is consistent with the southern position and lower altitude of Careser and the consequent major impact of pollutants and sea-salt transport from the south.

However, Ca^{2+} flux is one order of magnitude lower at Careser than Ortles. This decrease indicates a significantly lower deposition of carbonate dust on Careser as Ca^{2+} is the prevailing crustal ion in the snowpack from the mountain areas dominated by carbonate-rich bedrock. The detected fluxes are consistent with the geological characteristics of these two sites. The area near Careser is characterized by metamorphic rocks (mica-schist, gneiss, granites), while the Ortles group is comprised of sedimentary rocks including dolomite and black-banded limestone. This flux difference is consistent with the literature, where measured Ca^{2+} concentrations in Eastern Alpine winter snow differ between limestone ($300\text{--}600 \text{ ng g}^{-1}$) and metamorphic ($80\text{--}220 \text{ ng g}^{-1}$) bedrock (Gabielli et al., 2008).

Very few Total Organic Carbon (TOC) data in snow and ice from high altitude Alpine sites are presented in the literature. In an ice core from Colle Gnifetti, the TOC concentrations increased from 66 to over 614 ng g^{-1} in the time period between 1890 and 1975 (Lavanchy et al., 1999). TOC concentrations in the Ortles samples range from 180 to 1620 ng g^{-1} , with a median value of 310 ng g^{-1} and a median TOC flux of $245 \text{ mg m}^{-2} \text{ yr}^{-1}$.

6505

3.2 Stratigraphic and glaciological observations

Two main density transitions were detected at 240 ± 30 cm and 360 ± 30 cm of depth from twelve snow depth soundings carried out on the upper part of the Glacier Alto dell'Ortles. A comparison of the physical and chemical profiles sampled in the snow pit is reported in Fig. 2. The vertical variations in grain shape and size, snow density and hardness index are compared to the vertical profiles of $\delta^{18}\text{O}$ and NH_4^+ . The upper 60 cm of the snowpack are characterized by medium-size rounded particles, with the presence of partially decomposed precipitation particles. The snow density ranged from 270 to 310 kg m^{-3} , and the hardness index is approximately 250 N. These features are consistent with recently deposited dry snow subjected to destructive metamorphic processes. A visible weak dust horizon above a melt-freeze crust was recorded at 60 cm. This layer represents the first clear stratigraphic discontinuity that differentiates the recent 2009 spring snow from the 2008/2009 winter snow. From 60 to 270 cm, the density increased from 300 kg m^{-3} to $400\text{--}440 \text{ kg m}^{-3}$, and the hardness to from 250 N to 1000–1500 N. In the layers between 60 to 90 cm, medium size rounded particles (0.8 mm), faceted rounded particles and solid faceted particles were recovered, indicating kinetic growth processes triggered by temperature gradients. From 90 to 140 cm, a succession of small/medium size (0.2–1.0 mm) rounded particles layers and thin ice lenses formations (< 10 mm) were visible. Considering that no evidence of winter melting was found, the origin of these mm-scale ice lenses is probably due to wind activity, which is particularly intense on the Alto dell'Ortles glacier during winter. The dust layer at 130 cm is probably due to a weak Saharan deposition occurring on the 1 and 2 April 2009. This deposition can be inferred by considering the back-trajectories from Alto dell'Ortles glacier (see Sect. 3.5) and the Saharan event recorded at the Jungfraujoch (Collaud Coen et al., 2004) high alpine research station (2580 m a.s.l.; $46^\circ 33' \text{ N}$, $07^\circ 59' \text{ E}$; Collaud Coen, personal communication). From 140 to 270, the snow layers were characterized by large rounding-faceted crystals (1.5–3.0 mm), which are indicative of growth regime transition forms typical of the cold and dry snowpack.

6506

The second strong stratigraphic discontinuity is constituted by the thick ice lens (about 5 cm) at 280 cm. Below this discontinuity, all of the crystals that are characteristic of a dry-snowpack disappear and melt forms were observed. The density and the hardness index progressively increased up to 450–500 kg m⁻³ and 2000–2500 N, respectively. The grain shape was dominated by melt forms and, in particular, by large rounded polycrystals (3.0–3.5 mm) which are generally produced by sequential melt-freeze cycles in low water content conditions such as a pendular regime. Since the particle size of the polycrystals increases as a function of the number of melt-freeze cycles, these layers can be formed only during the summer ablation period at the high elevation of the Alto dell'Ortles glacier. The discontinuity at 275 cm likely represents the transition between the 2009 and the 2008 snow. Solid faceted particles were found above a thick melt-freeze crust at 60–65 cm and above the thick ice lens at 280 cm. This kinetic-growth form appears when the rounded particles are subjected to a large increasing vertical temperature gradient in the snow. This suggests that ice and melt-freeze layers act as an effective physical barrier, able to influence the small-scale thermal regime and, perhaps, the meltwater percolation and wet/dry migration processes of both particulate and soluble trace species trapped in the snow. At 395 cm we observed a dust layer in correspondence with a thick ice lens (2.0 cm) while the layers from 395 to 450 cm (the base of the snow-pit) were characterized by large rounded polycrystals. This thick ice lens and associated dust layer could indicate the transition between the 2007/2008 snow but, since no other information could be inferred from the stratigraphy, is instead corroborated by additional chemical evidence (e.g. high Cu and Cd concentrations, see below).

The $\delta^{18}\text{O}$ profile which can be used as proxy of air temperature during precipitation confirms the seasonal reconstruction inferred from the snow-pit stratigraphy, showing higher values during warm periods (between 0–60 and 260–345 cm) and lower during cold periods (between 60–260 and 345–400 cm). We also verify a correspondence between the highest $\delta^{18}\text{O}$ values and peaks in NH_4^+ , which is an anthropogenic component that is mostly deposited in the summer (Gabrielli et al., 2010). The chemical

6507

signature of the 2008/2007 snow transition appears less evident, and may be due to the smoothing effect of meltwater percolation during the 2007 and 2008 summers. A visible dust layer and a corresponding slight increase in NH_4^+ were observed at 395 cm concentrations was recorded, perhaps suggesting the presence of the 2007 summer layer below 390–400 cm. The seasonal $\delta^{18}\text{O}$ pattern is complicated and variations may be due to water percolation between the layers more than the advection history of the wet air masses that deliver precipitation. In summary, the results of the snow-soundings and the physical and chemical stratigraphic observations indicate that the transitions between the 2009/2008 and the 2008/2007 snow were at about 280 and 385 cm, respectively.

3.3 Principal Component Analysis (PCA)

A PCA has been applied to the entire dataset, of 82 snow samples where each sample was analyzed for 22 trace elements, 8 major ions, $\delta^{18}\text{O}$ and TOC to evaluate the aggregation between variables in light of different trace species provenance and sources. PCA is an statistical method in which linear combinations of the original variables are created that characterize maximum possible variance in the data (Scott et al., 2000). The PCA is a multivariate statistical technique often used for explore large and awkward datasets, and here this method has been applied to confirm the stratigraphic observations.

Figure 3 shows the biplot graph which represents both the variables (vectors) and the cases (points) distribution. The first four principal components account for more than 80% of the total variance in the dataset. The first component (PC1) which accounts for 57% of the total variance has comparable negative loadings for all the trace elements and major ions. The second PCA component (PC2) accounts for 12% of the total variance and has positive loadings for Mg^{2+} , Ca^{2+} , Li, Rb, Sr, Ba, Al, Ti, Fe, Ga, Mn, Co, U and negative loadings for $\delta^{18}\text{O}$, TOC, NO_3^- , SO_4^{2-} , Cl^- , Na^+ , NH_4^+ , As, Cd, Sb, Pb, Bi, V, Ni, Cu, Zn, and therefore separates crustal materials from anthropic and marine variables.. Cr, Tl and K^+ are not discriminated by PC2 indicating that

6508

the sources of these elements are various. In particular, the K^+ depositions may not only be linked to marine sources but also with terrestrial emissions, such as biomass burning (Simoneit, 2002).

5 The association between $\delta^{18}O$ and anthropogenic species indicates the predominant seasonal pattern of the anthropogenic pollutant deposition. In contrast, the crustal element inputs do not appear to be seasonally dependent. All of the samples characterized by negative scores in the PC2 correspond to summer layers, as inferred from the stratigraphic analysis. Interestingly, this seasonal separation is extremely well defined except for a few samples (summer samples at 55, 60, 260 and 305 cm and a winter
10 sample at 120 cm).

Despite having different sources, the concentrations of Cl^- and Na^+ the two major proxies of sea-salt, and anthropogenic species are well correlated indicating a similar origin area or transport pathway. This correlation is in contrast with results from an ice-core from the Grenzgletscher glacier (Eichler et al., 2004), where sea-salt related
15 species correlated with crustal dust elements. We suggest that the origin of the sea-salt aerosol deposited on the Eastern Alps is either the Adriatic Sea or it is injected into the air masses during the transport over the Pò Valley, whereas in Western Alps the sea-salt aerosol mainly arrives from the southwest.

3.4 Seasonality of the chemical variables

20 Profiles of selected ionic compounds and trace elements are reported in Fig. 4a and b. The $\delta^{18}O$ record shows a well defined seasonal pattern, with maximum values of up to -5.8‰ (summer) and minimum values of -24.1‰ (winter), which are typical values for Alpine precipitation at high altitude sites (Schotterer et al., 1997). All of the anthropogenic ions (NO_3^- , NH_4^+ , SO_4^{2-}) show a pronounced seasonal pattern with low
25 winter concentrations which increase in spring and peak in summer. NO_3^- and NH_4^+ show the most pronounced seasonality with summer to winter mean concentrations ratios of 4.2 and 5.3, respectively. For SO_4^{2-} , the summer to winter ratio is 3.6 while the

6509

sea salt contribution to SO_4^{2-} does not show any evident seasonal variation but always accounts for 10–20% of the total.

The seasonal variations of K^+ , Mg^{2+} and Ca^{2+} are less pronounced, demonstrating a quite constant deposition of crustal elements. Concentrations of the marine species
5 Cl^- and Na^+ follow a seasonal pattern comparable to those of NH_4^+ and other anthropogenic species, except for a few large isolated peaks in winter. The Cl^-/Na^+ ratio fluctuates around the mean value of 1.4, close to the average sea salt value of 1.8, except in the snow pit section from 320 to 340 cm of depth, where this is ranging between 2.4 and 3.0. According to the stratigraphy (Sect. 3.2), this layer is characterized by large
10 rounded polycrystals (3.5 mm) produced as a consequence of subsequent melt-freeze cycles. The ionic compounds are leached from snow during melt post-depositional process with different efficiencies on the base of the atomic characteristics of the ions and their interaction with the ice crystal lattice. For instance, the elution sequence derived both from laboratory and field experiments demonstrate that Cl^- is well preserved while
15 SO_4^{2-} and Na^+ are strongly affected by meltwater (Eichler et al., 2001). The TOC profile records the highest concentrations from the surface to a depth 65 cm, corresponding to the beginning of the 2009 warm season, while displaying few seasonal variations in the deeper sections of the snow pit. This behavior suggests a more efficient leaching by meltwater percolation than that of NH_4^+ and other anthropogenic compounds.

20 The EFc profiles of Cd, Sb, Zn, Cu and Pb correlate with each other where their respective concentrations peak in tandem (Fig. 4b). The largest mean EFc seasonal variations for trace elements are displayed by V (by a factor of 3.8), Sb (3.3), Cu (3.3), Pb (2.9), Bi (2.8), Cd (2.1), Zn (1.9), Ni (1.8), Ag (1.8), As (1.7) and Co (1.6). For elements which are most likely anthropogenic, EFc values increase during summer
25 periods by factors of 1.3 (Ti) to 3.8 (Cu) but, even during the winter season, their values remain largely higher than 10, indicating a predominant anthropogenic origin. As reported for the terrigenous ions K^+ , Mg^{2+} and Ca^{2+} the crustal trace elements also demonstrate limited EFc seasonal variations, ranging from factors of 1.0 (Ti, Be, Li, Al, Sr) to 1.4 (Ba, Rb, U). This diminished seasonality confirms that although the

6510

magnitude of the crustal inputs is influenced by different sources, seasonal transport and deposition processes, the main anthropogenic and natural sources are common during all the seasons.

3.5 Meteorological and atmospheric conditions

5 In order to explain the observed differences in the seasonal deposition of trace species to the Alto dell'Ortles glacier we have investigated the atmospheric pathways from the source regions to the study area. We computed the daily back-trajectories from the Alto dell'Ortles glacier (at 3850 m a.s.l.) from 2007 to 2009, using the Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT 4.8), provided by the National Oceanic and Atmospheric Administration (NOAA), which is a tool to simulate air particles transport and deposition (Draxler and Rolph, 2010; Draxler, 2003). We used the global dataset archive (GDA) containing 29 meteorological single level variables (at the surface) and 6 upper levels variables (for a total of 23 vertical levels from 1000 to 20 hPa) to calculate 48-h back-trajectories. For each day, we performed two model runs at 00:00 and 12:00 UTM. The model results are summarized in Fig. 5. Air masses from western quadrants (from SW to NW) represent more than 84% of the total during summer (JJA), and 63–73% in the other seasons. Northern trajectories (NW to NE) are larger in autumn (SON), and fewer in winter (DJF), representing 28% and 14% of the wind sources, respectively. Southern air masses (SE to SW) characterize the 32% of spring winds (MAM), 27% in autumn and about 21% in winter and summer. The longest 48 h trajectories originate from the west and cover a mean distance of 2450 km, while the trajectories from the northern, southern and eastern quadrants are shorter (1710, 1310 and 1220 km, respectively). These trajectories are generally longer in DJF and SON than in MAM and JJA. In DJF the mean trajectories lengths from W and SE are 1270 and 3050 km, respectively, while in JJA they are 705 and 1955 km (about 40% shorter). The back-trajectories containing a predominant ascending behavior, which are often associated to cyclonic fields, are more frequent in JJA where they comprise 65% of the total and comprise 55% of the trajectories for all the other periods of the

6511

year. Ascending air masses originate generally from the south and southeast (64–85% of the total) but in JJA ascending air mass trajectories from the east represent more than 80% of total eastern fluxes.

5 Despite the significant seasonal differences in the origin and behavior of air masses, as inferred from the evaluation of 48-h back-trajectories, these origins hardly explain the large changes in concentrations that are observed in the snow pit chemical profiles. In fact, a fundamental parameter that has to be taken into account to explain the seasonal variation in concentrations is the vertical structure of the troposphere at a regional scale. In winter, the Alto dell'Ortles glacier lies within the free troposphere because the vertical motions are inhibited by low-altitude thermal inversions with very stable atmospheric stratifications (Kappenberg and Kerkmann, 1997). In 10 Fig. 6, we summarize the averaged monthly variations in the maximum boundary layer depth (BLD), at the meteorological station of Milano-Linate Airport (~ 100 km SW of Mt. Ortles), obtained by analyzing the daily balloon data over 2007–2009. The BLD was deduced by analyzing the thermal profiles inferred from balloon launches (every day at 15 00:00 and 12:00 UTM and, in case of particularly unstable meteorological conditions, also at 06:00, 09:00, 15:00, 18:00 and 21:00 UTM), and by identifying the daily maximum altitude of the thermal inversion. The balloon data are available at the University of Wyoming website: <http://weather.uwyo.edu/upperair/europe.html>. We choose 20 the Milano-Linate station because it is indicative of the tropospheric vertical structure of the Pò Valley, the main anthropogenic area which affects the air quality over Alps (Seibert et al., 1998). The maximum daily boundary layer depth is much higher during summer than winter due to stronger insolation that enables more effective convection. In December and January, during only 15–20% of the days the boundary layer depth is 25 higher than 2000 m while during 52–57% of the days a very stable layer below 500 m caps the well-mixed boundary layer below 500 m. In these conditions, the pollutants emitted at the bottom of the valley cannot be lifted by thermal convection and are confined in a relatively small volume. During the spring, the BLD rises rapidly and, from April to September, the maximum daily BLD was higher than 2000 m a.s.l. and remains

6512

at this elevation for ~70% of the days. With this rapid rise in the BLD, pollutants are lifted by a synoptically influenced flow, or directly injected to the free troposphere and then transported horizontally by the synoptic flow and then are able to move across Europe.

5 Figure 8 summarizes the averaged monthly stability situations during the period 2007/2009, according to the Pasquill classification (Pasquill, 1961) at the Milan Linate airport and over the Alto dell'Ortles glacier. This stability is estimated by using the meteorological data (GDA meteorological archive) from the open-source READY system (Real-Time Environmental Applications and Display sYstem), provided by the Air
10 Resources Laboratory of NOAA. In Milan about 60–80% of the days from October to February are characterized by stable or neutral atmospheric conditions, with 17–38% of days characterized by slightly unstable conditions and only 2–4% by moderately and extremely unstable conditions. From March to September, unstable meteorological situations dominate, representing 70–80% of the total. At the Alto dell'Ortles glacier,
15 stable meteorological conditions are rare when compared to Milan. In general we note a higher frequency of moderately and extremely unstable conditions during the entire year with a particular increase from October to February when unstable conditions predominate for about 20–25% of the total compared with only 2–4% of the time at Milan. From March to June even slightly stable situations are completely absent while
20 neutral conditions account for only 12–16% of the total days. In July, moderately and extremely unstable conditions represent more than 74% while 26% of the days are slightly unstable.

The pollutants emitted from the heavily industrialized and populated Pò Valley during the winter season are thus trapped by the very stable low-altitude boundary layer
25 produced by the strong thermal inversion which therefore limits transfer to the free troposphere. Low velocity vertical winds are often not sufficient to penetrate the boundary layer and to lift polluted air from the lower to the upper tropospheric levels. For this reason during winter when the Alto dell'Ortles glacier almost permanently lies above the boundary layer altitude, is likely uninfluenced by local/regional anthropogenic

6513

emissions produced in the Southwestern Pò Valley. The winter western atmospheric fluxes and depositions to the Alto dell'Ortles glacier likely represent continental air quality background conditions at similar elevations, except during the rare unstable winter
5 meteorological conditions such as Foehn events. The Alpine Foehn, is a rain shadow wind which results from the subsequent adiabatic warming of air which has released most of its moisture on windward slope. The geographical position and altitude of Mt. Ortles suggests that it is directly affected by the northern upslope wind which can effectively transport pollutants from the bottom valley areas of Austria and Southern
10 Germany.

During the rest of the year, the meteorology is characterized by vertical exchanges
10 between the low level and free troposphere, allowing the mass transfer from local (Val Venosta in the north and Val di Sole in the south) and regional sources (Pò Valley) to high elevations. Pollutants from the Pò Valley are transferred vertically to the injection layer and then dragged by synoptically influenced flows to the Alpine barrier where they
15 are effectively lifted by upslope winds triggered during the daytime by the solar radiation. These vertical motions often produce shallow cumulus clouds above the crests and linked small-scale convective precipitation allows wet deposition of transported pollutants and trace species.

4 Conclusions

20 This work provides an initial insight into the occurrence of numerous trace elements and major ions in fresh snow from Alto dell'Ortles, the highest glacier in the Eastern Alps. The fluxes of Ba, Mn, Fe and Al are 50–75% lower with respect those on Colle Gnifetti during the last 50 years providing evidence for relatively low recent crustal dust deposition on Mt. Ortles. The ionic fluxes to Mt. Ortles are similar to those to
25 Colle Gnifetti, Careser and Stubai but much lower than to Col du Dome, Fiescherhorn-gletscher and Grenzgletscher. The PCA applied to the entire dataset provides a clear separation between trace species originated from crustal, (Mg, Ca, Li, Rb, Sr, Ba, Al,

6514

Ti, Fe, Ga, Mn, Co, U), anthropogenic (Organic Carbon, NO_3^- , SO_4^{2-} , NH_4^+ , As, Cd, Sb, Pb, Bi, V, Ni, Cu, Zn) and marine sources (Cl^- , Na^+). In addition, a pronounced seasonality in deposition is apparent. Summer snow appears more affected by anthropogenic and marine contributions while the aerosol flux is dominated by crustal and terrigenous sources during the winter. All anthropogenic ions (NH_4^+ , NO_3^- , SO_4^{2-}) and trace elements (Cd, Sb, Zn, Cu, Pb) demonstrate a pronounced seasonal pattern, with low winter concentrations that increase in spring and peak in summer. Stable oxygen isotopes ($\delta^{18}\text{O}$) also demonstrate a defined seasonal pattern. The origin and behavior of air, as inferred from the evaluation of 48 h back-trajectories, show significant seasonal differences. However, the large seasonal changes in major and trace element concentrations seem to be more related to the vertical structure of the troposphere at a regional scale rather than the synoptic weather patterns.

Acknowledgements. This work is a contribution to the Ortles project, a program supported by the Fire protection and civil division of the Autonomous Province of Bolzano (Michela Munari) in collaboration with the Forest division of the Autonomous Province of Bolzano (Paul Profanter, Barbara Folie) and the National Park of Stelvio (Wolfgang Platter). This is the Ortles project publication 2. For the field operations we thank: Volkmar Mair, (Geologic Office of the Autonomous Province of Bolzano), Reinhard Pinggera (Forest Division of the Autonomous Province of Bolzano) Philipp Rastner (EURAC), Karl Krainer (University of Innsbruck) Paul Val-
 20 lalonga (Niels Bohr Institute, Copenhagen), Matteo Cattadori (Museo Tridentino di Scienze Naturali) and Toni Stocker (Alpine Guides of Solda). We also thank Anselmo Cagnati and Andrea Crepaz (Arabba Avalanche Centre, ARPAV), for the useful comments about the stratigraphic observations. We are also grateful to Ping-Nan Lin (Byrd Polar Research Center, The Ohio State University) for the stable isotopes analyses. Finally, the authors gratefully acknowledge
 25 the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (<http://www.arl.noaa.gov/ready.php>) used in this publication.

6515

References

- Barbante, C., Van de Velde, K., Cozzi, G., Capodaglio, G., Cescon, P., Planchon, F., Hong, S., Ferrari, C., and Boutron, C.: Post-world war II uranium changes in dated Mont Blanc ice and snow, *Environ. Sci. Technol.*, 35, 4026–4030, 2001.
- 5 Barbante, C., Schwikowski, M., Doring, T., Gaggeler, H. W., Schotterer, U., Tobler, L., Van de Velde, K., Ferrari, C., Cozzi, G., Turetta, A., Rosman, K., Bolshov, M., Capodaglio, G., Cescon, P., and Boutron, C.: Historical record of European emissions 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.
- 10 Barbante, C., Gabrieli, J., Gabrielli, P., Vallelonga, P., Cozzi, G., Turetta, C., Hong, S., Rosman, K., Boutron, C., and Cescon, P.: A historical record of heavy metal pollution in Alpine snow and ice, in: *Persistent Pollution – Past, Present, Future*, edited by: Quante, M., Ebinger, R., and Flosser, G., Springer Verlag, Berlin, 2009.
- Baroni, C. and Orombelli, G.: The Alpine “Iceman” and the Holocene climate change, *Quaternary Res.*, 46, 78–83, 1996.
- 15 Boliu, D.: Paleo climate reconstruction based on ice cores from the Andes and the Alps, PhD thesis, Universität Bern, Switzerland, 2006.
- Cagnati, A. (Ed.): *Strumenti di misura e metodi di osservazione nivometeorologici*, AINEVA, Trento (Italy), 2003.
- 20 Collaud Coen, M., Weingartner, E., Schaub, D., Hueglin, C., Corrigan, C., Henning, S., Schwikowski, M., and Baltensperger, U.: Saharan dust events at the Jungfraujoeh: detection by wavelength dependence of the single scattering albedo and first climatology analysis, *Atmos. Chem. Phys.*, 4, 2465–2480, doi:10.5194/acp-4-2465-2004, 2004.
- Davis, B. A. S., Brewer, S., Stevenson, A. C., Guiot, J., Data Contributors: The temperature of Europe during the Holocene reconstructed from pollen data, *Quat. Sci. Rev.*, 22, 1701–1716, 2003.
- 25 Desio, A. (Ed.): *I ghiacciai del Gruppo Ortles-Cevedale*, Comitato Glaciologico Italiano, Torino, Italy, 1967.
- Doescher, A., Gaggeler, H., Schotterer, U., and Schwikowski, M.: A 130 years deposition record of sulfate, nitrate and chloride from a high-altitude glacier, *Water Air Soil Poll.*, 85, 603–609, 1995.
- Draxler, R. R.: Evaluation of an ensemble dispersion model, *J. Appl. Meteorol.*, 42, 308–317,

6516

- 2003.
- Draxler, R. R. and Rolph, G. D. (Eds.): HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY, NOAA Air Resources Laboratory, Silver Spring, MD, available at: <http://ready.arl.noaa.gov/HTSPLIT.php>, 2010.
- 5 Eichler, A., Schwikowski, M., and Gaggeler, H.: An Alpine ice-core record of anthropogenic HF and HCl emissions, *Geophys. Res. Lett.*, **27**, 3225–3228, 2000.
- Eichler, A., Schwikowski, M., and Gaggeler, H.: Meltwater-induced relocation of chemical species in Alpine firn, *Tellus*, **53**, 192–203, 2001.
- Eichler, A., Schwikowski, M., Furger, M., Schotterer, U., and Gaggeler, H. W.: Sources and distribution of trace species in Alpine precipitation inferred from two 60-year ice core paleo-records, *Atmos. Chem. Phys. Discuss.*, **4**, 71–108, doi:10.5194/acpd-4-71-2004, 2004.
- 10 Fierz, C., Armstrong, R. L., Durand, Y., Etchevers, P., Greene, E., McClung, D. M., Nishimura, K., Satyawali, P. K., and Sokratov, S. A. (Eds.): The international classification for seasonal snow on the ground, IHP-VII technical documents in hydrology No. 83, IACS Contribution No. 1, UNESCO-IHP, Paris, France, 2009.
- 15 Frei, C. and Schär, C.: A precipitation climatology of the Alps from high-resolution rain-gauge observations, *Int. J. Climatol.*, **18**, 873–900, 1998.
- Gabrieli, J.: Trace elements and polycyclic aromatic hydrocarbons (PAHs) in snow and ice sampled at Colle Gnifetti, Monte Rosa (4450 m), during the past 10 000 years: environmental and climatic implications, PhD thesis, University Ca' Foscari of Venice, Italy, 2008.
- 20 Gabrieli, J., Decet, F., Luchetta, A., Valt, M., Barbante, C., and Pastore, P.: Occurrence of PAHs in seasonal snowpack of Eastern Italian Alps, *Environ. Pollut.*, **158**, 3130–3137, 2010a.
- Gabrieli, J., Vallenga, P., Cairns, W., Cozzi, G., Spolaor, A., Sigl, M., Schwikowski, M., Boutron, C. F., and Barbante, C.: A new melting system for high resolution trace elements determination in alpine firn and ice cores, in preparation, 2010b.
- 25 Gabrieli, P., Cozzi, G., Torcini, S., Cescon, P., and Barbante, C.: Trace elements in winter snow of the Dolomites (Italy): a statistical study of natural and anthropogenic contributions, *Chemosphere*, **72**, 1504–1509, 2008.
- Gabrieli, P., Carturan, L., Gabrieli, J., Dinale, R., Krainer, K., Helmut, H., Davis, M., Zagardnov, V., Seppi, R., Barbante, C., Dalla Fontana, G., and Thompson, L. G.: Atmospheric warming threatens the untapped glacial archive of Mt. Ortles, South Tyrol, *J. Glaciol.*, **56**, 843–853, 2010.
- 30 Hong, S., Lee, K., Hou, S., Hur, S. D., Ren, J., Burn, L. J., Rosman, K. J. R., Barbante, C.,

6517

- and Boutron, C. F.: An 800-year record of atmospheric As, Mo, Sn, and Sb in Central Asia in high-altitude ice cores from Mt. Qomolangma (Everest), Himalayas, *Environ. Sci. Technol.*, **43**, 8060–8065, 2009.
- Jenk, T. M., Szidat, S., Boliuss, D., Sigl, M., Gaggeler, H. W., Wacker, L., Ruff, M., Barbante, C., 5 Boutron, C. F., and Schwikowski, M.: A novel radiocarbon dating technique applied to an ice core from the Alps indicating late Pleistocene ages, *J. Geophys. Res.*, **114**, D14305, doi:10.1029/2009JD011860, 2009.
- Kappenberger, G. and Kerkmann, J. (Eds.): *Il Tempo in Montagna, Manuale di Meteorologia Alpina*, Zanichelli, Bologna, Italy, 1997.
- 10 Kaspari, S., Mayewski, P. A., Handley, M. J., Osterberg, E. C., Kang, S., Hou, S., and Qin, D.: Recent increase in atmospheric concentrations of Bi, U, Cs, Ca and S from a 350-year Mt. Everest ice core record, *J. Geophys. Res.*, **114**, D04302.1–D04302.14, doi:10.1029/2008JD011088, 2009.
- Kuhn, M., Haslhofer, J., Nickus, U., and Schellander, H.: Seasonal development of ion concentration in a high alpine snow pack, *Atmos. Environ.*, **32**, 4041–4051, 1998.
- 15 Lavanchy, V. M. H., Gaggeler, H. W., Schotterer, U., Schwikowski, M., and Baltensperger, U.: Historical record of carbonaceous particle concentrations from a European high-alpine glacier (Colle Gnifetti, Switzerland), *J. Aerosol Sci.*, **30**, S611–S612, 1999.
- Maupetit, F. and Delmas, R. J.: Snow chemistry of high altitude glaciers in the French Alps, *Tellus B*, **46**, 304–324, 1994.
- 20 McConnell, J. R., Lamorey, G. W., and Hutterli, M.: A 250-year high-resolution record of Pb flux and crustal enrichment in central Greenland, *Geophys. Res. Lett.*, **29**, 2130–2133, 2002.
- Novo, A. and Rossi, G. C.: A four-year record (1990–94) of snow chemistry at two Glacier fields in the Italian Alps (Careser, 3090 m; Colle Vincent, 4086 m), *Atmos. Environ.*, **32**, 4061–4073, 1998.
- 25 Pacyna, J. M. and Pacyna, E. G.: An assesment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide, *Environ. Rev.*, **9**, 269–298, 2001.
- Pasquill, F.: The estimation of the dispersion of windborne material, *Meteorol. Mag.*, **90**, 33–49, 1961.
- 30 Planchon, F., Van de Velde, K., Rosman, K. J. R., Wolf, C. F., Ferrari, C., and Boutron, C. F.: One hundred fifty-year record of lead isotopes in Antarctic snow from Coats Land, *Geochim. Cosmochim. Ac.*, **67**, 693–708, 2003.

6518

- Preunkert, S., Wagenbach, D., Legrand, M., and Vincent, C.: Col du Dome (Mt. Blanc massif, French Alps) suitability for ice core studies in relation with past atmospheric chemistry over Europe, *Tellus*, 52, 993–1012, 1999.
- Puxbaum, H. and Tscherwenka, W.: Relationships of major ions in snow fall and rime at sonnblick observatory (SBO, 3106 m) and implications for scavenging processes in mixed clouds, *Atmos. Environ.*, 32, 4011–4020, 1998.
- Schotterer, U., Frohlich, K., Gaggeler, H. W., Sandjordj, S., and Stichler, W.: Isotopes records from Mongolian and Alpine ice cores as climate indicators, *Climatic Change*, 36, 519–530, 1997.
- Schwarb, M.: The Alpine precipitation climate. Evaluation of a high-resolution analysis scheme using comprehensive rain-gauge data, PhD thesis, Naturwissenschaften ETH Zürich, 2000.
- Schwikowski, M.: Reconstruction of European air pollution from Alpine ice cores, in: *Earth Paleoenvironments: Records Preserved in Mid- and Low-Latitude Glaciers*, edited by: Cecil, D. L., Green, J. R., and Thompson, L. G., Kluwer Academic Publisher, Dordrecht, Netherlands, 95–119, 2004.
- Schwikowski, M., Doscher, A., Gaggeler, H., and Schotterer, U.: Anthropogenic versus natural sources of atmospheric sulphate from an Alpine ice core, *Tellus B*, 51, 938–951, 1999.
- Schwikowski, M., Barbante, C., Doering, T., Gaeggeler, H. W., Boutron, C., Schotterer, U., Tobler, L., Van de Velde, K., Ferrari, C., Cozzi, G., Rosman, K., and Cescon, P.: Post-17th-century changes of European lead emissions recorded in High-Altitude Alpine snow and ice, *Environ. Sci. Technol.*, 38, 957–964, 2004.
- Scott, A. and Clarke, R.: *Multivariate Techniques*, edited by: Clark, T., John Wiley and Sons, New York, 2000.
- Seibert, P., Kromp-Kolb, H., Kasper, A., Kalina, M., Puxbaum, H., Jost, D. T., Schwikowski, M., and Baltensperger, U.: Transport of polluted boundary layer air from the Po Valley to high-alpine sites, *Atmos. Environ.*, 32, 3953–3965, 1998.
- Shoty, W., Zheng, J., Krachler, M., and Zdanowicz, C.: Predominance of industrial Pb in recent snow (1994–2004) and ice (1842–1996) from Devon Island, Arctic Canada, *Geophys. Res. Lett.*, 32, 21814.1–21814.4, 2005.
- Sigl, M.: Ice core based reconstruction of past climate conditions from Colle Gnifetti, Swiss Alps, PhD thesis, Universität Bern, Switzerland, 2009.
- Simoneit, B. R. T.: Biomass burnings – a review of organic tracers for smoke from incomplete combustion, *Appl. Geochem.*, 17, 129–162, 2002.

6519

- Smichowski, P.: Antimony in the environment as a global pollutant: a review on analytical methodologies for its determination in atmospheric aerosols, *Talanta*, 75, 2–14, 2008.
- Van de Velde, K., Boutron, C., Ferrari, C., Bellomi, T., Barbante, C., Rudnev, S., and Bolshov, M.: Seasonal variations of heavy metals in the 1960s Alpine ice: sources versus meteorological factors, *Earth Planet. Sc. Lett.*, 164, 521–533, 1998.
- Veysseyre, A., Moutard, K., Ferrari, C., Velde, K. V. D., Barbante, C., Cozzi, G., Capodaglio, G., and Boutron, C.: 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.
- Wedepohl, K. H.: The composition of the continental crust, *Geochim. Cosmochim. Ac.*, 59, 1217–1232, 1995.
- Weiss, D., Shotyk, W., Appleby, P. G., Kramers, J. D., and Cheburkin, A. K.: Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources, *Environ. Sci. Technol.*, 33, 1340–1352, 1999.

6520

Table 1. Main statistics of the species determined in the snow pit on the glacier Alto dell'Ortles. The concentrations of the trace elements are expressed in pg g^{-1} while the ionic compounds in ng g^{-1} .

	Mean	SD	Median	Min	Max	Max/Min
Li	19	13	15	4.9	74	15
Be	1.8	1.6	1.1	0.47	9.3	20
Al	3440	4290	1785	65	2.1E ⁴	321
Ti	450	240	440	11	1120	105
V	140	180	77	7.5	790	105
Cr	45	99	25	3.1	86	28
Mn	825	1060	495	19	6850	356
Fe	5340	5810	3290	95	2.5E ⁴	257
Co	13	13	9.0	1.0	81	80
Ni	190	146	143	74	910	12
Cu	155	142	122	18	730	41
Zn	955	790	690	285	5610	20
Ga	3.2	2.8	2.3	0.43	13	30
As	19	14	15	3.7	91	25
Rb	44	62	25	3.6	425	117
Sr	680	1260	265	9.7	7300	755
Ag	1.4	1.7	0.93	0.14	11	76
Cd	6.6	5.3	5.0	1.2	28	23
Sb	16	15	13	0.71	70	98
Ba	380	460	214	8.5	2360	278
Tl	5.3	2.9	4.7	1.6	20	13
Pb	108	102	74	7.5	514	68
Bi	2.1	1.8	1.7	0.18	8.0	45
U	2.0	1.6	1.5	0.12	7.5	61
Cl ⁻	60	61	42	5	291	58
NO ₃ ⁻	377	410	226	58	2210	38
SO ₄ ²⁻	297	410	150	16	1920	120
Na ⁺	44	44	23	5	214	43
K ⁺	19	18	13	1.2	99	99
Mg ²⁺	45	37	35	2.0	162	81
Ca ²⁺	281	310	199	10	2040	204
NH ₄ ⁺	207	229	133	3.4	1170	390
TOC	383	221	306	179	1630	9

6521

Table 2. Average concentration and fluxes of trace elements in snow samples collected in the Glacier Alto dell'Ortles snow pit and in the Colle Gnifetti ice core, Monte Rosa, in the time periods 1950–1980, 1980–1993 (Gabrieli, 2008) and pre-1700 (Barbante et al., 2004).

	Concentration (pg g^{-1})				Flux ($\mu\text{g m}^{-2}\text{ yr}^{-1}$)			
	Ortles 2007–2009	Pre-1700	Colle Gnifetti core		Ortles 2007–2009	Pre-1700	Colle Gnifetti core	
		1950–1980	1980–1993			1950–1980	1980–1993	
Cr	45	144	61	54	36	48	27	24
Cu	155	39	350	214	122	13	159	96
Zn	955	171	4200	3410	755	56	1890	1535
Co	13	70	33	38	10	23	15	17
Ni	191	24	–	–	151	7.9	–	–
Cd	6.6	1.6	88	38	5.2	0.5	40	17
Sb	16	24	–	–	13	7.9	–	–
Bi	2.1	1.6	9.9	3.6	1.7	0.5	4.5	1.6
U	2	2.9	21	13.6	1.6	1.0	9.5	6.1
Pb	108	130	4570	1655	85	43	2060	745
Ba	380	–	1640	1680	300	–	740	755
V	140	–	228	223	111	–	103	100
Mn	823	–	2400	2140	650	–	1080	960
Fe	5340	–	13740	16800	4220	–	6180	7560
Al	3440	–	17510	24320	2715	–	7880	10950

6522

Table 3. Mean concentration and fluxes of major ions in snow and ice samples in different Alpine sites: Glacier Alto dell’Ortles snow pit (mean accumulation ~ 800 mm w.e.), Colle Gnifetti firn/ice core (Monte Rosa; mean accumulation 330 mm w.e.), Col du Dome firn/ice core (Mont Blanc, mean accumulation 2450 mm w.e. yr⁻¹), Fiescherhornngletscher firn/ice core (Bernese Alps; mean accumulation 1400 mm w.e. yr⁻¹), Grenzgletscher firn/ice core (Monte Rosa; mean accumulation 2700 mm w.e. yr⁻¹), Careser (Ortles-Cevedale, Italian Eastern Alps; accumulation 1040 mm w.e. yr⁻¹), Stubai (Austrian Tyrolean Alps; accumulation 1250 mm w.e. yr⁻¹), Sonnblick (Austrian Tyrolean Alps), Dolomites (Eastern Italian Alps). The “w” associated with the period indicates that only winter snow was sampled.

Site	Altitude (m a.s.l.)	Period	Mean concentration (ng g ⁻¹)					Mean fluxes (mg m ⁻² yr ⁻¹)				
			NH ₄ ⁺	Ca ²⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Ca ²⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻
Alto dell’Ortles snow-pit	3850	2005–2009	208	281	297	377	60	166	225	238	302	48
ColleGnifetti ^{a,b}	4450	1500–1700	38	104	100	87	40	13	34	33	29	13
a,b	4450	1950–1980	118	159	671	208	47	39	52	221	69	16
a,b	4450	1980–1990	152	263	677	335	47	50	87	223	111	16
a,b	4450	1990–2003	211	407	670	447	73	70	134	221	148	24
Col du Dome ^c	4250	1988–1993	97	46	400	280	30	238	113	980	686	74
Fiescherhornngletscher ^d	3890	1945–1983	79	100	366	167	52	111	140	512	234	73
Grenzgletscher ^d	4200	1945–1983	89	92	384	151	26	240	248	1037	408	70
Careser ^e	3090	W–1994	73	24	345	412	260	76	25	359	428	270
Stubai ^f	3106	1992–1995	41	42	163	329	39	51	53	204	411	49
Sonnblick Glacier ^g	2950	1992–1995 (w)	259	64	336	763	96	–	–	–	–	–
Trentino-Veneto ^h	1025–3040	1995 (w)	–	510	530	900	162	–	–	–	–	–
Dolomites ⁱ	1610–2150	2005 (w)	172	712	462	1297	300	–	–	–	–	–

^a Bolius, 2007

^b Sigl, 2009

^c Preunkert et al., 1999

^d Eichler et al., 2004

^e Novo et al., 1998

^f Kuhn et al., 1998

^g Puxbaum et al., 1998

^h Gabrielli et al., 2008

ⁱ Gabrielli et al., 2010

6523

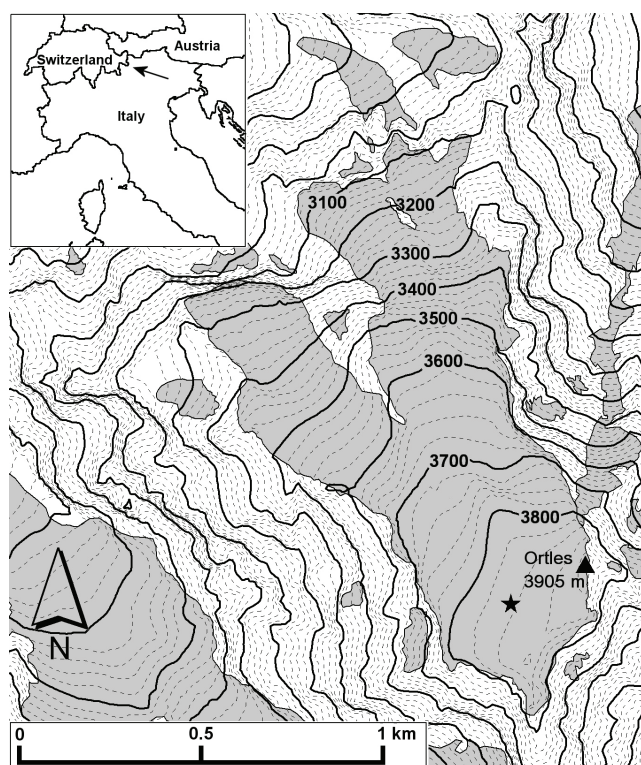


Fig. 1. Map of the Alto dell’Ortles glacier, Southern Rhaetic European Alps, (Provincia Autonoma di Bolzano Alto Adige, Italy). In grey the glacierized areas are reported. The star indicates the sampling site while the glacierized areas are reported in grey (adapted from Gabrielli et al., 2010).

6524

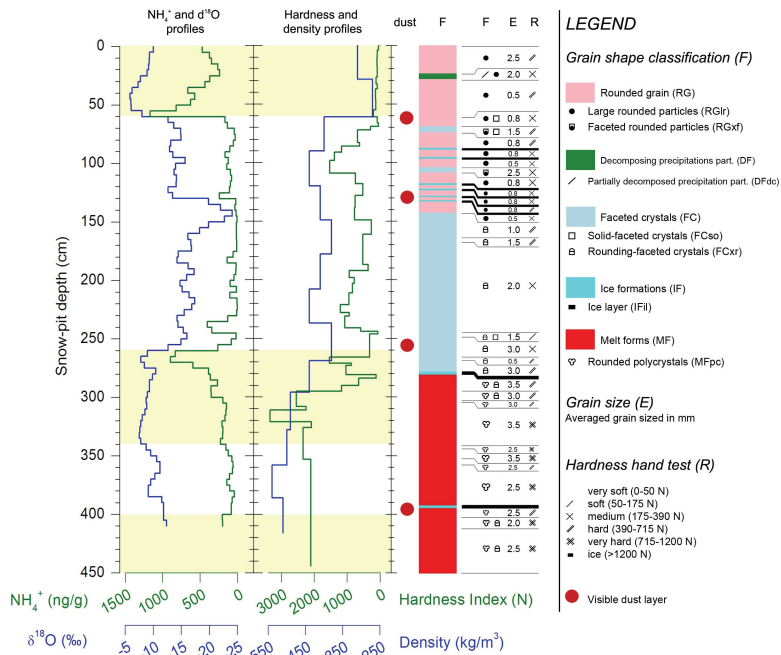


Fig. 2. Stratigraphic observations (grain shape and size), density, hardness index, $\delta^{18}\text{O}$ and NH_4^+ profiles inferred from the snow pit dug on the Alto dell'Ortles glacier. The grain shape has been classified in accordance with the International Classification for Seasonal Snow on the Ground (Fierz et al., 2009); in brackets the synthetic crystal shape code is reported.

6525

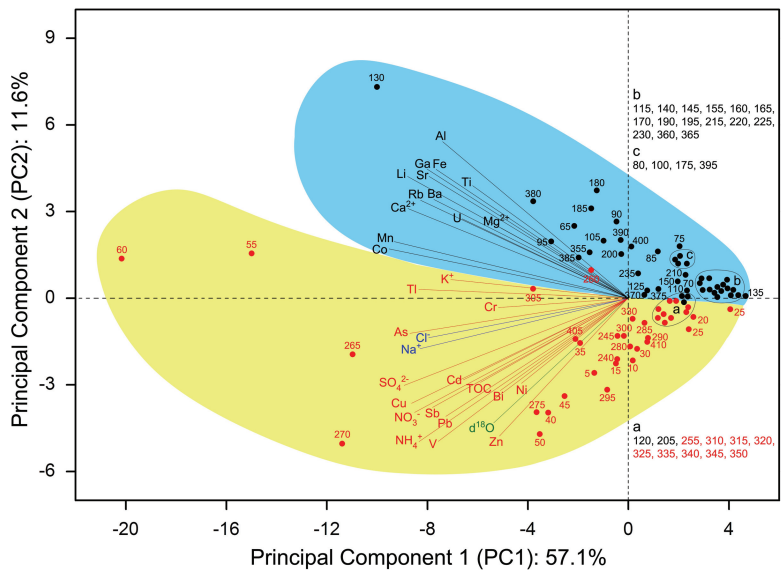


Fig. 3. Principal Component Analysis (PCA) biplot of all the chemical variables (lines with the variable name) and cases (points indicating the depth of the corresponding sample) on the first two PC which explain 57.1% and 11.6% of the total variance, respectively. The red-written cases correspond to the samples from warm periods while the black those from cold periods, as inferred from the stratigraphic observations.

6526

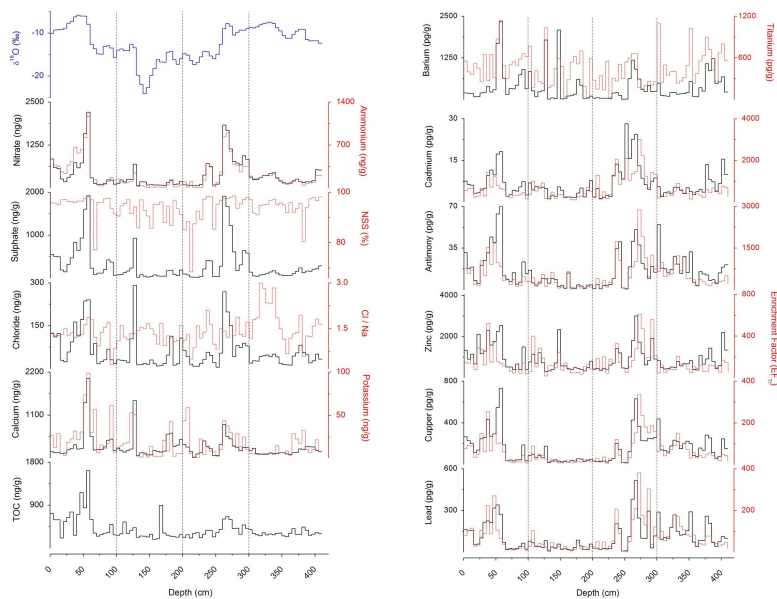


Fig. 4. Depth profiles of $\delta^{18}\text{O}$, major ions concentrations and TOC **(a)** and of some selected trace elements, and relative enrichment factors **(b)** in snow samples from the 420 cm snow pit on the Alto dell'Ortles glacier. The yellow bars indicate proposed summer layers, as inferred from the stratigraphic analysis and the PCA.

6527

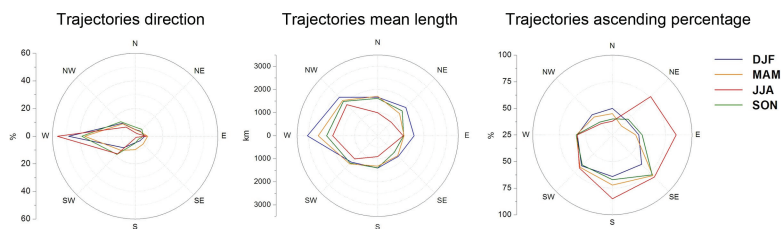


Fig. 5. Summary of seasonal behaviors of air mass back-trajectories, calculated using the NOAA HYSPLIT model, in the three years 2007–2009 time period.

6528

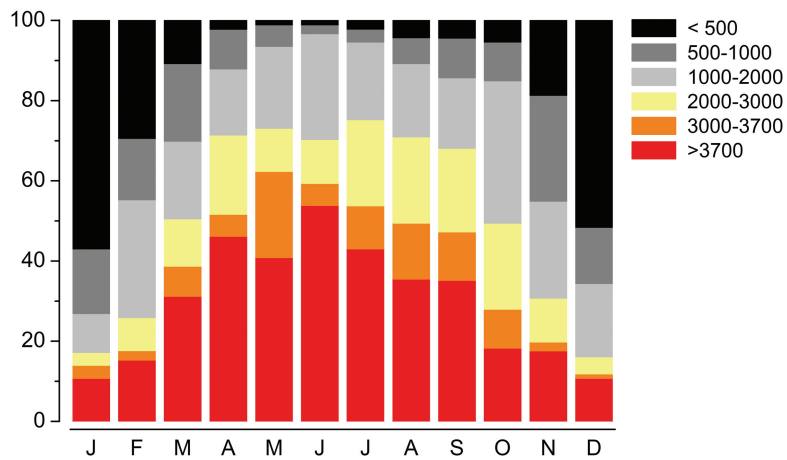


Fig. 6. Monthly averaged maximum boundary layer depth, inferred from the balloon data analysis at the Milano-Linate Airport meteorological station over the 2007–2009 years period.

6529

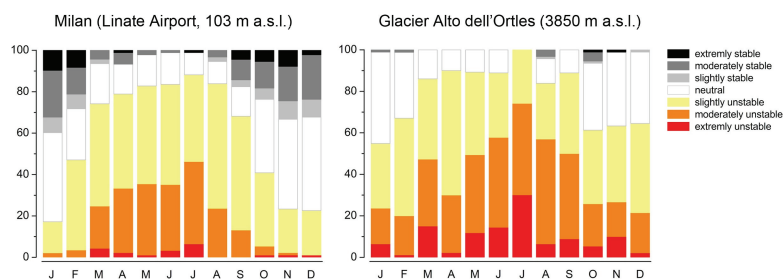


Fig. 7. Monthly variations of the calculated Pasquill Stability Classes calculated at Milano-Linate Airport meteorological station and at the Alto dell'Ortles glacier, over the 2007–2009 years period. The atmospheric turbulences are categorized into six stability classes from the most unstable to the most stable condition.

6530