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Major element chemistry in inner alpine snowpacks (Aosta Valley Region, NW Italy)

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ABSTRACT

Major element chemistry of the snow cover was investigated at 15 sampling sites at about 2000 m a.s.l. in the Aosta Valley Region (North Western Italy), an inner alpine region characterized by a continental climate, during late winter 2005–2006. Snowfall in winter 2005–2006 was primarily due to westerly, Atlantic air flows, while southerly flows were not a significant source of precipitation. These two factors (i.e. the inner alpine topography and the peculiar air flow patterns) determined a unique ion distribution compared to rest of the Alps. Calcium and magnesium concentrations in snowpacks were low, consistent with the absence of Saharan dust events and local geological sources. Sodium and chloride concentrations were higher than the average for the Alps, supporting the influence of the Atlantic air masses on the ionic composition of snowfall. Sulfate concentrations were in the range of background concentrations reported for high altitude and latitude sites, indicating that industrial emissions were not a main source of chemicals in Aosta Valley snowpacks for winter 2005–2006. Ammonium and nitrate values were comparable to concentrations found in other sites of the Alps for low-emission winters. We estimated dissolved inorganic nitrogen stored in snow to range between 0.25 and 0.75 kg N ha^{-1}, corresponding to about 2–6% of the over-winter-N mineralization in Alpine soils in the Western Alps. In the Aosta Valley, local biogenic pollution rather than long-range transport may contribute substantially to the ionic load in the snowpack when westerly air masses are the main source of precipitation. Although conducted over only one winter season, this study suggests a peculiar and previously unreported pattern of snowpack chemistry, that may be representative of the inner alpine, continental valleys in the absence of strong anthropogenic pollution or dust deposition. Due to the fact that inner alpine valleys cover a non-negligible surface of the Alps, we suggest these patterns to be taken into account while modeling ion depositions at a global scale.

1. Introduction

Snowpacks can accumulate significant amounts of particulates and solutes from atmospheric deposition. In much of western North America and mountainous regions of Europe and Asia, deep snowpacks form through the late autumn, winter and early spring (Kuhn, 2001). The mountain snowpack accumulates wet and dry atmospheric deposition, which may be held in storage until release during a melt period. For example, at Niwot Ridge in Colorado as much as 80% of the annual water input and more than 50% of the annual inorganic N deposition can be stored in the snowpack and released during snowmelt episodes (Brooks and Williams, 1999).

Snowmelt is the dominant hydrologic event on an annual basis in high-elevation areas (Williams and Melack, 1991a; Caine, 1996). Liquid water, particulates, and solutes stored over the winter period are released in a relatively short time period, usually on the scale of several weeks. Field and laboratory experiments have demonstrated that initial stages of snowmelt often have ionic concentrations many times higher than averages for the whole snowpack, referred to as an ionic pulse (Johannessen and Henriksen, 1978). Physical and chemical processes that determine the occurrence, magnitude and extent of an ionic pulse are not sufficiently understood to predict the ionic concentrations of snowpack meltwater at a point in time (Williams and Melack, 1991a,b).

The rapid release of water and solutes from the seasonal snowpack has the potential to exert a significant impact on terrestrial and aquatic ecosystems (Williams and Melack, 1991b; Williams et al., 1996a,b; Lepori et al., 2003; Edwards et al., 2007; Williams et al., 2009). In the last few years, a great deal of research has been devoted to the evaluation of the impact of anthropogenic pollution in remote areas. In the US, for instance, the National Atmospheric Deposition Program (NADP) was initiated in order to "collect data on the chemistry of precipitation for monitoring of geographical and temporal long term trends" (e.g. Williams and Tonnessen, 2000). In the Alps, an "ad hoc" program (SNOSP) was initiated in the early '90s to "investigate seasonal and geographical distribution of snow concentrations and deposition fluxes

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of environmentally relevant ionic species" (Puxbaum et al., 1991). Within SNOSP program, snowpack chemistry investigations in the Alps have been carried out since the early '90s. Study sites were mainly in the Eastern Italian Alps (e.g. Tyrol and Trentino regions, Nickus et al., 1998) and in the Southern Alps (e.g. the Tyrolean Alps, Kuhn et al., 1998), with relatively few studies conducted in the Western Alps.

There is particular concern that atmospheric deposition of pollutants in combination with changes in climate may be affecting soil and water processes in inner alpine valleys of the Alps. The rugged terrain and steep elevation gradients in the Alps influence air circulation and meteorology in unknown ways, resulting in a poorly understood, inner alpine, continental climate (Mercalli et al., 2003). The impact of such topographic conditions on snowfall quality has been poorly studied (e.g. Kuhn et al., 1998), although inner alpine valleys represent over 40% of the surface of the entire Alp chain. Preliminary analyses of snow chemistry based on synoptic sampling were conducted in inner alpine areas of the Alps such as the Aosta Valley of the Italian Alps about a decade ago (Nickus et al., 1997; Novo and Rossi, 1998). However, evaluation of the evolution of snowpack physical properties and chemistry over time within a snow season has not been attempted, nor has a regional evaluation been conducted.

Here we report the major element chemistry from snowpacks of the Aosta Valley (Fig. 1), before and during spring snowmelt 2006. This study was devoted to:

(1) Obtain a basic understanding on deposition and accumulation processes over the Aosta Valley snowpacks, that could be representative of the inner alpine valleys of the Alps.
(2) Investigate potential spatial and temporal patterns in the distribution of ion loads, in particular inorganic nitrogen.
(3) Determine relative contributions of certain sources (anthropogenic vs. natural, regional vs. local) to the ionic content of the Aosta Valley snowpacks.

2. Methods

2.1. Study area

Sampling sites were located in Aosta Valley (AV, Western Alps, Italy) at an elevation between 1850 and 2200 m a.s.l., at various aspects and on gentle slopes. The Aosta Valley surface area is 3262 km^2, the mean altitude is 2106 m a.s.l., the mean annual air temperature at 2000 m a.s.l. ranges from −0.2 to 3.1 °C. The climate of the region is strongly affected by the presence of surrounding high mountains, resulting in a typical inner alpine continental climate (Mercalli et al., 2003). Topography in this region exerts a major influence on several climatic variables, as for example on the precipitation: while on the south-eastern boundary of the region the external mountain side receives as much as 2000 mm y^{-1}, the 70% of the AV receives less than 1000 mm y^{-1} precipitation with minima of less than 500 mm in the inner core of the region (Mercalli et al., 2003). These precipitation patterns are the consequence of the strong influence of surrounding mountains.

The AV Region is divided into 3 sub-regions (Fig. 1) according to different precipitation conditions: (1) the North-West sub-region (NW) is characterized by the highest mountains; precipitations in this sub-region are usually related to West, North-West and South-West humid air masses coming from the Atlantic Ocean; (2) the Central sub-region (C) includes many different climatic areas and precipitations are influenced by the presence of surrounding high mountains and are generally low; and (3) the South-East sub-region (SE) is mainly affected by humid air masses coming from the Po Plain which contribute to high precipitation during spring and summer and low winter precipitations. The abundance of snow in this sub-region depends mainly on the occurrence of South and South-East humid air masses. For a more detailed description of the climate of the region see Mercalli et al. (2003).

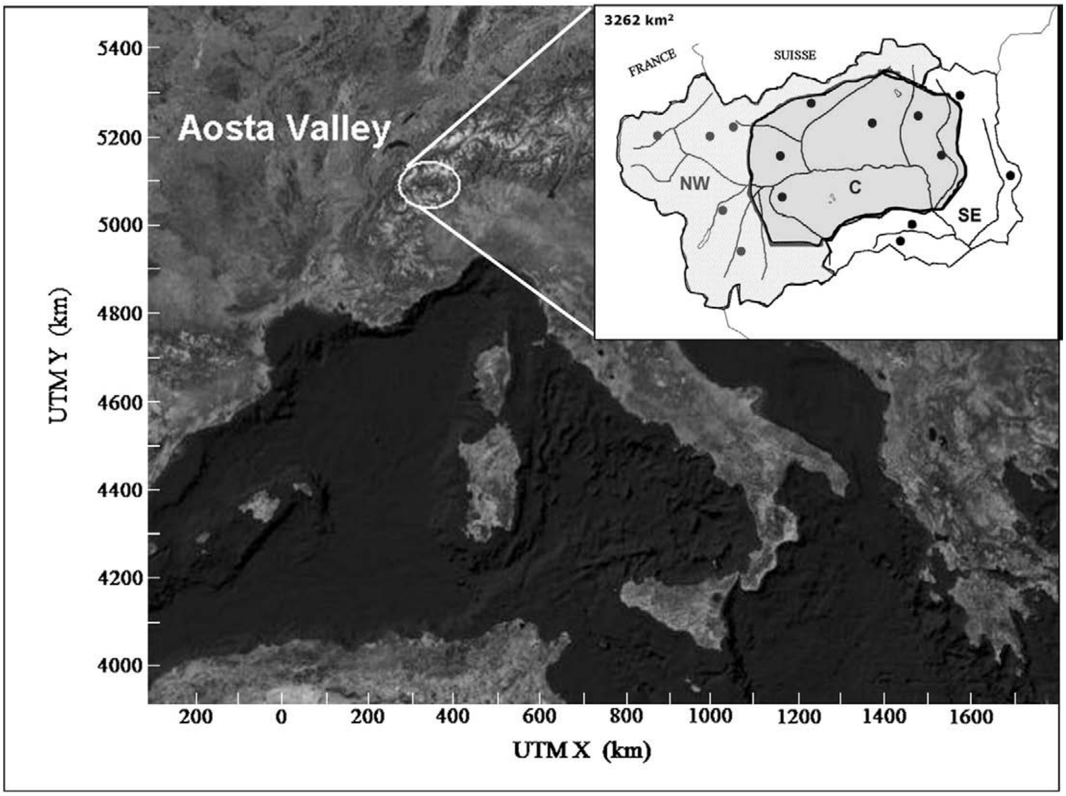

Fig. 1. Location of the study area. In the small picture the 15 sampling sites (solid circles) and the three sub-regions (NW: North-West, in light grey; C: Central, in dark grey; SE: South-East, in white) are shown. Image provided by Regione Autonoma Valle d'Aosta (Aut. n. 1072).

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Fifteen sampling sites were selected to provide comprehensive coverage of the region and were about equally distributed within the 3 sub-regions described earlier (Fig. 1). Sampling sites were not influenced by avalanches or excessive snow drifts. Snow samples were taken for all sites in early March and early April, in order to evaluate chemical distribution and ionic load before and during spring snowmelt. The selected sites are covered by alpine grasslands.

2.2. Snow sampling

In each of the 15 sampling sites, one snow profile was excavated per each sampling date. Snow was generally sampled at increments of 10 cm, up to 20 cm in case of homogeneous snowpacks higher than 2 m. Snow profiles were described following the AINEVA (Interregional Association for Snow and Avalanches) procedure (Cagnati, 2004). Snow density was determined and snow grains were described. Snow samples for chemical analysis were collected using pre-cleaned (by rinsing five times with ultra-pure water), 120 mL polypropylene tubes, transported in cooling box and stored at −15 °C until chemical analysis.

2.3. Chemical analysis

After thawing, pH was measured using a pH meter Ion 83 Ion Meter and conductance was analyzed using a Crison microCM 2201. Anions in undiluted samples were analyzed by ion chromatography, using a Dionex DX-500 device equipped with an ASRS-ULTRA Self Regenerating chemical suppressor (regenerant: 0.05 M H_2SO_4). Anions were separated on an Ion Pack AS9 column (6 mM Na_2CO_3/12 mM $NaHCO_3$). The detector was a Dionex Pulsed Electrochemical Detector used in conductivity mode. NH_4^+ was determined colorimetrically (Crooke and Simpson, 1971) while other cations (Na^+, Ca^{2+}, Mg^{2+} and K^+) were determined by flame emission spectroscopy in atomic absorption using a PerkinElmer AAnalyst 400. Instrumental detection limits were below 0.5 μeq L^{-1} for all ions. Empty pre-cleaned sample tubes were air-exposed at some of the field sites, filled with ultra-pure water and analyzed together with the samples. Blank values obtained were always under instrumental detection limit. As a quality test, ion percent differences (IOD) were calculated for each sample. IOD is the difference between the sum of cations and anions divided by the sum of cations plus anions. A threshold of ±60% of IOD was set by the NADP quality assurance guidelines (Peden, 1983) for charge totals less than 50 μeq L^{-1}. Above this value samples should be re-analyzed. On 303 samples, only 9 had an IOD slightly higher than 60%. Thus, chemical analysis was considered as sufficiently accurate.

2.4. Measure units and statistical analysis

Mean ion concentrations are presented as volume weighted means, calculated as Eq. (1):

$$VWM\,[\mu eq\,L^{-1}] = \sum([X]_i * SWE_i)/\sum SWE_i \tag{1}$$

where $[X]$ is ion concentration in [μeq L^{-1}] and SWE_i is the snow water equivalent in [cm] of a known 10 cm increment *i*.

Ion loads are reported as meq m^{-2}, except for dissolved inorganic nitrogen (DIN) which is also reported as kg N ha^{-1}.

Statistical analyses were carried out using SPSS 12.0 for Windows. Differences in snow physical and chemical properties between sampling dates and sub-regions were tested with a two-way ANOVA. Correlations between chemicals were carried out using the Pearson correlation coefficient. A varimax normalized principal component analysis (PCA) was performed in order to evaluate the major sources contributing to the ion content in the snow cover.

3. Results

3.1. Meteorological and snowfall patterns in winter '05–06

Winter '05–06 was characterized by relatively low air temperatures, with a mean of −6 °C for the Dec–Apr period at 2000 m a.s.l. at 8.00 a.m. Snow remained on the ground for 126 days and a cumulative snowfall of 289 cm was recorded as an average for the whole region (Borney et al., 2007). Both cumulative snowfall and the snow-covered season length were comparable to the long term averages. Snow precipitation was distributed during winter as reported in Table 1. During December and January, relatively small precipitation events were associated with Atlantic air flows from West and South-West (Borney et al., 2007). Starting from mid February and till April, a regular humid air mass coming from the West (Atlantic Ocean) was the source of several precipitation events and caused March to be the highest snowfall month (Table 1). Air masses coming from the South were not a significant source of snow precipitation during the whole season (Borney et al., 2007).

3.2. Physical properties of snowpacks

Physical properties of snow in the 15 sampling sites showed a great variability both between sites and sampling periods. Snow depth ranged from 58 to 290 cm. There was no significant difference between the depth of the snowpack in March (111 ± 44 cm) and April (104 ± 82 cm) ($n = 30$, Fig. 2a). The mean snow density was 254 ± 48 kg m^{-3} in March and increased significantly to 358 ± 39 kg m^{-3} in April ($p < 0.001$, $n = 30$) (Fig. 3). Snow Water Equivalent (SWE) ranged from 10 to 60 cm.

Both snow depth and SWE decreased significantly from sub-region NW to C to SE ($p < 0.01$, $n = 30$) indicating a different pattern of total precipitations (Fig. 2b). In sub-region NW spring precipitation resulted in an increase in the average snow depth in April compared to March, while in the same interval in the SE there was an average snowmelt loss of more than 50% of snow.

Snow temperature profiles indicate generally a positive gradient from the surface to the ground in March and isothermal conditions in April (Fig. 3). Moreover, snow grain type and size changed widely with time, with an increase in abundance of freeze–thaw grains and ice lenses in April, consistent with a shift from dry to wet snow metamorphism.

3.3. Ion concentrations in the snowpacks

Volume weighted means for main ions are reported in Table 2. Mean Electrical Conductivity (EC) was 6.5 μS cm^{-1}. H^+ mean concentration was 1.2 μeq L^{-1}. Cl^- was the most abundant ion: the mean concentration in March was 5.8 μeq L^{-1} and increased significantly in April to 8.7 μeq L^{-1} ($p = 0.05$, $n = 294$). NO_3^- followed with a mean concentration of 6.0 μeq L^{-1}. SO_4^{2-} was the anion with

Table 1
Monthly average snowfall (cm) in winter '05–06, relative contribution (%) to the total cumulative snowfall and main source of air masses determining precipitation events.

	Average snowfall (cm)	Rel. contribution (%)	Source of precipitation
December	36	12	South-West, North-West (Atlantic Ocean)
January	57	20	South-East (Sirocco wind)
February	70	24	West (Atlantic Ocean)
March	99	34	West (Atlantic Ocean)
April	29	10	West (Atlantic Ocean)
Total	289	100	

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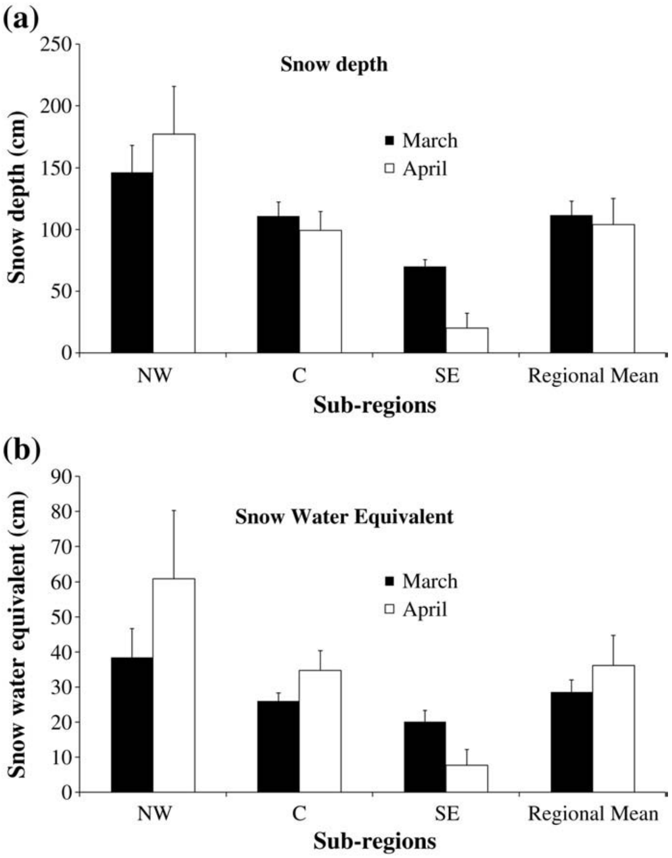

Fig. 2. Mean snow depth (a) and snow water equivalent (b) for the three sub-regions in March and April 2006. Error bars are SE. Abbreviations are as in Fig. 1.

the lowest mean concentration (1.9 μeq L^{-1}). NH_4^+ was the most important cation: the mean concentration was 3.6 μeq L^{-1} in March and it increased to 5.0 μeq L^{-1} in April ($p = 0.012$, $n = 294$). Na^+ concentration was found to be 3.5 μeq L^{-1}. Ca^{2+} and Mg^{2+} mean concentrations were 1.7 and 0.4 μeq L^{-1}, respectively. K^+ mean concentration in March was 0.8 μeq L^{-1} and it increased in April to 2.0 μeq L^{-1}.

3.4. Ion load in the snowpacks: DIN winter deposition rate

The regional variability of both snow water equivalent and ion concentrations combined to give great differences in the deposited ionic loads (Table 3).

Mean Na^+, Ca^{2+} and Mg^{2+} pools were found to be 1.3, 0.6 and 0.2 meq m^{-2}, respectively. SO_4^{2-} mean pool was 0.8 meq m^{-2}. These pools did not show a significant change over time or a significant spatial distribution in the three sub-regions.

We found a significant increase with time (i.e. from March to April) of NH_4^+ ($p = 0.027$), K^+ ($p = 0.027$) and Cl^- ($p = 0.013$) ($n = 30$). Among regions, we saw a consistent decreasing pattern of some species along the NW to SE transect. Ammonium pool was 2.5 meq m^{-2} in NW, 1.2 meq m^{-2} in C and showed a minimum of 0.7 meq m^{-2} in SE. The nitrate pool showed a decreasing trend from 2.9 to 1.7 to 1.1 meq m^{-2} in NW, C and SE, respectively. Potassium and chloride pools followed the same trend (Table 3). The DIN deposition rate was higher for NW (0.75 kg N ha^{-1}), and decreased along the NW–SE transect to 0.40 in C, down to 0.25 kg N ha^{-1} for SE.

3.5. Major sources contributing to the ion content

We performed a varimax rotated, normalized principal component analysis (PCA) in order to evaluate the major sources contributing to the ion content of the AV snow cover. Therefore, we show here the results of PCA on March samples, since in April snowpack the source signal seemed to be obscured by chemical redistributions along snow profiles during snow melt. This phenomenon of preferential elution has been demonstrated in several studies (e.g. Nickus, 2003; Cragin et al., 1996). We derived three factors from the PCA, that had Eigenvalues >1 (Kaiser Criterion), explaining 73.2% of the total variance (Fig. 4, Table 5). Factor 1 was loaded with Mg^{2+}, Ca^{2+}, K^+ and SO_4^{2-} and covered about 37.5% of the variance. The second factor covered 19.6% of the variance and was loaded with Na^+ and Cl^-. The third factor covered 16.1% of the variance and was loaded with N species, i.e. NH_4^+ and NO_3^-.

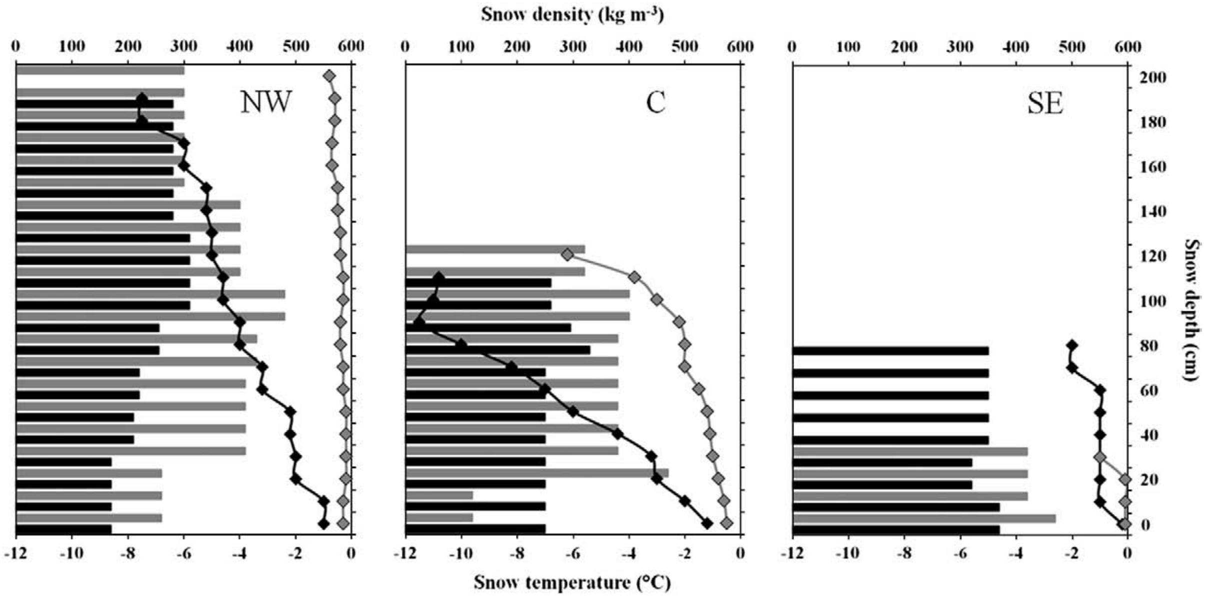

Fig. 3. Vertical profiles of snow density (kg m^{-3}, bars) and temperature (°C, lines) for three selected sites of the three sub-regions in March (black) and April (grey) 2006. 0 cm represents the snow–soil interface. Abbreviations are as in Fig. 1. Data have typically been collected between 8 and 10 am.

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Table 2
Volume weighted means (VWM) of ion concentrations and mean electrical conductivity (EC) of the seasonal snow cover. All data are coupled with relative standard errors. When both data for March and April are reported (i.e. K^+, NH_4^+ and Cl^-), there is a significant difference between means (see text). All concentrations are shown as μeq L^{-1}, except EC (in μs cm^{-1}). RSE are as % of the mean.

Date	K^+	NH_4^+	Cl^-	Mg^{2+}	Ca^{2+}	Na^+	NO_3^-	SO_4^{2-}	H^+	EC
March	0.8 RSE% 17 N = 15	3.6 RSE% 10 N = 15	5.8 RSE% 11 N = 15							
				0.4 RSE% 9 N = 30	1.7 RSE% 9 N = 30	3.5 RSE% 9 N = 30	6.0 RSE% 6 N = 30	1.9 RSE% 15 N = 30	1.2 RSE% 12 N = 30	6.5 RSE% 25 N = 30
April	2.0 RSE% 26 N = 15	5.0 RSE% 9 N = 15	8.7 RSE% 16 N = 15							

4. Discussion

4.1. Comparison of winter '05–06 with long term data

Cumulative seasonal snowfall during winter '05–06 (289 cm) was around 10% lower than the average value for period 1970–2005. Considering that minimum and maximum registered for the same period were 160 and 800 cm, respectively (data provided by Regione Autonoma Valle d'Aosta), snowfall amount during winter '05–06 was considered comparable to the long term pattern.

From Table 1, 80% of the over-winter snowfall was associated with west-originated humid air masses coming from the Atlantic Ocean. A particularity of winter '05–06 was the total absence of Saharan dust deposition events. Evidence of these depositions was reported for the Western Alps by previous studies (e.g. Nickus et al., 1997; Novo and Rossi, 1998; Schwikowski et al., 1995). The requested meteorological conditions for these phenomena are South-to-North air masses that allow a direct transport of dust from North Africa across the Mediterranean Sea to the Alps (Prodi and Fea, 1979). In winter '05–06 these meteorological conditions occurred rarely, and none of them was the source of snow precipitations (Table 1).

4.2. Ion concentrations

4.2.1. Calcium and magnesium

The high correlation between Ca^{2+} and Mg^{2+} (Table 4) indicates a common behavior and the presence of Ca^{2+} and Mg^{2+} in snow as dust-derived species has been reported by many studies carried out worldwide (e.g. Nickus, 2003; Hidy, 2003); thus these two elements will be discussed together.

Ca^{2+} and Mg^{2+} mean concentrations were considerably lower than those reported by several researchers for the Western and Eastern Alps (Nickus et al., 1997, 1998; Novo and Rossi, 1998; Edwards et al., 2007) who concluded that Saharan dust deposition events were responsible for such high concentrations.

On the contrary, for years without strong deposition events calcium concentrations were comparable with AV. Moreover, Nickus et al. (1998) reported that high calcium concentration (18 μeq L^{-1}) was associated with a local source from the bedrock. Mg^{2+} had a similar pattern in the earlier mentioned studies, being generally related to local dust or Saharan events. Our low calcium and magnesium concentrations are consistent with the absence of Saharan dust events for winter '05–06 and with the absence of a local extended geological source of calcium and magnesium. In fact, calcium and magnesium concentrations in AV may be representative for the winter mid-troposphere not influenced by long-range pollutant transport or Saharan dust (Novo and Rossi, 1998).

Table 3
Mean ionic loads in the 3 sub-regions. Different letters indicate significant differences between means. All loads are shown as meq m^{-2}. The mean is the average value for the 15 sampling sites (n = 30).

	Mg^{2+}	Ca^{2+}	Na^+	K^+	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}
	meq m^{-2}							
NW	0.2	0.7	2.0	0.7 a	2.5 a	2.9 a	3.7 a	0.8
C	0.2	0.5	1.1	0.5 ab	1.2 b	1.7 b	2.2 a	0.5
SE	0.1	0.4	0.7	0.1 b	0.7 b	1.1 b	0.9 b	1.1
Mean	0.2	0.6	1.3	0.5	1.5	2.0	2.4	0.8

4.2.2. Sodium, chloride and potassium

The mean Na^+ concentration in AV, at 3.5 μeq L^{-1} is 2–3 times higher than the rest of the Alps (Novo and Rossi, 1998; Nickus et al, 1997; Kuhn et al., 1998; Hidy, 2003; Edwards et al., 2007). Nevertheless, our mean concentration is comparable to the range provided by Nickus et al. (1998) for the Eastern Alps for year 1991. Furthermore, sodium concentrations are comparable with the 3.0 μeq L^{-1} reported for the Sierra Nevada-Cascade (Laird et al., 1986). In a similar fashion, the comparison of chloride concentrations shows the same behavior. The PCA, discussed later, suggests a sea-salt signal for Na^+, Cl^-, and partially for K^+.

4.2.3. Dissolved inorganic nitrogen

NH_4^+ (3.6 and 5.0 μeq L^{-1} in March and April, respectively) and NO_3^- (6.0 μeq L^{-1}) were two of the most abundant ions in AV snowpacks, and were comparable with concentrations over the Alps (Novo and Rossi, 1998; Edwards et al., 2007) which occurred in years without significant anthropogenic emissions. In contrast, our data were 2 to 3 times lower than the ones reported for years 1993–94 in Colle Vincent Glacier (Monte Rosa Massif), when strong anthropogenic events occurred (Novo and Rossi, 1998). We compared our data with some reported for the US: many US regions have experienced relatively high emissions of SO_4^{2-} and NO_3^- and consequent high values in precipitation (Stoddard, 1994). NO_3^- release from storage in the seasonal snowpack in the Rocky Mountains, for instance, was found to cause in many alpine ecosystems N saturation and several problems of surface water acidification (Williams and Tonnessen, 2000). For the Rocky Mountains, Turk et al. (2001) reported a mean concentration for ammonium and nitrate of 5.5 and 8.0 μeq L^{-1}, respectively. While AV nitrate concentration is lower than in the Rockies, ammonium is comparable. This may roughly indicate a lower anthropogenic emission component at the AV sites and a biogenic emission comparable with the Rocky Mountains. The low anthropogenic component hypothesis is corroborated by the low concentration of sulfate (see discussion later) in AV snowpacks. Moreover, the lack of correlation between nitrate and sulfate could suggest different sources for the two acidifying compounds.

Furthermore, NH_4^+ had a significant increase with time, showing a spring deposition effect. This increase could be explained by the transition from temperature inversion and stable atmospheric stratification in winter to strong temperature contrasts and convective mixing in spring (e.g. Maupetit et al., 1995; Kuhn et al., 1998).

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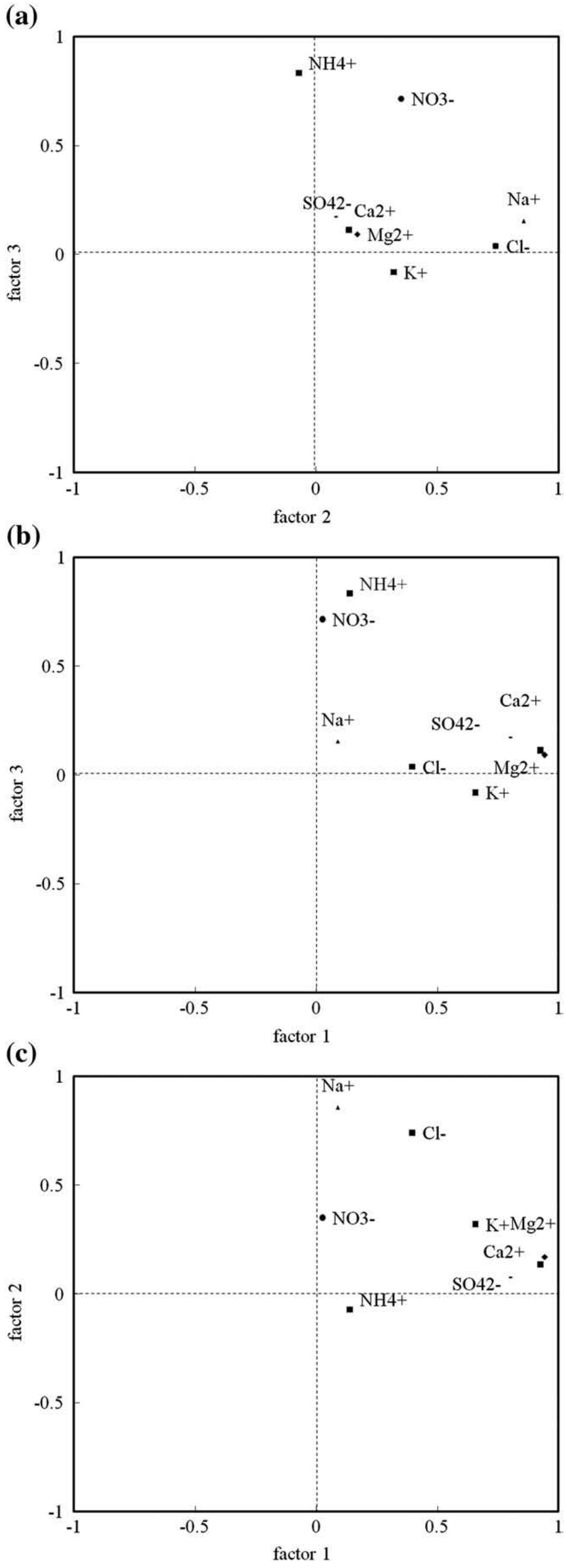

Fig. 4. Results of the varimax rotated PCA on March dataset (n = 167). Each point on the biplots represents loadings of a variable on two of the three factors. Factor 1: dust dissolution signal, Factor 2: sea-salt signal, and Factor 3: biogenic N signal.

Table 4
Correlation matrix between main ions in March snowpack (Pearson r coefficient, n = 167).

	Mg^{2+}	Ca^{2+}	Na^+	K^+	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}
Mg^{2+}								
Ca^{2+}	0.857							
Na^+	0.306	0.290						
K^+	0.588	0.403	0.343					
NH_4^+	0.217	0.152	0.301	0.213				
NO_3^-	0.187	0.271	0.241	0.111	0.361			
Cl^-	0.459	0.370	0.382	0.527	0.251	0.206		
SO_4^{2-}	0.669	0.764	0.260	0.146	0.129	0.213	0.210	
H^+	0.048	-0.023	0.092	0.116	0.051	0.052	0.105	0.050

NH_4^+ is generally associated with a biogenic emission due to local vegetal and animal source (e.g. Valsecchi et al., 1999). The increased NH_4^+ concentration in snowpack in April is coincident with the starting of agricultural activities and use of N-fertilizers, especially in the Po Plain but even at a more local scale. The resulting NH_4^+ spring deposition is therefore explained by the double effect of increased N emissions in the atmosphere and increased transport of N-enriched air to remote areas.

4.2.4. Sulfate

The presence of SO_4^{2-} in snowpacks has been associated worldwide to the industrial emissions (e.g. Barrie and Vet, 1984; Dash and Cadle, 1985). SO_4^{2-} mean concentration is 1.9 μeq L^{-1}, around 7-times lower than the one reported by Novo and Rossi (1998) for a low-emission year at the Colle Vincent Glacier and comparable with Greenland or Antarctica values (1.3–2 μeq L^{-1}) (Whitlow et al., 1992). According to Hidy (2003), who reported a background of anthropogenic contributions of 1–2 μeq L^{-1} for remote sites, AV sites can be ascribed to the baseline concentration range seen in very low-emission-affected sites in remote areas. In addition, the background concentration determined by Novo and Rossi (1998) for the Colle Vincent Glacier was around 2 μeq L^{-1}, in agreement with our observations that sulfate concentration in AV snowpacks is in the range of the background emissions found in high altitude and latitude sites.

The SO_4^{2-}/NO_3^- molar ratio for AV snowpacks is 0.7. Puxbaum and Wagenbach (1994) reported a SO_4^{2-}/NO_3^- molar ratio ranging from 1.8 for the Western Alps to 1.1 in the Eastern Alps. More recent works (Hiltbrunner et al., 2005) report a value of 1.1 for the Central Alps (Switzerland). The SO_4^{2-}/NO_3^- molar ratio is often used to understand the relative importance of SO_2 over NO_x emissions. In areas affected by high SO_2 emissions this value is usually greater than 1. Nickus et al. (1998) explained the increasing ratio of SO_4^{2-}/NO_3^- in snowpacks as a clear signal of anthropogenic influence in snow chemistry in the Eastern Alps affected by southerly air flow from the Italian Peninsula. In agreement with this explanation, and with precipitation patterns that occurred during winter '05–06 (Table 1), AV snowpacks appear to show little influence from local sources of SO_2 emissions. As a further confirmation, several studies report a peak concentration of sulfates during spring (e.g. Kuhn et al., 1998). This peak is explained by the transition from temperature inversion and stable atmospheric stratification in winter to strong temperature contrasts and convective mixing in spring. This process was responsible for an increase in SO_4^{2-} concentration on the Tyrolean Alps as high as 2 μeq L^{-1} (Kuhn et al., 1998). Our results show there was no significant increase in sulfate during the snowmelt period, thus we can assume that SO_4^{2-} contribution by anthropogenic emission sources was not significant.

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Furthermore, Kuhn et al. (1998) reported a SO_4^{2-}/NO_3^- value of 0.6 for the Southern Alps. They concluded that the Southern Alps apparently receive less of SO_4^{2-} pollution compared to the rest of the Alps. Since their study site is an inner alpine valley surrounded by high mountains in all directions except North-East, reasonably most of the precipitations occurred from orographic clouds. In AV, in winter '05–06, most of the precipitations (80%) were due to westerly air masses (Table 1) passing through the Monte Bianco Massif (Fig. 1). In both sites air masses have to pass through an orographic obstacle before the precipitations. We suggest that this common topographic condition could play a role in the scavenging of sulfate from air masses in both sites.

Summarizing, such a low concentration of sulfate in AV snowpacks could therefore be caused by three coupled factors. First, a low-emission winter for '05–06: sulfate concentrations in AV snowpacks were comparable to the background values calculated for geographically very close sites (Colle Vincent). Our findings suggest that long-range transport of sulfates does not show a great influence on snow chemistry at the AV sites. Second, orography could play a role in the scavenging of sulfates during precipitations, causing inner alpine regions to receive less SO_4^{2-} pollution compared to the rest of the Alps. Third, the low concentrations could be due to a decreasing trend in the troposphere sulfate concentration over the last years (Rogora et al., 2006). Further, recent studies on the Alpine snowpacks of inner alpine valleys and a multi-year comparison for AV snows are needed in order to discriminate quantitatively between these three components and for a better overall understanding of processes.

4.3. Regional variability of ion loads

There is a significant decreasing trend for ionic loading over the NW–SE transect, especially for K^+, NH_4^+, NO_3^- and Cl^- (Table 3). Nickus et al. (1998) found a general increasing trend in concentration from the Western to the Eastern Alps, of about 2–5 μeq L^{-1} for sulfate, nitrate and ammonium. This increase, however, did not determine substantial differences in terms of ion loads, since the distribution of snowfall followed an opposite gradient. In AV, the differences in ionic loading are driven by differences in the amount of snowfall (Fig. 2), which determines, at the local scale, the trend NW>C>SE in the distribution of ion loads.

SO_4^{2-} distribution among the sub-regions shows a different pattern. It decreases from NW to C and then there is an increase in SE (though not statistically significant). The SE sub-region is potentially affected by industrial emissions from the Po Valley. Even if these emissions seem to have little significant impact among the AV snowpacks, the partially different pattern in SO_4^{2-} distribution could be due to that. This hypothesis is consistent with the precipitation patterns described in Sections 3.1 and 4.1: air masses driving precipitations in SE are usually coming from the Po Valley, and in winter '05–06 these air masses determined only 20% of the precipitations, but were sufficient to apparently cause an increase in sulfate for the SE sub-region.

4.4. Major sources contributing to the ionic content

The results of PCA (Fig. 4, Table 5) were used to evaluate the major sources contributing to the ion content of the AV snow cover. Mg^{2+}, Ca^{2+}, K^+ and SO_4^{2-} are mainly loaded on factor 1. We associated at this factor a signal of non-sea-salt source. We believe that most of this factor can be explained with particle dissolution of dust in snow cover, as discussed earlier. Thus, we believe that the presence of these elements is due to a common, crustal source and the low concentrations of the three reflect the meteorological patterns of winter '05–06, characterized by the absence of the long-range transport of dusts. Results of PCA are in partial agreement with findings by Maupetit and Delmas (1994), that coupled magnesium and calcium as soil dust-derived cations in the French Alps. The behavior of K^+, however, is not totally clear, since it has a non-negligible loading on factor 2 (Fig. 3). Moreover, factor 1 may include some influence of industrial emissions on chemical composition, due to the fact that SO_4^{2-} is included. However, while discussing the sulfate behavior, the low influence of industrial emissions on AV snowpacks was discussed. Therefore, we consider the industrial emitted fraction of ions to be too small to show up another factor.

Table 5
Results of the varimax rotated PCA on March dataset (n = 167). % of the total variance explained by each factor and respective Eigenvalue are reported.

	Factor 1	Factor 2	Factor 3
% Variance	37.5	19.6	16.1
Eigenvalue	3.56	1.28	1.01

The second factor covered 20% of the variance and was loaded with Na^+ and Cl^-. It was associated with sea-salt aerosol. The influence of sea-salt aerosol can be seen in the high concentration of both Cl^- and Na^+ discussed earlier. Moreover, K^+ shows a relatively high loading on factor 2, even if the maximum is on factor 1 (Fig. 3). Following Maupetit and Delmas (1994), who reported a PCA factor loading sodium, potassium and chloride, we can hypothesize that K^+ contribution could be due mainly to particle dust dissolution, but partially to sea-salt aerosols.

The third factor covered 16% of the variance and was loaded with N species, i.e. NH_4^+ and NO_3^-. This factor was associated with biogenic emissions related to local sources. While in many other studies only NH_4^+ is generally associated with biogenic emissions (e.g. Nickus, 2003) in our case also NO_3^- seems to be related to the same source. This peculiarity could be explained by the low NO_3^- and SO_4^{2-} concentrations in AV snow, compared to other environments, which suggest a low influence of industrial emissions transported on the long range on the chemistry of snow at our sites. In such a condition, biogenic NO_3^- could be a non-negligible fraction. This hypothesis is corroborated by the lack of correlation between NO_3^- and SO_4^{2-} that is usually shown in industrial-emissions-affected snow (e.g. Maupetit and Delmas, 1994). Moreover, Williams and Melack (1991a,b) reported a high correlation between NH_4^+ and ($NO_3^- + SO_4^{2-}$), explaining that by the formation of NH_4NO_3 and $(NH_4)_2SO_4$ in aerosol. In our study, we confirm the possible formation of ammonium nitrate but we could not find any evidence of ammonium sulfate formation.

Nitrate production within the snowpack has been reported for high latitude ecosystems as the result of microbially-mediated nitrification (Amoroso et al., 2010; Wynn et al., 2007); in contrast Williams et al. (1996b) reported no nitrification in a temperate snowpack in Colorado. In this study, we cannot exclude microbially-mediated nitrification in the snowpack, but we have no direct evidence of such process.

As reported earlier, results of the PCA are presented for the March dataset only, since in April the preferential elution of chemicals seemed to obscure the PCA signals. Additionally, PCA was also performed separately for the three sub-regions, without getting any further information. The explained variance in those cases was always much lower than the one obtained by analyzing the whole dataset.

Non-sea-salt components (i.e. nss-sulfate, nss-potassium and nss-calcium) were computed from either sodium or chloride concentrations. Calculations were done according to Teinilä et al. (2003). Nss-sulfate and potassium were in about 80% of cases under detection limit, thus indicating that anthropogenic signal (for sulfate) and residential wood-burning (for K) were not a significant source of those compounds. Corrected concentrations were also used in the PCA but none of them were useful to further explain the source of chemicals in AV snowpacks.

Generally, the PCA suggests a strong correlation between calcium and magnesium as crustal weathering/particle dissolution signal. This

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is the strongest signal shown by PCA (38% of variance). Sea-salt aerosol signal (factor 2) couples sodium and chloride and represents the long-range transport signal. It includes partially potassium as well. K^+ source is not totally clear, since it could be included in the crustal weathering signal as well as in the sea-salt signal. Most likely, potassium pool comes from both the sources. The third factor, loading ammonium and nitrate, is the biogenic, local, short-range transport signal.

4.5. Nitrogen storage in snowpack of the Western Alps and its relevance to alpine ecosystems

Dissolved inorganic nitrogen pool in AV snowpacks was higher for NW (0.75 kg N ha^{-1}), and decreased along the NW–SE transect to 0.40 in C, down to 0.25 kg N ha^{-1} for SE. In all of the three sub-regions NO_3^--derived N accounted for about 54–59% of the total. Geographical distribution of different ionic loads depends on different snow accumulation in the three sub-regions and not on different concentrations in NW, C and SE. Snow accumulation is therefore the main process determining the load of chemicals in the snowpacks in AV. For DIN, the pattern in distribution of precipitations caused a 3-fold difference in the N loaded in the snowpack.

AV DIN load is higher than what was reported by Nickus et al. (1997) for Breithorn (3900 m a.s.l.), a site geographically close to the AV Region. We assume this difference to be due to an altitude decreasing gradient of chemical loadings. Hiltbrunner et al. (2005) reported a DIN pool in snowpacks of the Central Alps (2500 m a.s.l.) ranging between 0.5 and 1.7 kg ha^{-1}. Kloeti et al. (1989) reported for Swiss sites at an elevation of 1600 m a.s.l. a nitrogen load of 0.78 kg ha^{-1}.

In alpine ecosystems, DIN stored in the seasonal snowpack could contribute substantially to plant demand during the melting period. Hiltbrunner et al. (2005) estimated that in the Swiss Alps N pools in the snowpacks correspond to 10–34% of the N released by over-year mineralization. A study conducted in the Aosta Valley Region provides data to compare N pool in snowpacks with N mineralization rates at these sites. To highlight the ecological meaning of N input by snowmelt, we compared our values to the over-winter mineralization rates, in order to quantify the contribution of N coming from snowpack to the early spring N budget of Alpine soils. Freppaz et al. (2008) reported a net mineralization rate of 1.1 g N m^{-2} $winter^{-1}$ for a site in the South-East of the AV Region. The N contribution from the snowmelt was estimated to be 6%, 4% and 2% of the over-winter N mineralization for NW, C and SE, respectively. This appears to be a relatively small pool, but its strong influence on alpine ecosystems is determined by the fact that such pool is fast released to soil.

5. Summary and conclusions

Meteorological patterns of winter 2005–2006, coupled with the topographic characteristics of the Aosta Valley, an inner alpine valley, determined a peculiar distribution of chemicals among the snowpacks. Low anthropogenic emissions, low long-range transport of pollutants and the absence of Saharan dust reduced the concentrations of sulfate and crustal-dust species to background values.

Biogenic, agricultural, local emissions became the most important source of chemicals for AV snowpacks, ammonium and nitrate contributing to about 40% of the ion balance. Short term transport and subsequent deposition of chemicals appear to be the main processes controlling chemistry of snow in this inner alpine valley.

Although based on only one season of data, we suggest that the distribution of chemicals in the snowpacks of inner alpine valleys may show an overall different pattern, resulting in potentially different effects of N and S depositions in such sites. Given the not negligible extent of inner alpine valleys in the Alpine chain, such pattern should be taken into account while modeling N and S deposition at a global scale.

In the last years, a number of environmental data have been collected, by means of high altitude ice core drilling (e.g. Schwikowski et al., 1999). The low concentrations of anthropogenic N and S compounds found in the present study may be representative of winters characterized by peculiar air trajectories that lead to the absence of strong anthropogenic deposition or dust events. By combining historical meteorological data with data found in this study it may be possible to further explain the process of ion deposition at pristine high altitude alpine sites.

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