

## Monitoring of Solid Particulate Airborne Samples from Mountain Snow in Some Sites of the Alps, Italy

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### **ABSTRACT**

In the last decades, few days a week, several city centres in Italy are closed at vehicular traffic in order to limit the presence of particulate matter, often exceeding the limits set by law [1,2]. The particulate matter have an impact on human health [3,4], in the cultural heritage and natural environment deterioration [5,6]. Many studies have been the carried out in air monitoring in urban areas while the targeted surveys to assess the impact on air quality of snow dispersion for ski activities are rare. Thanks to the Autonomous Province of Trento it has been possible to sample the snow-pack in some ski areas in Italy and thanks to stratigraphic profiles it has been possible to observe variations of the chemical composition over time. Natural contribution is strictly related to winds and currents movement, for this reason a deep knowledge of these factors can help in the determination of the prevalent trajectories during the year [7,8]. During a penetrometeric and stratigraphic profile on Presena glacier, the main nivo-meteorological features, air temperature and temperature inside the different layers of the snowpack have been measured. Some snow samples has been collected and analyzed by SEM-EDS, ICP-MS and IC. These qualitative and quantitative analyses allow to obtain chemical and mineralogical composition to define the emitting source.

**Keywords:** Air Quality; Dolomites; PM<sub>10</sub>; PM<sub>2.5</sub>; SEM-EDS; IC; ICP-MS

#### 1. Introduction

The study of particulate matter in the snow is not common and few studies are related to the campaigns carried out in Antarctica. Most of the scientific works in Europe verifies the impact of large communication structures on the quality of the snow. This analysis assesses the contributions of local impact on air quality but also verifying the contributions of transboundary aerosol and defines the levels of background, to estimate the impact. It is assumed that the snow sampling particulate matter in the atmosphere during the fall, providing information on the chemical characteristics of the air column crossed. Quantify the changes in the chemistry of snow can be useful to complete the balance of the contributions of particulate matter to the soil and their effects on the ecosystem, knowing that they have potential negative environmental [9-11]. In addition, the trace elements may allow to recognize traces of various sources of aerosols both natural

and anthropogenic [12].

Precipitation, liquid and solid, are important mechanisms of atmospheric deposition, especially in remote areas. Several studies, from the last 20 - 30 years [13], have shown that collect samples of precipitation often is efficient in trace the sources and reconstruct the transport routes. In fact, some studies have emphasized the importance of know the falling snow to recognize both the aerosol particles and the phases of volatile organic compounds from the atmosphere [14,15]. These empirical and theoretical studies suggest that the snow has a great efficiency in both maintain the particles that the gaseous phases of organic compounds with respect to the rains, for this reason the snow plays an important role in contamination of the environment [16].

The monitoring stations of particulate are difficult to be managed in mountainous areas, which are characterized by long periods with thermal states below zero. Nevertheless, these areas are particularly interesting for the analysis of transboundary aerosol, both for the low

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human impact that for their localization at high altitudes. Therefore, the present study evaluated the potential of chemical and morphological characteristics of the particles, to determine local and transboundary contributions through samples of stratigraphic sections of snow that have taken place during the entire winter 2010. Some researchers have shown that it is not negligible the impact that the contaminants accumulated during the winter season can have on natural resources during and after the melting of snow in spring [17,18]. In areas of permanent snow and glaciers, contaminants may be subject to deep burial resulting in inclusion in the layers of ice [19,20]. Hence the possibility of having information on the evolution over time of the particulates, through the study of carrots performed in glaciers [19,21,22].

The estimation of the particulate in the snow also has repercussions on the evaluations of the overall energy balance, since the impurities and the sizes of the particles control the absorption of solar radiation, while the temperature controls the emission of radiation at low wavelengths [23]. At visible light (0.4 to 0.7  $\mu$ m), the ice is weakly absorbing and particles in the snow will trigger the light. Consequently, the pure snow has an albedo very large (>0.9) (radius of the radiative flux reflected on the incident radiative flux). The albedo of snow visible is very sensitive to impurities, such as soot, dust and fragments of vegetation.

Some models have shown that the high absorption of small particles in concentrations of about 1 ppm may decrease the albedo of the visible snow, mainly due to the reduction of the coefficient of scattering. In some studies it has been shown that the albedo decreases exponentially from 20% to 60% in perennial snow with a particulate concentration from  $10^2$  to  $10^3$  -  $10^4$  µg/m³ [24,25].

In literature, studies carried out on the snow and ice of Greenland and Antarctica have shown the presence of toxic trace elements (lead and cadmium). On the basis of stratigraphic position and historical assessments based on light isotopes, it was possible to interpret the causes of these enrichments, attributing the anomalies in atmospheric emissions from anthropogenic sources in the period of the Greek-Roman two millennia before the Industrial Revolution, probably due to ancient mining and smelting activities [26,27]. These anomalies are characterized by relations between elements for emission sources of the industrial revolution. Air pollution from 1700 to the present has been documented for several heavy metals, including Pb, Cd, Cu and Zn [28-30], Hg [31], Pt, Pb e Rh [32]. Studies on the snows and glaciers of Antarctica have made it clear that the natural cycles of trace elements such as Cr, Cu, Zn, Ag, Pb, Bi and U, were widely disrupted in the oldest Antarctic atmosphere, especially in recent years, and these disturbances reflect the stage of advancement of technology and metallurgical processes.

This is mainly due to long-range transport of pollutants from artificial sources of the surrounding areas, such as South America, South Africa and Australia [33-38], Geochemical data obtained from the study of snow and glaciers in Greenland [39] and in the remote regions of Antarctica [40] and in the Arctic [41], have shown that the development of pollution with trace elements has become of global importance, and reflects the extent of human impact on natural geochemical cycle of these same elements. Recently, several studies have demonstrated the different relationship between trace elements and human activities in the snows and glaciers of the Alps and in the high altitudes of the glaciers Bolivia [32,42-49]. In recent studies, the concentrations of trace elements were measured in the snow at high altitudes in eastern Tien Shan [50], eastern Pamirs Mountains Muztagh Ata in northern China [51,52], on Mount Everest in the Himalayas [53-55], in the Scottish mountains [56], in America [23] and in the Italian Alps [16,57]. From all these studies it is understandable that the concentrations of some trace elements vary from area to area.

The interest on the study of trace elements present in the snows and glaciers at mid-latitudes is of great interest, because of rapid economic growth and industrialization developed in recent decades, resulting in high levels of anthropogenic pollution in the atmosphere [58,59]. These studies have been done both in relatively remote areas, such as the Andes Mountains [60] and in populated areas as the European Alps [43,48]. The deposits of snow in the Alps testify the effects of anthropogenic emissions in Europe [61]. Recent samplings on Alpine glaciers have allowed to reconstruct the history of pollution of trace elements in the last century [48,62]. Nevertheless, detailed studies on the sources of the trace elements present in the Alpine snows are quite rare [63,64]. The importance of these studies is to find markers of anthropogenic emission potentially toxic in the snow and to implement defense mechanisms to protect the terrestrial and marine environment and to protect human health.

In this study we analyzed samples of snow, to distinguish the contributions of anthropogenic origin from those of natural origin, taking samples in the Dolomites in winter 2010. All samples were analyzed in ion chromatography and ICP-MS in order to know the chemical composition and in SEM-EDS for morphological characterization.

## 2. Methods

The samples were made in the central Dolomites and in the Adamello-Presanella Massif (Trentino Alto Adige-North of Italy), near Alpe Pampeago (Tesero-Val di Fiemme-Trento), in the snow fields of Monsorno (altitude 2010 m), Tresca (altitude 2080 m) and Presena Gla-

cier (altitude 2730 m). The Monsorno field presents an exposure S while the Tresca field with an exposure NNW, they are far from each other less than one kilometre (**Figure 1**). The Capanna Presena field present exposure N and is located at the base of the glacier. The sampling site is chosen mainly in remote areas to avoid contamination from nearby emissions from roads, villages, tourist stations, alpine huts and artificial snow cannons.

Val di Fiemme is one of the main valleys of the Dolomites and is located in eastern Trentino. Together with Val di Fassa and Val di Cembra, is the catchment area of Avisio, left tributary of the river Adige. This area is very large (~400 Km<sup>2</sup>) and it is approximately 180 Km from Adriatic Sea. It is surrounded to the N with Dolomites of Gardena and Fassa (Bolzano), to E with Dolomites of Feltre and the Pale di San Martino (Community Primiero), to SE with Pre Alpes Bellunesi (Community Valsugana), to S with Pre Alpes Vicentine, to W with Dolomites of Brenta and Alps of Val di Non (Community Cembra Valley), to NW with Alps Sarentine. The Dolomites di Fiemme are called mountains and not Dolomiti for their composition non-dolomitic, they shall consist, in fact, by silicate (granites and metamorphic rocks as porphyry) with a minor presence of carbonate and dolomite, and are located entirely in Trentino Alto Adige. The highest peak is Cima d'Asta with its 2847 m above sea level. During the winter season, Dolomitic area is often affected by strong continental thermal anticyclones that determine a mostly stable and very cold weather and lead to a strong minimum rainfall between December and February. The snowy weather conditions derived from passages of warm fronts from the Atlantic or the cyclogenesis on the Genoa Gulf, that attract masses of very hot and humid air from the Mediterranean (mainly orographic snowfall).

During the different phases of sampling, the main meteorological characteristics were collected at an altitude from 1760 m to 2730 m: air temperature and temperature of the superficial layer of the snow. Through the penetrometric battage profile, it was possible analysed a layer of snow of 4 m depth (Ghiacciaio Presena—2730 m), identifying each individual substrate. Then, through a process of dec-climatological analysis it was possible to



Figure 1. Map of the sampling site.

know the sources that produce volcanic ash, or desert sands, or other contributions of transboundary aerosol. During the stratigraphic analysis, some samples were collected through coring and they were subsequently analyzed by SEM, ICP-MS and ion chromatography in the Department of the University of Ferrara, allow to obtain qualitative and quantitative analysis of the snow, and defining the chemical composition to know the source of emission.

The sampling was done in Pampeago Alp and in Presena Glacier at different times of the year 2010, during monitoring season of avalanches. February 18, March 11, April 11, May 12, therefore different meteorological conditions cannot be avoid. The meteorological data (temperature, humidity, wind direction and wind velocity) were respectively provided by METEOTRENTINO weather station of Cavalese-Alpe Cermis and Capanna Presena (2750 m). The first weather station is situated at 2200 m and was the nearest station to Pampeago Alps. The distance from station to sampling sites ranged from 4 to 5 km from SSW. Near the snow field of Capanna Presena automatic weather station complete with snow gauge ultrasonic is placed.

The sampling during the first campaign (February 18, 2010) was carried out from 10 am to 13 pm (UTC + 1). The synoptic situation is characterized by a depression centred on Ireland, with a secondary low pressure field located on the ground near the Corsica Island and at high altitude (500 hPa geopotential) on the south of Sardinia. This facilitated the arrival of humid and warm current from southern Mediterranean basin (Libeccio at middle altitude and Scirocco at ground) to the Dolomites, with moderate snowfall above 1200 m. The average wind speed were 3 Km/h and direction to the south (the trajectories were created using the software online NOAA HYSPLIT MODEL-GDAS Meteorological Data—Figure 2(a)). High values of relative humidity (about 74%), associated with mild climate even in the mountain (0°C level at 1600 m with temperatures between -3°C and -1°C at 2200 m) and snowfall events, reduced the aerosol particles resuspension. Three samples were collected. These samples were all used for the SEM-EDS analysis. The sampling during the second campaign (March 11, 2010) was carried in Pampeago out from 10:30 am to 12:30 am (UTC + 1). During March, the depression migrated from NW to NE Italy. This created mild and very moist southern currents to the dolomitic area. The average wind speed were 7 Km/h and the direction were from south-east (Scirocco-Figures 2(b) and 3(b)). High values of relative humidity (68%) and mild temperatures (at 2200 m temperatures between -3°C and +1°C) during the day, with a light snowfall caused the reduction of the aerosol resuspension. For this sampling, three samples were collected: 30 cm depth, 70 cm depth and 130 cm depth.

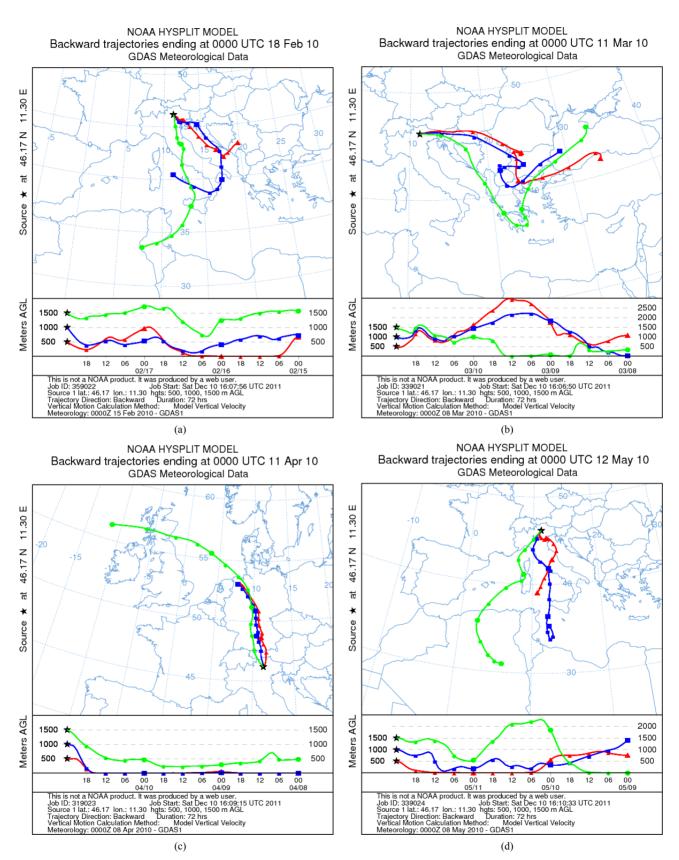


Figure 2. Back trajectories of the sampling days in the Dolomites (Software online NOAA HYSPLIT MODEL): (a) February, 18; (b) March, 11; (c) April, 11; (d) May, 12.

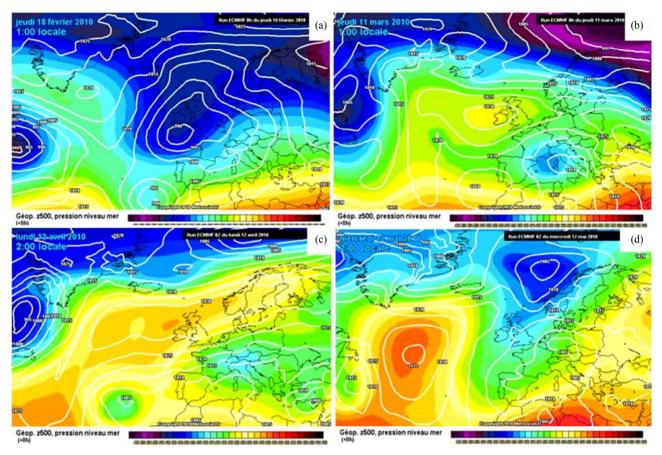


Figure 3. Atmospheric pressure on the ground and geopotential at 500 hPa to 00UTC: (a) February, 18; (b) March, 11; (c) April, 12; (d) May, 12.

The sampling during the third campaign (April 11, 2010) was carried out at the Presena Glacier (2750 m from 12 am to 2:30 pm (UTC + 1). The synoptic situation is characterized by inflow of cold air from the northeastern and arising from thermal contrast between the Russian anticyclone and a depression extending from eastern France and Styria. These currents cause a sudden drop in temperature, with variable weather and isolated snow showers over 1000 m. At 2500 m, the average wind speed and direction were 9 Km/h and from the north (**Figures 2(c)** and **3(c)**). Low values of relative humidity (37%) and temperature (T<sub>min</sub> -8°C and T<sub>max</sub> -3°C at 2730 m) maintained the environment stable and wet during the sampling. Also for this sampling, three samples were collected: 40 cm depth, 100 cm depth and 140 cm depth.

The sampling during the fourth campaign (May 12, 2010) was carried out from 11 am to 2:30 pm (UTC + 1) at Presena Glacier. The synoptic situation shows a range of pressures levelled to a low centre of south-western Europe with a strong anticyclone located on North Africa (**Figure 3(d)**). Therefore, on observe an active moderate humid south westerly flows. Sky mostly cloudy both without precipitation. The average wind speed and direc-

tion were 5 Km/h and from the south (**Figure 2(d)**). At 2750 m, values of relative humidity is around 84% while the temperatures are quite high and between -2°C to 4°C. For this last sampling, five samples were collected: on the ground level (surface layer), 170 cm depth, 250 cm depth, 300 cm depth and 310 cm depth.

#### **Analysis**

The instruments used for sampling were simple plastic tins, previously cleaned with MilliQ<sup>®</sup> water, with double-sealed cap. After collection, all samples were transported in a refrigerated cooler to UNIFE laboratory in Ferrara and stored under refrigeration until microscopy analysis was performed [65].

The samples were used for SEM-EDS analysis to characterize the shape and morphology and the elemental composition of aerosol particles collected. Morphological characteristics, size and elemental analysis of individual particles were performed with a Scanning Electron Microscopy (SEM) (Zeiss EVO 40) equipped with an Energy Dispersive X-ray Spectrometer (EDS) (INCA 300 OXFORD) for X-ray microanalysis. The particle size and the surface morphology of sampled aerosol par-

ticles were investigated in high resolution mode (up to 20.000×) with a working voltage of 20 kV which correspond to the detection limit of 1 um particle size. The analyses were qualitative and were performed in the manually mode. SEM-EDS is often employed to identify airborne particulate deposits and biological materials [66]. In EDS, the X-ray detector measures the number of emitted X-rays as a function of their energy. Since elements have a characteristic energy, the EDS spectrum can be used to identify the quantity of elements present [67]. EDS technique is able to characterize the chemical composition of particles whose diameter is greater than 1 micron [68]. The Scanning Electron Microscopy is a technique employed in numerous atmospherically studies [65,68-73]. It is important to know that chemical and physical characterization of individual particles by SEM-EDS instrument can reveal source information which cannot be determined through bulk chemical characterization. Each snow solution was placed in a specific centrifuge. There by the aerosol particles are attached to a film of titanium, which was subsequently analyzed by SEM. Other that, the filters, which were used for the preparations of the samples to analyzed in ICP-MS, were mounted on aluminum support SEM "stubs" with double-sided tape which had a conductive graphite-based. The samples were then coated with a thin layer of gold (coating) film by electric arc high vacuum method and then analyzed by SEM.

The multi-element analysis was carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, X Series spectrometer, collision/reaction cell CCT<sup>ED</sup>, Thermo Electron Corporation), which has become an increasingly popular technique for characterization of atmospheric aerosols [74]. Multi-element characterization is done using a small sample volume, it has a large dynamic range (ppt or ppb) and a short analysis time [75-79]. For the ICP-MS the blank solution were prepared with 8 cc H<sub>2</sub>O MilliQ<sup>®</sup>, 1cc of standard Rh Re (100 ppb) and 1 cc of HNO3. The Limits of Detection (LOD) values were calculated as three times the standard deviation (3 s) of blanks. This analysis allows to recognize the geochemical fingerprint of the snow solution and to provide markers to identify anomalies related to the contributions of particles. Two different samples for each snow solution were prepared:

- 1 cc of the snow solution was diluted with 8 cc H<sub>2</sub>O MilliQ<sup>®</sup> and 1 cc of standard Rh Re (100 ppb);
- 50 cc of the snow solution were filtered by syringe with a polypropylene VWR filter 0.45 μm. Then, 1 cc of the snow filtered solution was diluted with 8 cc H<sub>2</sub>O MilliQ<sup>®</sup> and 1 cc of standard Rh Re (100 ppb).

For the IC analysis we used the ion chromatograph Dionex ICS2000, which uses of an eluent of carbonatebicarbonate. The anions are separated by an ion-exchange resin, low-capacity and highly basic and direct in a strong acid cation exchanger (suppressor), where they are converted into an acid form with high conductivity and the eluent is transformed into carbonic acid with weak conductivity. Therefore, the anions are measured for conductometry and compared with the standards on the basis of the retention times. The quantization is done by measuring the peak area or height. For IC analysis, 100 cc of each snow solution samples were injected in the instrument and analyzed.

#### 3. Results and Discussions

## 3.1. Morphological Classification by SEM Analysis and Elemental Composition by SEM-EDS Microanalysis

For each sample, SEM measurements were conducted on particles which were not in contact with any others. High-resolution images of particles were obtained by regulation of vacuum inside the instrument chamber. Several distinct particle shapes were observed, which were single particles rounded (Figure 4(a1)), angular (Figure 4(a2)) and amorphous (Figure 4(a3)); and agglomerate: rhomboedral/schalenoedral (Figure 4(b1)) and amorphous (Figure 4(b2)). The single particles were presents in a minor percentage (38%) respect the agglomeration particles (62%). The majority of single particles, randomly selected, were classified as amorphous particles (20%), less rounded as particles (12%) and a minority as angular particles (6%). Instead of agglomerate particles were classified as amorphous particles (40%) and a minority as rhomboedral/schalenoedral particles (22%).

Aerosol composition of single particle was determined using EDS microanalysis which detected the presence of C, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn and Fe. The chemical composition of the analyzed particles can be divided in five main categories: allumo silicate (**Figure 4(a1)**), silica (**Figure 4(a2)**), organic material (**Figure 4(a3)**), carbonate (**Figures 4(b1)** and (**b2)**) and sodium chloride (observed on the titanium film analyzed by SEM-EDS).

**Figure 5** shows the chemical characterization of the particles analyzed by SEM-EDS. It can be noted that the majority of the particles were allumo silicate and sodium chloride and only a minority were silica and carbonate. This means that the particulate resuspended in the sampling zone in the Dolomites, is predominantly composed of resuspension of artificial snow and particles of anthropic local pollution.

# **3.2. Chemical Composition by ICP-MS Technique**

The average concentrations in ppm and in percentage are reported in **Figure 6**, that shows variations in abundance

between different elements as a function of the two solutions analyzed: "suspended" means the original snow solution and "filtered" means the solutions filtered by syringe with a polypropylene VWR filter 0.45  $\mu m$ . The elements with negligible concentration are: B, Mn, Cu, Zn, Sn, Co, Mo, V, Cr, Ni, Rb, Sr, Ba, U. Toxic metals such as mercury, arsenic, vanadium nickel and cadmium were not found in any samples.

In general the concentrations are not representative, because so low, but it is important tom know the chemical composition of the snow, because the elements inside contributing to the water chemistry.

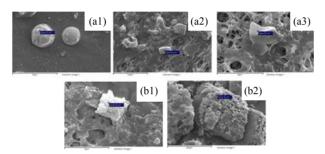


Figure 4. Images of representative particle shapes analyzed by SEM-EDS on the filters: single ((a1) round particle, (a2) angular particle, (a3) amorphous particle) and agglomerate ((b1) rhomboedral/schalenoedral particles, (b2) amorphous particles).

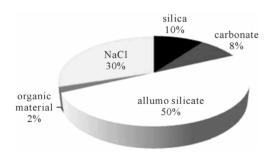


Figure 5. Characterizations of the particles in snow samples of each sampling (winter 2010) by SEM-EDS.

In all snow samples analyzed, it can observed high concentrations of calcium (%) respect the other elements, that confirms the high presence of carbonates in the sampling area.

Ca and K change so much from one sample to another. This could be due to the presence of artificial snow produced with local groundwater, which is carbonate.

The graphs show that the chemical composition of snow is not constant, but changes in several months. This could be due to the presence of transboundary events, which may be studied with isotopic analyzes in the future.

**Table 1** shows the ratio between the filtered snow solution and the original snow solution of the main elements analysed by ICP-MS, in each samples of the three periods of sampling.

In the samples of March, particles very large are probably derived from transboundary and no local. The samples taken in correspondence of chair lifts, are the most polluted, and being greater the amount of coarse particles which remain in suspension, the ratio is low (ratio < 1).

In the samples of April, the ratio filtered/suspended of aluminum is lower than in the samples of March, this represent the stop of the chair lifts. While the sample (140 cm) could connect to the period in which the sample (30 cm) was taken in the month of March.

In the May samples, the high anomalies in the samples (250 cm) and (300 cm) is probably due to the temperature in the sampling period, which was higher than in the two months before. These anomalies could represent the melting snow surface which favored the accumulation of particulate league in the snow below.

Between the concentration of sodium, potassium and aluminum there is a positive correlation. This indicates that the alkaline elements in the Dolomites, being related mainly to allumo silicate, are generally concentrated in the suspended fraction (ratio of filtered/suspended < 1) (**Table 1**). Despite the lower concentrations of cations,

Table 1. Ratio between the filtered snow solution and the original snow solution of the main elements analysed by ICP-MS, in each samples of the three periods of sampling.

|     | March 11  |           |           | April 11  |           |           | May 12    |           |           |           |           |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| ppm | (30 cm)   | (70 cm)   | (130 cm)  | (40 cm)   | (100 cm)  | (140 cm)  | (0 cm)    | (170 cm)  | (250 cm)  | (300 cm)  | (310 cm)  |
|     | filt/susp |
| Al  | 2.0       | 1.9       | 0.0       | 0.4       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       |
| Fe  | 0.0       | 3.8       | 0.0       | 0.2       | 0.5       | 3.4       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       |
| Ca  | 0.1       | 1.0       | 0.2       | 2.8       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       |
| Mg  | 0.3       | 1.2       | 0.2       | 1.6       | 0.0       | 0.6       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       |
| K   | 0.0       | 0.2       | 0.0       | 0.9       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       |
| Na  | 0.0       | 0.7       | 0.7       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       |

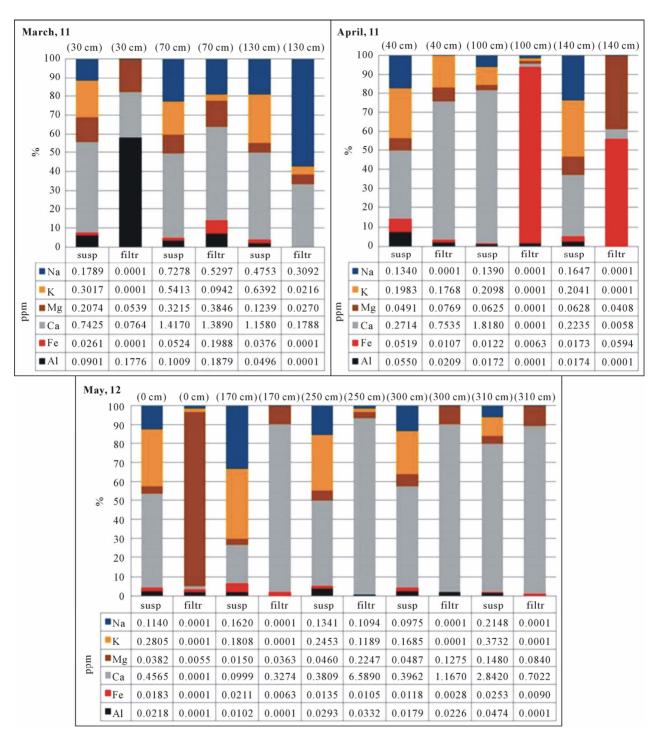


Figure 6. Average concentration of elements analysed by ICP-MS: March, 11; April 11; May, 12.

in the mountain areas there is a greater presence of silicates rich in iron and lower concentration in soluble salts, probably the silicates derive from transboundary sources. The diagram of the particulate sampled in May 2010 (**Table 1**) shows negative anomalies of sodium, potassium, aluminum and iron, representatives silicate minerals. While higher is the local contribution of carbonates (Ca and Mg).

#### 3.3. Chemical Composition by IC Technique

The concentrations of anions analyzed are low. In some samples, nitrates and phosphates are under the detection limit (LOD), which represents the minimum concentration of analita detectable (**Table 2**). Fluorides and phosphates under the detection limit. The symbol "n.d." means "value comparable with white value".

The sulfate characterizes a mineral acidity in the snow sample. The abnormal presence of sulphate ions could be due to transboundary aerosol. In Italy, the sulfates are destroyed by reducing the amount of fuel with the introduction of geothermal energy and gasoline without sulfur, but in the foreign countries, especially in the east part of Europe, these are not adopted.

The presence of chlorides may be due to pollution anthropic, being the sampling area close enough to the chairlift. It should be noted, in fact, that the concentration of chloride ion decreases from March to May.

The presence of nitrate ion confirms the anthropic activity of the chairlift. Generally, the nitrate ion is very soluble and does not persist in the snow. The high presence of this ion could be explained by the transformation of nitrate ion in nitrite ion. Nitrites are an intermediate metastable and toxic within the chain of bacterial oxidation of proteins (protein-ammonium ion-ion nitrite-nitrate ion). This ion is, therefore, an important indicator of the presence of pollution by organic material, like bacterium Pseudomonas syringae, in the artificial snow. This bacterium is a protein of the cell wall capable of accelerating the crystallization of the water droplets. Normally it is founded on the leaves of many plants and it is rarely free in the soil. Bacterial cells are lyophilized and dissolved in water for the production of artificial snow [80,81]. On this basis, it appears that further study of the particles of particulate present in the snow, especially with microbiological investigations, because the snow itself can be resuspended and with it also these compounds that can be harmful to human health if inhaled.

Table 2. Analysis results by ion chromatography of samples taken in the Dolomites in winter 2010.

| Ion Chromatography-ANIONS (mg/L) |        |                 |                  |                  |             |  |  |  |  |  |
|----------------------------------|--------|-----------------|------------------|------------------|-------------|--|--|--|--|--|
| Date                             | Sample | Cl <sup>-</sup> | NO <sup>2-</sup> | NO <sup>3-</sup> | $SO_4^{2-}$ |  |  |  |  |  |
| 11/03/10                         | 30 cm  | 0.0704          | n.d.             | 0.3824           | 0.0500      |  |  |  |  |  |
| 11/03/10                         | 70 cm  | 0.5710          | n.d.             | 2.7652           | 0.9788      |  |  |  |  |  |
| 11/03/10                         | 130 cm | 0.6846          | n.d.             | 0.6575           | 0.4724      |  |  |  |  |  |
| 11/04/10                         | 40 cm  | 0.0873          | n.d.             | 0.5942           | 0.2843      |  |  |  |  |  |
| 11/04/10                         | 100 cm | 0.0754          | n.d.             | 0.6293           | 0.1330      |  |  |  |  |  |
| 11/04/10                         | 140 cm | 0.1826          | n.d.             | 0.9560           | 0.0940      |  |  |  |  |  |
| 12/05/10                         | 0 cm   | 0.0299          | n.d.             | 0.2493           | 0.1725      |  |  |  |  |  |
| 12/05/10                         | 170 cm | 0.1613          | 0.148            | 0.0687           | 0.0766      |  |  |  |  |  |
| 12/05/10                         | 250 cm | 0.0937          | n.d.             | 0.2509           | 0.1964      |  |  |  |  |  |
| 12/05/10                         | 300 cm | 0.0559          | n.d.             | 0.1379           | 0.3874      |  |  |  |  |  |
| 12/05/10                         | 310 cm | 0.0899          | n.d.             | 0.2258           | 0.3450      |  |  |  |  |  |

#### 4. Conclusions

In this project have been addressed issues of sampling and analytical procedures related to snow samples with very low concentrations and subject to easy contamination. Sampling procedures were determined and the identification of the particulate matter in samples of snow was made by chemical methods (ICP-MS and IC) and observations by SEM-EDS.

The experimental results have allowed for a good response that the analysis of snow can give to estimate the transboundary contributions and possible anthropic impacts.

The snow has not homogeneous composition, which reflects transboundary contributions and it is a good indicator for assessing the regional and local impact.

The SEM analysis, carried out on larger particles, have allowed the identification of the morphology and chemical composition of the various types of particles, which are formed by silicates, allumo silicates, carbonates and organic particles.

From the ICP-MS analysis, the alkaline elements are concentrated in the fraction suspended and they are present as allumo silicates with dimensions larger than those of the filter (>0.45 m). This indicates that the sea spray and chlorides emitted from incinerators do not have strong effects in mountainous areas.

The strong vertical variations were testimony to the different origin of the snow, which according to its path could be sampled more or less high concentrations of particulate matter but also of a different nature and composition.

The presence of nitrates is important and it is related with nitrites, which were produced by artificial snow. Data obtained from the analysis in IC.

The results suggest a method to use to continue the study of particulate matter in the snow, because it is particularly interesting to estimate the contribution of various pollution sources and to understand the risk factors for people and ecosystems in the sampling area. The snow melted, in fact, favors the interaction of the particles contained in it with biomass. Furthermore, the solid particles in the snow can then be resuspended and be inhaled by humans, with the melting of the snow.

The study of aluminum will be interesting to analyzed because it may be a good tracer to study the formation and the residence time of snow in the upper atmosphere.

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