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# Characterization of PM in Snow Samples of Po Valley and Dolomites: Petro Chemistry and Morphology

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**Abstract:** ***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. Two test areas were studied (Ferrara city in the Po Valley and Alpe Pampeago in the Dolomites) using SEM-EDS technique to identify the morphology of the particles and IC and ICP-MS technique to characterized the chemical composition to better understand the environmental impact of some potential pollutant sources.***

**Keywords:** Air Quality, Snow, SEM-EDS, ICP-MS.

## 1. Introduction

Generally, the snow on the surface of the roads is compacted into a hard crust making it difficult or impossible to remove [1]. This crust provides good driving conditions with very low temperatures (>0°C), while it becomes slippery at temperatures around 0°C [2]. Chemicals, such as sodium chloride (salt), are added especially during the early hours of snowfall for preventing compaction [3], making it possible to quickly recover good driving conditions. However, the salt has negative effects on vegetation [4], on aquifers of fresh water [5], causes corrosion in some parts of vehicles [6], bridges, road beds and other infrastructures [7]. The application of salt on roads, also, lowers the freezing point of water [8], so that snow and ice melted, forming saline water which flowing into surrounding rivers or filtrating into the ground. Consequently, the resources of freshwater, terrestrial habitats and aquatic ecosystems are degraded. The salinization of freshwater could cause acidification of waterways, alteration of mortality and aquatic biodiversity [9]-[10]-[11]. The first portion of the melted snow contains high concentrations of impurities [12], which are mainly related to particulates from anthropogenic pollution in the air. The snow is compacted to the ground with impurities, which may increase the damages to groundwater when snow melts. For this reason, quantify the chemical composition of snow could be useful recognizing the negative contribution of particulate matter on soil and environment [13].

Several studies shown that it is possible to reconstruct the transport routes collecting samples of solid or liquid precipitation [14] and to characterize anthropogenic or natural transboundary contributions [13].

The objective of this research was to characterize the chemical composition of snow to give information on aerosol chemistry and transboundary contributions of anthropogenic sources. This paper briefly describes the comparison of the chemical composition of snow collected during winter 2009-2010 in the Dolomites and in Ferrara city (eastern part of Po Valley). It was important to characterize the anthropogenic contribution of salt in the snow sampled in Ferrara, area susceptible to subsidence and infiltration of water into the ground. The high presence of salt in melted snow could penetrate deep into groundwater of the city and affect the quality of aquifers recharges.

## 2. Methods and Analysis

Several measurement campaigns were carried out during winter 2009-2010 in Ferrara (north-east of Italy) (Fig.1) in four areas more or less close to busy roads: December 2009, February and March 2010. The meteorological data (temperature, humidity, wind direction and speed) were provided by ARPA Emilia Romagna [15]. The Po Valley is a subsiding sedimentary basin between Alps and Apennines. Moreover, the subsidence is not homogeneous, but is strongly influenced by tectonic structures deep that cause large differences in the thickness of the sediments. To expand the geological context must be taken into account the distribution of aquifers [16], which is important because the snow melts slowly promotes the absorption of water by the soil, feeding the aquifers. Sampling in Dolomite were made in Alpe Pampeago (Tesero, Val di Fiemme - northern Italy - 2080m) (Fig.1). The sampling site was chosen in remote areas to avoid contamination by emissions from roads and villages. The samplings were carried out during the monitoring of avalanches in 2010. The meteorological data were provided by Meteotrentino Station Weather Cavalese - Alpe Cermis and Capanna Presena (2750m) [17]. The descriptions of instruments were in [17].

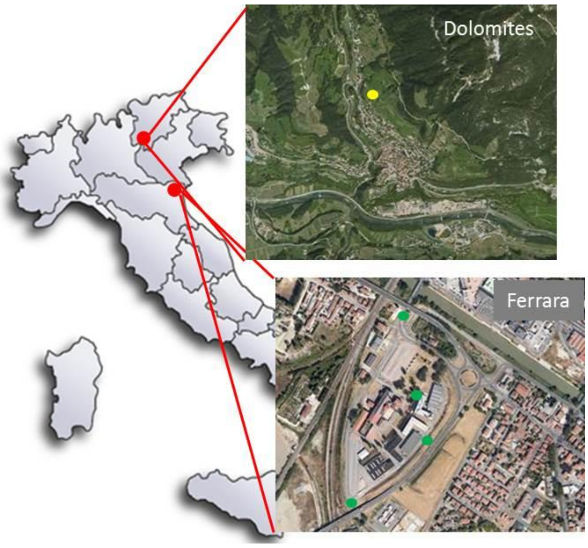



**Figure 1:** Map of sampling sites (in yellow sampling area in Dolomites, in green sampling areas near the scientific center of Ferrara University).

## 3. Results and Discussions

The sampling was effective in capturing the heterogeneous class of solid pollutants collected, although with the SEM are unable to characterize particles <1µm, which is the analytical limit of the instrument. In detail, the snow samples collected in Ferrara show mainly inorganic particles with a prevalence of clay minerals and allumo silicate (50%). Particles of sodium chloride (30%), quartz (10%), magnesium carbonate (8%) and rare organic particles (2%) were also characterized (Fig.2). This means that particles resuspended in the eastern part of Po Valley in winter was mainly made up from the resuspension of local soil. While most of the particles observed in the samples of Dolomite were particles of sodium chloride (90% - Fig.2), representing the chemical composition of water, and then of snow.

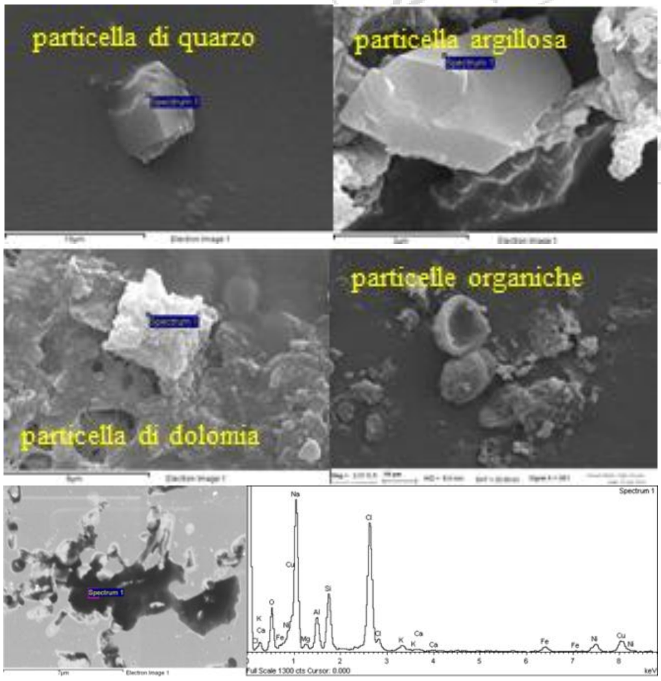


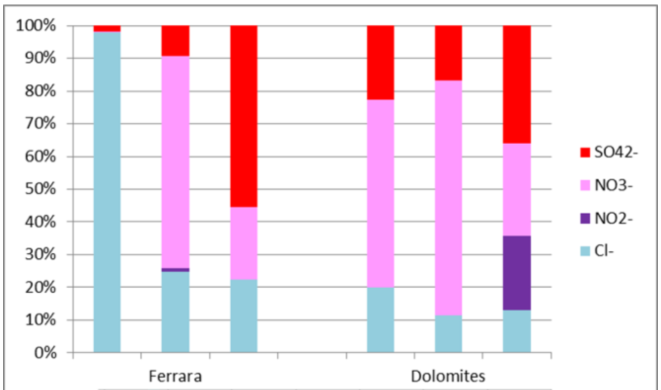

**Figure 2**: Particles observed by SEM-EDS in snow samples collected.

Fig. 3 shows a bar graph of the percentage concentration of anions analyzed by Ion chromatography (IC) in Ferrara and Dolomite. The results show that in snow samples of Ferrara the concentrations of anions were higher than in the Dolomite. Some elements such as chloride, nitrates and sulfates were relatively high in the samples of Ferrara, especially in snowfall of December. This can be explained by the fact that sampling was performed two days after the snowfall, probably the snow had already absorbed part of the smog of traffic.

The concentration of $Cl^-$ in Ferrara in the snowfall of December was high (1599mg/L), probably due to the addition via road salt to maintain road clean. [18] show that $Cl^-$ concentrations between 50-1000mg/L indicate water contaminated by road salt. Previous work on the impact of road salt, in fact, demonstrate the importance of knowing the concentration of $Cl^-$ in snow samples [19[-[20]-[21]. These studies explain that increasing trends of $Cl^-$ suggest anthropogenic sources, such as increased road salt use. The effect of sodium chloride solution content on snow hardness in Ferrara was different from that observed in the Dolomite (as in [22]). The presence of chlorides in the samples of the Dolomites was probably due to anthropogenic pollution, being the sampling area close enough to the chairlift. It was observed that the concentration of $Cl^-$ decreases from March to May. This reflects the decrease in sky activity: high concentrations in March during the height of skiing, low concentrations in May after the close of activity in April.

The presence of nitrates and sulfates may indicate mineral acidity of snow in both sampling areas. These ions, in fact, were formed in the atmosphere by oxidation and subsequent reaction with water of oxides of nitrogen (NOx) and sulfur dioxide ($SO_2$). The presence of nitrogen oxides in the atmosphere was mainly due to the placing of sulfuric and sulphurous anhydrides by combustion industries (gas turbine and incinerators).

Ions concentrations decrease from the snowfall of December to March in Ferrara and from the snowfall of March to May in the Dolomites. In the Dolomites this was related to the stop of sky activity, instead of in Ferrara is related to the proximity of the snowfall of March to the previous snowfall of February, which had taken the particulate in the air column crossed and bring it to the ground.




| (mg/L) | dec-09 | jan-10 | mar-10 | mar-10 | apr-10 | may-10 |
|---|---|---|---|---|---|---|
| Cl- | 1599 | 1,539 | 0,606 | 0,442 | 0,115 | 0,086 |
| NO2- | 0,036 | 0,072 | 0,0000 | 0,000 | 0,000 | 0,148 |
| NO3- | 3,275 | 4,023 | 0,598 | 1,268 | 0,727 | 0,187 |
| SO42- | 30,7 | 0,581 | 1,507 | 0,500 | 0,170 | 0,236 |

**Figure 3**: Ionic characterization of snow sampled in Ferrara and Dolomites (n.d. means "not detected" = value comparable with white value).

Fig.4 shows the chemical composition of particles analyzed by ICP-MS. The graphs show the relationship between filtered solution (filtered) and melted solution (suspended): Ferrara (A) and Dolomite (B). Li-Be-Cr-Co-Ni-Ga-As-Mo-Ag-Cd-Sb-Sn-Hg-Tl-Bi-U were below the detection limit. The chemical concentration of the samples collected during the first snowfall in Ferrara was more enriched in cations than the last (from December to March). Samples collected during snowfall in December were more concentrated in chlorides and sodium, probably due to the application of salt in the roads. This impact was absent in the samples of March, in which the concentrations of alkaline elements were low, or even absent. We could deduct that the low concentration of particulate during the last snowfall of March was due to the proximity of this event to the previous snowfall of February. Comparing the results of the sampling collected in December in areas with low human impact with the subsequent snowfall, the concentration of metals in the snowfall in December is higher. This seems to confirm the important role of snowfall in breaking of air pollutants. Similar consideration can be performed for potassium which is correlated with sodium ($R^2$=0.99) due from anthropogenic sources. There is a strong difference between the samples of Ferrara and those of the Dolomites, as in the Po Valley enrichment in sodium and potassium is not correlate with an enrichment of aluminum and iron, indicating that the elements derived from alkaline salts of anthropogenic pollution (spreading of salt), while in Dolomite there was a presence of silicates rich in iron and alkaline elements and lower concentration in soluble salts (positive correlation between sodium potassium and aluminum). While in the samples of Po Valley the presence of chlorides was linked to the shedding of salt on roads, in the Dolomite was linked to human activity connected with the activity of the lift.
The high chemical concentrations in the samples of May, is probably related to the sampling period when temperatures began to rise. The anomaly may therefore represent the melting snow surface that favors the accumulation of particulate collected in the snow below. The local contribution from carbonates is higher in samples of March and subsequent decreases in snowfall.

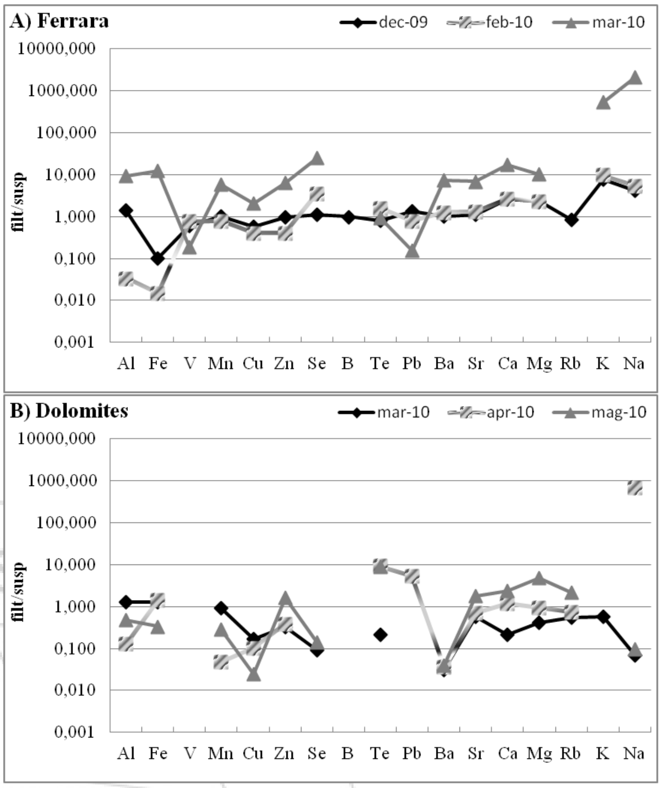



**Figure 4**: Chemical characterization of snow sampled in Ferrara (A) and Dolomites (B).

## 4. Conclusions

The difference between the two sampling area testify the different composition of the snow, which could collect concentrations of particulate matter from different sources: natural or anthropogenic.

In Ferrara, chloride was due to the addition of salt on the roads; in Dolomite was due to the anthropogenic activity of the chairlift.

Chloride, NOx and sulphate in Ferrara were higher than in Dolomite, this cause a higher pollution in the aquifer recharge of Ferrara during snowmelt.

High contamination of snow from traffic in Ferrara, which could facilitate deposition of metals near the main traffic roads.

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## Author Profile

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