

Metal Concentrations in Snow Samples in an Urban Area in the Po Valley

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Abstract

This study shows a chemical and morphological characterization of snow samples collected near crossroads of urban area of Ferrara and near the Technological College of University of Ferrara (Italy) during three important snowfalls. The field campaigns were carried out in the eastern part of Po Valley (Italy) in winter 2009-2010. The chemical composition of melted snow was compared with analyses of the same filtered samples of melted snow so as to give the composition of particles smaller than a few nm. The metal concentrations in the aerosol particles were analyzed with ICP-MS and IC methodologies, while the morphological features were described by SEM-EDS analyses. The results showed that snow samples were characterized by important amounts of allumo silicates with dimensions larger than 0.45 µm, from resuspension of the local soil, and IC analysis confirmed the anthropogenic pollution of the snow. Six main particles were classed and recognized: silica, carbonate, allumo silicate, sodium chloride and organic compounds, including biogenic materials and pollen (agricultural aerosols which are composed for 92% of single particles and for the remaining 8% of agglomerations of particles). We present here initial data on heavy metals in snow collected in Ferrara. They were obtained by analyzing fresh snow deposited during three snowfall events in December 2010, February and March 2011. The analyses were performed by the inductively coupled plasma mass spectrometry (ICP-MS), ion chromatography (IC) and scanning electron microscopy (SEM-EDS).

Keywords

Air Quality, Snow, SEM-EDS, IC, ICP-MS

1. Introduction

Studies of the chemical characterization of the snow to quantify the contribution of natural or anthropogenic

sources have increased in recent years [1]-[6].

In the last period, many of the Italian urban areas have recorded numerous and repeated events exceeding the limit concentrations of particulate (PM_{10}) for the environment and for the protection of human health [7] [8]. The high presence of particulate matter in the atmosphere produces effects on health [9] [10] and the deterioration of monuments [11] [12]. Epidemiological and environmental studies have shown that these negative effects are related with size and chemical composition of the particles [13] [14], especially with the presence of trace elements [15]. Trace elements occur naturally in the Earth's environment in low concentrations. However, human activity, such as industry, fuel combustion, metal smelting, agriculture, can result in concentrations of some elements greater than their natural background levels [16]. This can alter the rate at which elements are transported into the atmosphere within air masses, moving through ecosystems with adverse effects for the environment and human health depending upon their toxicity [15] [16].

Aerosol found in urban areas represents a mixture of primary particles emitted from several sources, which could be anthropogenic and/or natural.

Aerosol particles are important carriers of metals, some of which possess toxic properties. The major metals and trace elements in the aerosol may result from: crustal origin form resupsended dust could be Ca, Mg, Fe and AI [17] [18]; Sr could replace Ca in minerals like calcite and gypsum and Rb, Li and Cs can be constituent of aluminum silicate minerals [19]; Ni, Cr, Mn, Cu and Zn might have originated from industrial activities [18]. Ni associated with V could be associated to fuel use, in particular petroleum coke or fuel oil from cement and ceramics industries [20]-[22]; coal combustion processes could be Al, Fe and Ca [23]; K, Cu and Zn could be products of refuse incineration [24]; products of oil combustion include Mn, Fe and Pb [25] and products of refuse oil burning include Pb, Cd and V [26]-[28]; Pb, Fe and Zn could be products of vehicle exhausts [29]; Ca and Zn are often added to motor oil [30]; wood burning processes result in generation of K for domestic and commercial purposes [18] [31]; Cu, Zn, Sn and Sb could be products of tire and brake abrasion [21] [32]-[35]; the important uses of Cd are as alloys, in electroplating industry, in pigments, as stabilizers in polyvinyl plastics and in Ni-Cd batteries [36]; sodium chloride (NaCl) could be considered to be a pollutant from the de-icing agents used to secure the road condition [37].

It is important to know the metals and trace elements present in the atmosphere to better understand the sources of these pollutants and implement mitigation plans in the areas most subject to pollution, especially during winter season, in which weather conditions facilitate the stationing of pollutants.

Some researchers have shown that it is not negligible that the contaminants accumulated during the winter season can have an impact on natural resources during and after the melting of snow in spring [38]. In areas of permanent snow and glaciers, contaminants may be subject to deep burial resulting in inclusion in the layers of ice [39] [40]. Snowpits and ice cores retrieved from high-latitude/high-elevation glaciers are an ideal archive for documenting the modern and past composition of the atmospheric chemistry because they provide high-resolution, well-preserved, multiparameter archives of the atmospheric signature from remote areas worldwide. Previous investigations of trace elements in snow and ice from Greenland [41]-[44], the Canadian Arctic [45]-[47] and Antarctic [48]-[51] have enhanced our understanding of the current status of the atmosphere, past anthropogenic perturbations, and the response of these areas to changing emissions from industrial activities in Eurasia, North America and central Asia. In recent studies, the concentrations of trace elements were measured in the snow at high altitudes in eastern Tien Shan [52] [53], eastern Pamirs Mountains Muztagh Ata in northern China [54]-[56], on Mount Everest in the Himalayas [57]-[59], in the Scottish mountains [60], in America [61] and in the Italian Alps [61]-[73]. From all these studies it is understandable that the concentrations of some trace elements vary from area to area.

In regions with cold climatic conditions, snow surveying has become a major environmental research topic [74]-[77]. According to Engelhard *et al.* (2007) [78], snowflakes accumulate more pollutants from the atmosphere than raindrops because of their larger surface area and slower fall velocity.

Snow acts as a natural filter for various chemical elements and particles, especially those originating from anthropogenic activities (e.g., industry, road traffic) [79]. As suggested by Viskari *et al.* (1997) [80] snow appears to be a good collector of organic and inorganic pollutants from the atmosphere and can be used to monitor local airborne pollution from road traffic. Recently, deposition of polyaromatic hydrocarbons (PAH) [81], heavy metals [72] [82]-[88], platinum-group elements (Rh, Pt, Pd) [86] and concentrations of particles in different size fractions [73] [89] on snow have been reported.

Snow sampling can be applied to assess the load of anthropogenic emissions on local [86] [90] and regional

scales [85] [91].

Several studies have emphasized the importance of knowing the falling snow to recognize both the aerosol particles and the phases of volatile organic compounds from the atmosphere [92] [93]. These empirical and theoretical studies suggest that the snow has a great efficiency in both maintaining the particles that are 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 [69].

Results presented in this paper showed a chemical and morphological characterization of snow samples collected near crossroads of urban area of Ferrara and near the Technological College of University of Ferrara (Italy) during three important snowfalls and analyzed by SEM-EDS, ICP-MS and IC techniques. Snow was used as a sampling medium because it is an efficient scavenger of air pollutants, and usually remains on the ground for sampling after the event and snowmelt contaminates soil [6].

Several analytical techniques have been used in the past for the determination of trace elements in snow and ice [1] [94] and ICP-MS has emerged as a useful technique owing to its multi-element capability, high detection power and low sample consumption [95]. The analysis of the chemical composition of snow provides useful information on aerosol chemistry and long-range distribution patterns of anthropogenic substances emitted into the atmosphere [96]-[101]. Concentrations of dissolved elements in melted and filtered snow may be used to estimate deposition during winter [102]. However, total deposition can be seriously underestimated if particulates within the snow are omitted [85] [90].

The objectives of the work presented in this paper were: to analyze the metal concentration in snow collected near and far the crossroads in an urban area in Ferrara and in a rural area in Codigoro; to find out its correlation with the fine particle fraction that stay suspended in melted snow after filtration; to understand if anthropogenic or natural sources have a predominant role in snow pollution.

2. Methods

2.1. Field Site

Several measurements campaigns were carried out during winter 2009-2010 in the city of Ferrara (north-east of Italy) (**Figure 1**). The sampling areas are located in the east part of Emilia Romagna in the Po Valley. The first field site is an area in the city of Ferrara, inland (44°50'42"N - 11°37'5"E), instead of the second field site is an area in the suburb of Ferrara near the Adriatic Sea called Codigoro (44°50'0"N - 12°7'0"E).

Four sampling areas were selected in Ferrara: Sample 1 = overpass near a main street; Sample 2 = overpass behind the University; Sample 3 = parking; Sample 4 = garden. These areas were located near a main road, for this reason it can be possible to find elements of anthropogenic pollution from vehicular traffic.

Two sampling areas were selected in Codigoro: Sample 5 = urban area; Sample 6 = rural area.

The first area in Codigoro is an urban area, for this reason it can be possible to find elements of anthropogenic pollution from vehicular traffic, as in the samples collected in Ferrara. Instead of the second area in Codigoro is a rural area, and elements of anthropogenic sources it can be difficult to find.

In general, the soil is a silt clay soil, made from terrigenous sediments transported and deposited by the river



Figure 1. Map of the sampling site.

Po (Bianchini *et al.*, 2001) [103]. The rural area is far enough from the Adriatic Sea and therefore the contribution of particulate matter from sea spray is negligible.

2.2. Sampling

All the campaigns were carried out after and during the snowfall in December 2009, February 2010 and March 2010. The main goal was to investigate the spatial and temporal distribution of trace elements in an urban and rural area. The meteorological data (temperature, humidity, wind direction and wind velocity) were provided by ARPA Emilia Romagna weather station. For the city of Ferrara the nearest meteorological station is "Ferrara urban", which is 26 m u.s.l. (Lat: 44.832498 - Long: 11.621138 26). For Codigoro the nearest meteorological stations are in Copparo, which is 30 Km far from the sampling area (1 m u.s.l.; Lat: 44.916303 - Long: 11.821301) and in Volano, which is only 15 Km from the sampling area but it is located near the Adriatic Sea (1 m u.s.l.; Lat: 44.812868 - Long: 12.250367).

The sampling during the snowfall in December was carried out in the morning of the 21/12/2009, two days later the snowfall. The wind parameters had allowed speed of 2 m/s, high values of relative humidity 93%, low temperature (max: -5° C, min: -7° C) and pressure 1015 mb. The data of the monitoring station of ARPA Ferrara shown a high concentration of PM₁₀ and PM_{2,5} in day of the sampling (21 December 2009, Figure 3). In Ferrara PM₁₀ = 79 µg/m³ and PM_{2,5} = 56 µg/m³ (Ferrara CorsoIsonzo monitoring station far 1.8 Km from the sampling site in Ferrara); near Codigoro PM₁₀ = 55 µg/m³ and PM_{2,5} = 45 µg/m³ (Gherardi monitoring station far 15 Km from Codigoro).

The sampling during the snowfall in February was carried out in the morning of the day 01/02/2010. The value of wind speed was 3 m/s. High values of relative humidity 71% and low temperatures (max: 2°C, min: -7°C) and pressure 1013 mb. The data of the monitoring station of ARPA Ferrara shown a low concentration of PM₁₀ and PM_{2,5} in day of the sampling (01 February 2010, **Figure 3**). In Ferrara PM₁₀ = 48 µg/m³ and PM_{2,5} = 35 µg/m³; in suburb PM₁₀ = 37 µg/m³ and PM_{2,5} = 33 µg/m³.

The sampling during the snowfall in March was carried out in the morning of the day 10/03/2010. The value of wind speed was 9 m/s. High values of relative humidity 91% and low temperatures (max 1°C, min 0°C) and pressure 1010 mb. The data of the monitoring station of ARPA Ferrara showed a low concentration of PM₁₀ and PM_{2,5} in day of the sampling (10 March 2010, **Figure 3**). In Ferrara PM₁₀ = 22 μ g/m³ and PM_{2,5} = 13 μ g/m³; in suburb PM₁₀ and PM_{2,5} not detected.

The backward trajectories (software online NOAA HYSPLIT MODEL – GDAS Meteorological Data) shown that the wind direction was from North in the first two sampling and from the east during the thirty sampling (Figure 2(a) 21/12/2009, Figure 2(b) 01/02/2010, Figure 2(c) 10/03/2010).

The instruments used for sampling were simple plastic tins, previously cleaned with MilliQ[®] water, with double-sealed cap.

The graphs in Figure 3 showed the concentrations of PM_{10} and $PM_{2.5}$ ($\mu g/m^3$) in Ferrara and Codigoro before and after the sampling days (ARPA Emilia Romagna).

Only the samples in December 2009 were collected during a high pollution event, in which the contributions of PM_{10} and $PM_{2.5}$ exceed the limit value (50 µg/m³ - D.M. 2 aprile 2002, n.60) in Ferrara (PM_{10} and $PM_{2.5}$) and in Codigoro only for PM_{10} .

The concentrations of PM_{10} and $PM_{2.5}$ during the snow event in February were lower the limit value (Figure **3(b)**), because the snow event started the day before the sampling (31 January 2010) but with a mixture of snow and rain. This could have reduced the concentrations of particulate matter in the atmosphere. The snow mixed with rain melted in contact with the ground dispersing the collected particulate, which was present in high concentration before the snow event. During the last snow event, March 2010, the concentrations of PM_{10} and $PM_{2.5}$ were already under the limit value before the sampling (Figure 3(c)).

3. Analysis

After collection, the snow samples were transported in a refrigerated cooler to UNIFE laboratory in Ferrara and stored under refrigeration until microscopy and chemical analysis was performed [104].

3.1. SEM-EDS Analysis

The snow samples were used for SEM-EDS analysis to characterize the shape and morphology and the elemental



NOAA HYSPLIT MODEL Backward trajectories ending at 0000 UTC 10 Mar 10 GDAS Meteorological Data



Figure 2. Images of backward trajectories (72 hours) representative the direction of the winds during the sampling campaigns: 21/12/2009 (a), 01/02/2010 (b), 10/03/2010 (c).







Figure 3. PM_{10} and $PM_{2.5}$ concentration in the monitoring station near Ferrara (C. so Isonzo) and Codigoro (Gherardi) during the snow events. (a) December 2009, (b) February 2010, (c) March 2010.

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 particles were investigated in high resolution mode (up to 20.000X) with a working voltage of 20 kV which correspond to the detection limit of 1 µm 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 [105]. 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 [106]. EDS technique is able to characterize the chemical composition of particles whose diameter is greater than 1 micron [107]. The Scanning Electron Microscopy is a technique employed in numerous atmospherically studies [104] [107]-[112]. SEM-EDS measurements were performed on an adhesive support. Portions of the substrate 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.

3.2. ICP-MS Analysis

Chemical analysis has carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Samples analysis has been performed with a Thermo Electron Corporation Xeries spectrometer, with a collision/reaction cell (CCT^{*ED*}) for the reduction/exclusion of main polyatomic and isobaric interferences. This technique is suitable for revealing in solutions most of the elements present in the periodic table. Results are expressed as a concentration in $\mu g/m^3$. In the fine tuning of the procedure for the samples treatment for ICP-MS analysis the samples were prepared with a solution of standard (Rh - Re 100 ppb). Two different kinds of samples were prepared for each samples of snow, one represented the solution sampled, and one represented the solution filtered with a filter 0.45 μ m porosity, to analyze only the fine particles. All samples were analyzed by ICP-MS to determine the major, minor and trace elements. The samples collected were dissolved by acid digestion in a hotplate open system in different steps with HF, HNO₃ and H₂O₂. The Limits of Detection of this technique is the minimum significant concentration. This analysis allows to recognize the geochemical fingerprint of the snow and to provide markers to refer the local origin and to identify anomalies related to the contributions of transboundary particles.

3.3. IC Analysis

For the IC analysis we used the ion chromatograph Dionex ICS2000, which uses of an eluent of carbonate-bicarbonate. 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, 100cc of each snow solution samples were injected in the instrument and analyzed.

4. Results and Discussions

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

For each sample, high-resolution images of particles were obtained by SEM regulating the vacuum inside the instrument chamber. Several distinct particle shapes were observed on substrate, and they can be classified in four distinct categories: square particles (Figure 4(a)), rounded particles (Figure 4(b)), amorphous particles (Figure 4(c)), agglomerations of multiple amorphous particles (Figure 4(d)) [104]. The majority of particles were classified as amorphous particles (~60%), less as square particles (~20), rounded particles (~12%) and a minority as agglomerations of particles (~8%).

The 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 [113]. The chemical composition of the analyzed particles can be divided in two main categories: the first category of particles contains inorganic compounds, like silica (Figure 4(a)), carbonate (Figure 4(e)), allumo silicate (Figure 4(c)), amphibole (Figure 4(f)), ferrous particle (Figure 4(g)),



Figure 4. Images of representative particle shapes: square particles (a), round particle (b), amorphous particle (c) and (g), agglomerate (d), scalenohedral/rhombohedral (e), amphibole (f).

micrometeorite (Figure 4(b)); the second category of particles contains smaller organic compounds, including biogenic materials and pollens.

The concentration of organic particles observed by SEM-EDS is not abundant (less than 5%), respect the inorganic fraction (~95%). These qualitative results allow comparing the chemical composition of the aerosol sampled by the snowfall. The SEM-EDS measurements also showed that particulate matter was dominated by particles with diameters greater than 2.5 μ m.

Carbonates, silica and clay mineral were originated from soil erosion and its resuspension and they had the typical morphology of crustal mineral: carbonate crystalline (rhombohedral and scalenohedral morphology), allumo silicate lamellar, angular or rounded silica. The particles with original morphology indicate that the sources are local, while the particles with rounded morphology suggest that the particles travelled and their angular morphology was eroded by wind or snow.

Figure 5 shows the chemical composition of particles analyzed by SEM-EDS. In all samples allumo silicate is the most abundant component of the inorganic fraction, followed by NaCl, silica, carbonate and only a minority were organic materials.

In December samples, the clay mineral particles were prevalent. This lamellar morphology suggested a local source. Few quartz and calcite particles were observed. The rhombohedra and scalenohedra morphology of calcite particles suggested that they were formed through chemical and physical processes in the presence of water, so called: a chemical precipitation source.

In February and March samples, the inorganic particles were prevalent clay minerals with a lamellar morphology produced from local sources. Few quartz with square morphology, calcium carbonate particles and ferrous amorphous particles were also observed. Figure 4(b) shows typically rounded particles that could be a micro meteorite [114] [115]. The low presence of organic particles observed in all samples of different snow events were characterized by crushed pollen, paradoxically these pollens are typical of arid environment.

4.2. Chemical Composition by ICP-MS Technique

The snow samples were analyzed by ICP-MS. For sampling preparation see [73].

Li - Be - B - Cr - Co - Ni - Ga - As - Rb - Mo - Ag - Cd - Sb - Sn - Hg - Tl - Bi - U were under the detection limit, that indicates low concentration of metals. The precision of the measurements, in terms of their repeatability, was determined on snow samplescollected in Ferrara. The standard deviations of each trace elements determined in the sample (%) are: Al 0.3, Fe 0.5, V 0.5, Mn 0.4, Cu 0.3, Zn 9, Se 0.4, Te 0.5, Pb 0.2, Ba 0.4, Sr 0.5, Ca 51, Mg 7, K 4, Na 25.

Chemical analysis and particles size analysis were obtained by analyzing the content of filtered samples. The filtered used was a PTFE filter with 0.45 µm porosity.

Figure 6 shows the chemical composition of particles analyzed by ICP-MS. The graphs show the relationship between the filtered solution (filtered) and the real solution (suspended) for the main elements and metals analyzed by ICP-MS of the three snow events: December (A), February (B) and March (C).

Some elements are below the limit of detection (<0.0001 ppm) in the filtered solution.





Figure 6. Chemical composition of particles analyzed by ICP-MS. Relationship between filtered and suspended: December (a), February (b) and March (c).

The elements under the limit value 1 represent soluble particles or particles with dimension under 0.45 μ m (porosity of the filter). The difference between filtered and suspended indicates the size of the particles: ratio < 1 represents coarse size; ratio > 1 represents particles with size <0.45 µm and/or elements in solution.

Figure 6 shows that concentration of the snow of December 2009 is more enriched in cations compared to the last of March 2010.

The concentration of Na found at all sampling sites was due to the fact that sodium chloride had been used as de-icing agent on the roads [116].

Some samples show high concentrations of metals represented by the low ratio for the elements Iron and Aluminum, which tend to form insoluble hydroxides. Iron is represented by a ratio filtrate/suspended ≤ 1 , in almost samples, especially in the snow of December 2009 and February 2010. In the snow of March 2010 the ratio filtrate/suspended is major than 1 (samples C2 and C4, **Figure 6(c)**), probably due to the presence of bivalent Iron partially soluble. The Aluminum concentration showed the same trend of the Iron. The Aluminum ratio filtrate/suspended is major than 1 in some samples collected distant main road (sample A2 of December 2009 - **Figure 6(a)**, sample B6 in February 2010 - **Figure 6(b)**; samples C2, C3 and C6 in March 2010 - **Figure 6(c)**). In general, the Aluminum is the element that changes more, in some samples is in solution but not in other. It is important to better understand the behavior of Aluminum, to know if it could be a pollutant that could create damage to groundwater. Ferrara is an area where the aquifer recharge is given by the rains, if the snow is polluted, when it melts and recharges aquifers, pollutes the water.

The high concentration of Zinc in some samples confirms the anthropogenic pollution, especially in the sample A1 of December 2009, which was collected near a main road. From literature, Zinc enrichment in the solid and liquid formations is an indicator of pollution [117].

Some researchers have founded that the correlation between suspended solid and chemical element decrease with the increase of the particle size [6] [118] [119].

Our results of heavy metal concentrations are in agreement with those reported by [2] [116] [120]. They have found that heavy metals concentration of Pb, Cu, Cd, Zn, Al, Mg and Fe increase with the increase of the particle size, especially in snow samples exposed to urban traffic.

Figure 6 shows the correlation found between the concentration of elements mainly originating from anthropogenic sources (Fe, Zn and Al) and the fine particles, especially in the snowfall of December and February.

Table 1 shows the total ratio between filtered and suspended of the samples collected in Ferrara in the three snow events, to know the anthropogenic contribution from vehicular traffic. The samples collected in Codigoro not appear, because they weren't collected in December.

Samples 1 and 2 were collected near main street and were more polluted than samples 3 and 4. In these two samples (3 and 4) the ratio was major than 1 in all the snow events. This indicates a lower contribution from vehicular traffic.

Figure 7 shows metal concentration in snow samples at different locations analysed by ICP-MS. The data are obtained by averaging the results of sampling in December, February and March. Some of the elements are below the detection limit: Fe at one location (6) and Pb at one location (5), instead of Ca, Na, K, and Cu have very low concentrations, near the detection limit (Ca and Na in the samples 2, 4, 5, 6; K in the samples 2 and 6; Cu in the samples 6). The highest concentration of Na in the sample 1 confirmed the fact that sodium chloride had been used as de-icing agent on the road. It is important to remember that sample 1 was collected near the main road of the sampling area [6].

Гab	le 1.	Total	ratio	between	the	filtered	snow	solution	and	the	original	snow	solution	of	the
sam	ples	collec	ted in	Ferrara a	inal	ysed by	ICP-N	MS.							

Comple	December	February	March filt/susp		
Sample	filt/susp	filt/susp			
1	0.84	0.50	0.93		
2	0.58	0.30	0.90		
3	1.08	2.19	2.16		
4	3.74	2.07	1.60		

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Figure 7. Metal concentration in snow samples at different locations analysed by ICP-MS.

The concentrations of Ca is probably due to contribution from mineral particles comprising carbonate (as in **Figure 4(e)** analysed by SEM-EDS). The higher concentration of Ca in the samples 1 (near the main road) confirms the use of de-icing agent on road. It is know that Ca is an impurity of de-icing salt [116].

Mn is higher in the samples collected near the main road (1 and 5). This is probably due to the fact that Mn has benne used as an additive to enhance vehicle performance [121].

Al, Cu, Fe, Ni, Mn and Pb represent pollution from anthropogenic activity.

Correlations

Correlation analysis was performed to estimate the relationship between selected metals (Al, Fe, V, Mn, Cu, Zn, Se, Te, Pb, Ba, Sr, Ca, Mg, K) against each other. **Table 2** show the correlation coefficients calculated for filtered solution in the three different snowfall (A = December 2009; B = February 2010; C = March 2010). Instead of **Table 3** show the correlation coefficients calculated for suspended solution in the three different snow-fall (A = December 2009; B = February 2010; C = March 2010).

 Table 2. Correlation coefficient for the measured parameters for suspended solution in December 2009, February 2010,

 March 2010.

		Fe	V	Mn	Cu	Zn	Se	Те	Ph	Ra	Sr	Ca	Μσ	к	Na
	Δ1	0.412	0.378	0.581	0.947	-0.426	nd	nd	0.644	0.491	0.588	0.0.569	0.581	0.591	0.576
	Бо	0.412	0.078	0.001	0.747	-0.900	n.d.	n.d.	1 000	1.000	0.084	0.086	0.084	0.083	0.976
	v		0.970	0.960	0.506	-0.940	n.u.	n.d.	0.022	0.945	0.954	0.950	0.956	0.954	0.056
	v Mn			0.900	0.500	-0.071	n.u.	n.u.	0.922	0.945	1.000	1.000	1.000	1.000	1.000
	Cu				0.030	-0.971	n.u.	n.u.	0.992	0.960	0.626	0.610	0.621	0.620	0.622
_						-0.446	n.a.	n.a.	0.001	0.515	0.030	0.019	0.031	0.039	0.625
600	Zn						n.a.	n.a.	-0.958	-0.997	-0.972	-0.977	-0.974	-0.971	-0.976
oer2	Se							n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
emł	Те								n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dec	Pb									0.975	0.993	0.990	0.992	0.994	0.991
Ţ	Ba										0.987	0.990	0.988	0.987	0.990
DEI	Sr											1.000	1.000	1.000	1.000
EN	Ca												1.000	1.000	1.000
JSP	Mg													1.000	1.000
SI	K	0.470	0.740	0.004	0.040	0.050		0.000	1 000	0.057	0.067	0.007	0.000	0.000	1.000
	AI	0.470	0.742	0.994	-0.249	-0.353	n.d.	-0.282	1.000	0.957	0.967	0.986	-0.998	0.990	0.780
	re v		0.940	0.575	0.165	0.913	n.d.	-0.062	n.a.	0.707	0.537	0.376	-0.519	-1.000	0.401
	V M			0.357	-0.505	0.009	n.a.	0.308	0.866	0.459	0.554	0.385	-0.307	0.462	0.562
	MIN Cu				-0.142	-0.519	n.a.	-0.209	0.800	0.945	-0.454	-0.207	-0.881	0.907	-0.504
0	Cu 7n					-0.398	n.u.	-0.818	-0.594	0.500	-0.434	-0.397	-0.615	-0.181	-0.304
201	So						n.u.	0.928 n.d	0.594	0.590 n.d	0.028	0.170 n.d	0.015 n.d	0.502 n.d	0.184 n.d
ary	Т							n.u.	-0.722	0.680	0.030	-0.046	-0.821	-0.220	n.u. 0.403
pru	Ph								0.722	1.000	0.922	0.710	1 000	0.220	-0.954
-Fe	Ba									1.000	0.969	0.921	-0.952	0.962	0.237
ď	Sr										01202	0.964	-0.970	0.908	0.377
IQ	Ca												-0.926	0.928	0.183
PE	Mg													-0.806	-0.392
SUS	ĸ														-0.060
•1	Al	n.d.	n.d.	0.077	0.972	0.559	n.d.	-0.366	-1.000	n.d.	n.d.	-0.156	0.701	n.d.	-0.139
	Fe		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	\mathbf{V}			n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mn				0.832	0.026	n.d.	0.842	n.d.	n.d.	n.d.	-0.392	0.858	n.d.	0.665
	Cu					0.593	n.d.	-0.325	n.d.	n.d.	n.d.	-0.699	0.720	n.d.	0.832
	Zn						n.d.	-0.269	-1.000	n.d.	n.d.	-0.815	-0.134	n.d.	0.034
010	Se							n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ch 2	Te								1.000	n.d.	n.d.	-0.159	0.686	n.d.	0.676
Iarc	Pb									n.d.	n.d.	1.000	1.000	n.d.	n.d.
2 	Ba										n.d.	n.d.	n.d.	n.d.	n.d.
ED	Sr											n.d.	n.d.	n.d.	n.d.
UN	Ca												0.318	n.d.	-0.315
SPE	Mg													n.d.	0.858
SU	К														n.d.

			• •			Ũ		
Date	Location	Sample	FI ⁻	Cl⁻		Br⁻	NO ₃	\mathbf{SO}_{4}^{2-}
23/12/09	Fe: overpass front	A1	0.0109	<u>6243.1</u>	n.d.	1.0449	3.4993	<u>113.41</u>
23/12/09	Fe: overpass back	A2	0.0360	1.3083	n.d.	n.d.	3.2622	1.9267
23/12/09	Fe: parking	A3	0.0301	<u>148.85</u>	n.d.	n.d.	2.1404	4.2348
23/12/09	Fe: garden	A4	0.0306	1.5692	0.0359	n.d.	4.1996	3.0752
01/02/10	Fe: overpass front	B1	0.0148	3.8236	n.d.	n.d.	3.1449	0.4542
01/02/10	Fe: overpass back	B2	0.0176	0.5308	0.0314	n.d.	3.1747	0.4762
01/02/10	Fe: parking	B3	0.0363	0.9935	0.1131	n.d.	3.1403	0.7509
01/02/10	Fe: garden	B4	0.0371	0.8268	n.d.	n.d.	6.3607	0.6445
01/02/10	Codigoro: urban	B5	0.0269	2.0895	0.0112	n.d.	1.9847	0.7573
01/02/10	Codigoro: suburban	B6	0.0007	1.3404	n.d.	n.d.	1.5169	0.4464
10/03/10	Fe: overpass front	C1	0.0005	0.6059	n.d.	n.d.	0.5945	1.4595
10/03/10	Fe: overpass back	C2	0.0008	0.7031	n.d.	n.d.	0.5728	1.6401
10/03/10	Fe: parking	C3	0.0009	0.5535	n.d.	n.d.	0.6011	1.4232
10/03/10	Fe: garden	C4	0.0002	0.5614	n.d.	n.d.	0.6220	1.5041
10/03/10	Codigoro: urban	C5	0.0003	1.4129	n.d.	n.d.	0.2037	0.4763
10/03/10	Codigoro: suburban	C6	0.0004	0.1865	0.0545	n.d.	0.2168	0.3710

Table 3. Analysis results (mg/L) by ion chromatography of samples taken in the Ferrara and Codigoro in winter 2009/2010.

Table 2 shows a strange correlation between Na concentration and Zn concentration. In the snowfall of December the correlation was negative [6], instead of in the snowfall of February and March the correlation was positive [122].

The analysis showed a strong positive correlation between Na and Ca both for the snowfall of December ($R^2 = 0.99$) and February, This suggest the same sources, and it is probably a consequences of the fact that salt used as a de-icing agent contain calcium impurities [6].

Table 2 shows a strange correlation between Na concentration and K concentration. In the snowfall of December the correlation was positive ($R^2 = 0.99$), instead of in the snowfall of February the correlation was negative. The salt used as a de-icing agent probably contains potassium as impurities [6].

Some metals from anthropogenic sources are strongly correlated. Positive correlations were found between Al and Cu in the snowfall of December ($R^2 = 0.87$) and March ($R^2 = 0.94$), instead of negative correlation in the snowfall of February. The opposite was for Fe and Zn, in the snowfall of December a negative correlation, instead of positive correlation in the snowfall of February ($R^2 = 0.17$).

A positive correlation was observed between Ca and K, thus indicating that these elements originate from the same sources (December $R^2 = 0.99$ and February $R^2 = 0.85$). The same positive correlation was observed between Ca and Pb.

4.3. Chemical Composition by IC Technique

In some samples, nitrates and bromides are under the detection limit (LOD), which represents the minimum concentration of analita detectable (**Table 3**). Phosphates under the detection limit. The symbol "n.d." means "value comparable with white value". The concentrations of the fluorides analyzed are low in all samples.

Table 3 shows that some elements (chloride, nitrates and sulfates) are relatively high, especially in the snowfall of December 2009. This can be explained by the sampling carried out two days after the snowfall. Probably the snow had already absorbed part of smog of the vehicular traffic. This high contribution can therefore be related to anthropogenic sources.

The high concentration of chlorides found at all sampling sites, especially near the main road in the snowfall

of December, was due to the fact that sodium chloride had been used as de-icing agent on the roads (confirmed by the high concentration of sodium analyzed by ICP-MS).

The presence of nitrates and sulphates may indicate mineral acidity of the snow sample. These ions, in fact, are formed in the atmosphere by oxidation and subsequent reaction with water of the oxides of nitrogen (NOx) and sulfur dioxide (SO₂). The presence of nitrogen oxides into the atmosphere is mainly due to the presence of sulfuric and sulphurous anhydrides by the combustion of the gas turbine central and/or incinerators. In recent years, the sulfate ion has had a strong reduction in Western countries, in which people use sulfur-free petrol, while in countries without environmental legislation this ion continues to be injected. For this reason, the presence of the sulfate ion may be indicative of cross-border contributions (SO₂) formed during the combustion of coal and fuel oils.

In Ferrara city, the sulphates are brought down by reducing the amount of fuel with the introduction of geothermal energy and using gasoline without sulfur. The abnormal presence of sulphate ions could be an indicator of transboundary sources from foreign countries, where this is not adopted.

From the snowfall of December to March, the ion concentrations decrease, especially in the city of Ferrara:

- from 0.03 mg/L to 0.0006 mg/L for fluorides;
- from 3.3 mg/L to 0.6 mg/L for nitrates;
- from hundreds of mg/L to 0.5 mg/L for chlorides;
- from hundreds of mg/L to 1.5 mg/L for sulphates.
 Even in Codigoro, the concentration decrease from February to March.

5. Conclusions

In this project, issues of sampling and analytical procedures related to snow samples with very low concentrations and subject to easy contamination have been addressed [73].

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.

SEM-EDS analysis of snow samples shows that the particles are single or agglomerate.

The major components of snow are the inorganic particles as shown by SEM-EDS measurements, which 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 μ m). This indicates a resuspension of local soil.

The presence of chloride, nitrate and sulphate is important and it is related with anthropogenic sources (smog of the vehicular traffic). Data were obtained from the analysis in IC.

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.

This study suggests that there is a direct contamination of snow in the Po Valley from the activity of vehicular traffic and therefore an important deposit of trace elements is close to the busiest streets.

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.

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