Atmospheric Pollution Research

The composition of PM_1 and $PM_{2.5}$ samples, metals and their water soluble fractions in the Bologna area (Italy)

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ABSTRACT

In this study the metal composition of PM_1 and $PM_{2.5}$ samples collected in the surroundings of a municipal incinerator located in a suburban–farming area, less than 10 km away from Northeast of Bologna (Italy) was investigated. Seven out of eight monitoring stations were installed in a domain of 8x9 km^2 around the incinerator plant; the eighth station was placed inside the urban area of Bologna. The coordinates of four monitoring stations were selected on the basis of a preliminary study by using a dispersion model. Eleven metals (Al, Sb, As, Cd, Fe, Mn, Ni, Pb, Cu, V, Zn) were quantified in both the filter acid–digests and in the water extracts. The $PM_{2.5}$ collected in all the sites of the domain were highly correlated with exception of the urban site. The daily average metal concentrations in summer were 1.84% and 1.14% for $PM_{2.5}$ and PM_1 respectively, indicating that fine particles are less enriched in metals. Fe, Al and Zn were the most abundant elements, and they represented about the 80% of the total amount of the analyzed ones. The average water soluble metal compositions were 0.71% and 0.41% for $PM_{2.5}$ and PM_1 respectively. In the sites of the suburban–farming studied area the Principal Component Analysis (PCA) and Cluster Analysis revealed differences between water soluble metal compositions in PM_1 and $PM_{2.5}$. The urban sites were characterized by lower total and soluble metals contents than the other $PM_{2.5}$ stations installed around the incinerator plant. However, no noticeable difference in the concentrations of metals in the particulate matter between the sites chosen as maxima of incinerator emissions and the control sites was observed.

Keywords: $PM_{2.5}$, PM_1, water soluble metals, air quality, waste incinerator

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1. Introduction

In recent decades, due to the demographic growth and industrialization of advanced societies, waste production has consequentially increased. At present, various technologies including landfills, resource recycling and incineration processes have been applied to manage waste disposal. Among them incineration is one of most widespread. Nevertheless, during incineration treatment, a small amount of pollutants can be emitted in atmosphere and this can represent a threat to living organisms including humans. It is well known that incineration, like every combustion process, can generate fine particles and, for a given particle composition, the finest ones are the most harmful. In particular PM_1, that is particulate with an aerodynamic diameter of less than 1 μm, is able to penetrate into the human respiratory and circulatory systems, resulting in adverse health effects (Chow et al., 2006; Pope III and Dockery, 2006).

From the point of view of particles chemical composition, the exhaust gases of incinerators may contain many potentially harmful substances (Besombes et al., 2001), including metals (Chang et al., 2000; NRC, 2000; Hu et al., 2003). Furthermore, the presence of transition metals in PM can induce pro–inflammatory responses in human airways through their ability to form reactive oxygen species via Fenton or Fenton–like reactions (Prophete et al., 2006; Verma et al., 2010). In particular, water–soluble metals have been shown to be the key drivers of oxidants generation (Knaapen et al., 2002; Cheung et al., 2012).

These aspects cause a high perception of health risk related to the presence of incinerators, especially for local communities living nearby these plants. Although, it has been proved that nowadays Municipal Waste Incinerators (MWIs) represent a minor source of anthropogenic aerosol emissions compared to fossil fuel power plants and vehicle emissions (U.S. EPA, 2000; Cheng et al., 2009). This is especially true for efficient plants since the number and the chemical composition of the particles generated from MWIs are strongly affected by various operating parameters of the plant such as the combustion temperatures, the composition of the waste feed, the kind of filters installed. In such a contest, to assess the impact of incinerator (Donnelly, 1992), it is important to frame the emission of the plant with respect to the other possible sources (Ntziachristos et al., 2007).

The present work deals with the composition of PM_1 and $PM_{2.5}$ collected near a MWI located in the Emilia–Romagna (ER) region and exactly in the Bologna area. It should be mentioned that, in this geographical area, high levels of ambient particulate matter, often exceeding air quality limits, are encountered. Consequently, a number of studies dealing with Po Valley air monitoring have already been reported (Lonati et al., 2005; Vecchi et al., 2007). However, despite the number and quality of chemical data, most of these studies focused on the pollution properties and source apportionment of PM_{10} and the effects due to incinerator have only been investigated pertly. To acquire new knowledge about the air quality in the proximity of incinerators, the local ER Administration promoted a wide research project called MONITER

(http://www.moniter.it). In this work, which is a part of the MONITER project, the daily evolution of the metal content of aerosol particulate as a function of particle size and seasonal conditions is reported, with the aim of differentiating patterns of aerosol composition driven by local meteorology or local sources. Specifically, this study includes the following four aspects: (1) a comparative analysis of the temporal variation of the PM_1 and $PM_{2.5}$ in different functional areas in Bologna; (2) a comparative analysis of levels of 11 elements in PM_1 and $PM_{2.5}$, focusing on the pollutant properties of heavy metals; (3) the seasonal composition of PM_1 and $PM_{2.5}$; (4) the comparison of the levels of the water soluble metals in different locations of the domain.

2. Experimental

2.1. Sampling locations

The plant under study is located in a suburban–farming area, less than 10 km away from northeast of Bologna (Italy), in the Po Valley, which is a well–known polluted critical area. The incinerator plant has the following main features: 600 tons day^{-1} of incinerating capacity, two 80–m–high stacks and BAT (Best Available Technique) purification devices.

Seven out of eight monitoring stations were installed in a domain of 8x9 km^2 around the plant; the eighth station (MGA) was placed inside the urban area of Bologna, in a site used for urban background measurements by ARPA–ER (Emilia–Romagna Regional Agency for Prevention and Environment).

A preliminary study with ADMS–Urban (Cerc, Cambridge, UK) dispersion model was performed to select monitoring station coordinates, using PM_{10} emissions as the pollutant tracer. The details of the simulation are described elsewhere (Bonafe and Rossi, 2011). A first station (MXW) representative of maximum deposition of plant emissions, in the averaged meteorological winter conditions, was placed in the east side, not too far from the incinerator, along the wind main–direction axis. A second station (CTW), used as a "control" of the first one, was chosen in a position representing both the minimum deposition of plant emission and whole extra–incinerator emissions, according to the PM_{10} simulation. A second maximum (MXS) was placed on the west side of the plant on the same wind axis, in the averaged meteorological summer conditions and a second control (CTS) was chosen to represent both the minimum deposition of plant emission and whole extra–incinerator emissions, according to the PM_{10} simulation in summer. The other stations were placed to represent different air conditions in the domain:

- MXD: The site is in a position of high traffic, it receives emissions from nearby freeways and railroad. Due anthropic emission sources, like vehicular traffic, domestic heating, railways and industrial activities it was also indicated as the most polluted site in the preliminary simulation study.
- MND: The site is surrounded by agricultural land. There are no major roadways in the vicinity of the site and nearby traffic emissions are negligible. It represents the minimum of the domain of the pollution due to industrial and traffic sources, as evidenced by the preliminary simulation study.
- CAS in a suburban area. It is close to CTS, but it is located in an inhabited area. It was chosen to compare the PM composition of the control site CTS to that of a suburban area characterized by anthropic emission sources.

The location of the monitored sites is reported in Figure 1.

2.2. Sampling methods

The meteorological conditions of the Po Valley are characterized by weak circulation of air masses in the winter period, and alternation of hot–dry and humid days in summer

(Larsen et al., 2012). On the contrary, in spring and autumn, atmosphere with frequent unstable to neutral conditions is encountered. Consequently, extremely high PM concentrations are usually recorded in summer and winter, and especially during the cold season. Therefore, the domain was monitored in the seasons that can lead to acute episodes. In particular, the sampling campaign was conducted from the 3rd of June to the 24th of July 2008 (herein referred as summer and notated with S) and from the 14th of January to the 12th of March 2009 (herein referred as winter and notated as W). In both seasons, samples were collected daily; sampling collection continued for about 8 weeks. During the moni-toring periods, some meteorologycal parameters were recorded, i.e. temperature, pressure, relative humidity, wind velocity and direction, mixing height (H_{mix}) (see Table S1 in the Supporting Material, SM). Meteorological parameters (temperature, pressure, relative humidity, solar radiation, rainfall, wind speed and direction) were available from ARPA–ER meteorological station (ARPA–ER, 2008; ARPA–ER, 2009). The summer campaign was meteorologically characterized by light winds. The wind roses of the campaign periods are reported in Figure 2a.

The simulation of the incinerator impact in the studied domain was performed based on PM_{10} emitted in the recorded meteorological conditions (see Figure 2b). The details of the simulation are reported elsewhere (Bonafe and Rossi, 2011).

Identical units, each consisting of a Skypost PM TRC Tecora (Tecora, Paris, France) were set up in the sampling sites to collect daily $PM_{2.5}$ and PM_1 on quartz fiber filters 47 mm diameter (Whatman, Maidstone, UK). The height of the sampler head was placed 2 m above to the ground level. PM_1 samples were collected solely in MXW, MXD and CTW (herein notated as MXW–1, MXD–1 and CTW–1, respectively) whereas $PM_{2.5}$ samples in these three sites were notated as MXW–2.5, MXD–2.5 and CTW–2.5, respectively. The data referring to the other sites, where solely the $PM_{2.5}$ was monitored, were notated with the site label. After gravimetry, chemical analysis was carried out on a sampling periods of 48 h, by joining filters of two subsequent days, for all sites. The analyses were carried out on a 24 h basis for the MXW site. The frequency of the analysis of this site was increased since the simulation indicated MXW as representative of maximum deposition of plant emissions, in the averaged meteorological conditions (see Figure 2b). For all the other sites, each daily filter was cut in 4 portions: two quarters of two subsequent days were pooled together to be used for chemical analysis of water soluble constituents, while the others to be used for analytes that are not water soluble.

The total number of samples was 309 for the summer campaign and 345 for the winter and eleven metals (Al, Sb, As, Cd, Fe, Mn, Ni, Pb, Cu, V, Zn) were quantified on every sample.
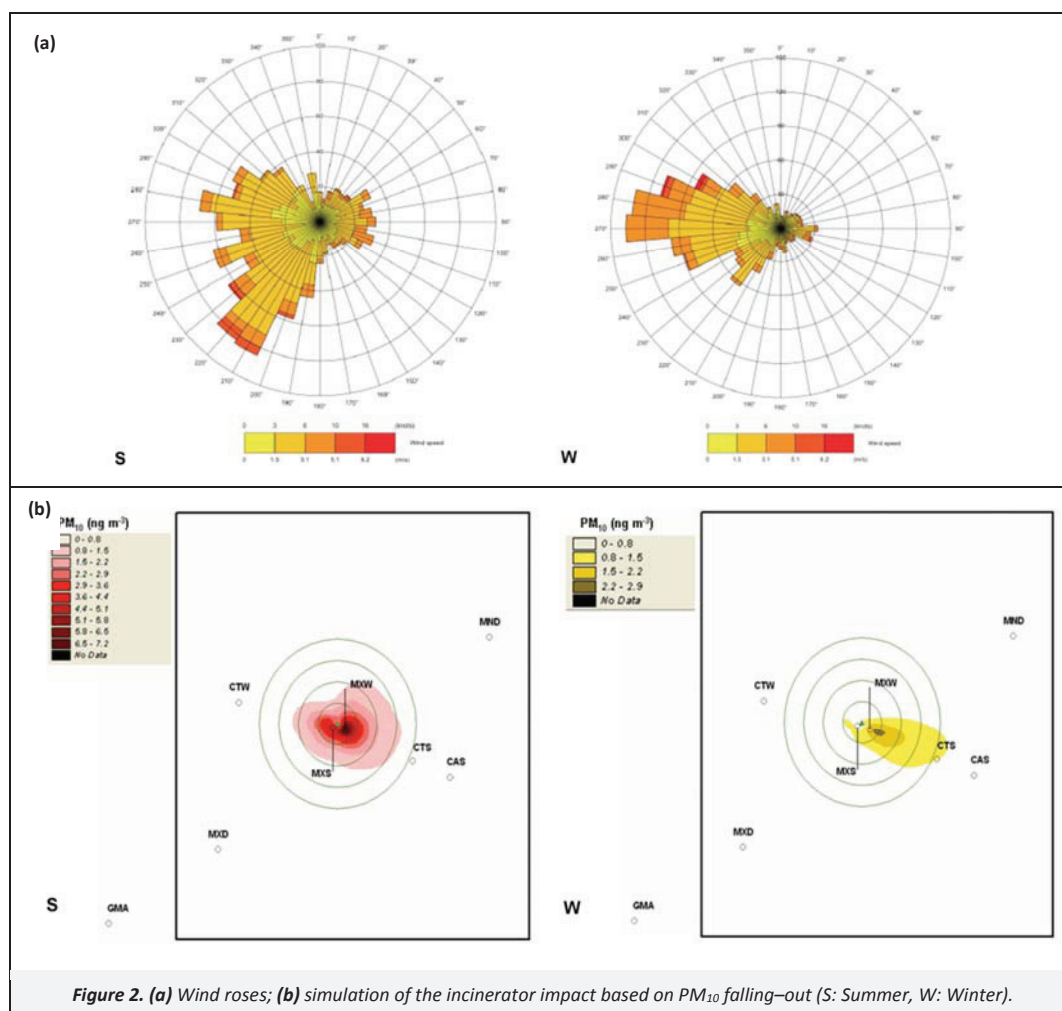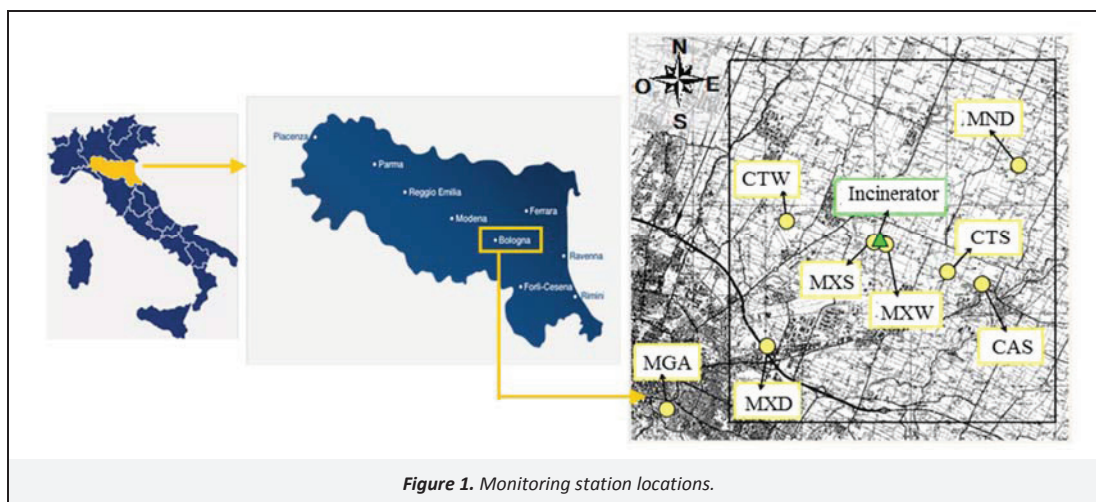
2.3. Chemical analysis

PM_1 and $PM_{2.5}$ mass concentrations were determined by weighing the filters before and after the ambient sampling under controlled temperature (21±2 °C) and relative humidity (30±5%), using a microbalance Mettler (Mettler–Toledo, Columbus, OH, USA) with a resolution of 0.01 mg.

The total metal content was determined on samples mineralized through microwave digestion, using nitric acid and hydrogen peroxide, according to UNI EN 14902 2005 method (European Standard, 2005). The solutions obtained were analyzed through inductively coupled plasma–mass spectrometry technique (ICP–MS) with an Agilent 7700 (Agilent Technologies, Santa Clara, CA, USA) instrument.

For the determination of water soluble elements, the filters were extracted in 11 mL of deionized water (DI, Milli–Q, >18 MΩ, Millipore, Bedford, MA, USA) via sonication in a water bath for

20 min. These extracts were then filtered using 0.2 μm PTFE (polytetrafluoroethylene) filters (Puradisc, Whatman, USA). The filtered extracts for metals were acidified by adding nitric acid (high–purity trace metal grade, 2% w/v final solution), consistent with current protocols (Henshaw et al., 1989). The levels of water soluble metals were quantified using Graphite Furnace Atomic Absorption Spectroscopy (GF–AAS) with a PerkinElmer Analyst 800 (PerkinElmer, Waltham, MA, USA) instrument equipped with Zeeman background correction.

Blank concentrations for the filters, including the contribution from filter handling during sampling, were measured and used to correct the concentrations measured in the dissolved filters. The blank contribution to the total concentration was regularly under 20% for all the elements. In some sites, Zn concentrations in the acid digest were below the detection limit (LOD) in some days, whereas they were above the LOD in the water extracted, due to different detection limits of the two methods.

Figure 1. *Monitoring station locations.*

Figure 2. (a) *Wind roses;* **(b)** *simulation of the incinerator impact based on PM$_{10}$ falling–out (S: Summer, W: Winter).*

The detection limits were calculated from the calibration curves and their values fell in the range 1.9×10^{-5}–3.6×10^{-2} µg m^{-3} for ICP–MS and 1×10^{-5}–3.2×10^{-3} µg m^{-3} for GF–AAS. In the computation, the average values were calculated assuming the concentration equal to 1/2 of LOD if the concentration was below the instrument detection limit (Lampa et al., 2012). Accuracy and precision (repeatability) were measured using Standard Urban Dust Reference Material (NIST, SRM–1648).

3. Results and Discussion

3.1. Particle mass concentrations

Seasonal differences were observed in the particle matter concentrations, with PM$_1$ and PM$_{2.5}$ highest concentrations during winter (see Figure 3) The average concentrations were 15.52 ± 0.31 µg m^{-3} and 19.68 ± 0.78 µg m^{-3} for PM$_1$ and PM$_{2.5}$ respectively, during the summer period (June–July), 22.38 ± 0.59 µg m^{-3} and 33.7 ± 1.9 µg m^{-3} and for PM$_1$ and PM$_{2.5}$ respectively, during the winter period (January–March). These data agree well with other studies previously reported in this area (Bigi and Ghermandi, 2014). In a recent publication (Bernetti et al., 2010) it has been reported that the SNAP (Selected Nomenclature for Air Pollution) sectors responsible for particulate matter are few, with road transport (SNAP sector 7) and commercial, institutional and residential combustion plants (SNAP sector 2) being the main sources of PM$_{2.5}$.

The PM$_{2.5}$ data measured during week–days were not significantly different from those of weekends, only a moderate decrease in PM$_{2.5}$ concentrations (about 10%) was observed during the weekends. PM$_{2.5}$ in the Po Valley has been shown to have a fraction of secondary aerosol in the range of 32 and 47% in Bologna (Matta et al., 2003). The contribution from re–suspended dust to PM$_{2.5}$ is expected to be smaller in comparison to larger PM fraction (Amato et al., 2009). For these reasons a weekly cycle in PM$_{2.5}$ is generally not observed.

The PM$_{2.5}$ concentrations measured in the eight sites during both the campaigns were highly correlated (see Table 1). In particular, a correlation coefficient higher than 0.887 was calculated for the winter PM$_{2.5}$ data, whereas the correlation was generally lower for the summer data, with a minimum value of 0.713. Furthermore, PM$_1$ and PM$_{2.5}$ in co–located measurements were highly correlated with a minimum value of 0.779 in summer and 0.922 in winter.

It could be supposed that when the meteorological conditions favor the mixing of the lower atmosphere, the concentration levels are quite uniform in the whole domain, regardless of the PM sources: usually in winter, atmospheric dilution was lower due to stagnation conditions, resulting in the accumulation of air pollutants. In fact, the mixing height in winter was significantly lower than during the summer campaign (see the SM, Table S1).

A good correlation was also observed between PM$_{2.5}$ collected in the high traffic site (MXD) and in the rural site (MND). Since these sites are located at the opposite ends of the domain, this finding indicates that the sources of the major constituents of PM$_{2.5}$ were similar. Spatial homogeneity, in the particulate matter amount in the Po valley, has been found also for sampling sites located in proximity of an industrial area (Canepari et al., 2014).

3.2. Total metal concentrations

The sum of all elements constitutes a small fraction of particulate matter (about 1.8% of PM$_{2.5}$ in summer). It was similar to those found in Toronto (Celo and Dabek–Zlotorzynska, 2010) and in Milan (Marcazzan et al., 2001) equal to 1.2 and 1.4%, respectively.
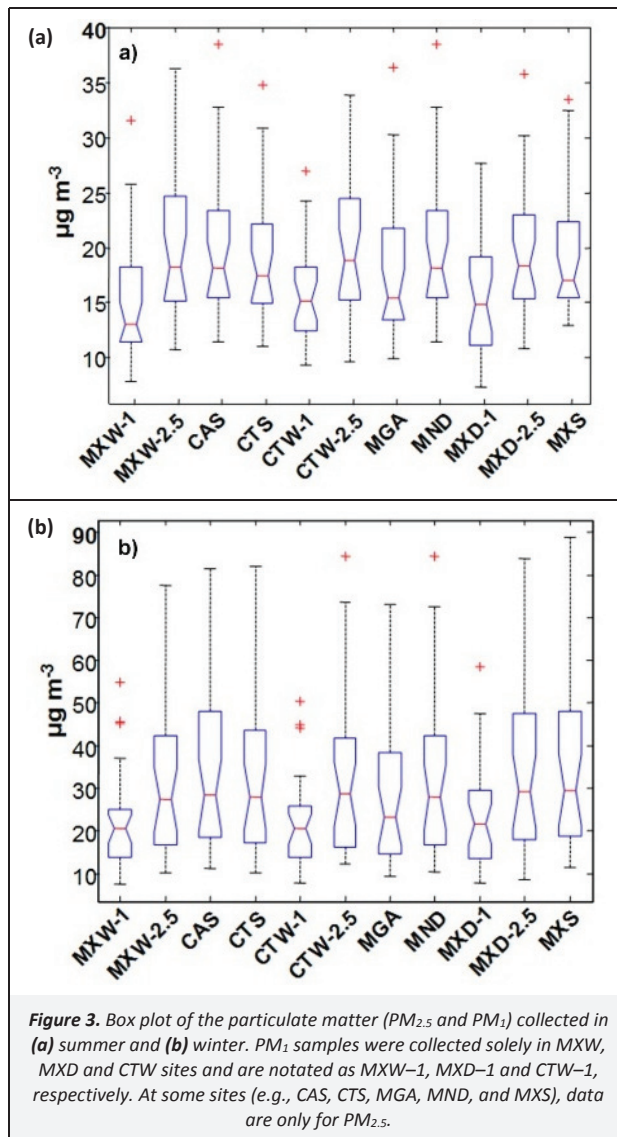
Figure 3. Box plot of the particulate matter (PM$_{2.5}$ and PM$_1$) collected in **(a)** summer and **(b)** winter. PM$_1$ samples were collected solely in MXW, MXD and CTW sites and are notated as MXW–1, MXD–1 and CTW–1, respectively. At some sites (e.g., CAS, CTS, MGA, MND, and MXS), data are only for PM$_{2.5}$.

The main metal components of PM$_{2.5}$ were Al and Fe, in fact, they accounted for about 60–80% of the metal concentrations in summer. A significant contribution of these elements to the particulate collected in Phoenix, Arizona, USA, was evidenced previously (Kegler et al., 2001). Moreover, the mean concentrations of As, Cd, Cu, Fe, Mn, Ni, Pb, Sb and V in PM$_{2.5}$ were in good agreement (see the SM, Table S2), with those recently found in the Po Valley (Canepari et al., 2014). The winter data showed a similar trend. Zn was abundant in both the fractions of the particulate matter, and its concentration was in agreement (see the SM, Table S2) with that reported for Po Valley aerosol (about 20 and 30 ng m^{-3} in PM$_1$ and PM$_{2.5}$ respectively) as reported by Perrone et al. (2010).

The concentrations of elements in the PM$_{2.5}$ collected at different locations of the domain were similar. This finding suggests a reasonable uniformity in the contribution of the different metal sources to PM$_{2.5}$. To investigate this hypothesis, the correlation between the metal content of PM$_{2.5}$ collected at MXD and MND sites (see Sampling Locations) was considered. A good correlation for a major constituents like Fe was observed ($R^2 = 0.849$, $p = 2 \times 10^{-8}$, $n = 28$), on the contrary, for a trace element like As, the correlation was less significant ($R^2 = 0.443$, $p = 0.023$, $n = 28$).

Table 1. Matrix of correlation coefficients of PM at different sites in summer and winter

MXW–1	MXW–2.5	CAS	CTS	CTW–1	CTW–2.5	MGA	MND	MXD–1	MXD–2.5	MXS
					Summer					
1.0000	0.8763	0.8152	0.7904	0.6962	0.7637	0.8513	0.7599	0.7931	0.7279	0.6917
	1.0000	0.7760	0.7820	0.5633	0.7192	0.8253	0.7807	0.6626	0.7853	0.6666
		1.0000	0.8835	0.7660	0.7803	0.9235	0.8218	0.8175	0.8207	0.8262
			1.0000	0.7054	0.8780	0.9021	0.9238	0.7668	0.8554	0.7767
				1.0000	0.7783	0.7647	0.6656	0.8691	0.7429	0.7471
					1.0000	0.8525	0.8853	0.8209	0.8728	0.7129
						1.0000	0.8660	0.8506	0.8378	0.7686
							1.0000	0.7788	0.8654	0.7510
								1.0000	0.7795	0.7198
									1.0000	0.8003
										1.0000
					Winter					
1.0000	0.9367	0.9055	0.9398	0.9649	0.9405	0.8427	0.9379	0.9520	0.8886	0.9420
	1.0000	0.9869	0.9883	0.9062	0.9879	0.9643	0.9835	0.9463	0.9799	0.9911
		1.0000	0.9864	0.8715	0.9752	0.9726	0.9774	0.9170	0.9777	0.9853
			1.0000	0.9113	0.9880	0.9548	0.9857	0.9499	0.9717	0.9921
				1.0000	0.9224	0.8123	0.9145	0.9378	0.8596	0.9138
					1.0000	0.9481	0.9812	0.9471	0.9691	0.9884
						1.0000	0.9462	0.8842	0.9823	0.9550
							1.0000	0.9429	0.9640	0.9855
								1.0000	0.9332	0.9633
									1.0000	0.9787
										1.0000

The metal contents in both the PM modes were compared for the three sites where both $PM_{2.5}$ and PM_1 were monitored (i.e. MXW, MXD and CTW). In Figure S1 (see the SM) the concentrations of the metals normalized by PM are reported. Some elements such as As and Al showed a preferential partition into the PM_1 fraction, whereas Fe, Mn and Cu tend to accumulate in the coarse mode. The other elements studied showed a similar distribution between the two size fractions. It has been reported that the elements associated to road traffic abrasion products (mainly from tires and brakes) such as Cu, Mn, and Fe (Schauer et al., 2006; Wahlin et al., 2006) are preferentially distributed in the coarse mode (68–95% in the fraction $PM_{10–1}$). These elements possibly derive from topsoil erosion and dust resuspension (Perrino et al., 2014). On the contrary, for trace elements, it has been reported that elements associated with fossil fuel combustion (V and Ni) or other high temperature industrial processes (As, Cd and Pb) mostly occur in fine particles (50–82% in the PM_1 fraction).

To investigate the extent of the contribution of anthropogenic emissions to atmospheric elemental levels, the enrichment factor (EF) was estimated as the ratio of each element's abundance in PM samples to its average abundance in the upper continental crust (UCC), by selecting Al as the reference element. The EF for any element X relative to crustal material is defined by:

$$EF_X = \left(X/Y\right)_{air} / \left(X/Y\right)_{crust} \tag{1}$$

where, EF_X is the enrichment factor of X, Y is a reference element for crustal material (Al, see above), $(X/Y)_{air}$ is the concentration ratio of X to Y in the aerosol sample, and $(X/Y)_{crust}$ is the average concentration ratio of X to Y in the crust.

The UCC composition was retrieved from Mason (1966). Typically, elements with an EF greater than 10 are considered to derive mostly from anthropogenic sources, whereas elements with an EF approaching 1 are considered mainly of crustal origin (Birmili et al., 2006). In Figures 4a and 4b, it can be seen a remarkable enrichment for Cu, Zn, Pb and Sb in $PM_{2.5}$ indicating their possible anthropogenic origin. A similar trend was observed also for PM_1 (see Figures 4c and 4d). Incinerator plants are potential sources of these elements. However these metals can be originated also by other combustion sources and in particular from vehicular emissions and fossil combustion (Lough et al., 2005; Schauer et al., 2006). Similarly, Ni was enriched in both PM modes, but to a lesser extent, suggesting its mainly anthropogenic sources such as oil combustion, vehicular emissions and industrial activities (Marcazzan et al., 2001; Lough et al., 2005).

3.3. Water solubility of individual metals

The water soluble metal (WSM) components of particles have been shown to be one of the main responsible for PM–induced toxicity (Knaapen et al., 2002; Cheung et al., 2012). The averaged WSM concentration of the studied elements, calculated on all sampling sites, constitutes solely the 0.71% of the total $PM_{2.5}$ mass in summer and it decreases in winter (0.41%).

The most soluble metals in the $PM_{2.5}$ fraction were Zn, Cd, As and Sb, the least soluble were Al and Fe, while elements with medium solubility (10–40%) were Mn, Cu and Pb (see Figure 5a). For some elements (Cd, Sb and Pb) a size–dependent solubility was detected: in particular, solubility was higher in the fine size range (see Figure 5b).

This behavior can be due to diverse sources of metal compounds characterized by different solubilities. Moreover, the chemical and dimension fractionation of the aerosol can increase the selectivity of elements as source tracers (Canepari et al., 2014). In general, anthropogenic sources give rise to particulate matter containing a higher proportion of WSM. This is especially true for

the particulate generated from high–temperature combustion processes. On the contrary, metals from crustal sources, such as from alumino–silicate samples, are generally weakly soluble (Desboeufs et al., 2005). It can also be noticed that the elements having high water solubility were also characterized by a large EF values (see Figures 4 and 5), thus confirming the contribution of anthropic sources for these elements. The water soluble fractions determined for $PM_{2.5}$ (see Figure 5a) were in good agreement with those reported in a previous study carried out in Birmingham, UK, particularly for Fe, Mn, Cu, Ni (<0.1, ~0.3, ~0.25, ~0.25, respectively) (Birmili et al., 2006). Principal component analysis (PCA) was performed on the data of metal concentrations and their soluble fractions (see Sections 3.4 and 3.5).
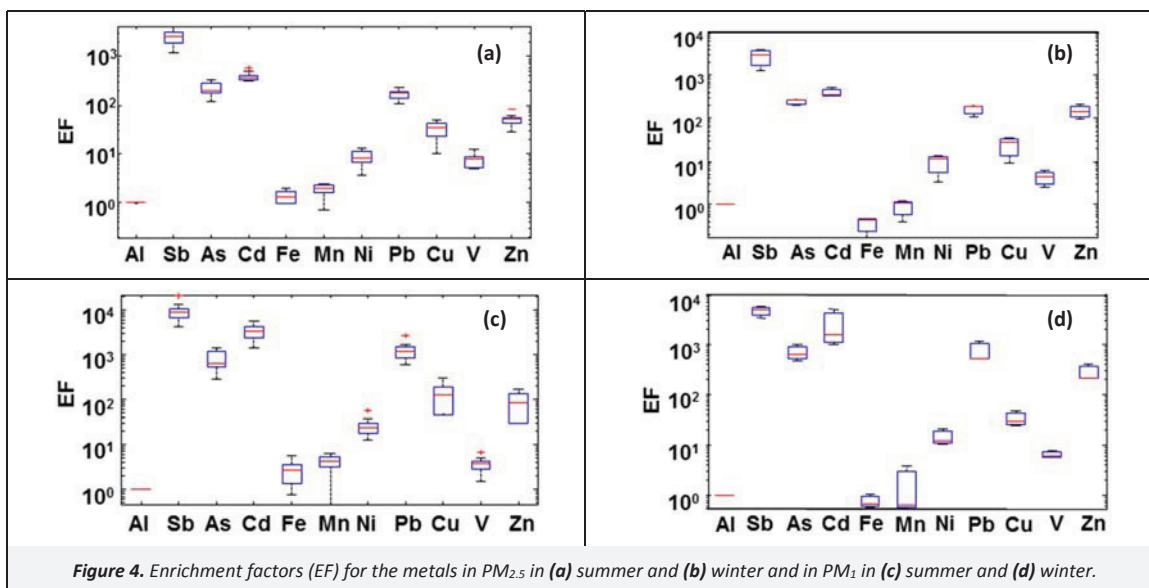
3.4. Seasonal variation

The concentration ($\mu g\ m^{-3}$) data of the two campaigns were divided by the particulate matter concentration in $\mu g\ m^{-3}$ to obtain data in $\mu g\ \mu g^{-1}$ unit. These transformed data were analyzed by PCA and the corresponding 3D plots are shown in Figures S2 and S3 (see the SM). The scores of the total metals (see Figure S2) are clearly separated into two clusters along PC1 corresponding to winter (W) and summer (S) data respectively. A similar trend was also observed for the metal soluble fraction (see the SM, Figure S3). The sum of the metal concentrations in $\mu g\ m^{-3}$ in summer and winter were similar to each other, but, at the same time the quantity of particulate matter increases in the cold season, the result of combining these two effects was a reduction of the metal concentrations (in $\mu g\ \mu g^{-1}$), in the suspended solid collected in winter. The increase of particle concentration in winter was attributed to the frequent and persistent thermal inversions at ground level during the cold season in the Po Valley (Marcazzan et al., 2001; Daher et al., 2012). Possibly, it was also due to increased accumulation of particles of the nucleation mode due to the high relative humidity of the atmosphere, as well as to the less efficient removal of particles of the finest size fraction by rains. The loadings of PC1 with respect to the PM composition indicated that the concentrations of trace elements for unit PM weight in winter was lower than in summer with exception of Cd and Pb. Vehicles emissions, industrial processes and resuspended road dust could be ascribed as Pb sources whereas Cd mainly originates from metal smelting and combustion processes (Vecchi et al., 2004; Schauer et al., 2006). A higher concentration of anthropogenic elements in the cold season has already been reported (Marcazzan et al., 2001; Bell et al., 2007). Cold/warm concentration ratios higher than 1 were observed in the 0.8–1.3 μm size fraction for some metals such Cd (3.6), Cu (3.7), Pb (2.8) On the contrary, concentration ratios below

1 were observed for Fe, Cu and Mn suggesting preferable air intake of these metals during the dry period of the year, probably from road resuspended dust (Samara and Voutsa, 2005). The different chemical composition of the two size classes (i.e. PM_1 and $PM_{2.5}$) are discussed in the following section.

3.5. Multivariate data analysis

PCA and cluster analysis (CA) were performed on average chemical compositional data obtained from the two campaigns separately (expressed as $\mu g\ \mu g^{-1}$, see above), in order to minimize the effects due to seasonal variation. In this work, solely the PCA of the WSM concentrations in PM_1 and $PM_{2.5}$ were considered.

Figure 6 shows the scores of WSM for the PM collected during summer and the variable loadings in the space of the first three principal components, which explain for more than 70% of the total variance. The first principal component (PC1) differentiates the PM_1 from $PM_{2.5}$. Since almost all variables have similar weights on the first PC, it can be hypothesized that this PC is related to the elemental concentration and not to the concentration of some specific metals; indeed, the two PM fractions (i.e. PM_1 and $PM_{2.5}$) differed in almost all metal concentrations, independently of the sampled site. Generally, the metal concentration for unit weight of particle matter was lower for the finest fraction as indicated from the low PC1 scores of PM_1. Among the $PM_{2.5}$, PC1 discriminates urban and suburban sites (MGA and CAS, respectively) from all the other ones, thus revealing that the content of soluble metals (especially Fe, Mn, Cu, Sb) in these two sites was lower than the average. The compositional differences of the urban sites are more evident in the PC2/PC3 scores and are related to a higher content of Zn and V than the average. This finding agrees well with the fact that MGA and CAS seem to be more influenced by traffic. In fact, MGA represents the urban background, so it is reasonable to suppose that traffic markers were found there, whereas the contributions due to industrial activities or fossil combustion processes were scarce. A previous study carried out in the same geographical area (Morselli et al., 2003) indicated fuel burning as a possible source of Zn and V, although it was mentioned that these metals could also derive from metallurgical activities, in particular those involving alloy steels. Finally, MGA is characterized by high PC3 loading, with a Ni water soluble content higher than the average. Ni has also been classified as a metal associated to vehicular traffic (Manoli et al., 2002). The sites of the suburban area around the incinerator have similar PC1 scores. This finding indicates that these sites showed a similar composition in water soluble metals.
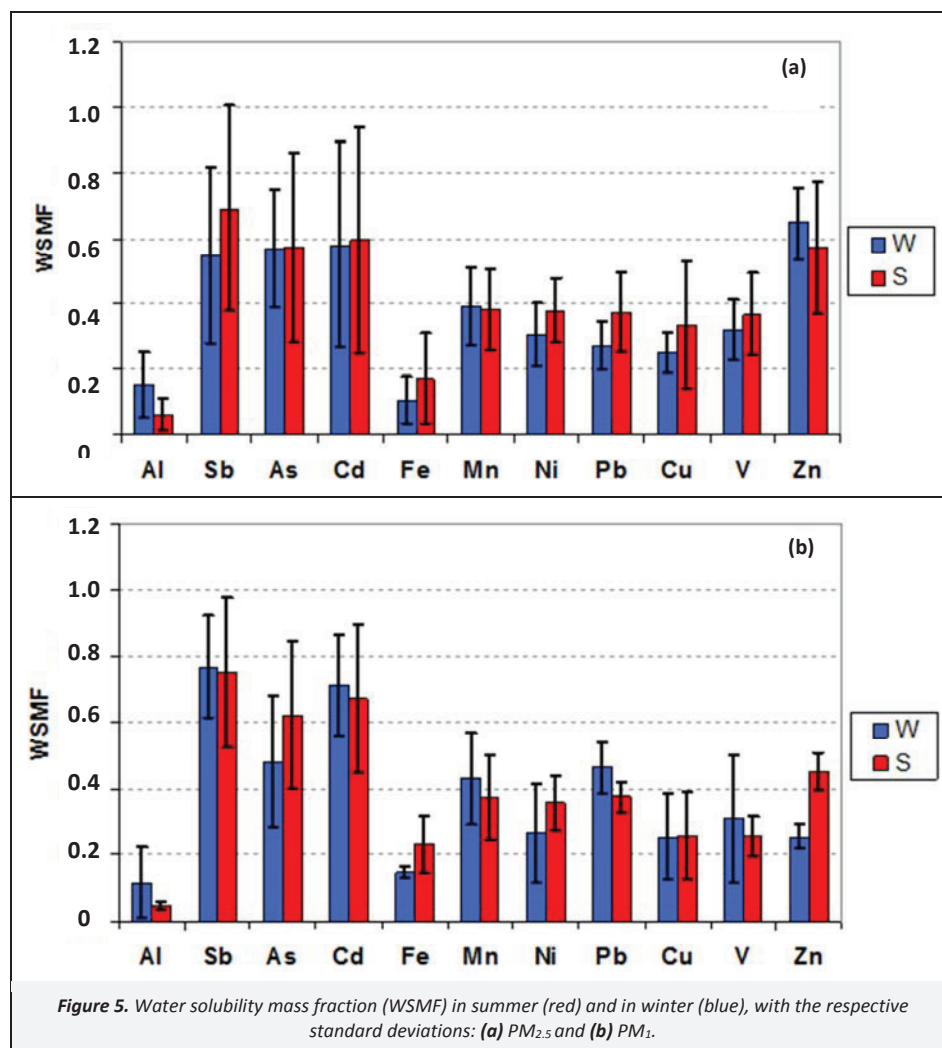

Figure 4. Enrichment factors (EF) for the metals in $PM_{2.5}$ in **(a)** summer and **(b)** winter and in PM_1 in **(c)** summer and **(d)** winter.

Figure 5. *Water solubility mass fraction (WSMF) in summer (red) and in winter (blue), with the respective standard deviations: **(a)** PM$_{2.5}$ and **(b)** PM$_1$.*

Figure 7 shows the scores and loading plots obtained by PCA for the samples collected during the cold season. The sites can be grouped into four clusters. Similarly to the data collected in summer, also in winter the PM$_1$ composition differed from that of PM$_{2.5}$. This difference is conditioned by the variables which mainly contribute to PC1, characterized by high positive loadings of Fe, Mn, Cu and high negative loadings of Ni and Pb. Therefore, in winter the fine particulate was enriched in elements which are characteristic of anthropic sources (Ni and Pb). This behavior is more evident for MXD–1 which differs from the others PM$_1$ in Cd and Zn concentrations (high positive loadings on PC3), indicating the presence of a variety of anthropic combustion sources impacting on this site. It can also be observed that the WSM in PM$_{2.5}$ had quite similar concentrations for all the sites, in fact they have similar weights on PC1.

However, the PM$_{2.5}$ can be divided into two clusters by PC2, which is characterized by high negative loadings for As, V, Cd and positive loading for Sb. Along PC2 the urban (MGA), the suburban (CAS), the summer falling–out maximum and its control (MXS and CTS respectively) sites are located in the positive semi–axis. The high traffic and the rural sites (MXD and MND respectively), the winter falling–out maximum and its control (MXW and CTW respectively) sites are located in the negative semi–axis. Therefore, in these last four sites, As, V and Cd concentrations higher than average have been found, possibly coming from industrial activities or combustion processes. To discriminate between the possible

sources, it should be considered that Morselli et al. (2003) ascribed Ni, Cd and V to industrial and manufacturing activities, which are widespread in the Bologna area. Among combustion processes, waste incinerator doesn't seem to be the main source of these soluble metals in the particles, since their contents in stack emissions were generally very low, in particular the As concentrations were below the detection limit (see Tables S4 and S5 in the SM). Therefore, it could be inferred that these elements mostly derived from industrial activities. In Figure 7, it can also be noticed that the scores of the sites of the maximum falling–out are close to those of their control sites. Therefore, it could be assessed that these two classes of sites exhibit compositional homogeneity of PM$_{2.5}$.

4. Conclusions

In this study the concentrations of 11 metals were measured in airborne PM$_{2.5}$ and PM$_1$ collected at 8 sampling sites around a municipal incinerator. The mass concentrations revealed greater PM amount collected in winter than in summer. A high correlation between the particulate matter in different sites of the domain and also between PM$_1$ and PM$_{2.5}$ in co–located sampling sites was observed. In winter, the correlation was higher than in summer, probably due to atmospheric stagnation conditions. Al and Fe were the most abundant metals while Zn, Cd and As were the elements with higher solubility in water.
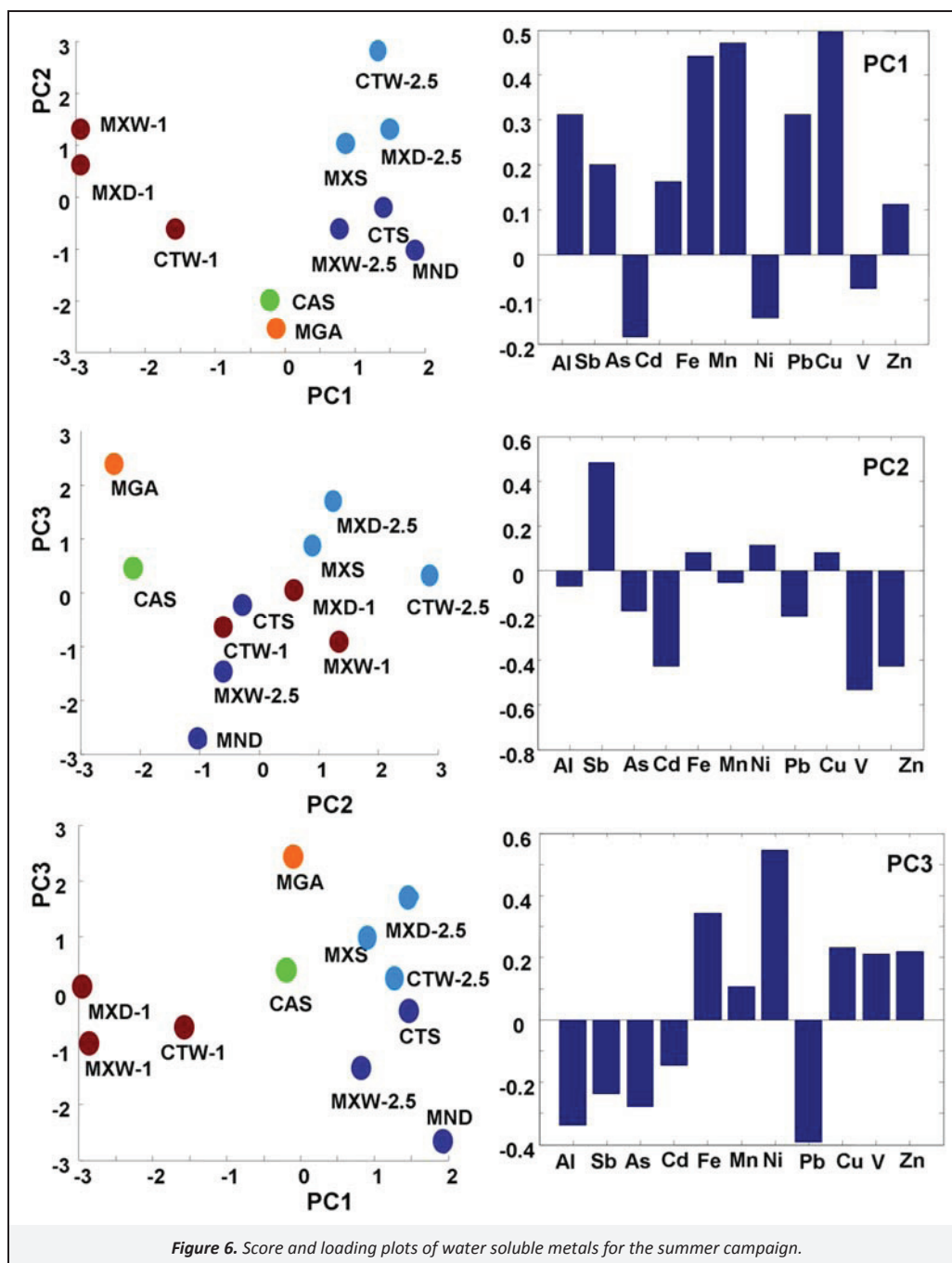
The enrichment factor confirmed that Al and Fe were partially of crustal origin, while the most soluble elements were attributed to anthropogenic sources.

PCA was performed on metals concentrations normalized by the PM amount. Both total content and the water–soluble fraction in PM collected in winter is statistically different from summer, especially for Cd and Pb concentrations. The PCA performed on the data obtained from the two campaigns separately showed that the chemical composition of PM_1 is different from that of $PM_{2.5}$. Generally, the metal concentration for unit weight of particle matter is lower in the fine fraction. For what concerns the coarser dimensional mode, no differences between the sites chosen as maxima of falling–out and their respective controls was observed.
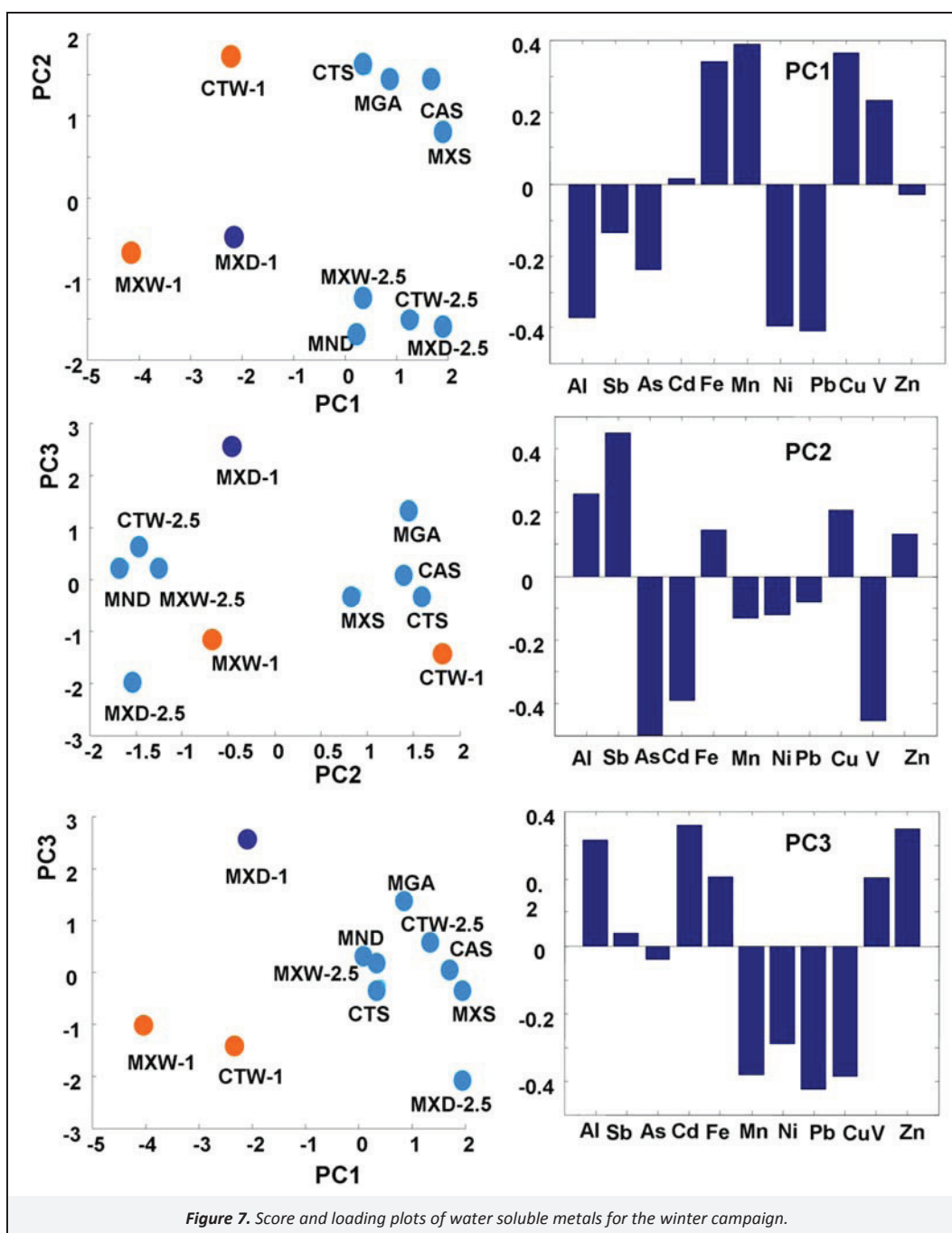
The urban MGA and the suburban sites CAS generally were characterized by lower total and soluble metals content than other $PM_{2.5}$ stations.

Acknowledgements

Figure 6. *Score and loading plots of water soluble metals for the summer campaign.*

Figure 7. *Score and loading plots of water soluble metals for the winter campaign.*

Supporting Material Available

Stack emissions (S1), Averaged meteorological data recorded at MXW site during the monitoring program (Table S1), Total metal concentrations (ng m^{-3}) in all sampling stations (Table S2), Stack emissions gravimetric data (Table S3), Stack emissions total metal concentrations (µg m^{-3}) in particulate matter, condensed phase and after each of the three bubblers (Table S4), Stack emissions of water soluble metal concentrations (µg m^{-3}) in the 3 aliquots of particulate matter (Table S5), Average metal concentrations in PM$_{2.5}$ and PM$_1$ monitored in winter (Figure S1), Scores plot and loadings plots of total metals during the whole sampling period (Figure S2), Scores plot and loadings plots of soluble metals during the whole sampling period (Figure S3). This information is available free of charge via the Internet at http://www.atmospolres.com.

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