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by

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Spatial distribution and potential sources of trace elements in PM_{10} monitored in urban and rural sites of Piedmont Region

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Abstract

The results on elemental composition of aerosol (PM_{10}) sampled during 2011 in Piedmont region (Italy) are interpreted using meteorological data, Enrichment Factors (EF), chemometric processing by Principal Component Analysis (PCA), Factor Analysis (FA) and Hierarchical Cluster Analysis (HCA).

Daily concentrations of about 30 elements were measured using HR-ICP-MS in five monitoring sites. A clear seasonal pattern, with higher concentrations in autumn and winter, was observed, particularly in the urban sites. Levels of As, Cd, Ni and Pb in most of the samples were within the limits imposed by the European legislation. Spatial differences in PM_{10} and metal concentrations were significant, with rural and urban sites showing different metal patterns, indicating different sources. K and Ca were used, respectively, as marker of biomass burning and industrial marker (cement plant); EFs showed that Ca was enriched just in one area and K was enriched only in the winter period considered and in some stations.

Data analysis through PCA, FA and HCA allowed us to identify correlations among the investigated elements and similarities between sampling sites in order to individuate specific emission sources, such as non-exhaust vehicle emission.

Keywords

Piedmont

Trace elements in PM_{10}

Spatial variability

Chemometric processing

Inductively coupled plasma-mass spectrometry

1. Introduction

Particulate matter pollution is nowadays one of the major problems in big cities, despite remarkable improvements have been made in terms of air quality over the last decades. PM_{10} (aerodynamic equivalent diameter lower than 10 μm) fraction is studied as carrier of many harmful trace metals (such as As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, V and Zn) into the human respiratory system (Brunekreef and Holgate, 2002; Dockery and Pope III, 1994). The association between PM and adverse health effects (Alessandrini et al., 2013; Dockery and Stone, 2007) had led to the Directive 1999/30/EC and, in recent years, to the Directive 2008/50/CE and to the Directive 2004/107/CE, that determined specific target values for the presence of PM_{10}, $PM_{2.5}$ and the concentrations of several chemical elements, namely arsenic, cadmium, nickel and lead, in PM_{10}.

In this study we determined about thirty elements, by high resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS), in airborne PM_{10} samples collected in 2011 at five sampling sites in Piedmont Region (Italy), three of them categorized as urban and two as rural stations.

Results of major, minor and trace element levels, as well as the comparison with previous data obtained in Turin and in some other cities in the Po valley, which is the most industrialised region in Italy, are reported.

We applied the most common chemometric techniques: Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), to evidence the spatial and seasonal variability in the chemical composition of Piedmont aerosol. This data treatment has permitted to confirm the great effectiveness even of the chemometric tools used by most of the scientific community.

Overall, we tried to identify and characterize the emission sources influencing particulate matter in a critical region like Piedmont, which presents very different environmental situations and is characterized by diverse industrial areas and districts. Although, Piedmont is the gateway to the Po valley, so far it has seldom been studied as a whole (Romanazzi et al., 2014; Malandrino et al., 2013; Casazza et al., 2013; Malandrino et al., 2013).

This study is the result of a cooperation between the University of Turin and the regional agency for the environmental protection (ARPA Piemonte).

2. Material and methods

2.1 The study area

Piedmont (Figure 1) is a large region located in the North-western part of Italy, surrounded on three sides by mountains. Its central part corresponds to the upper part of the Po valley. Due to its topography, as the Alps and the Apennines shield the valley, this area is characterised by adverse atmospheric dispersion conditions, especially during wintertime, when the mixing layer height is low and thermal inversion is frequent. Thus, prolonged periods with high pollution occur, during which air quality standard is exceeded, especially in cities and industrial zones: in Turin city centre, we had 134 exceedances of the daily average limit (50 $\mu g/m^3$) for PM_{10} mass (*D.Lgs. 155*, 2010) in 2011 (ARPA Piemonte, 2012).

Three of the investigated sampling sites are in the Turin area: one site, called TO1, is localised in the historical centre (Via della Consolata), mainly affected by vehicular traffic and heating emissions; the second one, called TO2, is in the northern out-skirts of the town, in an area of high vehicular traffic density, being close to an highway and subjected to various industrial emissions, since several plants (foundries, plastic material stamping, etc.) are present in its neighbourhood; the third one, called DR, is located in the small town of Druento, within a regional park, without any direct influence of urban activities and, hence, considered as a background station.

Two sampling sites are in the Cuneo province: one is close to Borgo San Dalmazzo, a small town with low traffic density and also few residential and industrial (e.g. cement plant) emission sources; the other one is in Saliceto (SA), a village on the border with Liguria region, with only residential influences and no specific emission sources. This site was chosen also in consideration of its proximity to a heavily polluted area caused by the presence of ACNA, a former chemical plant located in the village of Cengio, that polluted waters and soils of the valley until 1999; since 1998 the area of the plant is listed among national interest sites with a high environmental risk (Abollino et al., 2007; *Act n. 426*, 1998). As this area has undergone remediation, SA is now classified as rural background site by ARPA Piemonte.

2.2 Sampling and mass determination

Samples were collected daily for the whole year 2011 by ARPA Piemonte; among these 140 specimens were selected for this study: 28 samples per station, one week in February, May, August and November months, i.e. choosing a month for every season. We chose a week in which the daily amount of particulate was varying significantly, but with a weekly average comparable to the average recorded for the season. Our selection criterion has permitted us to compare days with a high and a low concentration of particulate and to provide information on the dominant sources of atmospheric aerosol in the investigated area, even if we cannot consider this selection as representative of the possible patterns of atmospheric pollutants in the whole year. Sampling was carried out using low-volume samplers (2.3 m^3/h) equipped with size-selective inlets: particles with d_{ae} < 10 µm (PM_{10}) were collected on quartz fibre filters with a total diameter of 47 mm and a diameter of the deposition area of 38 mm.

All filters have been analysed to determine the mass of particulate collected using a gravimetric technique according to MD 155/2010 (*D.Lgs. 155*, 2010).

2.3 Analytical method

Acid digestion (Milestone MLS-1200 Mega) was chosen as dissolution procedure. The filters were cut in two parts, which were separately weighed and treated, using a mixture of 2 ml of HNO_3 and 0.5 ml of H_2O_2, in PTFE bombs. The digestion program consisted in 5 heating steps of 5 minutes each, except for the first one that lasts 1 minute (at 250, 200, 350, 550, 250 W respectively). Nitric acid was purified by sub-boiling distillation and ultrapure H_2O_2 (30%, Sigma Aldrich) was used. Resulting solutions were filtered on cellulose filters (Whatman Grade 5) and diluted to 30 ml with Milli-Q (Millipore) ultrapure water (18.2 MΩ/cm).

The metal contents were determined using Thermo-Finnigan Element 2 high resolution ICP-MS. Mass resolution and isotope selection were optimized for each element to ensure resolution of spectral interferences and maximize sensitivity. A minimum of triplicate 180 s analyses when working at low resolution, and quadruplicate when working at medium resolution, was conducted on each sample following a 60 s uptake and stabilization period. After each sample the nebulizer system was rinsed for 2 min with 2% sub-boiling HNO_3, to eliminate carry-over. Sets of instrumental blanks and calibration verification checks were run at frequent intervals during the sequence.

Three unexposed backup filters were also analysed, using the same procedure as for the samples, and the calculated elemental concentrations were then subtracted from each sample.

NIST SRM 1648a (Urban Particulate Matter) was used to verify that analyte concentrations were within 20% of the expected values before proceeding with sample analysis. The metal recovery rates of certified elements were within 80% and 120% for all analytes, except Al, Ti, Cr, extractable completely only with HF. Finally, the relative standard deviations of the results were generally within 5%.

2.4 Chemometric tools

A statistical-chemometric elaboration was applied in order to identify the principal sources of pollution and to highlight similarities and differences between the five sampling sites. Between the several source apportionment techniques (Viana et al., 2008) we used Principal Component Analysis (PCA), Factor Analysis (FA) and Hierarchical Cluster Analysis (HCA), since these methods are largely known and used by most of the scientific community and do not require an a priori knowledge about sources.

PCA is a technique that reduces the number of dimensions, summarising a set of multivariate data in few linear combinations of the variables (called principal components), without a significant loss of information (Otto, 1999). Results of PCA can be plotted to simplify the interpretation of the positive and negative correlations among variables (in this case the elements determined in PM_{10}), and the valuation of the behaviour of objects (in this case PM_{10} samples). Factor analysis was used to explore the relationship between variables using a Varimax rotation procedure to maximise the explained variance.

HCA is an effective statistical method for the study of atmospheric aerosol composition, and can be used to confirm the groups of variables and samples obtained with PCA, identifying the groupings not well detectable with the latter, since HCA considers all the information contained in the data set, not only a part of it, as in PCA (Contini et al., 2010). The method groups data by similarity: objects with the maximum of similarity are arranged into a single group, or cluster, and the calculation is iteratively repeated.

Data elaboration was performed with XlStat 2013.2.04 and The Unscrambler X 10.2 software Package.

3. Results and discussion

3.1 PM_{10} concentration and chemical composition

The means and the ranges of concentrations for PM_{10} and analysed elements at each of the five sampling sites are shown in Table 1. The mean values for PM_{10} mass compare well with the mean values reported by ARPA Piemonte for 2011 (50, 59, 31, 29, 29 $\mu g/m^3$, respectively for TO1, TO2, DR, BSD, and SA stations), indicating the representativeness of the group of samples selected. Therefore we can discuss the data evaluating possible seasonal patterns and suggesting aerosol sources, taking into account that one week of sampling for season cannot be considered completely representative of the whole season. As expected the highest mean values occurred in Turin, as well as the maximal seasonal variability.

Concerning analyte concentrations, the highest levels were found for the soil-derived elements (e.g. Al, Ca, Fe and Mg), indicating the significant contribution of soil and resuspended mineral particles to atmospheric PM. Most analytes show a clear seasonal pattern (Fig.2) with higher concentrations in the cold season, behaviour observed also in previous works and by other researchers in Northern Italy (Malandrino et al., 2013; Marcazzan et al., 2001; Prodi et al., 2009). This pattern is particularly noticeable for the anthropogenic elements (e.g. Co, Cu, Pb and Zn) and in TO1 and TO2 sites. The most likely explanation for this behaviour is the different intensity of anthropogenic emissions in different parts of the year and, mainly, the typical Po valley meteo-climatic conditions. Indeed, in winter, severe and frequent thermal inversions and ground level fog cause the stagnation of air in the valley floors and, consequently, the accumulation of pollutants; this scenario is particularly evident where the atmospheric pollutants concentrations are higher, i.e. in Turin city.

If we divide the sampling days into two groups according to the PM_{10} concentration (high and low concentration), we find that the highest differences between the two sample sets are in TO1 and TO2 sites. It is interesting to note that, in Turin, percent variations are greater for geogenic elements (Mg, Al, Ti, Mn and Ce), whereas in the other sites this behavior is not observed. This might be due to a variation in the anthropogenic fraction of PM, particularly the resuspended soil dust could have varied, as a result of more frequent construction activities (e.g. railway bypass).

During the week chosen in February, there was a snow event between January 30th and February 1st, which allowed us to prove the homogeneous response of the elements: indeed we see a clear reduction of all the concentrations (greater than 75% for most of them) in the first day of the snowfall (January 30th) and a progressive increase in the following days (Fig.3). In this study we do not have a direct comparison with a rain event, but this strong reduction could be due to the fact that snow is a better scavenger of aerosol particles than rain per equivalent water content (Lei and Wania, 2004; Paramonov et al., 2011).

To make conjectures about the possible sources of particulate matter, we need to understand if there are significant differences between the five sites: we applied a one-way ANOVA (Tukey HSD test; $p = 0.05$) on all the element concentrations and, excluding Ti, clearly of geogenic origin in all stations, we found significant differences between the sites for all the elements investigated. The two urban sampling stations (TO1 and TO2) are statistically different from all other sites for all the elements (excluding Ca and K).

Splitting the samples by season, Mg, Al, Ti, Ce, La, Sb and Cr have not showed statistically relevant differences between the seasonal periods examined, vice versa all the other elements are characterized by average concentrations in autumn and winter significantly different from those in spring and summer, showing a possible seasonal cycle, probably conditioned by human inputs.

Considering the target values of As, Cd and Ni, reported in the European legislation (respectively 6, 5 and 20 ng/m^3), and the limit value for Pb imposed by the European legislation (0.5 µg/m^3)(*D.Lgs. 155*, 2010), it is significant noting that the concentrations of these elements in almost all samples are one order of magnitude lower than these values; the exception is Ni that, in some DR samples, exceeds its target value (16 and 18 November 2011, 249 and 140 ng/m^3 respectively), probably because of a contamination of the samples during collection or weighing. However high concentrations of this element had already been observed in PM_{10} collected in Turin for 1996 and 2001 (Malandrino et al., 2013); it is therefore not possible to exclude the presence of an anthropogenic source, especially combustion processes in motor vehicles, affecting the concentration of this element.

In this study Ca was used as tracer of a cement plant, as done in previous studies (Predicatori et al., 2009). In four sites Ca has crustal origin, but in BSD we may have a contribution from a plant, located few kilometers far from the sampling site. Concentrations of calcium in BSD station are significantly higher compared with all other sites and with the other crustal components determined in this site. Taking wind direction and atmospheric conditions data into account and running deposition simulations through NOAA Hysplit Dispersion Model (Draxler and Rolph, 2015) we are able to explain the overall tendency and, therefore, we can say that the cement plant is an important emission source for this area but, in the absence of data on possible

different processing cycles, and periods in which the plant could be turned off, we cannot fully explain the observed trend for Ca.

Regarding element concentrations, we found a significant level of potassium in airborne particulate matter collected in SA, sampling site in which the concentrations of the other elements are low. K is considered a marker of biomass burning (Andreae and Merlet, 2001; Caseiro et al., 2009), thus, in this case, it is indicative of the use of wood for home heating.

In every site we found a seasonal pattern for K (Fig. 2), with higher concentrations in winter and autumn but, in SA, we detected winter concentrations even higher than in Turin city center. This confirms the massive use of wood as heating source in this small village and likely makes potassium a good marker for this site in the chemometric study.

Table 2 shows a comparison of the average elemental concentrations (ng/m^3) for PM_{10} in Turin with those from past campaigns and in other Italian and European locations. While keeping in mind the great variability present in these data, some general considerations can be made. The Cr, Ni, Zn and Zr concentration in Turin atmospheric particulate matter is similar over time, while Cu, Fe, Mg and Zn present variable concentrations. However, all the elemental concentrations reported in this study are comparable with those obtained in other cities. Overall, it is evident that the values obtained in Turin, Milan and Madrid are higher, compared to coastal cities, which have a higher air turnover.

To facilitate interpretation of the major categories of sources contributing to the trace metal contents in PM, Enrichment Factors (EFs) of elements in aerosol relative to Earth's crustal composition were computed according to:

$$EF = \left(\frac{C_{Me}}{C_{Al}}\right)_{Sample} / \left(\frac{C_{Me}}{C_{Al}}\right)_{Crust}$$

where $(C_{Me}/C_{Al})_{Sample}$ is the concentration ratio between the metal and Al in the sample and $(C_{Me}/C_{Al})_{Crust}$ is the same ratio in Earth upper-crust as reported by Wedepohl (Hans Wedepohl, 1995). Results are shown in Table 3. We have used Al as reference element since soil is considered to be the major source of Al in aerosol and also commonly found in literature for urban sites (Cesari et al., 2012; Jiang et al., 2014). Moreover, the EFs relative to Ti (Supplementary Material) have also been calculated and the deductions are basically the same as the ones obtained using Al as reference.

The values of EFs have been calculated separately by season and sampling site, with the aim of making some hypotheses about both their seasonal and spatial trends. The Ni spikes found for some samples were discarded as presumably contaminated. Average results for each element are shown in Fig.4.

We may assume that elements having an EF larger than 100 are mainly of anthropogenic origin, while elements with EFs up to 10 are mainly of crustal origin (Gharaibeh et al., 2010; Kaya and Tuncel, 1997).

The analysis of EFs can only provide qualitative information on the element sources because of the wide variation of the elemental concentrations in the upper crust (Hans Wedepohl, 1995). Taking into account this feature, for some pollutants we have also computed EFs relative to the local background values in soil, calculated according to the ISO 19258/2005 norm by ARPA Piemonte, using Al as reference element (ARPA Piemonte, 2014). In particular, for Pb, Cu, Zn, and Sb the natural-anthropic background, instead of the natural

background has been calculated: this value originates from the sum of the concentrations due to natural and diffuse anthropic sources, such as atmospheric deposition and agronomic operations, and is calculated from the concentration data in the topsoil (0-10cm). Results are shown in Table 3.

As Fig. 4 shows, Mg, Fe, Ti, K, Ca, Mn, Sr, Co, Ce, La and Zr, are mainly of crustal origin, even if we see that Ca and K are more enriched, respectively, in BSD and in SA than in other sites. The EFs for Ce and La are higher in SA, probably because of the soil composition.

Finally V, Ba, Cr, Ni, Cu, As, Zn, Sb, Pb, Mo, Cd and Hg are moderately or highly enriched in all stations: they can arise from different anthropogenic sources (vehicle emissions, heating, industry, dye industry for SA) (Sanderson et al., 2014; Sternbeck et al., 2002).

EFs were also computed considering the local soil composition instead of the average concentrations in Earth crust. The values obtained (Fig. 4b) present some similarities and differences compared with EFs relative to the upper crust. In particular, V has, also in this case, the highest EF in SA. Vanadium is emitted from all sources using heavy fuel oils such as ship engines and power plants (Becagli et al., 2012; Moreno et al., 2010; Toscano et al., 2011): therefore, this result is probably due to the input of air from the sea, as SA is relatively close to an important harbour and to a great coal power station localised in Savona city (Liguria region). To evaluate this hypothesis we calculated back-trajectories Taking wind direction and atmospheric conditions data into account and running deposition simulations by NOAA Hysplit Dispersion Model (Draxler and Rolph, 2015) and found that, particularly during summer days, air masses arriving in SA originate mainly from sea.

Secondly, we have a clear reduction in EF values for Ni and Cr, probably due to a relevant natural contribution from the soils: Piedmont plains originated during past fluvio-glacial events and are therefore made of sediments, which partly derive from serpentinitic areas; this, as already documented by other researchers (Biasioli et al., 2006; Bonifacio et al., 2010), causes high background levels of Ni and Cr in soils. Finally, we notice an overall decrease of the EFs for anthropogenic elements: this is unsurprising, especially in Turin sites, where the soil is already contaminated by diffuse sources, including atmospheric PM deposition. This decrease, indeed, is less evident in the background sites, namely DR and SA, for typical urban pollutants like Pb and Zn: as a consequence, the EFs calculated for these elements considering local soil background are 10 times higher in these sites than in Turin.

Figure 4c shows that, for most of the metals, the EFs computed for the winter and autumn weeks are higher than those calculated for summer and spring weeks. This demonstrates once again that the lower air turnover in cold periods determines a general accumulation of all the metals in airborne particulate matter in Piedmont Region.

3.2 Chemometric data handling

The chemometric treatment of the experimental data was carried out both on the whole data set (135 samples with 23 variables) and considering the data for the five sites separately. For the concentrations below the detection limit and the spikes for nickel, a value generated applying NIPALS (Nonlinear Iterative Partial Least

Squares) method was inserted in order to thoroughly apply PCA, FA and HCA without losing any data. All the data sets considered were normalized and autoscaled site by site and as whole data set.

The PCA results indicate that the first three principal components explain about 70% of the data variance, with only Sb, V and Ni presenting also high loadings on PC4, PC5 and PC6, respectively.

The scores plot of the first two principal components, for all the samples, is reported in Fig.5.

An evident differentiation exists on PC2 among the sites, forming clusters with centroids separated from each other. This principal component is particularly influenced by the variables characterizing SA samples (mostly K and V), therefore these samples have high scores on PC2 and are all grouped in a compact cluster. At the opposite side of the plot we find BSD samples: PM from this site does not display a particular pattern, with the exception of the high content of Ca, so the samples are not well grouped or extended along a direction. At the centre there are samples from TO1, TO2 and DR. The samples collected in Turin are arranged along PC1, which represent variables related to the anthropic pollution; these samples, in particular from TO2 site, are more scattered, owing to a clearer seasonal pattern in their elemental content: the PM_{10} samples collected in the cold seasons show higher score values on PC1 because they are in greater extent influenced by pollutant and geogenic variables, for the reasons previously pointed out. Instead the PM_{10} from DR site is the least influenced by the pollution variables; indeed, all the samples are contained in a very compact cluster, characterized by negative values on PC1.

Table 4 presents the factor loadings obtained for the PM_{10} samples from all the five sites. Six factors were obtained summing about 78% of the total variance in the entire data set. The first factor, accounting for 43% of the total variance, presents highest loading for Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sr, Zn and Zr. Many of these elements (e.g. Ba, Cu, Fe, Mo and Zn) have often been reported as deriving from brake abrasion and tyre wear (Monaci and Bargagli, 1997; Pant and Harrison, 2013; Thorpe and Harrison, 2008), while elements such as Al, Mn, Sr and Zr are usually associated with crustal material. Therefore we have hypothesized that this factor describes non-exhaust vehicular emissions and road dust resuspension. Pb is no more emitted from vehicles, but it has high correlations with Zn, Ba and Mo (Pearson correlation coefficients: Pb/Zn 0.854, Pb/Ba 0.795, Pb/Mo 0.824; P-value 0.05) suggesting its presence in the road dust fraction. The second factor may be associated with different mineralogy in SA because of the high loadings of Ce and La. The third factor is characterized by high loadings of Mg, Ca and Ti: therefore it can be associated with crustal contribution and, particularly for BSD, with typical contribution from a cement plant. Arsenic and antimony have high loadings in the fourth factor: therefore this factor can be associated with a possible industrial source, even if it is also likely that the correlation between these two elements arises from a common trend in atmosphere, due to their similar chemical properties. Finally the last two factors present high loadings for K and Ni and for V respectively; therefore they can be associated with fossil fuels combustion processes as well as biomass burning in residential heating systems and with ship and industrial emissions. These factors heavily influence SA samples for the reasons above reported (intensive use of wood for home heating and possible influence of air masses polluted by ship and industrial emissions from Savona city).

To clearly show the temporal evolution of the factors in each site we report in Fig.6 the averages of the scores for PM_{10} samples collected in the four sampling weeks computed separately for each factor and for each site. It is evident that each site has a characteristic temporal evolution of the factors (sources), demonstrating that different sources influence the composition of airborne particulate matter in these locations. Specifically we find that TO1 and TO2 sites are influenced by a greater number of factors and, particularly, by F1 than the other sites; the typical seasonal trend of the sources associated to this factor is clearer in these sites, particularly in TO2. DR site is not particularly influenced by any identified factor with the exception of F5 during cold weeks: this could be due to use of wood and other fuels in local residential heating systems. The factor temporal trend observed for BSD demonstrates once again the great importance of F3 for this site: this factor presents a seasonal trend though not as obvious as for TO1 and TO2. Finally SA site is clearly influenced by F2, F5 and F6; indeed, it is interesting to note that, while the influence of F2 is almost constant in the weeks studied, F5 and F6 have an opposite temporal trend since their contributions are high in cold and warm weeks respectively: this confirms further that our interpretation of these factors is correct.

We have also applied PCA to each site individually (28 samples per site): the information obtained for Turin sites confirm what has been reported for the entire data set, whereas different results were found for background sites (PCA plots for each sampling site are reported in the Supplementary Material).

In DR background site a larger number of elements, including also Sr, V, Cr and Zr, are related to crustal source elements. In BSD site Ca is only correlated with Mg and Cr but not with other typical geogenic elements, like Al, Mn and Fe, that in turn are strongly correlated with one another, so we can hypothesize that also Mg and Cr are emitted by the cement plant although to a lesser extent. In the SA site we have a greater dispersion of the variables, with the first principal component influenced by anthropic elements, like Mn, Ba, Cr, Mo and Zn, describing, probably, vehicular emissions and road dust resuspension. K has also high loadings on this component; this further confirms that potassium, in this site, has a prevailing anthropic origin, with a seasonal pattern linked to the use of wood for home heating.

Crustal elements, like Al, Ti, and Ce, and anthropic elements, like V, Ni, Pb and Cd have higher loadings on PC2. The correlation between these elements is likely attributable to the proximity of this sampling site to the harbour and industrial area of Savona. The air that comes from the sea (likely characterised by high input of pollutants as V, Ni, Pb and Cd) flows over the soil and is enhanced in crustal elements (Al, Ti and Ce) before arriving at the sampling site.

Eventually Q-mode Hierarchical Cluster Analysis (HCA) was applied to the total data set to highlight the similarities between variables, which can indicate common sources of atmospheric particulate matter and particularly to individuate smaller clusters among the elements characterizing factor 1. Overall the results are similar to ones obtained with PCA and FA, thus confirming the hypotheses about the sources. Specifically, the dendrogram (Fig.7) shows the following clusters: from the top, the first cluster observable is characterised by the link between As and Sb, probably due to their similar chemical properties, leading them to an analogous trend in atmosphere. This group is linked at a higher level of dissimilarity with Ni, suggesting that they could partially arise from a common source, identifiable with the emissions from industrial combustion processes of

fossil fuels. A second cluster is characterized by La, Ce, K and V, linked at different levels of dissimilarity. This group encloses the variables that characterize principally the composition of the PM sampled at SA. Particularly, the higher concentrations of La and Ce are, likely, linked to the area mineralogy, while the concentrations of K and V are probably higher for the reasons discussed above. A third group is characterized by more elements, namely Cu, Fe, Zr, Cr, Cd, Pb, Co, Ba, Zn, Mo, Mn and Sr, that are linked at different levels of dissimilarity, suggesting that they derive from multiple sources, all likely correlated with vehicular traffic. In greater detail this cluster is made-up by two sub-groups. For the first one we can hypothesize that Cu, Fe, Zr, Cr and Cd might originate from traffic emissions, like mechanical abrasion of metal structures of vehicles, tyres and brakes linings and road dust resuspension. The second group includes elements likely associated, in diverse extents, to traffic emissions (vehicle exhaust for Pb and Co and non-exhaust for Ba, Zn, Mo and Mn). These groups are linked with Sr, which is a crustal element and is positioned near the last cluster, characterized by the crustal elements, namely Mg, Al, Ca and Ti. Therefore, it is possible to affirm that HCA, considering all the information of the original data set, has permitted to obtain a more detailed identification of sources characterizing the first factor compared to PCA and FA.

4. Conclusions

This study shows that the values of PM_{10} content and the mean element concentrations in atmospheric particulate matter collected in various localities of Piedmont region are in tune with values found in urban sites in Italy and Europe. The highest PM_{10} concentrations for almost all elements were found in the Turin outskirts (TO2 site), affected by traffic, residential and industrial emissions. In most of the sites considered (namely four on five), element concentrations have a typical seasonal trend, ascribable to the higher contribution of combustion processes in industrial and residential heating systems and to the increase in vehicular traffic in the cold season, but especially to the thermal inversions at ground level that frequently occur during the winter in this area. The highest variations in massive concentrations of PM were found in TO1 and TO2 sites. This might be due to a variation in the anthropogenic fraction of PM, in particular in the resuspended soil dust. This influence is obviously higher in the great urban sites. Three marker metals were found: two of these were relative to the SA sampling station, namely K, marker of biomass burning for heating, and V, marker of the air coming from the sea. Ca was identified as marker of a cement plant in the atmospheric particulate matter of BSD station; in all other stations this element has crustal origin.

Chemometric elaboration of data allowed us to further confirm the seasonal pattern and the differences between the urban and the background sites; furthermore, for every site the possible sources influencing the concentrations of elements in PM_{10} were hypothesized by PCA, FA and HCA.

Finally, regarding the presence of As, Cd, Ni and Pb, it is significant noting that we found concentrations one order of magnitude lower than European limit values in almost all samples.

Further studies, addressing a wider suite of analytes on a larger number of samples, are necessary to better identify and quantify the different emissive sources of PM_{10} for the area investigated.

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Table 1 Mean, minimum and maximum concentrations of each element determined in PM10 samples at five monitoring sites. All values, except for PM, are expressed in ng/m^3. PM is expressed in µg/m^3.

	TO1*		TO2*		DR*		BSD*		SA*	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
PM_{10}	58	23-110	65	16-125	32	7-66	26	15-48	32	15-72
Mg	254	19-738	522	53-1592	148	6.77-314	400	48.9-1891	173	53.7-367
Al	203	17,8-428	383	11.9-1127	137	4.08-531	211	7.44-824	123	10.4-344
K	486	79.4-1285	395	130-909	232	56.8-472	325	60.8-851	459	128-1143
Ca	749	18.7-1517	1041	271-2721	482	146-1460	1925	328-7332	735	279-1416
Fe	1316	272-3164	2487	431-6810	356	57.4-658	382	105-848	259	93-391
Ti	23.5	2.29-54	26.7	5.7-65.4	18.5	4.99-33.7	23.9	6.33-63.2	19	8.2-49.5
Mn	17.3	3.63-37.5	28.4	6.2-95.8	8.23	2.04-31.3	9.61	3.51-45.8	7.14	3.9-12.5
Cu	22.3	5.04-52.4	67.3	13.4-176.4	3.9	0-15.1	11.4	3.37-33.2	1.73	0-8.46
Zn	64.3	19.6-164	83	14.6-228.8	37.9	4.81-79.3	30.9	0-79.4	26.1	6.4-64
Sb	11	1.9-48.3	10.1	2.6-27.5	2.03	0-5.92	4.23	0.6-12.8	0.16	0-1.2
Ba	32.1	12.4-76.9	40.2	7.4-101.5	16.7	7.39-54.5	13.8	7.74-40.3	6.01	0-15.5
Pb	16.3	3.8-44.6	13.7	0-39.9	6.06	1.7-13.2	10.9	1.13-171	6.18	1.91-18.8
Cr	8.24	1.9-14.3	12,1	2.6-34.3	5.22	0.51-12.5	3.58	0.83-10.1	3.21	1.84-7.82
V	3.15	1.06-5.73	2.77	0.73-5.71	1.44	0.67-2.5	1.97	0.39-7.83	3.21	0.6-8.93
Co	0.7	0.06-1.85	0.65	0.09-1.54	0.18	0-0.87	0.3	0.05-2.43	0.11	0.02-0.52
Ni	5.74	0-16.2	5.97	2.2-15.1	6.45	0-41.9	8.88	0.68-94.2	3.3	1.97-631
As	0.71	0.18-1.48	1.03	0.19-4.66	0.38	0.14-0.7	0.43	0.12-1.04	0.39	0.1-4.16
Sr	1.88	0.04-4.37	239	0.44-11.15	0.72	0-1.39	0.33	0-1.98	0.78	0.34-1.22
Zr	1.66	0.29-4.01	3.21	0.55-7.96	0.38	0-3.43	0.43	0-1.9	0.36	0.14-0.62
Mo	4.86	083-16.02	5.35	1.3-14.21	1.09	0.24-3.03	0.48	0.06-1.51	0.92	0.56-1.73
Cd	0.62	0,19-1,.8	1.1	0.32-5.51	0.31	0.05-1.01	0.31	0.01-1.36	0.33	0.15-0.5
Ce	0.22	0-0.88	2.57	2.12-5.95	0.15	0-1.53	1.52	0.43-3.71	2.77	2.55-3.23
La	<0.007	<0.007	2.39	2.09-4	0.02	0-0.47	1.16	0.05-2.76	3.08	2.83-3.41
Hg	0.44	0-2.77	4.49	0.45-6.9	0.91	0-3.42	0.75	0-9.4	4.13	232-16.44

*TO1: Turin area (Via della Consolata); TO2: Turin area (northern out-skirts of the town); DR: Druento; BSD: Borgo San Dalmazzo; SA: Saliceto.

Table 2 Comparison of average element concentrations in urban PM_{10} from different Italian towns. All values are expressed in ng/m^3.

Element	Turin[a]	Turin[b]	Milan[c]	Palermo[d]	Genoa[e]	Florence[e]	Naples[e]	Frankfurt[f]	Madrid[g]
Al	293		840	733	117	181	217		970
K	441		660		99	102	149		390
Ca	895		1880		381	753	547		1920
Mn	45.7		45	12	6	10	8	35	22
Cr	10.2	16.4	13	6.5	7	9	7	16	9
Pb	15		71	18	9	12	9	33	118
Cu	44.8	8.19	72	49	12	37	16	102	112
Fe	1902	274	1830	496	329	811	499		1930
Mg	388	1501			224	165	244		250
Ni	5.86	7.33	10	5.5	2	3	2	7	4
Zn	73.7	333	180	48	14	19	8	106	93
Zr	2.44	8.15	3		3	4	4		

a This study, mean concentrations from Turin (2011).

b (Malandrino et al., 2013a). c (Vecchi et al., 2007), daytime measurements. d (Dongarrà et al., 2007). e (D'Alessandro et al., 2003). f (Zereini et al., 2005). g (Salvador et al., 2004).

Table 3 Enrichment factors of elements computed with respect to the earth's crustal composition (ECC) and the local background values in soil (LB).

	TO1		**TO2**		**DR**		**BSD**		**SA**	
	ECC	LB	ECC	LB	ECC	LB	ECC	LB	ECC	LB
Al	0.1	0.2	0.1	0.2	0.2	0.4	0.2	0.4	0.2	0.3
Cu	29	6.3	47	10	18	11	49	20	9.9	4.1
Zn	34	9.1	23	6.4	81	42	64	20	72	31
Sb	1266	291	2265	521	871	200	1527	195	78	22
Pb	37	6.4	18	3.1	60	22	38	9.9	85	34
Cr	2.7	0.8	1.9	0.6	5.4	1.6	3.1	4	4.6	0.8
V	1.4	1.2	0.8	0.6	2.1	1.8	2.3	2.1	5.9	5.4
Co	0.9	0.9	0.5	0.5	0.8	0.7	0.9	1	0.7	0.6
Ni	3	0.6	2.3	0.4	11	1.9	7	5.8	11	1.8
As	16	3.1	14	2.7	34	6.6	40	4.8	37	5.1

Table 4 Variable loadings in the factors obtained by Varimax rotation for PM_{10} samples at five monitoring sites.

Element	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**	**Factor 6**
Al	0.680	0.094	**0.701**	0.030	-0.060	0.088
As	**0.624**	0.127	0.491	0.047	-0.200	0.251
Ba	0.397	0.283	0.045	0.052	**0.764**	-0.012
Ca	0,228	0.016	**0.776**	-0.014	0.168	-0.131
Cd	**0.966**	0.135	0.183	0.116	0.020	0.033
Ce	0.368	-0.018	**0.488**	0.082	-0.091	0.227
Co	**0.842**	0.167	0.265	0.058	0.122	0.063
Cr	**0.899**	0.259	0.185	0.207	-0.042	-0.036
Cu	**0.870**	0.062	0.166	0.101	0.352	0.027
Fe	0.129	-0.012	0.007	**0.835**	-0.017	-0.060
K	**0.912**	-0.010	0.102	0.129	0.190	0.013
La	**0.748**	0.070	-0.023	0.112	0.558	0.097
Mg	**0.827**	0.069	0.279	0.103	0.021	0.083
Mn	0.286	0.308	0.018	-0.026	0.004	**0.527**
Mo	**0.745**	-0.059	0.098	0.047	0.357	0.334
Ni	0.092	-0.048	0.033	-0.008	**0.116**	0.073
Pb	0.450	0.088	0.022	**0.813**	0.115	0.076
Sb	**0.598**	-0.018	0.244	0.049	0.093	0.282
Sr	**0.920**	0.156	0.102	0.216	0.059	0.047
Ti	**0.883**	0.003	0.060	0.097	0.261	0.275
V	**0.759**	0.259	0.087	0.085	0.165	-0.083
Zn	0.137	**0.959**	0.175	0.038	0.002	-0.113
Zr	0.173	**0.799**	-0.209	0.017	0.291	0.359

Fig.1. Geographical map of Piedmont and detail of sampling areas.

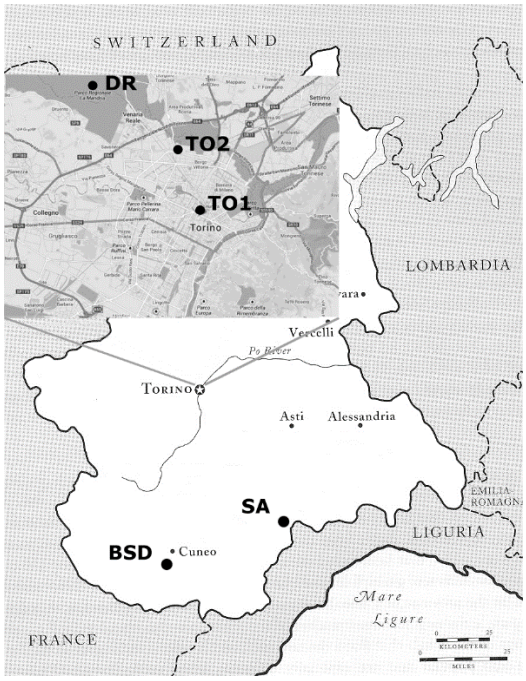
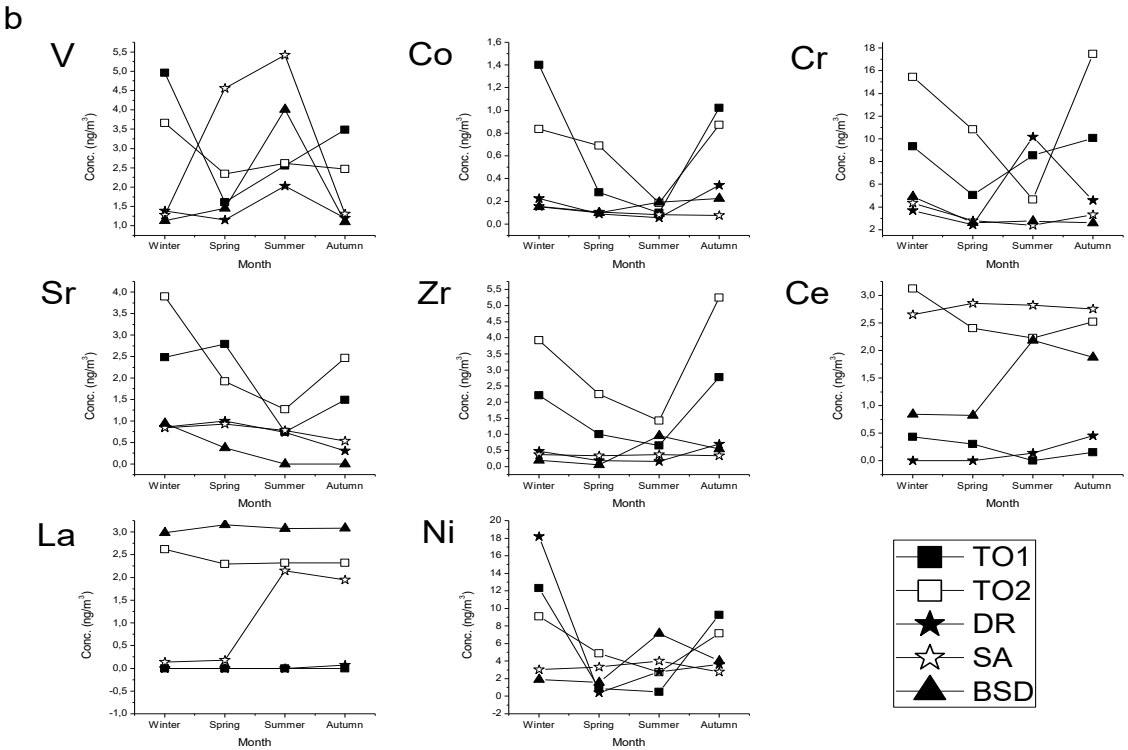


Fig. 2. Seasonal trends of element concentrations in PM10 samples: a) Mg, Al, K, Ca, Fe, Ti, Mn and Ba; b) V, Co, Cr, Sr, Zr, Ce, La and Ni; c) Cu, Zn, Sb, Pb, As, Mo, Cd and Hg.



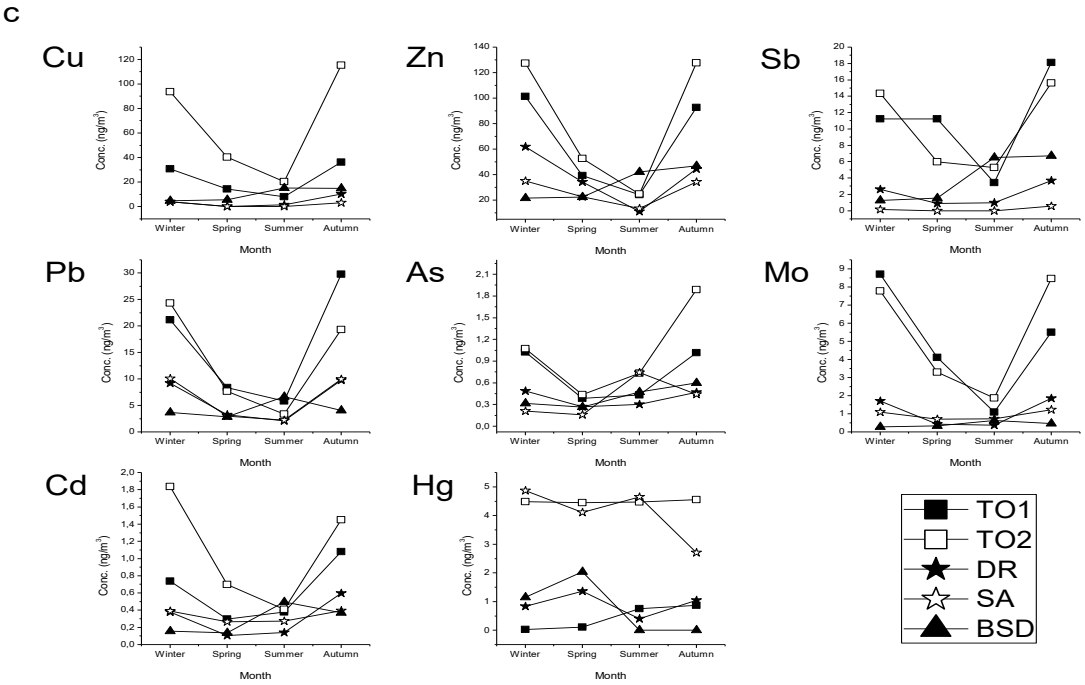


Fig. 3. Concentration trends of three elements of different origin (industrial, traffic, geogenic) during a snow event (snow fell during the first two days and, although with lower intensity, in the third).

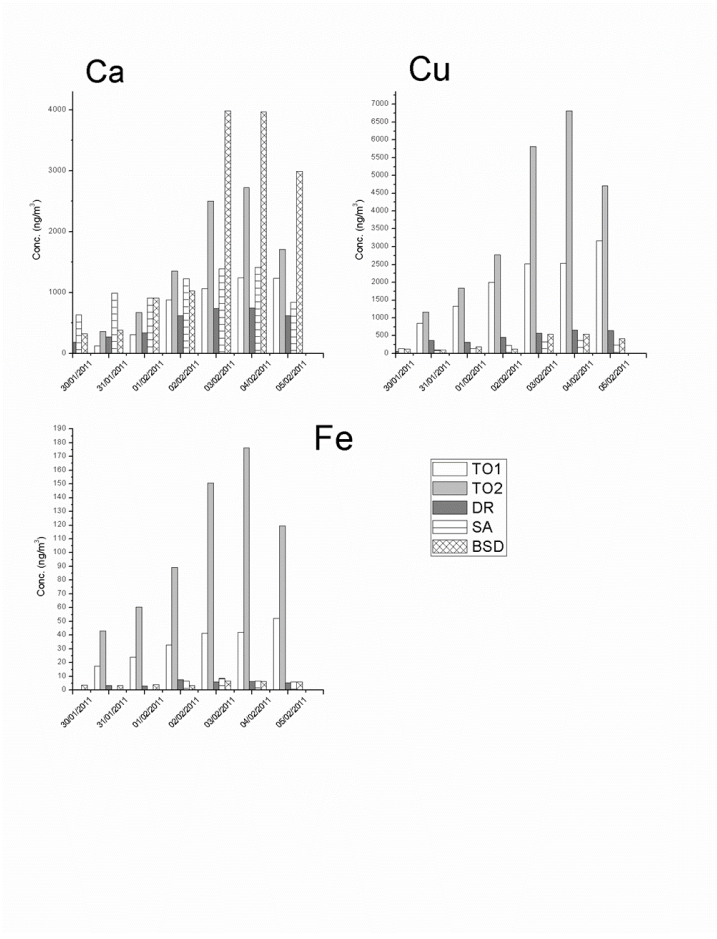


Fig.4. Enrichment factors in the study areas: a) average for sampling site computed considering concentrations in Earth Crust; b) average for sampling site computed considering the local soil composition; c) seasonal average.

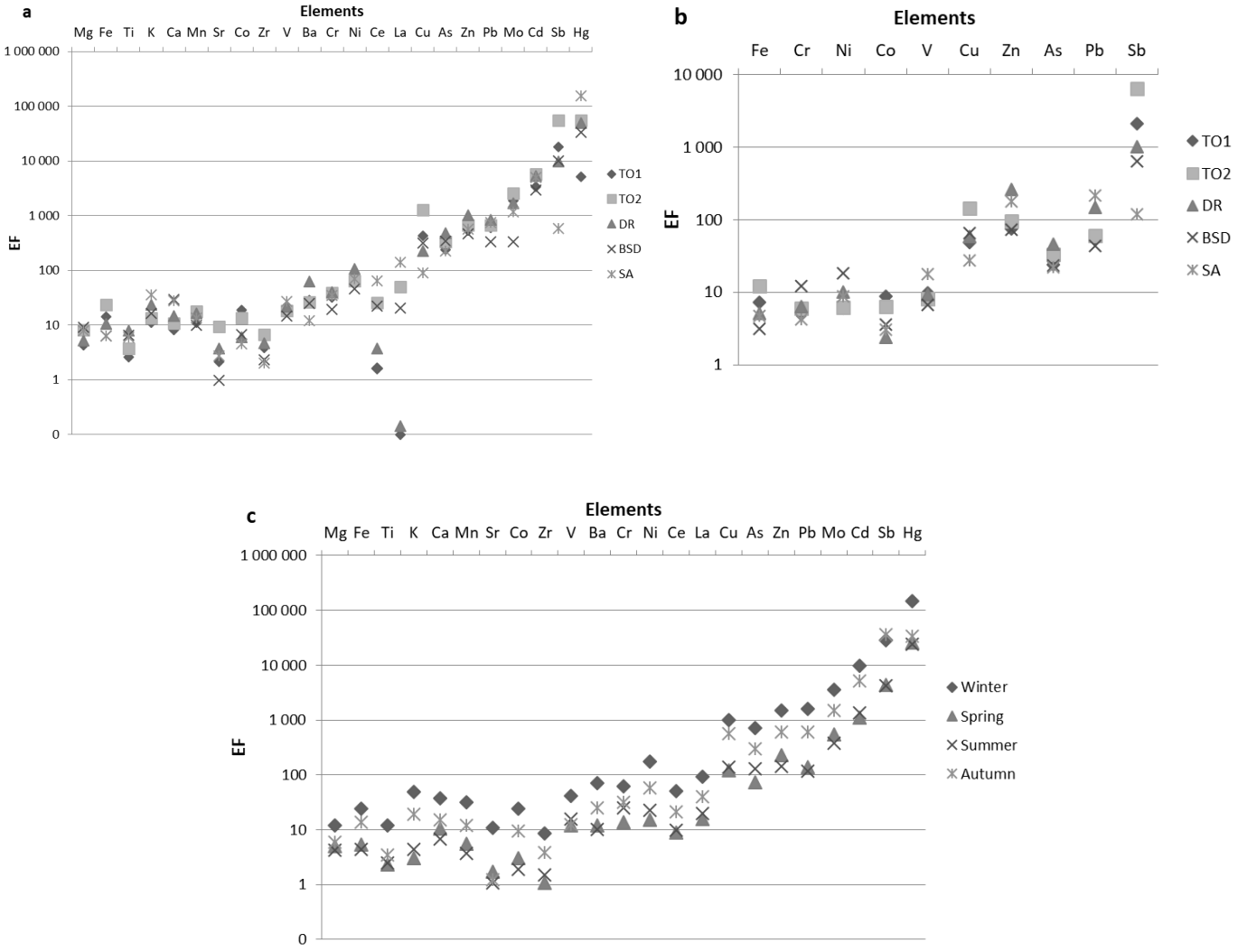


Fig.5. Scores and loadings plot on PC1-PC2 for all sites.

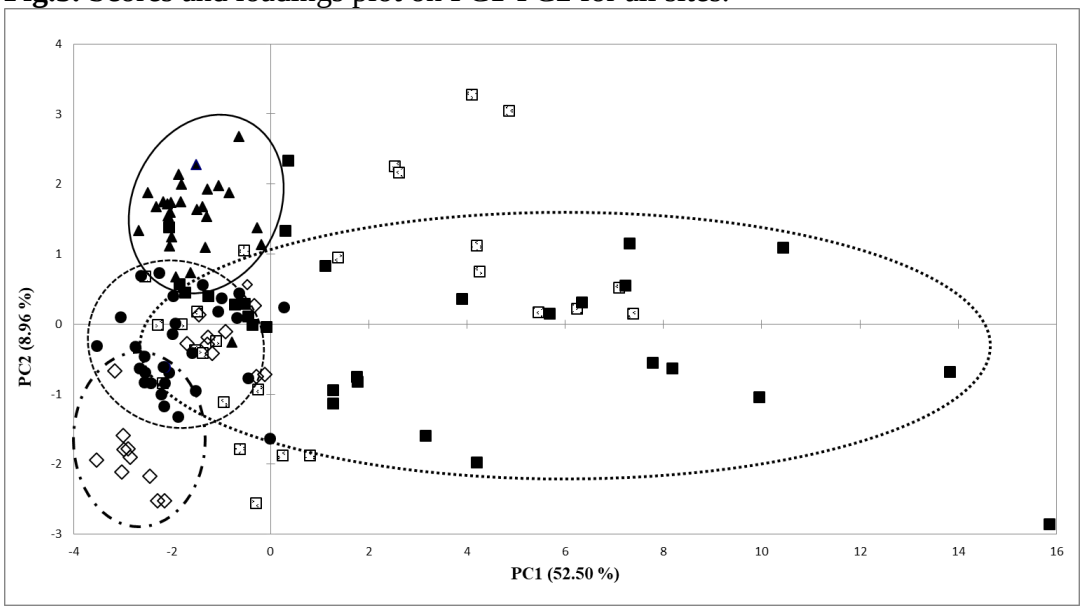


Fig. 6. Scores averages on each factor for PM_{10} samples for the four sampling weeks.

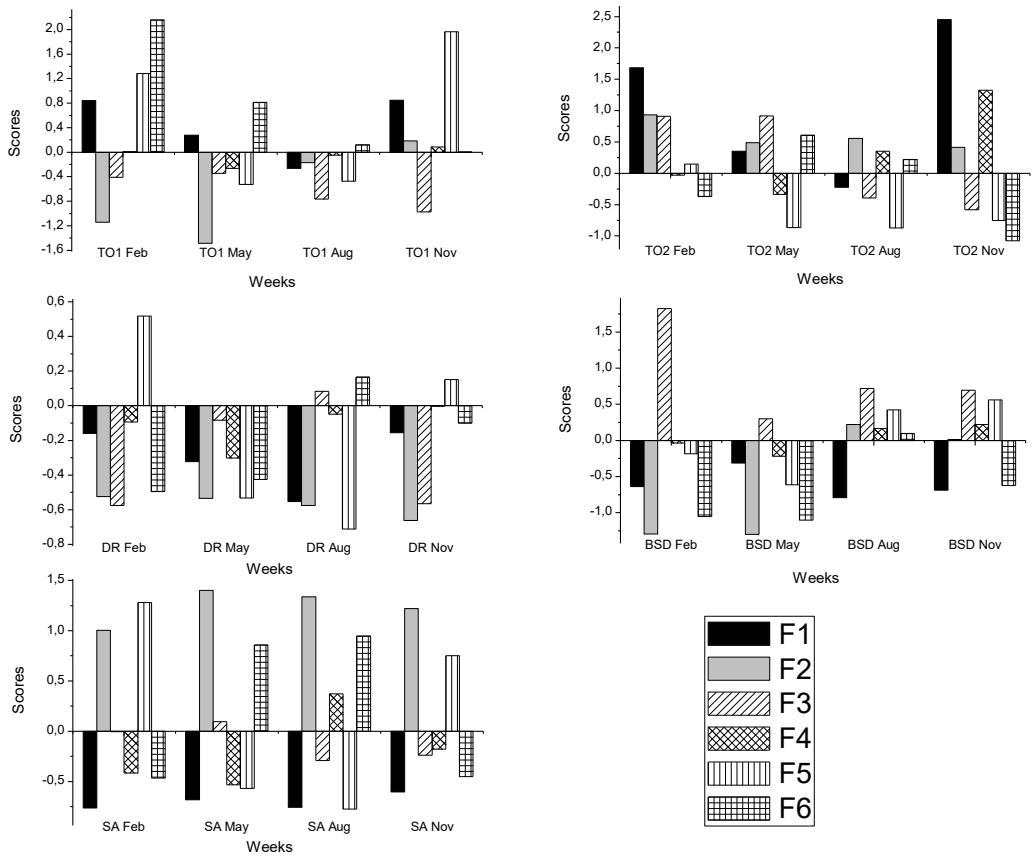
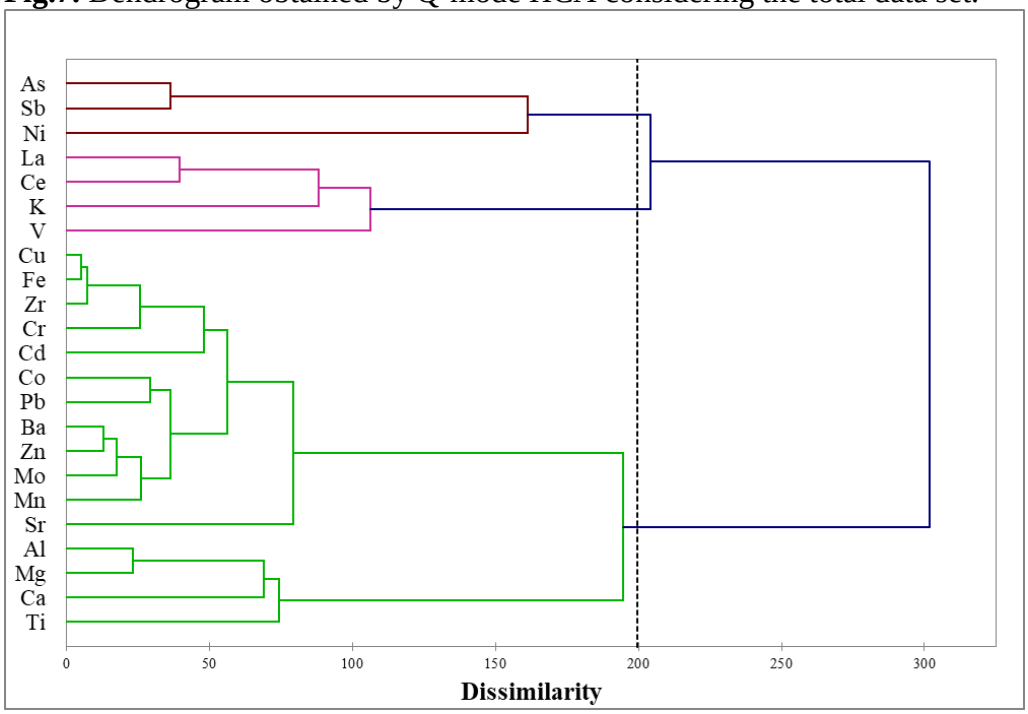



Fig.7. Dendrogram obtained by Q-mode HCA considering the total data set.