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Dispersion of Atmospheric Particulate Emissions in Built-up Areas Close to a Steel Mill

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In the nineties, a steel mill has been established in the south part of Udine municipality (Italy), in an industrial zone close to built-up areas, which were consequently affected by pollutants continuously released to the atmosphere by the firm. The amount of TPM, its PM_{10} content, the concentration and the distribution of metals within the two PM classes have been evaluate. Data analysis allows identifying several trace metals as representative of different kind of emissions released to the atmosphere; data concerning PM detected close to the industrial zone have been frequently compared with those obtained for urban traffic in the Udine urban area in order to highlight the steel mill contribution to the production and dispersion of atmospheric pollutants. Results concerning the amount of PM_{10} found in TPM and issues related to the distribution of metals into both substrates, PM_{10} and TPM, have been discussed. Several metals, such as Zn, Mn, Pb and Cd, showed interesting relationships based on their distribution between the two substrates, which allows for identifying markers of the metallurgical activities and emissions sources.

1. Introduction

In the south part of Udine municipality (Italy), where built-up areas are close to an industrial zone, the dispersion of airborne species of environmental and health concern, mainly ascribed to a steel mill established in the nineties within that area, has been found. From 1995 to 2002, several experimental campaigns have been carried out to regularly detect trace metals within the total particulate matter (TPM); since July 2002, considering the influence of main meteorological conditions on pollutants transportation in the atmosphere, a monitoring network, constituted by four monitoring stations located where the maximum pollutants concentrations at ground level could be expected, has been established in the neighbouring built-up areas. Products sampling has been done according to the EN 12341 (1998) EU directive and EN 14902 method, with ICP-MS determinations.

2. Results and discussion

As summarized in Table 1, to highlight the steel mill contribution to the production and dispersion of atmospheric pollutants, data concerning PM detected close to the

industrial zone (1200 m far from the steel mill) have been frequently compared with those obtained for urban traffic; in particular, a comparison among different dimensional classes has been made, evidencing also the composition of PTM both in terms of PM_{10} and $PM_{2.5}$. PM values detected at the urban site are in good agreement with results obtained in other experimental campaigns, carried out in different cities (Valentini et al, 1993; Ragosta et al., 2002) thus confirming that these results are non influenced by emissions of industrial metallurgical activities; moreover, this assumption is confirmed by the high content of $PM_{2.5}$ found in the collected PM, which contribution can be attributed to secondary sources, such as traffic and domestic heating. The particulate matter sampled at the industrial site is coarser than that found at the Udine site and this confirms that there is a not negligible contribution due to the steel mill presence upwind the monitoring stations; in this case, a source of PM can be both the industrial facilities, where PM is formed through agglomeration of fine particles emitted by melting and steel casting activities, and the dust dispersion from agricultural soils.

Table 1 Summary of data collected at urban and industrial sites (day-averaged results).

Site	Period	$\frac{PM_{10}}{PTM}$	$\frac{PM_{2.5}}{PM_{10}}$	$PM_{2.5}$ (µg/m^3)			PM_{10} (µg/m^3)			PTM (µg/m^3)		
				min.	avg.	max.	min.	avg.	max.	min.	avg.	max.
Urban (Udine)	oct 31,06 jan 02,07	0.82	0.93	9	43	114	7	49	151	19	53	101
Industr. zone	jun18,04 may07,05	0.87	nd	nd	nd	nd	8	39	152	6	47	195
Industr. zone	oct19,06 dec30,06	nd	0.71	8	27	100	8	44	132	nd	nd	nd

Table 2 Concentration of trace metals in PM_{10} (day-averaged results).

	Fe [µg/m^3]	Mn [µg/m^3]	Cr [ng/m^3]	Ni [ng/m^3]	V [ng/m^3]	Zn [µg/m^3]	Pb [µg/m^3]	Cd [ng/m^3]	As [ng/m^3]
Industrial site	0.67	0.06	7.22	5.12	3.02	0.17	0.03	0.62	1.61
Urban site (Udine)	0.78	0.02	3.84	5.65	3.37	0.05	0.01	0.34	1.03
Ratio (ind/urb)	0.86	3	1.88	0.91	0.9	3.4	3	1.82	1.56

Concerning trace metals detected within the PM_{10} fraction (Table 2), it is possible to notice that several elements were found in higher concentration in samples collected, in particular at the beginning of 2006, during winter, at the industrial site with respect to those of the urban site; this allows to identify Zn, Pb and Mn as reference pollutants emitted by the steel mill.

The trends of some metals have been evaluated; in particular Mn (Figure 1) and Zn have been considered as marker of the industrial activity, while V (Figure 2) emissions have been mainly attributed to energy production processes that use liquid oils, coal or wood as fuel (Win Lee et al., 2000). Concentrations recorded at the industrial site did not show the peculiar cyclic trend, characterized by high pollutants concentrations during fall and winter periods and low emissions during summer; as evidenced by the figures, after the January-March period, where high pollutants amounts have been found in the atmosphere, emissions of trace metals were progressively reduced until both trends, the industrial and the urban ones, became comparable. This behaviour could be explained

considering that at the steel mill facility, during summer, several equipments have been installed in order to contain and to treat secondary diffuse emissions produced by the ovens. Such a way, a large amount of the indoor air has been treated, thus contributing to a significant reduction of pollutants emitted and dispersed in the atmosphere and, as a consequence, detected from the monitoring station located downwind the industry.

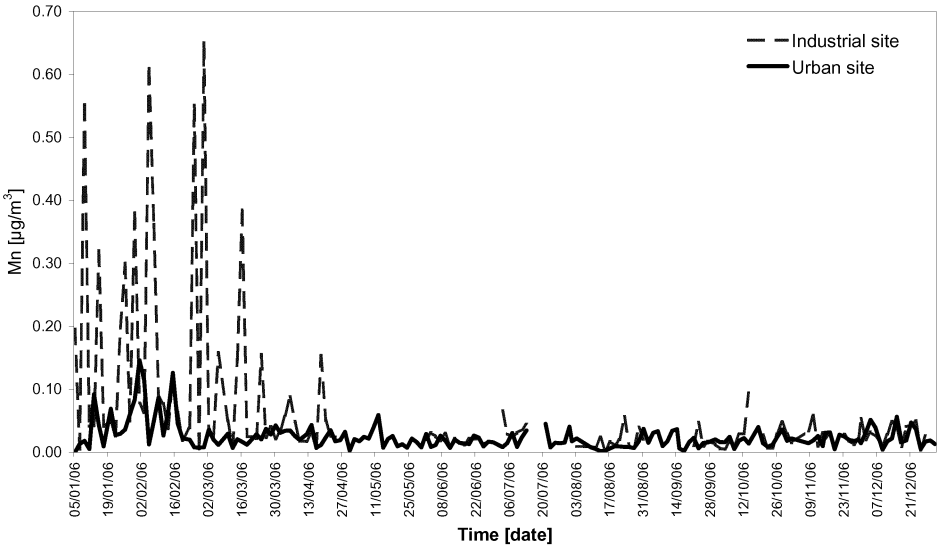

Figure 1 Trends of Mn concentrations (day-averaged results, PM_{10} fraction) for the urban and industrial sites.

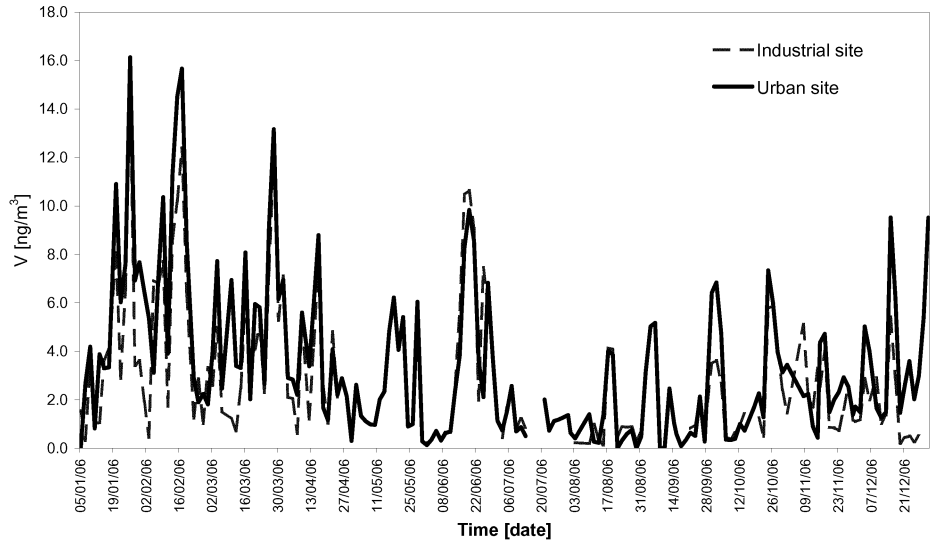

Figure 2 Trends of V concentrations (day-averaged results, PM_{10} fraction) for the urban and industrial sites.

Therefore, the correlation coefficients evaluated for the concentrations of several metals detected at both, urban and industrial, sites evidenced that Mn (R^2 = 0.141) e Zn (R^2 = 0.008) are poorly correlated and they are statistically independent, so they can be assumed as good markers of the industrial steel activity. A low correlation was also found for iron, Fe (R^2 = 0.374), and this is probably a suggestion that there are different sources for the investigated sites: emissions from buildings and vehicles in the urban area, while the steel mill in the industrial zone. On the other hand, V (R^2 = 0.562) showed concentrations values and trends very similar in both environments; these results are in according with other studies (Win Lee et al., 2000), which considered V as a typical pollutant of anthropic environments produced, as previously said, by the combustion of liquid or solid fuels.

In the industrial zone, in particular, the monitored trace elements were mainly found within the PM_{10} fraction, showing ratios, which are time independent, in the range 72-97% for metals found in high or low concentrations, respectively. These results, confirmed also by other studies (Baiutti et al, 2006; Cazzuli et al, 2006; Sammut, 2006), evidenced the possibility to have a comparison and to identify a relationship between new detailed measurements and historical data produced by TPM monitoring campaigns. Concerning trace metals, it was found that correlation coefficients are very similar for both particulate fractions, PM_{10} and TPM.

With the aim to identify specific industrial sources that are responsible of the dispersion in the atmosphere of the detected trace metals and to understand if some of them are significantly correlated, cluster analysis have been applied on the experimental data. Therefore, it was assumed that two or more elements could be emitted by the same source and/or behave in the same way in the atmopshere.

Cluster analysis, also called segmentation analysis or taxonomy analysis, seeks to identify homogeneous subgroups of cases which both minimize within-group variation and maximize between-group variation. An *Agglomerative Hierarchical Clustering* approach has been used and a distance matrix has been drawn using correlation of items as a similarity measure. In particular, the square values of the Pearson correlation coefficient, have been used to indicate similarity and an average linkage method has been selected in order to form clusters of events. In detail, the *Average linkage within groups* is the mean distance between all possible inter- or intra-cluster pairs and, considering two clusters, A and B, it is computed as:

$$d_{A,B} = \frac{\sum_i \sum_k d_{i,k}}{n_A \cdot n_B} \qquad (1)$$

where the number of elements which constitute the clusters A and B are n_A and n_B, respectively, and the distance between the elements of the two clusters is $d_{i,k.}$ In this way, the average distance between all pairs in the resulting cluster is made to be as small as possible. Cluster analysis results have been summarized in a hierarchical tree plot, called *dendrogram* (Figure 3), which shows the relative size of the proximity coefficients at which cases were combined. Cases with low distance/high similarity are close together, with a line linking them, indicating that they are agglomerated into a cluster. When, on the other hand, the linking line extends to the right of the dendrogram the linkage occurs a high distance coefficient, indicating the cases/clusters were agglomerated even though much less alike.

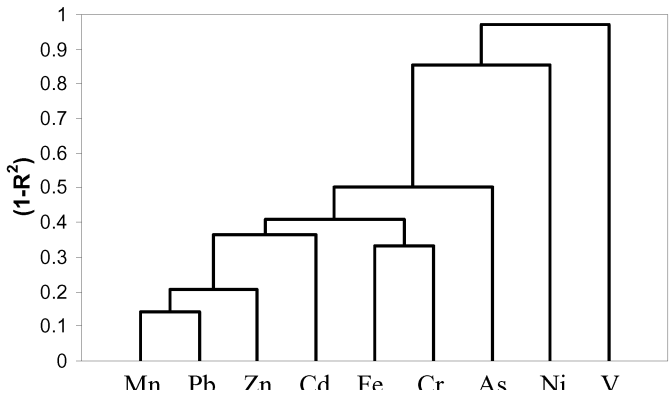

Figure3 Dendrogram showing correlations of metals found in PTM (industrial site).

As shown by Figure 3, Mn and Pb have the higher similarity, since they refer to analogous generation mechanisms that could be secondary emissions produced by feeding operations for Pb and by ladle operations involving steel for Mn. In addition, Zn and Cd evidenced a good similarity with the first Mn-Pb cluster; for this reason, it was assumed that they are generated by paints and coatings of the treated scraps used in melting processes. Moreover, another cluster, constituted by the main steel components, Fe-Cr, can be logically identified in iron and steel works; therefore, it is possible to point out the presence of a group made by Mn-Pb-Zn-Cd-Fe-Cr, representative of the overall industrial impact of steel activities on the trace metals emissions and on their presence within the PM fraction of the atmospheric particulate. A lower similarity has been shown with As, that could be emitted by scraps coatings, but the results for As emissions still need to be confirmed. Lastly, Ni and V are poorly correlated with the aforementioned metals; they showed, both in urban and industrial zones, similar trends as a function of time, so it seems that they are emitted by anthropic sources, rather than by the steel mill (Valentini et al, 1993). These correlations were confirmed by measurements performed in indoor working areas, in proximity of the possible sources (Borroni et al, 1989).

Thanks to the presence of several monitoring stations located at different distances from the steel mill, it was also possible to evaluate and to compare the trends of trace metals found in PTM; in particular, measurements collected at two sites that are downwind the industry, at a distance of 500 and 1200 m, respectively, have been considered. Due to the lack of space, only the concentration profiles of Mn have been here reported (Figure 4); the profiles of metals, such as Zn, Pb, Cd and As, could be omitted since they were very similar and correlated to the trend of Mn, as previously discussed. Therefore, V can be chosen as representative marker of those compound that are not strictly related to the metallurgical activity. Concerning Mn, concentrations measured at the closest site were up to 4 times higher than those detected at the 1200 m site; it is so possible to evidence the presence of a dilution effect that is function of the downwind distance from the pollutants “sources”. A different behaviour can be highlighted for the V, which trends are practically overlapped, as found also when the emissions for the urban and

industrial environments were compared; this means that no dilution effect is present in this case and that V is distributed as a background pollutant in atmospheric emissions.

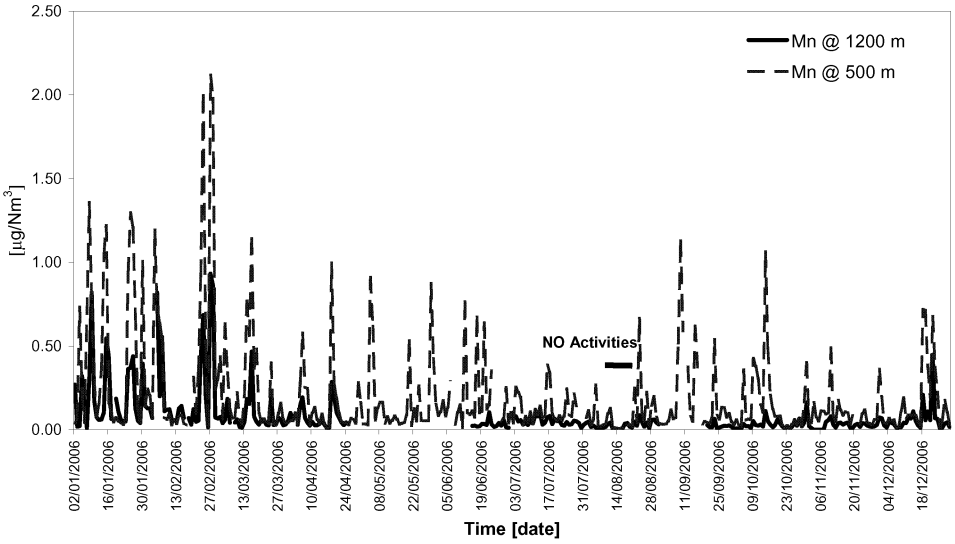

Figure 4. Trends of Mn concentrations (day-averaged results, PTM fraction) for the industrial sites located downwind the steel mill.

3. Conclusions

The differentiation of metals as a function of the PM_{10}/TPM ratio suggested that their emissions could be originated from dissimilar sources, with different generation and aggregation pathways of the elements. It was possible to identify elements that are involved in melting operations, such as Fe and Mn (usually related to primary emissions), or elements that are practically pollutants of the scrap, released during oven loading operations, such as Pb, Zn and Cd (mainly related to diffuse emissions). These results allow for foreseeing the possibility to use PTM and PM measurements, obtained by monitoring stations, to correctly identify sources of concentrated and diffuse emissions in order to address technological solutions able to reduce and to limit the impact of industrial activities on air quality and human health.

4. References

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