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## **A comprehensive approach to the investigation of atmospheric particulate PM<sub>2.5</sub>: preliminary results**

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### **Abstract**

Understanding the health effects induced in humans by the inhalation of air particulate matter requires first that airborne particles be characterized in detail. Aiming at elucidating some prominent mechanisms and processes involved in the atmospheric environment - human organism interaction, a comprehensive approach was adopted to thoroughly investigate PM<sub>2.5</sub> from a mineralogical, chemical and chemical-physical point of view.

In the present study, two summer and winter samplings collected from the Rome urban area were investigated by different techniques (SEM-EDS, XRD, ICP-MS, ICP-OES, TGA-DTA). Mineralogical and physical characterization gave important information on the prevalent phases (oxides, sulphates, silicates, carbonates, and abundant carbonaceous particles hosting metals) contained into the material under study. The bulk chemical composition evidenced the presence of heavy metals, in particular As, Cd, Cu, Cr, Fe, Pb, Ni, and Zn. Consequently, in order to verify the potential mobility of such heavy metals, batch kinetic leaching tests were carried out by using a physiological solution mimicking the lung environment and samples were collected from the solution at different times of treatment. Among the metals

contained into the particulate, a leaching trend was observed mainly for Pb, Cd and Cu, with Cd resulting the most mobile metal, whereas no Fe release was observed. The leaching solution mimicking the human intrapulmonary fluid will be exploited for future toxicological tests in cellular models, in order to assess the potentially harmful role of the above metals in biological systems.

*Key words:* PM<sub>2.5</sub>; particulate matter characterization; heavy metals leaching; multi-method approach; Rome urban area.

## Introduction and Background

Fine dusts and particulate matter with diameter < 10 µm, < 2.5 µm, and < 1 µm, PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>, respectively, represent a well-recognized environmental emergency. Since 1997, US EPA (Environmental Protection Agency) adopted new air quality standards imposing regulatory limits for PM. In European countries, the air quality is regulated by recent directives (European Parliament Directives, 2008/50/EC). According to these directives, Italy has set limits for concentrations only for PM<sub>10</sub> equal to 50 µg/m<sup>3</sup> (not to be exceeded more than 35 times a calendar year), even if the weather-climatic and orographic characteristics of the Italian territory do not always facilitate the dispersion of pollutants.

The airborne particles can originate from both natural phenomena (pedogenetic erosion processes, volcanic activity, forest fires, dispersion of pollen, etc.) and from human activities, mainly automotive traffic and combustion processes. PM is generally composed of fine mineral particles, organic and inorganic materials, such as elemental and organic carbon, ammonium salts and metals.

Among the particulate matter components, heavy metals and mineral fibres, especially the non-regulated ones (non-asbestos), deserve special attention as for the type of exposure (environmental) and health implications (Gunter et al., 2003; Burrigato et al., 2005; Fantauzzi et al., 2012). Atmospheric PM remain suspended in

air for long periods - few hours for the coarser fraction up to few weeks for the finer fraction - and can travel long distances, up to hundreds of kilometres. Consequently, pollution by PM exhibits the characteristics of a cross-border phenomenon.

Due to its composition, the particulate is endowed with intrinsic toxicity, which is exacerbated by its ability to absorb gaseous substances and heavy metals. Furthermore, as already reported in several papers (Bianchi et al., 1997; Daniels et al., 2000; Pope et al., 2002), the reduced dimensions of the particulate matter favour its progress along the windpipe and the bronchial tree down to reach the lung alveolus, so posing a serious risk of irreversible local and systemic health harm. Lung diseases related to dust inhalation are manifold, from mild inflammation up to calcified pleural plates.

Many studies concentrated on the dimensional range of particles, in particular the smallest ones (< PM<sub>2.5</sub>). Worth recalling, the macroscopic bulk properties usually change with particle size. It is generally accepted that the high specific surface of the particulate matter is a determinant factor for toxicity, given that the material identity depends on its structural and compositional properties. Depending on the particle physical and/or chemical characteristics, there is a complex interrelationship between the material size and composition, which may relate to both the bulk and surface properties of each particle and newly emerging properties localized at the interface. Usually, enhanced chemical reactivity

associates with reduced particle size, with intricate processes underlying such association.

The city of Rome, as most of urban areas, receives inputs to the aerodispersed particulate principally from geogenic source, bioaerosol, biomass combustion (heating), vehicular traffic and occasionally from sea-spray salts and desert dust, depending on atmospheric conditions, while the industrial input can be considered negligible or in any case due to medium or long-range transport to the city of Rome (Canepari et al., 2009). Previous investigations on  $PM_{2.5}$  from the city of Rome provided information about the inorganic compounds (Mazziotti Tagliani et al., 2009; Gianfagna et al., 2010; Mazziotti Tagliani et al., 2011), with significant Fe-sulphate associated to other mineral phases.

Again in Rome, a study performed by the ISS (Italian National Health Institute), reported slightly lower concentrations (10-17%) in a

typical urban background site (an urban park) in comparison with a site directly influenced by automotive traffic. From such evidence, it was suggested the concentration levels tend to be quite homogeneously distributed over large areas of urban land (Marconi et al., 2003).

In Figure 1, reprinted from a Regione Lazio report (Regione Lazio, 2010), the diffusion of emission sources of  $PM_{2.5}$  for Lazio region is shown. A major concentration value is evident for the Roma city area.

Previous studies showed that the PM soluble components are more directly linked to the adverse health effects than the total metal content (Costa and Dreher, 1997; Adamson et al., 1999). In particular, inflammatory reaction may be faster for soluble compounds due to their immediate internalization. Thus, the solubility of PM metals in the lung fluids is an important criterion in the global assessment of PM toxicity.

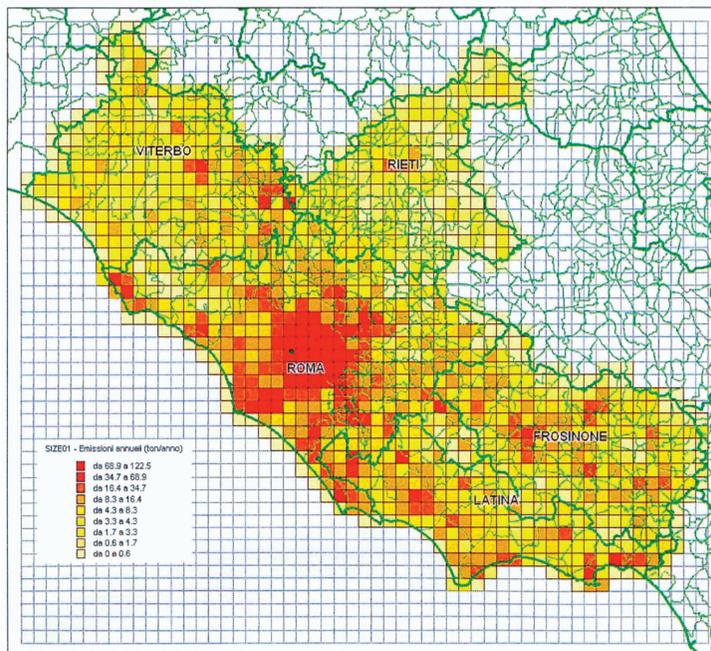


Figure 1. Annual emissions (tons/year) of  $PM_{2.5}$  in Lazio region (Regione Lazio, 2010).

In the literature, a number of papers report on the leachability of heavy metals from PM (Mukhtar and Limbeck, 2013 and references therein), and different extraction procedures and leaching agents such as high purity water (Birmili et al., 2006; Deshmukh et al., 2013), weak acids, chelating agents, buffer solutions and synthetic body fluids (Voutsas and Samara, 2002), have been proposed. The importance of experimental parameters such as pH, composition of the leaching solution, temperature, solid/liquid (S/L) ratio and time of extraction has been emphasized in several papers (Julien et al., 2011). Up to now, however, no in vitro measuring procedure for metal dissolution has still emerged as the gold standard method in the evaluation of PM lung bio-accessibility. With this in mind, in the present study the leaching tests were carried out after carefully selecting the experimental parameters in order to: i) use a leaching solution mimicking as closely as possible the human intrapulmonary fluid, also exploitable in subsequent in vitro cytotoxicity tests, ii) lower as much as possible the quantification limit (QL) of the analytical methods employed to quantify the leached components. A thorough characterization and analysis of the material under study has been also carried out, with special emphasis on the nature (origin, composition, morphology, size) and toxicity potential (heavy metal content, reactivity in biological media) of such material.

## Experimental

In the present work, a in-depth investigation on the PM<sub>2.5</sub> from two different sampling campaigns, was carried out. According to the standard procedures (Julien et al., 2011), both polytetrafluoroethylene (PTFE) and quartz (Qz) filters were utilized. To investigate the presence of heavy metals and their possible release in biological environment, a sufficient amount of material was collected. In order to verify the

potential mobility of heavy metals, a batch kinetic leaching test was carried out, using a physiological solution mimicking the pulmonary environment.

### Sampling

Two sampling campaigns for the collection of particulate matter were carried out in June 2011 and in February 2012, by ARPA LAZIO (Regional Environmental Agency) and ISS, at the following air quality monitoring stations in Rome (Figure 2):

1. CorsoFrancia: downtown - vehicular traffic oriented site;
2. Regina Elena: downtown - vehicular traffic oriented site;
3. Cinecittà: downtown - residential area;

Both campaigns were carried out at the first two sites (1 and 2, CorsoFrancia and Regina Elena, respectively), while the last site (3, Cinecittà) was added during the second campaign to gain additional data.

PM<sub>2.5</sub> sampling was carried out through automated sequential samplers (Figure 3) of the suspended particulate matter onto Ø 47 mm filter membranes. Aerosol sampling was conducted at medium-volume conditions (2.3 m<sup>3</sup>/h). Depending on analytical needs, either ultra-pure Qz or PTFE filters were used. Mass measurement of the gathered particulate matter was contextually carried out by using the beta rays attenuation method.

### SEM-EDS analysis

A scanning electron microscope (SEM, Zeiss 940A), equipped with a microanalysis EDS Link system, was used at 15 kV high voltage, 3.5 A filament current, 25 mm work distance operating conditions. Samples on both the Qz and PTFE filters were analyzed. From the morphological point of view, the particles onto the Qz filters were best visualized due to their good dispersion and separation among the silica fibers; instead, particles onto PTFE filter were embedded and



Figure 2. Sampling locations (1, 2, 3) in the urban area of Rome city.



Figure 3. FAI SWAM5a Dual-channel Monitor.

crowded, and not easily detectable. Silicate phases were not well detectable on Qz filters, but clearly visible on PTFE filters.

Back-scattered electrons (BSE) were utilized to detect the contrast between areas with different chemical compositions, since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), which makes them brighter in the image.

*X-Ray analysis*

X ray powder diffractometry (XRPD, Seifert MZIV diffractometer) was carried out on the samples without removing them from the PTFE filters; unfortunately, due to the high background noise, Qz filters resulted unsuitable to obtain a

good diffraction spectrum. The spectra were recorded at CuK $\alpha$  radiations, 40 kV and 20 mA operating conditions. Because of the presence of low angle diffractions, a glycolation procedure with ethylene glycol (80 °C, 4 hours) was performed to seek out the presence of clay minerals.

#### *Thermal analysis*

DTA/TGA analyses were performed in an air stream by using a Stanton Redcroft Model 1500 thermobalance with a sensitivity of 1  $\mu$ g, operated in the 20-1500 °C temperature range at a heating rates of 0.1-50 °C/min. The furnace winding is made of platinum-rhodium and the thermocouple is located under the rhodium-platinum crucible containing the sample. The analyses were carried out in the 20 to 850 °C range at 10 °C/min heating rate. Due to the little amount of particulate collected, which was also retained inside the filter pores, it was not possible to scratch off a proper amount of dust from the filter to obtain a representative specimen for thermal analysis, even after filter treatment in an ultrasonic bath. To overcome this difficulty, an analysis of the filter "as is" and an analysis of the particulate-bearing filter was carried out, from which the thermal behaviour of the particulate alone was obtained by comparison. To this purpose, the central circular portion of the filter containing the particulate was cut and transferred into the crucible of the thermobalance.

#### *Total metal content determination*

By assuming a homogeneous deposition of the particulate matter onto the filters, each loaded filter was carefully cut out in two equal pieces by using a ceramic blade. The weight of the particulate matter on each half-filter was calculated proportionally to the whole loaded filter. Successively, one half filter was digested to determine the total metal content, and the other half was leached by using the buffer solution described below.

In each experiment, a variable number of emitters was used. Such number was decided on the basis of the amount of the particulate matter collected onto the filters, being necessary to carry out the experiments having at least 10 mg of particulate matter available in order to assure sample representativeness and minimize procedural errors.

The portions of filters used for the determination of the total metal content were weighed and digested with a mixture consisting of 5 ml 69% HNO<sub>3</sub> (Hiperpur-Plus, Panreac) and 2 ml 30% H<sub>2</sub>O<sub>2</sub> (Ultrapure Reagent, J.T. Baker) in TFM vessels in a microwave system (Milestone 1200 Mega, Italy); the same procedure was also applied for blanks. The solutions obtained were diluted to 50 ml with ultrapure water and successively analysed by ICP-OES (Perkin-Elmer Optima 2000 DV) for Fe, Zn and by ICP-MS (Perkin-Elmer Elan 6100) for As, Cd, Cu, Ni and Pb.

#### *Leaching test procedure*

The leaching bath was a buffered solution with both pH and ionic strength / composition mimicking the lung deep interstitial fluid (130 mM NaCl, 5 mM KCl, 1.2 mM MgSO<sub>4</sub>, 5 mM NaHCO<sub>3</sub>, 1.5 mM CaCl<sub>2</sub>, 5.5 mM glucose, 10 mM HEPES, pH 7.4). Unlike other solutions widely used to simulate lung fluids, e.g. the Gamble solution and its variants, we kept the HCO<sub>3</sub><sup>-</sup> concentration to a minimum in order to avoid the progressive shift in both ion composition and pH due to the loss of CO<sub>2</sub> into the ambient air, where the CO<sub>2</sub> partial pressure is much lower than into the alveoli. pH stability was assured by including HEPES (4-(2-Hydroxyethyl)piperazine-1-ethanesulfonic acid), an organic buffer currently used in cell culture protocols; in our experimental setup, HEPES also simulated organic components of lung fluids such as organic acids, metabolites and proteins.

Weighed halves of the loaded filters, were suspended in 100 ml of the above buffer solution

in a polyethylene bottle (Kartell). The bottle was continuously shaken in a thermostatic oscillating bath at 37 °C in the dark. An analogous leaching test was carried out by using the same number of weighed halved blank filters. Kinetic experiments were performed by sampling the bottle content at 15 min, 60 min, 180 min, 24 h, 96 h (4 days), 168 h (7 days) and 264 h (11 days) time points. For each experiment, a 3 ml fraction of the leaching solution was withdrawn and filtered through a 0.45 µm membrane filter (Millex HA, Millipore). Throughout the experiments, temperature and pH of the solution were periodically checked and recorded. To 2.5 ml of the filtered solution transferred into a polypropylene tube, 1 ml 69% HNO<sub>3</sub>, 0.5 ml 30% H<sub>2</sub>O<sub>2</sub> and, after 2 h, 1 ml of ultrapure water were added in sequence. The solution was then diluted to 5 ml final volume and an aliquot was analysed by ICP-MS and by ICP-OES.

The amount of particulate matter samples utilized for both the total metal content determination and the leaching procedures was insufficient for the replicate determination of uncertainties associated with the analytical procedures for each sample. Hence, the Practical

Quantification Limit (PQL) and the coefficient of variation (CV%) (Table 1) were calculated by applying an analogous analytical procedure both to test filters (other than those analysed) obtained during the same sampling campaign and to certified reference material (NIST 1648a). In particular, the PQL (the lowest level that can be reliably achieved within the specified limits of precision and accuracy during routine laboratory operating conditions) was obtained as 10 times the standard deviation of the procedural blanks.

## Results and discussion

### *PM<sub>2.5</sub> characterization*

*Identification of mineral phases and possible attribution of metal contents.* By combining different analytical techniques (SEM-EDS, X-ray and DTA), sulphates, silicate, oxides, and carbonaceous phases resulted to be the most abundant chemical components. In particular, well-crystallized sulphates (melanterite) silicates (zeolites), and Fe-oxides, were identified. Subordinate carbonates, clay minerals, and various oxides and hydroxides were also found.

In particular, SEM observation allowed most

Table 1. Estimated Practical Quantification Limit (PQL) and Coefficient of Variation (CV%).

Element	Total Content		Leaching	
	PQL(mg/kg)	CV (%)	PQL (ug/L)	CV (%)
As	0.5	5	*	**
Cd	0.1	8	0.1	10
Cr	10	6	5	**
Cu	5	6	10	**
Fe	90	5	50	**
Ni	10	3	0.5	10
Pb	1	10	1	10
Zn	30	5	5	5

\* Not detectable due to the significant interference related to the composition of the leaching solution;

\*\*Not calculated as the leached concentration was below PQL.

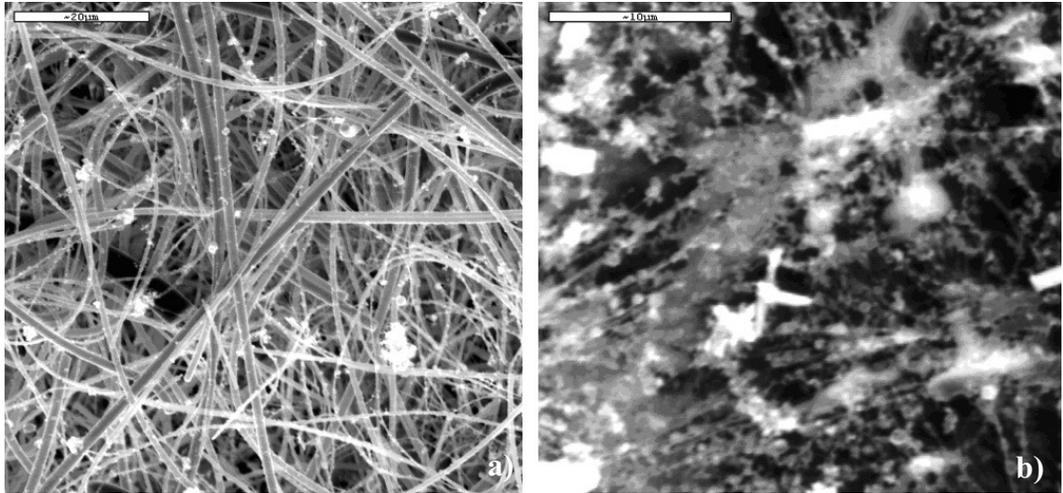


Figure 4. a) BSE images of PM sample on Qz filter, and b) on PTFE filter.

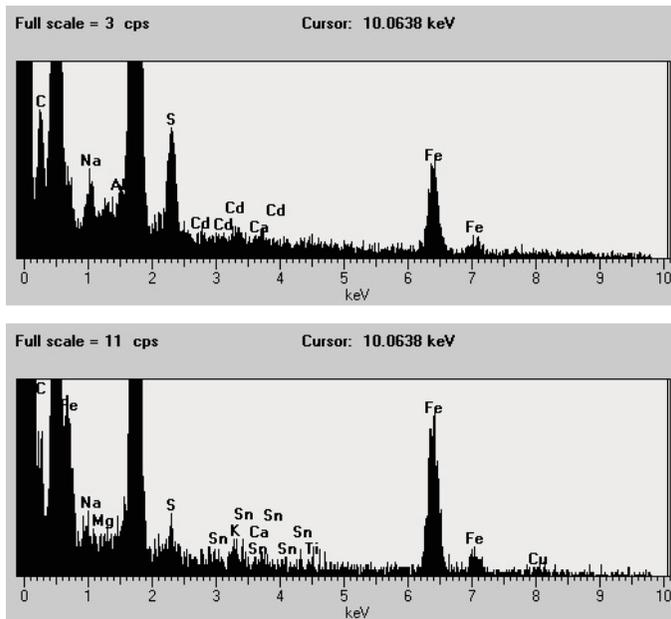


Figure 5. Different concentration of S respect to Fe: a) Fe-oxides-hydroxides + Fe-sulphate; b) Fe-oxides-hydroxides.

of the particles constituting the samples under study to be individuated and defined (Figure 4 a, b). By EDS microanalysis (Figure 5 a, b), iron -

associated to sulphur and other metallic and not metallic elements - was the most represented chemical element.

XRPD analysis showed that melanterite, an epta-hydrate iron sulphate ( $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ ), was the most abundant crystalline phase (Figure 6), while other sulphates, silicates, and various Fe-oxides were subordinately present. Interesting is the presence of a zeolite phase, well evidenced by glycolation treatment, which resulted in the increase of the  $2\theta$  angle causing shifting of the peak around  $6^\circ 2\theta$  (outwardly attributable to the clay group minerals), witnessing the typical behaviour of zeolite.

The DTA and TGA patterns of the PTFE filter alone (dotted line) and after collection of the particulate (thick line), are reported in Figure 7. Concerning the filter alone, the small endothermic effect at about  $330^\circ\text{C}$  originated from polymer melting (Stone, 1960). The exothermic effect at about  $570^\circ\text{C}$  was due to the combustion of the organic matrix of the filter taking place immediately after the lost of the fluorine atoms. The combustion was complete at

about  $580^\circ\text{C}$  but the weight loss slowly proceeded to reach about 100% around  $850^\circ\text{C}$ .

By analysing the particulate, the DTA pattern showed two endothermic effects, at  $110^\circ\text{C}$  (A) and at  $140^\circ\text{C}$  (B), with a corresponding weight loss of about 3% for each effect. A few hypotheses can be formulated about these effects. The former could be attributed to either the loss of hydration water from the sample (water in the gypsum, clays and zeolites) or the probable presence of ferrihydrite (Eggleton and Fitzpatrick, 1988), while the latter could be accounted for by water loss from melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) (Smykatz-Kloss, 1974; Wang et al., 2007), which was also revealed by SEM and X-ray analysis. Alternatively, the two endothermic effects could be also attributed to the largest polymorphic transition and to the phase transition (melting) of ammonium nitrate, respectively, even though such effects are reported to occur at slightly higher temperatures,

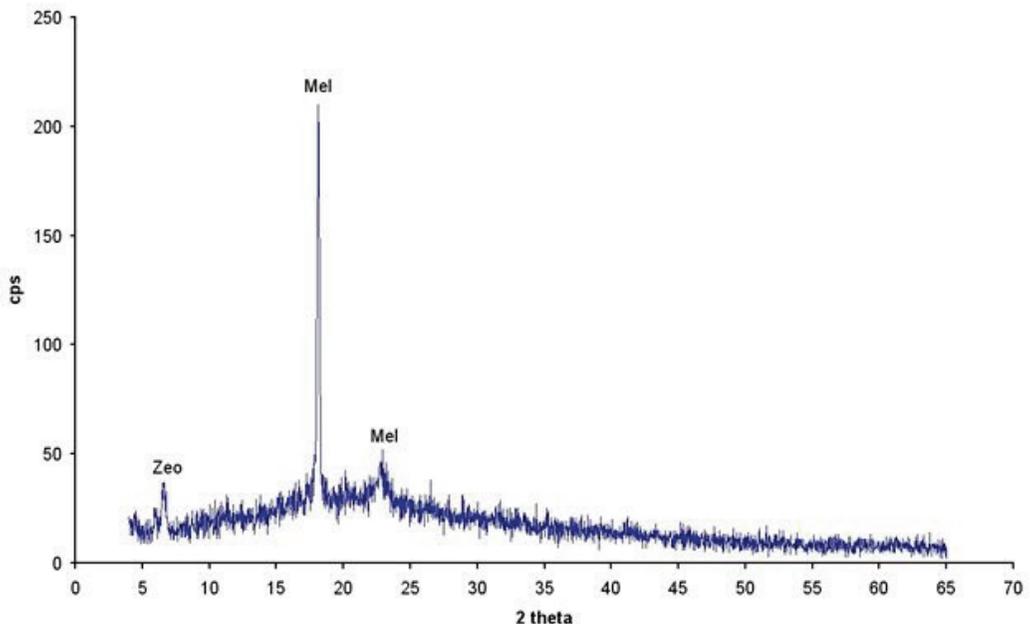


Figure 6. XRPD spectrum on a sample of Regina Elena site (Feb. 2012: Mel = melanterite, Zeo = zeolite).

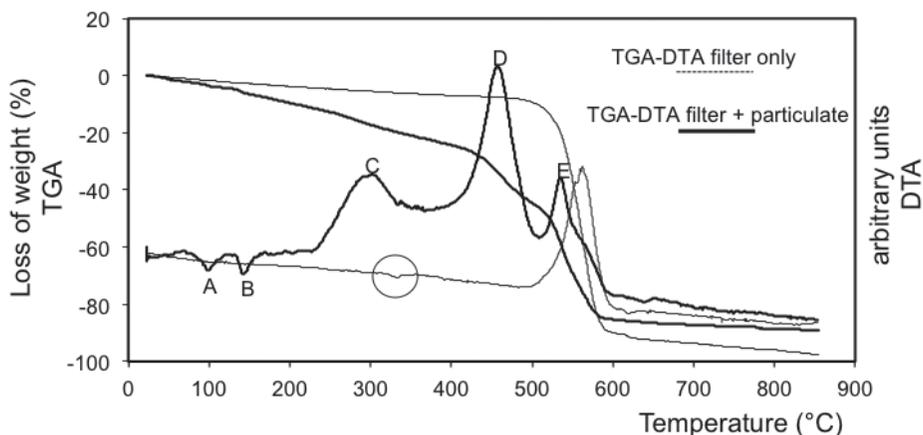


Figure 7. Thermal curves in air of atmospheric particulate. Dotted line: TGA/DTA of the PTFE filter used to collect the atmospheric particulate. Thick line: TGA/DTA of the atmospheric particulate-bearing PTFE filter.

125 and 169 °C respectively, (Mackenzie, 1972). Moreover, other researchers exclude that weight losses, and, consequently, DTA-effects, in the range 80-180 °C be ascribed to ammonium salts or to other inorganic ions (Perrino et al., 2012; Canepari et al., 2013). Finally, the two low-temperature endothermic effects could be also be ascribed to phase transitions of a mixture of potassium nitrate and ammonium chloride (Mackenzie, 1972), even though, again, they should take place at temperatures higher than those recorded in our sample.

At higher temperature, the pyrolysis in air of the organic matter in the particulate occurred and gave origin to organic vapours surrounding the sample. As soon as the vapours reach the proper concentration, combustion occurred at about 300 °C, with a corresponding weight loss of about 14%. Finally, the combustion of the organic residue occurred at about 460 °C, with a weight loss of about 19%. The combustion of the PTFE filter at about 530 °C (E) and a corresponding weight loss of about 51%, occurred at a lower temperature than that of the filter alone (570 °C), a behaviour probably due to the presence of a

large amount of iron in the particulate ash that acts as a catalyser for the scission of the fluorine atoms, whereby the combustion of the carbonaceous filter matter is accelerated.

The ash of the particulate accounted for about the total residue of the combustion (11%), as the total weight loss of the PTFE filter is about 100%.

#### *Total heavy metals concentrations*

Bulk chemical data evidenced the presence of heavy metals, in particular As, Cd, Cr, Cu, Ni, Pb, Zn, and Fe. These results were in good agreement with those obtained by exploiting other instrumental analyses, so offering comprehensive information on quantitative metal contents inside the particulate matter. Unlike iron, the relatively high amount of metals in the particulate matter samples seems not to be associated to the above crystalline phases, being prevalently enclosed in the clustered carbonaceous particles. This is clearly showed by the SEM-EDS spectra (Figure 5) for Cd and Cu, which are better singled out when the carbon line is higher respect to the other spectra in

which metals are not detected. DTA and TGA investigations confirmed the presence of high amount of carbonaceous constituent, associated to mineral phases that prevalently contain water (molecular H<sub>2</sub>O or hydroxyl group). In fact, melanterite and Fe-oxy-hydroxides phases were well highlighted.

As for the elements object of this study, previous investigations of PM<sub>2.5</sub> in the city of Rome (Canepari et al., 2009) attributed Fe and As as coming from crustal material due to the large extension of volcanic areas in the Lazio region and in the rest of central Italy, where the outcropping volcanic rocks are particularly rich in these elements. Moreover, in the study of Canepari et al. (2009), Cr, Cu, Ni and Pb were linked to traffic-related sources and the same source was also recognised for Cd and Zn, though not attributed to direct emission from tailpipe but generated by vehicular abrasive processes, like brake linings and tyre abrasion (Birmili et al., 2006; Moreno et al., 2006).

Our results (Tables 2 and 3) show that the highest quantity of particulate is collected during the winter season, being the weight/volume of

samples collected during summer about 70-75% of those collected during winter. This is in agreement with the usual trend found in urban areas, where the inputs from heating and from vehicular traffic are higher in winter.

The total concentration of As, Cd, Cr, Cu, Fe, Ni, Pb and Zn in the collected airborne particulate was comparable with that previously published for other Italian urban areas (D'Alessandro et al., 2003; Mazzei et al., 2008), for the city of Rome (Canepari et al., 2006; Canepari et al., 2008) and for other European areas (Ayrault et al., 2010; Voutsas and Samara, 2002; Johansson et al., 2009 and references therein).

None of the elements regulated by the Italian law (Dlgs. 155/2010) was present at concentrations exceeding the limit values, that are 6, 5, 20, and 500 ng/m<sup>3</sup> for As, Cd, Ni and Pb, respectively, in accordance with the European Directive 2008/50/EC.

Arsenic, cadmium and chromium showed a higher concentration per volume in winter, while the concentration per dry mass was constant in winter and summer. These findings suggest that such chemicals have the same source (same

Table 2. PM<sub>2.5</sub> metal concentrations, expressed as w/v (ng/m<sup>3</sup>), and total particle mass (µg/m<sup>3</sup>).

	June 2011		February 2012		
	Regina Elena	Corso Francia	Regina Elena	Corso Francia	Cinecittà
As	0.33	0.37	0.53	0.66	0.81
Cd	0.17	0.06	0.32	0.25	0.38
Cr	1.09	1.88	1.74	2.75	2.04
Cu	15.98	22.47	8.64	15.99	9.75
Fe	222.8	975.2	128.9	282.2	157.8
Ni	3.20	4.71	1.71	3.48	3.91
Pb	5.57	10.35	10.29	11.84	14.53
Zn	22.08	52.56	27.13	60.98	45.36
PM <sub>2.5</sub>	18.23	23.44	26.50	31.20	43.40

Table 3. Total metal concentrations in PM2.5 expressed as w/w dry weight (mg/kg).

	June 2011		February 2012		
	Regina Elena	Corso Francia	Regina Elena	Corso Francia	Cinecittà
As	20.7	15.2	19.6	18.5	20.4
Cd	10.6	2.4	12.0	8.8	7.8
Cr	68.1	77.2	64.5	47.2	83.3
Cu	997	921	320	225	486
Fe	13895	39953	4768	3636	8710
Ni	199	193	63.2	90.1	105
Pb	347	424	381	334	363
Zn	1377	2153	1004	1048	1869

concentration in the particulate) during the two seasons, while the amount of particulate containing these elements is higher in winter. Copper, iron and nickel showed a different trend, with higher concentration in summer both per volume and dry weight, suggesting that their source is variable during the two seasons. Lead and zinc concentrations showed no clear differences between summer and winter, probably linked to particulate emitted from the same sources and in the same amounts.

#### Leaching tests

In order to evaluate the potential of metal release into a biological environment (particularly lung), the same particulate samples (half filters) have been leached using the solution described in the method section. Among the metals analysed, only Cd, Cu and Pb were constantly detected in our experimental conditions, and As, Cr, Fe, were always below the detection limit in the leaching solutions. Ni and Zn were detected only in the leaching solutions of the winter campaign.

The leaching trends (Figure 8 a, b, c, d) are shown as logarithmic trendlines on scatter plots. A logarithmic trendline is a best-fit curved line

usefully adopted when the changing rate of the data values increases or decreases quickly and then levels out. This representation shows the trend (time and amount) of metal release in the given experimental conditions.

Pb (Figure 8a) showed a regular trend, with a plateau level attained at about 96 hours. Percentages of leached element were comparable in samples from the same sites during different seasons (about 25% Regina Elena, 30% Corso Francia). We can notice that the highest percentage was leached from the Cinecittà-winter samples (about 45%), suggesting that in this case Pb is associated to a more labile phase.

Cd (Figure 8b) is the most mobile element in our working conditions, having been leached up to about 99% in the Corso Francia site during summer. This sample showed a peculiar behaviour, being characterized by the lowest total concentration and the highest leaching rate, while the elements from the other samples were released to about the same percentage; on this basis, the presence in the sample of Cd bound to more labile phases is suggested.

For all samples, the time to reach the plateau values was relatively short, having such values

been attained within 180 minutes; however, in some samples the mobile fraction was extracted within the first step of treatment (15 minutes) and the successive variations in concentrations were comprised in the experimental variability.

The high Cd leachability rate is consistent with previous data obtained from other urban areas (Voutsas and Samara, 2002; Fernandez et al., 2000) and is in accordance also to the typical geochemical behaviour of Cd, known to be a very mobile element, and even more so in oxidizing environments (Kabata-Pendias and Mukherjee, 2007).

Cu showed an irregular trend, accountable for by the very small amounts detected (close to the detection limit). Consequently, the leaching curves for Cu are not reported here and only some general considerations can be drawn. During the first 15-60 minutes of leaching, 20-30% Cu was released, with no further variation up to the end of the treatment. The Cu leaching pattern was irregular in shape, plausibly because of concurrent re-adsorption / re-precipitation phenomena. The rapid dissolution of copper in our samples is consistent with previous literature data showing that this metal easily forms oxide derivatives associated to dust particles, a weak interaction easily overcome even by rainwater (Kabata-Pendias and Mukherjee, 2007).

Ni (Figure 8c) and Zn (Figure 8d) were detected only during the leaching of the winter samples and were comparable in behaviour (34% and 48% maximal extraction attained after about 96 hours of treatment, respectively). This result suggests a higher mobility of such chemicals in winter samples, since their total concentrations were similar either in summer and winter samplings.

It is worth noting the behaviour of iron during leaching, as in addressing the toxicity of airborne PM, the release of this element into physiological media is considered as a key factor in the production of reactive oxygen species (ROS) resulting in health effects (Ntziachristos et al.,

2007). In our experiments, although iron is present at high concentrations (up to  $1\mu\text{g}/\text{m}^3$ , and about 4% in weight) in the analysed particulate, it is not detected into the leaching solutions. This information leads us to suppose that in our samples Fe is present in its oxidized state ( $\text{Fe}^{3+}$ ), because generally  $\text{Fe}^{3+}$  compounds are water insoluble at the near neutral (7.4) pH conditions of our leaching experiment and are water soluble only in strongly acidic solutions (Brookins, 1988). The melanterite crystalline phase (detected by XRD), containing iron in its reduced and more soluble form  $\text{Fe}^{2+}$ , can be consequently supposed to be present in very small amounts in respect to the other phases with lower crystallinity, or even amorphous. The good detectability of melanterite by XRD can be therefore attributed to its good crystallinity, more than to its abundance. We can also hypothesize that the  $\text{Fe}^{3+}$  present in the samples is bound in poorly crystalline forms (hard to be detected by XRD), as usually found in Fe-oxy-hydroxide, especially when generated by neo-formation processes, as we can suppose occurring in atmospheric environment by the oxidation of  $\text{Fe}^{2+}$ . Thermal analyses confirmed the presence of hydrate and hydroxi-hydrate phases which can contain  $\text{Fe}^{3+}$  (Fe-oxy-hydroxides, e.g. ferrihydrite), as well as the BSE images reported in Figure 9, where the metallic particles and the relative EDS spectra with predominant Fe contents are well visible. Further investigations are in progress to better identify and characterize these microcrystalline phases.

### Concluding remarks

The comprehensive investigative approach adopted in the present work provided preliminary results of an in-depth characterization of the  $\text{PM}_{2.5}$  analysed. These significant results may represent a critical basis for successive studies on the toxicity of heavy metals from  $\text{PM}_{2.5}$ , the particulate matter fraction that usually accounts for the highest metal contents.

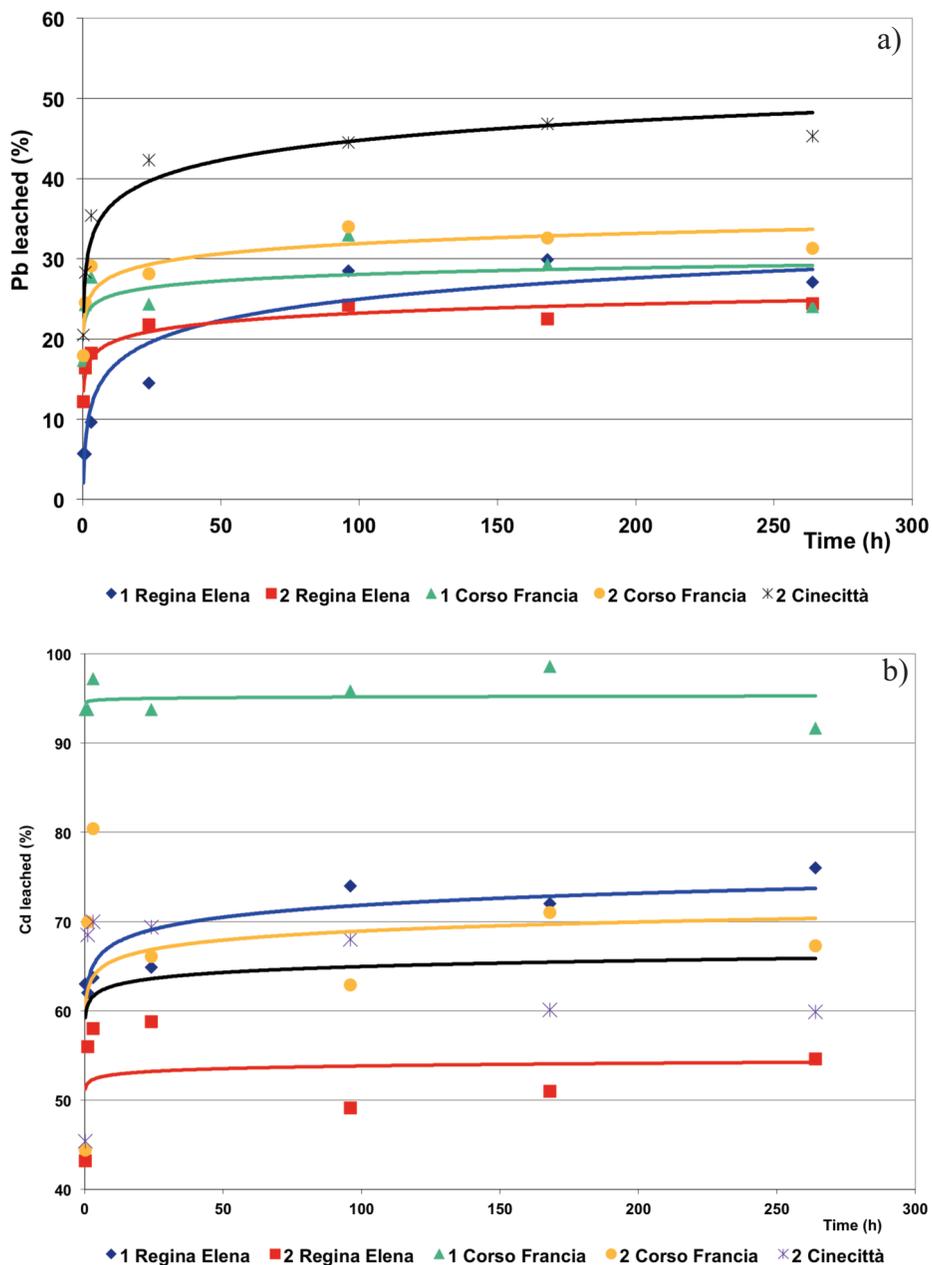


Figure 8. a) Pb leached (%). (1 summer, 2 winter); b) Cd leached %. (1 summer, 2 winter); c) Ni leached (%). Ni was detectable only for the sample of the winter campaign.; d) Zn leached (%). Zn was detectable only for the sample of the winter campaign.

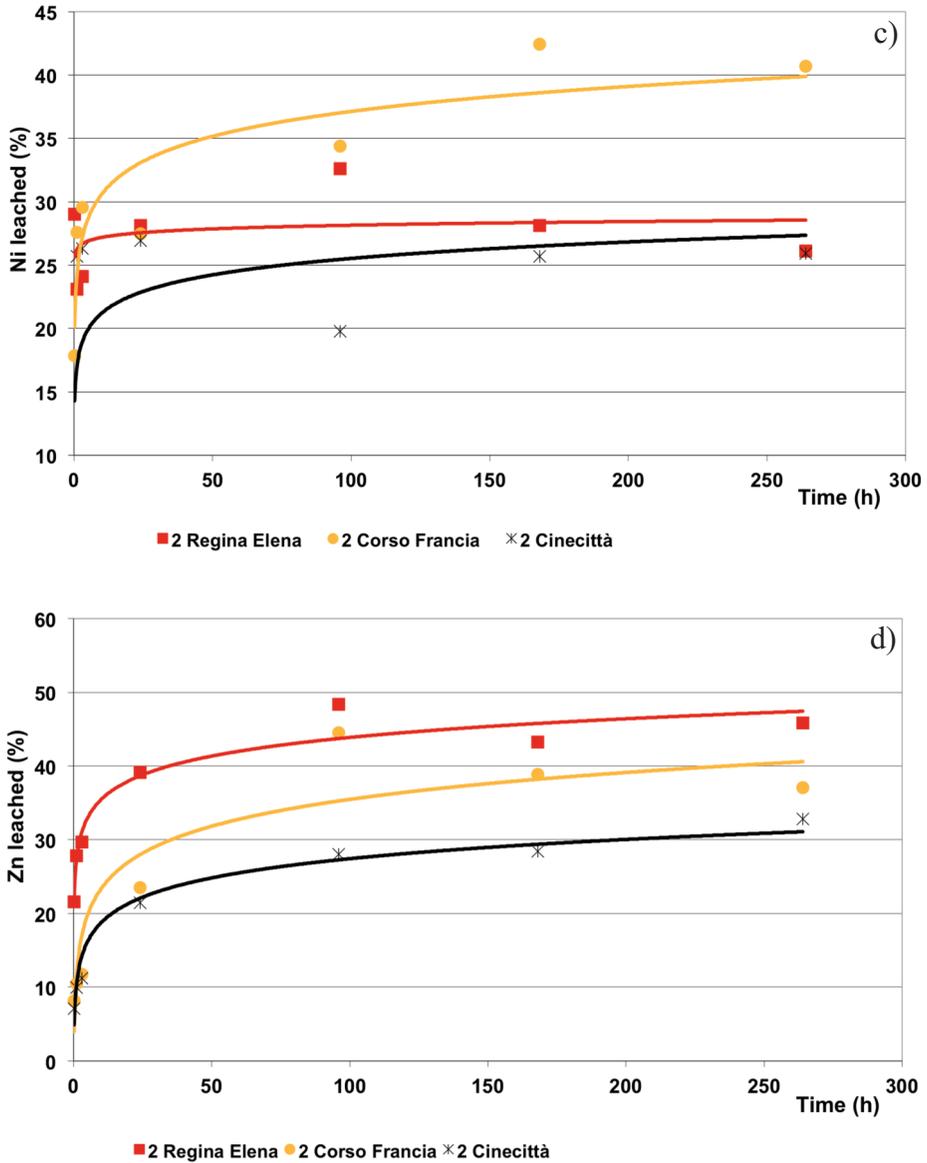


Figure 8. ...Continued

A good correlation between mineralogical and thermal results and chemical data has been possible. In fact, the bulk chemical analyses gave a chemical identity well comparable with the

mineralogical and physical investigations. Moreover, heavy metals leaching tests showed that metals behaviour is regulated by their hosting matrix and allowed us to hypothesize the

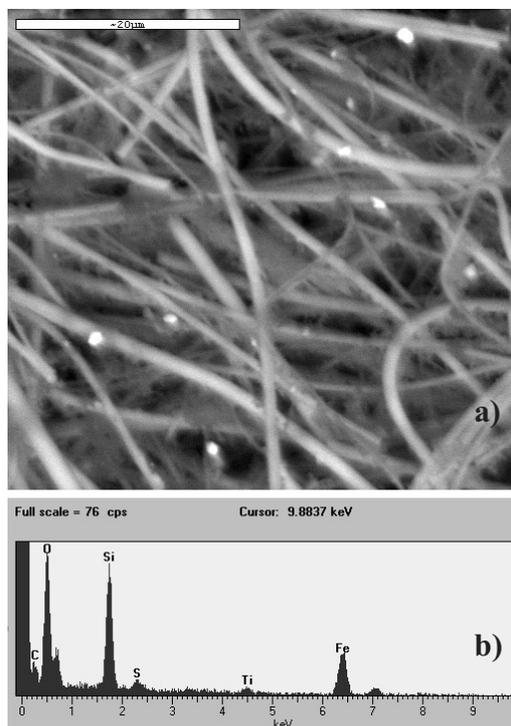


Figure 9. a) BSE image of particulate on Qz filter showing the metallic micro-particles. b) EDS spectrum of a micro-particle containing prevalently Fe. Note the very high oxygen line indicating oxides and/or hydroxides phases.

form in which the elements are present in the material under study. In particular, the evidence that the abundant Fe content measured in the PM was not detected in the leaching solutions, allows us to hypothesize that this element is present in its oxidized  $\text{Fe}^{3+}$  form, possibly forming oxy-hydroxides microcrystalline phases, as evidenced also by the results of the mineralogical investigation. Additionally, the findings of the present study allow to foretell that the leaching procedure adopted would be appropriate for toxicity studies on heavy metals released from PM; in fact, while providing consistent analytical information, our procedure allows the same

leaching solution to be also exploited in *in vitro* cytotoxicity experiments.

Finally, the absence of iron in the leaching solution, which simulates the pulmonary environment, casts doubts as for the effective role of this element as an aetiological factor in specific pulmonary pathologies and deserves further investigation.

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