ABSTRACT

The European ceramic tile industry is mostly concentrated in two clusters, one in Castelló (Spain) and another one in Modena (Italy). Industrial clusters may have problems to accomplish the EU air quality regulations because of the concentration of some specific pollutants and, hence, the feasibility of the industrial clusters can be jeopardized. The present work assesses the air quality in these ceramic clusters in 2008, when the new EU emission regulations where put into force. PM_{10} samples were collected at two sampling sites in the Modena ceramic cluster and one sampling site in the Castelló ceramic cluster.

PM_{10} annual average concentrations were 12-14 μg/m^3 higher in Modena than in Castelló, and were close to or exceeded the European limit. Air quality in Modena was mainly influenced by road traffic and, in a lower degree, the metalmechanical industry, as evidenced by the high concentrations of Mn, Cu, Zn, Sn and Sb registered. The stagnant weather conditions from Modena hindering dispersion of pollutants also contributed to the relatively high pollution levels. In Castelló, the influence of the ceramic industry is evidenced by the high concentrations of Ti, Se, Tl and Pb, whereas this influence is not seen in Modena. The difference in the impact of the ceramic industry on the air quality in the two areas was attributed to: better abatement systems in the spray-drier facilities in Modena, higher coverage of the areas for storage and handling of dusty raw materials in Modena, presence of two open air quarries in the Castelló region, low degree of abatement systems in the ceramic tile kilns in Castelló, abundance of ceramic frit, glaze and pigment manufacture in Castelló as opposed to scarce manufacture of these products in Modena. The necessity of additional measures to fulfil the EU air quality requirements in the Modena region is evidenced, despite the high degree of environmental measures implemented in the ceramic industry.

The Principal Component Analysis (PCA) identified four factors in Modena, attributed to: road traffic + metalmechanical industry, mineral, ceramic, and background; and three factors in Castelló, attributed to: mineral, ceramic (with influence of road traffic) and regional background. The additional measures to improve the air quality should be focused mainly on road traffic in Modena, and on the ceramic industry in Castelló.

KEYWORDS

Ceramic industry, PM, metals, cluster, road traffic

1 INTRODUCTION

It is well known that the exposure to ambient particulate matter (PM), either fine or coarse, has negative effects on human health (Brunekreef and Forsberg, 2005; Pope III and Dockery, 2006). PM has also effects on visibility (Watson, 2002), ecosystems (Grantz et al., 2003) and the Earth's radiative balance (Forster et al., 2007). European standards (Directive 2004/107/EC and Directive 2008/50/EC) regulate the levels of PM_{10}, $PM_{2.5}$, Pb, Cd, As and Ni.

Meeting the ambient target and limit values may be a challenge in some industrialized areas, especially in industrial cluster areas, where additionally to the urban PM sources, industrial PM emissions affect the air quality. Industrial clusters are common because they facilitate innovation and increase the competitiveness of the companies due to several advantages, such as easier raw materials and equipment delivery, constant interaction among companies, easier interaction with universities or research centres and financial institutions (Lunbdvall, 1993; Edquist, 2004). From the environmental point of view, industrial clusters tend to provoke the concentration of some specific pollutants (Querol et al., 2007a). One of these emitting industrial activities is the manufacture of ceramic tiles and ceramic glaze components (Konieczyński et al., 2007; Monfort et al., 2004, 2011; Palmonari and Timellini, 1982; Santacatalina et al., 2010; Timellini et al., 1993). Around 80% of the European Union ceramic tile and ceramic glaze components manufactures are concentrated in two areas, forming the so-called ceramic clusters, in Modena (Italy) and in Castelló (Spain), which implies a high concentration of industrial emission facilities. Moreover, within the area of the Modena ceramic cluster, metal mechanic industries are located, adding to the industrial emissions affecting the air quality of the area. Previous studies found that PM_{10} and heavy metal concentrations are the two parameters of major concern to fulfil EU legal requirements (Minguillón et al., 2007b; Querol et al., 2007a).

To meet the air quality standards, emissions of different pollutants (including PM) are also regulated. The European Directive 1996/61/CE (IPPC Directive: Integrated Pollution Prevention and Control) and subsequent amendments (replaced in the Directive on industrial emissions 2010/75/EU) establish the necessity of obtaining official emission permits for each industrial facility, based on the most effective and advanced techniques to prevent or reduce impacts, known as the Best Available Techniques (BAT). The application of these Directives is expected to reduce from 2007 onwards the differences in the emission limit values across EU at mid-term. Nevertheless, depending on national or regional previous legislation an adaptation period could be needed. So, in the year taken as a basis for this study (2008), the first of the actual application of the IPPC Directive, significant differences can be found between the emission limit values and degree of BAT implementation in the two studied clusters.

The Castelló ceramic cluster is located in a 400 km^2 area in Eastern Spain (Figure 1). It has a population of 336000 inhabitants, spread in towns 20 km far from each other, with a population density from 120 to 1600 inhabitants/km^2, depending on the town. It consumes a large supply of clayey raw materials (around 12 million ton/year) coming from sources which include opencast quarries within the cluster area. Other important raw materials used in the ceramic industry include a large variety of natural and synthetic products, such as feldspars, zircon or boracic components (Criado et al., 2004). In the Castelló cluster a major NW atmospheric flow prevails during winter. On the contrary, in summer, thermally induced local and meso-scale circulations give rise to the sea breezes regime, inland during the day and towards the coast during the night, which hinders air-mass renovation due to re-circulation of the air masses (Millán et al., 1997). The annual rainfall varies between 300 and 500 mm and depends on just a few days of rain (González Hidalgo et al., 2003); in 2008 the annual rainfall was 421mm, distributed in 67 days (Quereda et al., 2009) (Table 1).

The Modena cluster is located in an area of 400 km^2, situated in the Po Valley. It has a population of 287000 inhabitants, similar to that of the Castelló cluster, with a population density from 500 to 1000 inhabitants/km^2, with the different towns being 7-8 km apart from each other. No open quarries are located in the area, because the vast majority of raw materials are imported. The area has frequently occurring stagnant atmospheric conditions in winter hindering the dispersion of pollutants. These conditions are more intense in Modena than in Castelló region (see section 3.1). The annual rainfall in 2008 was 754 mm, and it was distributed throughout the twelve months of the year (111 days of rain) (http://www.arpa.emr.it) (Table 1).

The ceramic tile production in 2008 was similar in both clusters (300-450 10^6 m^2), whereas the production of ceramic frits, glazes and pigments was much higher in Castelló. On the other hand, in the Modena region there are several metalworking and metalmechanical facilities (about 400, mainly small or medium). As stated above, in 2008 the degree of application of the BAT was different in both ceramic clusters due to the previous legislation. Whereas all the ceramic facilities in the Modena cluster were using BAT, in the Castelló cluster the situation was different. The main differences in 2008 can be summarised as follows: a) the storage and handling areas of dusty raw materials were mainly outdoors (60% of the facilities) in Castelló and mainly indoors in Modena; b) the emission limit for existing and new spray-driers in Spain was 50 and 30 mg/Nm^3 (where N stands for normal conditions) (until 2015), respectively, and it was 30 mg/Nm^3 or less for all spray driers in Modena; c) the ceramic kiln facilities using fabric filters was less than 5% in Castelló (Minguillón et al., 2009) with the consequent emissions released directly to the atmosphere (implementation of BAT is in process nowadays) while in Modena all the ceramic kilns were equipped with fabric filters.

The identification and quantification of the PM sources in a given place is feasible if a complete PM chemical composition dataset, including major and trace elements, ions, elemental carbon (EC), and organic carbon (OC), is available (Viana et al., 2008). Previous studies assessed the impact of the ceramic industry on the air quality in the Castelló cluster (Minguillón et al., 2007a, 2007b, 2009; Querol et al., 2001a, 2007a; Vicente et al., 2012). As a consequence an Air Quality plan for this area was elaborated and published in 2008 (Generalitat Valenciana, 2008). The PM_{10} concentrations registered by these studies were higher than those recorded in the present study. Querol et al. (2007a) identified the tracers of the ceramic industry in the Castelló area: Zr, Zn, Pb and As, and probably Tl. Minguillón et al. (2007b) identified five PM sources. The mineral source, mainly attributed to the ceramic industry, but also with minor contributions from soil resuspension (maximum 1 μg/m^3) and African dust outbreaks (maximum 3 μg/m^3), contributed with 11.2 μg/m^3. The regional background + sea spray source, which was influenced by the industrial estate located on the coast (an oil refinery and a power plant fuelled by natural gas), accounted for 12.1 μg/m^3. The industrial source, attributed to the manufacture and use of glaze components, including frit fusion, accounted for 5.4 μg/m^3, although the contribution decreased notably from 2002 to 2005, coinciding with the implementation of PM abatement technology in the frit fusion kilns of the area. Finally, the road traffic source accounted for 3.7 μg/m^3. Hence, the total industrial contribution was estimated in approximately 12 μg/m^3, which was about 35% of bulk PM_{10}.

The Italian ceramic tile industry was the first in Europe to develop and adopt techniques for the reduction of the environmental impact, which has been studied since the early seventies by Centro Ceramico Bologna, the Regional Environmental Protection Agency (Agenzia Regionale Prevenzione e Ambiente dell'Emilia-Romagna, ARPA) and the ceramic tile industries (and their Association, Assopiastrelle). Several studies estimated the atmospheric emissions from ceramic plants, and identified Pb as the main tracer, among other metals (Palmonari et al., 1978; Palmonari and Timellini, 1989; Busani et al., 1995; Busani and Capuano, 2000). Some studies on the air quality in the Modena cluster were mainly performed by the Regional Environmental Protection Agency (ARPA) (Busani and Capuano, 1999; Busani and Capuano, 2000; ARPA, annual reports, http://www.arpa.emr.it/modena; ARPA, 2004, 2005). An Air

Quality Plan was published in 2007 (ARPA, 2007). Other general studies have been carried out (Picchi et al., 2001), such as studies on the Pb occupational exposure (Candela et al., 1998) and children exposure (Ferri et al., 1998). The regional inventory of atmospheric emissions elaborated by ARPA estimates the contribution to primary PM_{10} total emission from different sources. Considering both the urban area and the ceramic district, in 2007 road traffic and ceramic industry accounted for about 40% each of the total primary PM_{10} emissions; the domestic heating and the metalworking and metalmechanical industry accounted for 6% and 5%, respectively. A complete study on the Modena cluster, including chemical characterization of ambient particulate matter is currently missing, and this study aims to fill this research gap.

There is an open debate on the feasibility of the industrial clusters in EU, which can be jeopardised by the new EU environmental regulations. Within this frame, the objective of the present work is to assess the air quality in the two most important ceramic tile clusters in Europe (whose production accounts for around 90% of the EU), considering their social, meteorological and technological similarities and differences.

2 METHODOLOGY

2.1 Sampling sites, schedule and measurements

Two sampling sites in the Modena ceramic cluster and one sampling site in the Castelló ceramic cluster were selected. Parco Ferrari (PF, 44º38'24''N, 10º54'36''E, 30 masl) is an urban background site located in a park in the west part of the city of Modena. Maranello (MR, 44.53N, 10.87E, 110 masl) is an industrial site located in a city with the same name 18 km south of Modena, inside the ceramic cluster. L'Alcora (LA, 40º04'07''N, 00º12'43''W, 175 masl) is an urban background site located in the town of the same name in the Castelló ceramic cluster (Figure 1). L'Alcora was chosen among the possible sampling sites in the Castelló cluster because of its similarities with Maranello regarding the size of the town (11000 and 18000 inhabitants, respectively). Unfortunately, there was no sampling campaign in the town of Castelló, which would have been comparable to Parco Ferrari site. Nevertheless, sampling was carried out at three additional sites in the Castelló ceramic cluster: Vila-real (urban), Borriana (urban) and Onda (suburban). Sampling schedule and measurements were similar to those carried out at L'Alcora. For the sake of brevity, only some of the collected data at these three sites will be used in the present work, whereas data collected at L'Alcora will be discussed in detail.

The sampling period was determined by the availability of samples in the Modena cluster, which is limited to the year 2008. At MR and PF, samples were collected daily (00:00 to 23:55) during 2008 by low volume samplers on 47mm diameter quartz fibre filters (Whatman). At MR a 2025 Partisol Plus-Rupprecht & Patashnick working at 1 m^3/h was used. At PF a LSPM10 - Unitec working at 2.3 m^3/h was used. After sampling, PM_{10} concentrations were determined gravimetrically. One of every two daily samples was used for chemical analyses (173 daily samples from each of the sites). The analyses were carried out using composite samples, obtained by grouping 3-5 daily samples, resulting in 43 composite samples from each of the sites. At LA, PM_{10} samples were collected daily (00:00 to 23:55) during 2008 by a high volume sampler (30 m^3/h) DIGITEL DH-80 on 150mm diameter quartz fibre filters (QF20 Schleicher and Schuell). After sampling, PM_{10} concentrations were determined gravimetrically. Two randomly selected samples per week (including weekends) were used for chemical analyses.

2.2 Chemical analysis

Samples were analyzed following the procedure described by Querol et al. (2001b). A quarter of each filter was used for analyses of the selected samples. Filters were acid digested (HNO_3:HF:$HClO_4$), and the resulting solution was analyzed by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Mass Spectrometry (ICP-MS) for the major and trace elements concentration determination, respectively. Blank filters were analyzed and the corresponding blank concentrations were subtracted from each sample to calculate ambient concentrations. A few mg of the reference material NIST 1633b were added to blank filters and were analysed to check the accuracy of the analysis of the acidic digestions.

Due to the variable concentrations of some elements in the blank Whatman filtres (used for MR and PF), concentrations of the following elements could not be determined for the corresponding samples: Al, Ca, K, Na, Mg, Li, Cr, Ni, Rb, Sr, Y and Cs. To the contrary, these elements were analysed correctly for LA samples.

2.3 Principal component analysis

A receptor modelling technique was applied to identify the main PM_{10} sources. Given its simplicity and suitability for this type of data, a varimax rotated Factor Analysis (Principal Component Analysis, PCA) was chosen. The analysis was carried out for a global dataset including data from both Parco Ferrari and Maranello sites. Species with concentrations often below the detection limit or with detected analytical problems were not considered for the PCA. The selected species for PF and MR were: PM_{10}, Fe, SO_4^{2-}, Ti, V, Mn, Co, Cu, Zn, As, Se, Cd, Sn, Sb, La, Ce, Nd, Pb, Bi and Th. For LA, two analyses were performed: one of them including all the analysed species and the other including only the species valid for Modena. Given that the data was autoscaled during the PCA, factors with eigenvalues greater than 1 were retained, according to Kaiser's criterion (Kaiser, 1960). The species with higher loadings in each factor were interpreted as fingerprints of the emission sources, although sometimes the method is not able to separate different sources.

2.4 Additional tools

To investigate the air mass origin reaching the study areas, 5 day back-trajectories (modeling the vertical velocity) were calculated daily for three different altitudes (750, 1500 and 2500 masl) with the HYSPLIT model (Draxler and Rolph, 2003). This was done for both study areas. Moreover, to identify the North African dust outbreaks influence, a number of tools were used: SKIRON aerosol maps (provided by the University of Athens, Kallos et al., 1997), DREAM aerosol maps (http://www.bsc.es/projects/earthscience/DREAM, Nickovic et al., 2001), and NAAPs aerosol maps (Naval Research Laboratory, http://www.nrlmry.navy.mil/aerosol).

The boundary layer height was calculated using the HYSPLIT model from the NOAA Air Resources Laboratory (http://www.ready.noaa.gov/READYamet.php), using the information for stability time series. It was calculated for every three hours for the whole year 2008. For the Castelló region, the coordinates from L'Alcora were used and for the Modena region, the coordinates from Parco Ferrari were used.

3 RESULTS AND DISCUSSION

3.1 Meteorological conditions

General meteorological conditions in the Castelló and the Modena clusters are described in the introduction. It has been said that the Modena area is affected by stagnant atmospheric conditions in winter more than the Castelló region. The boundary layer height calculated specifically for this study is shown in Figure 2. Average daily pattern is shown for each of the months. The boundary layer depth is much higher in summer than in winter for both regions and higher during daytime as opposed to night-time. The strong winter stagnant conditions in the Modena region are evidenced by the low maximum average boundary layer depth (<500m) between November and January. A day per day analysis shows that 16 days in January had a boundary layer depth below 400m, this happening for 15 days in December and 4 days in November, whereas this is only true for 5 days in December in the Castelló region.

3.2 PM concentrations

PM_{10} annual average concentrations recorded at PF and MR were 39 µg/m^3 and 41 µg/m^3, respectively, which is 12-14 µg/m^3 above the corresponding average at LA. This evidences the differences in PM sources and atmospheric conditions between the two areas. In the Modena region, PM_{10} concentrations were quite homogeneous, as shown by the strong correlation between daily PM_{10} concentrations at PF and at MR (squared Pearson correlation coefficient R^2=0.80, Figure 3). The similar concentrations at the urban and the industrial sites may indicate a low local influence from the ceramic industrial sources, and/or strong mixing atmospheric conditions in the area where the two sites are located. Even though the stagnant conditions mentioned before hinder the air mass renovation and the dispersion of pollutants, the sites are close enough to be affected partially by the same sources in the same air mass, hence showing PM concentrations varying in tandem.

A clear seasonal trend with higher concentrations in winter and lower concentrations in summer was observed in the Modena region (Figure 4). This is attributed to the different atmospheric conditions throughout the year, hindering the dispersion of pollutants in winter and favouring it in summer. On the contrary, no clear seasonal pattern was observed at LA (Figure 4). The elevated PM_{10} concentrations recorded in the end of February and in October were partially due to the influence of North African dust outbreaks (indicated as NAF in Figure 4). This influence was not seen at LA in February because there were not available PM_{10} data for those days. In October, a clear increase in the PM_{10} concentrations was observed for both Castelló and Modena regions, indicating the wide area of influence of the North African episode.

3.3 Chemical composition

Table 2 shows the average annual concentrations of trace elements in PF, MR, LA, and the range at the three additional sites in the Castelló ceramic cluster, together with typical concentrations in Spanish urban areas, steel-industry-influenced areas and stainless-steel-industry-influenced areas (Querol et al., 2007b). The typical concentrations in Spanish urban areas were used as a reference to identify the elements in relatively high concentrations. Thus, for each of the species analysed, if the concentration is higher than the usual concentration in urban areas, the species can be identified as characteristic of the area and the possible sources of this species need to be investigated.

The elements Mn, Cu, Zn, Sn and Sb were registered in high concentrations at PF and MR compared to LA and/or compared to Spanish urban areas (Table 2). These relatively high concentrations at both PF and MR may be attributed either to abrasion products from tyres and brake pads from road traffic or to the influence of metalmechanical industry. Nevertheless, despite the concentrations were relatively high, they were lower than those registered in steel-influenced environments (Table 2), and therefore the influence of the metalmechanical industry in the Modena area may be considered moderate. Although the concentrations of these elements vary in tandem at PF and MR, indicating the homogeneity of the pollutants within the area, concentrations were generally similar at PF and MR during summer, whereas they were higher at PF in winter (Figure S1). This may indicate the local origin (road traffic), which results in higher concentrations in the emission area (Modena city, PF site) in winter due to stagnant conditions in winter.

At LA, Ti, Se, Tl and Pb concentrations were relatively high (Table 2 and Figure S1). These elements were attributed to the influence of ceramic industry in the area (Minguillón et al., 2007b; Querol et al., 2007a). Hence, despite the presence of ceramic industry in the Modena region, its influence on the air quality is not as evident as in the Castelló cluster. The causes for the different impact of the ceramic industry on the air quality in these two European areas are discussed below and summarised in **¡Error! No se encuentra el origen de la referencia.**.

The higher Ti concentrations (typical mineral tracer) recorded at LA compared to those recorded at PF and MR are attributed to higher mineral emissions in the Castelló cluster, due to: a) lower degree of high efficient systems implemented in the spray-drier facilities (responsible for a significant part of the mineral emissions generated by the whole ceramic industry (Minguillón et al., 2009)); b) higher percentage of facilities carrying out the storage and handling of dusty raw materials outdoors; c) more road transport of raw and pre-processed materials; d) presence of two open air quarries; and e) drier weather conditions and more occurrence of North African dust events.

Another significant difference between both clusters in 2008 is the degree of BAT implementation in the ceramic tile kilns. As stated above, it was less than 5% in Castelló (Minguillón et al., 2009) whereas it was 100% in Modena. Even though the emissions from the ceramic tile kilns are not very important in terms of bulk PM with respect to the emissions from the whole ceramic industry (Minguillón et al., 2009), the composition of these emissions includes different heavy metals. The abatement systems (fabric filters with addition of lime) are mainly implemented to reduce fluorine emissions (IPTS, 2007; Monfort et al., 2003, 2008), but they have also shown a very high efficiency in the abatement of some elements such as Tl and Pb (Celades, 2012). As a result, the ceramic tile kilns in the Castelló facilities may emit Tl and Pb, whereas in the Modena cluster these elements are retained in the abatement systems. This difference in the emissions is reflected in the ambient concentrations of Tl (<0.1-0.1 ng/m^3 in Modena and 1.7 ng/m^3 in Castelló, as annual means), and Pb (12-15 ng/m^3 in Modena and 69 ng/m^3 in Castelló). Nevertheless, the Pb and Tl concentrations were also influenced by the frit manufacture, very important in the Castelló cluster, whereas it is quite scarce in the Modena cluster. The emissions from frit kilns include these elements (Celades, 2012) even though all the frit kilns were equipped with abatement systems (fabric filters or electrostatic precipitators) in 2008.

Concentrations of As, identified as a tracer of ceramic emissions (Querol et al., 2007a), were similar in both clusters (1.3 ng/m^3 of As in Castelló and 1.8-1.9 ng/m^3 in Modena, as annual means). Concentrations of Zn, identified as a tracer of ceramic emissions (Querol et al., 2007a), were relatively higher in Modena (50 ng/m^3 of Zn in Castelló and 53-76 ng/m^3 in Modena, as annual means), which may be attributed partially to the influence of road traffic and in a lower degree the metalmechanical industry present in the Modena area.

Some of the increases in Fe concentrations can be attributed to African dust outbreaks (empty symbols in PM_{10} plot), e.g. those of February and October, identified already in Figure 4. The increase is also observed for LA in October, given that the African dust outbreak reached also the Castelló cluster. The increases in Fe concentrations due to African dust outbreaks are simultaneous with increases in Ti concentrations.

3.4 PM sources

The PCA applied to the global dataset for Modena cluster (PF + MR) identified four factors, attributed to: road traffic + metalmechanical industry, mineral, ceramic, and background (Figure 5). The model was not able to differentiate between the road traffic influence and the metalmechanical industry influence, probably because of common tracers. The factor was characterized by Fe, Mn, Co, Cu, Zn, Cd, Sn, Sb, Pb and Bi. The mineral factor was characterized mainly by Ti, Co, La, Ce and Nd, with Fe having a factor loading of 0.4. The rest of the typical mineral species (e.g. Al_2O_3, Ca, Mg) were not included in this analysis because of analytical problems as explained in the methods section. This factor may be attributed to the addition of road dust resuspension, natural dust outbreaks, and mineral emissions from the ceramic facilities. Given that these sources share the same chemical composition, the model is not able to separate them. The third factor was attributed to ceramics because its tracers (Zn, As, Se) coincide partly with the tracers of ceramic glaze components manufacture and use. Finally, the fourth factor, characterized by SO_4^{2-} and V, was attributed to the background, with influence of fueloil combustion. Typically this background factor includes also Ni (Viana et al., 2008), but this element was not included in the present analysis due to analytical problems explained in the methods section.

The PCA applied to LA including only the same species included for the Modena analysis allowed identification of three factors, attributed to: mineral, ceramic (with influence of road traffic) and regional background (Figure 5). When applying the PCA to LA dataset including all the analysed species, the same factors were identified, together with an additional sea spray factor. The factors identified by the different PCA analysis shared the same tracers (Figure 5). The mineral factor included the typical mineral species such as Fe, Ti, Mn, La, Ce, and Nd. In the analysis with all the species, this factor included also Al_2O_3, Ca, K, Mg, Li, Sc, Rb, Sr, Y, and Pr. The ceramic factor included Zn, As, Se, Cd, Pb and in the version with all the species Tl and Cs were also in this factor. Most of the tracers were also part of the ceramic factor in Modena. The regional background factor was characterised by SO_4^{2-} and V, including also Ni in the version with all the species. This profile coincides with the regional background factor identified in Modena, as well as in many other European sites (Viana et al., 2008). Finally, the sea spray factor was only identified in the version with all the species, given that its main tracer is the Na, excluded in the other analysis.

It should be noted that the species used in the present study do not include tracers from biomass burning, being unable to identify this source. Nevertheless, its influence is expected to be significant in the Modena cluster, due to the domestic heating. This could be an additional reason why the PM_{10} bulk concentrations are higher in the Modena cluster with respect to Castelló cluster, where the influence of the biomass burning is expected to be very low.

4 CONCLUSIONS

PM_{10} annual average concentrations registered at PF and MR were 12-14 μg/m^3 above the corresponding average at LA, evidencing the different PM sources and atmospheric conditions between the two areas. In the Modena region, PM_{10} concentrations were quite homogeneous indicating a low local influence from the ceramic industrial sources, and/or the mixing atmospheric conditions within the area where the sites are located.

The influence of the meteorology in the Modena region is evidenced by a clear seasonal pattern with higher concentrations in winter and lower concentrations in summer. The influence of North African dust outbreaks was also identified. Despite the very high degree of BAT implementation in the ceramic industry of Modena, PM_{10} concentrations were close or even higher than the PM_{10} annual limit, so additional measures should be implemented, which evidences the difficulties of some industrial areas with stagnant weather conditions to accomplish the EU air quality requirements.

High concentrations of Mn, Cu, Zn, Sn and Sb at both PF and MR were attributed to the influence of road traffic and/or, in a lower degree, the metalmechanical industry. Some of the ceramic tracers (Ti, Se, Tl and Pb) concentrations were registered in higher concentrations at LA compared to PF and MR, evidencing the lower influence of the ceramic emissions in the Modena region, probably due to the better abatement systems in the ceramic facilities (spray-driers, storage and handling of dusty raw materials and ceramic kilns) and lack of local quarries.

The heavy metals concentrations registered in both clusters are far below the EU limit/target values; however, the progressive implementation of BAT as a consequence of the EU emission regulations should reduce their levels, especially in the Castelló cluster.

The PCA identified four factors in Modena: road traffic + metalmechanical industry, mineral, ceramic, and background. In Castelló, the PCA carried out with all the analysed species identified four factors: mineral, ceramic (with influence of road traffic), regional background and sea spray. This last factor was not identified when running the PCA with only the species included in Modena. Even though some of the species could not be determined for Modena due to analytical problems, the main sources were identified. The test with the LA dataset including and not including all the species supports this conclusion. As explained, only the sea spray influence could not be identified at LA with the limited dataset. Anyhow the sea spray influence is expected to be negligible in Modena, given the location and characteristics of the region. Nevertheless, a more complete dataset, including all the species analysed by ICP-AES and ICP-MS, carbonaceous fractions analysis (elemental and organic carbon), nitrate, and ammonium would be necessary to be able to separate the metalmechanical industry source and to be able to quantify the contribution of each of the sources to the bulk PM, in addition to identifying them.

According to the reported data and the PCA results, the additional measures to improve the air quality in Modena should be mainly focused on road traffic. Further measures may be taken in the metalmechanical industry, although its influence on the air quality remains not quantified. In the Castelló cluster the additional measures should be focused on the ceramic industry, where there is a significant potential improvement.

FIGURE CAPTIONS

Figure 1. Maps of the Castelló and the Modena ceramic clusters with the location of the sampling sites.

Figure 2. Average daily pattern of the boundary layer depth in Modena and L'Alcora for 2008, calculated with the HYSPLIT model.

Figure 3. Daily PM_{10} concentrations at MR vs. daily PM_{10} concentrations at PF during 2008. Line and equation correspond to orthogonal distance regression. R^2 is the squared Pearson correlation coefficient.

Figure 4. Daily PM_{10} concentrations at PF, MR and LA during 2008, with indication of days under North African dust outbreak influence (NAF). Date format: dd/mm.

Figure 5. Factor loadings for the different sources identified for the global dataset for the Modena cluster (including Parco Ferrari and Maranello data) and for the Castelló cluster (including L'Alcora data).

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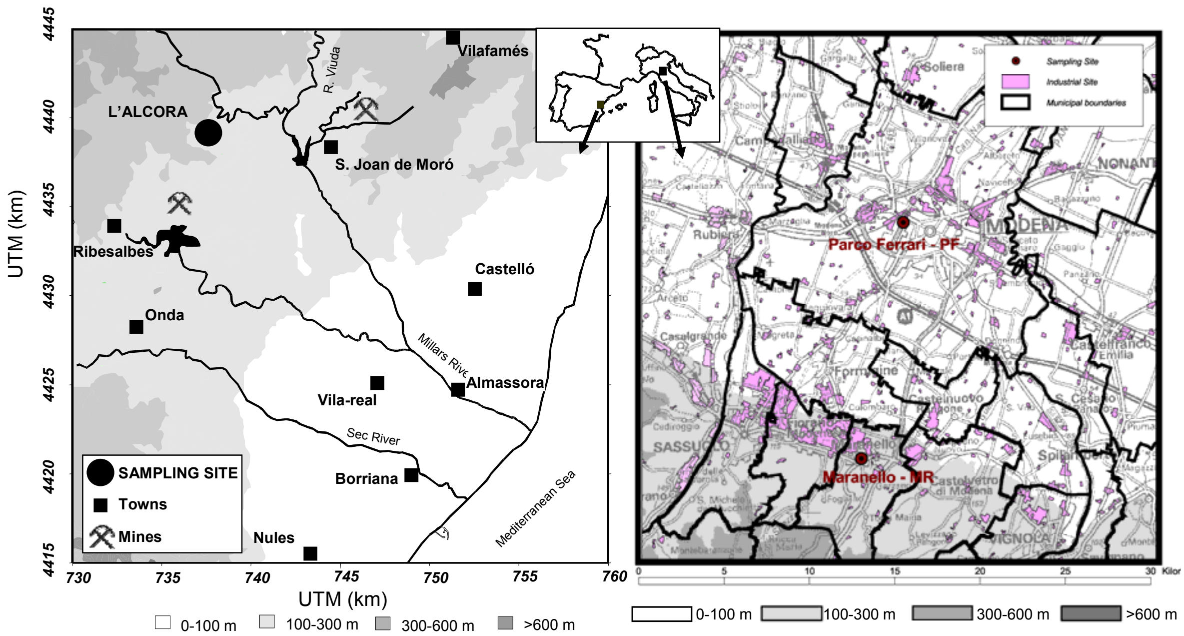
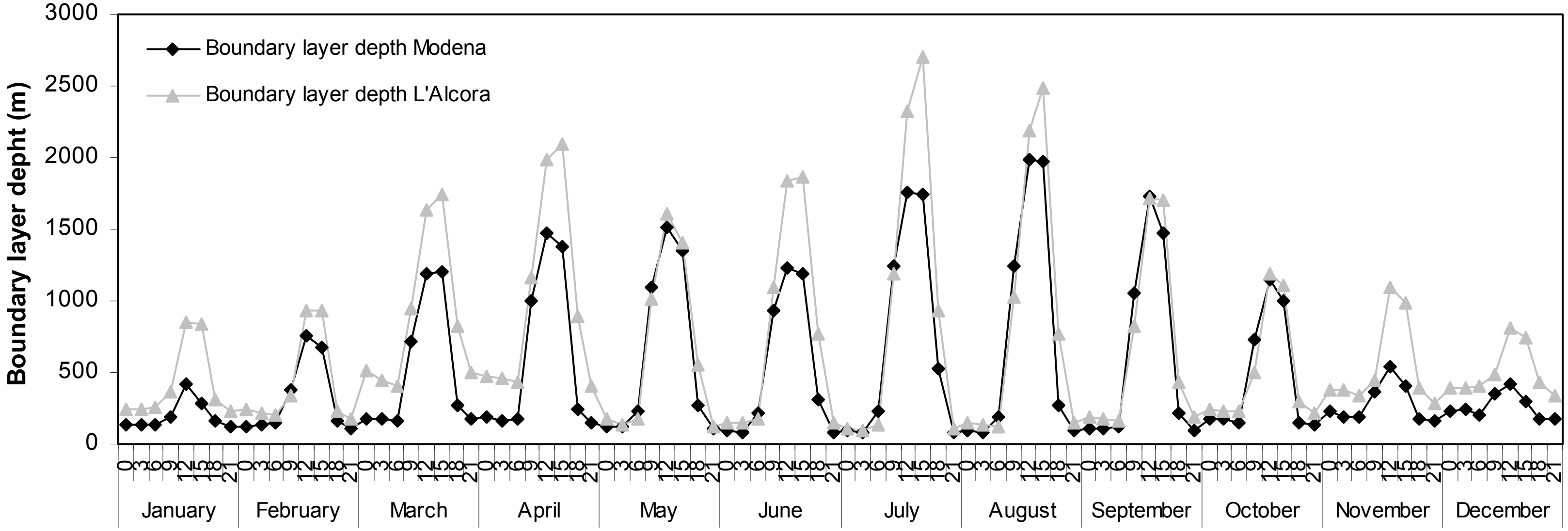

UTM (km)
L'ALCORA
Vilafamés
R. Viuda
S. Joan de Moró
Ribesalbes
Castelló
Onda
Millars River
Almassora
Vila-real
Sec River
Borriana
Nules
Mediterranean Sea
SAMPLING SITE
Towns
Mines
0-100 m
100-300 m
300-600 m
>600 m
Sampling Site
Industrial Site
Municipal boundaries
Parco Ferrari - PF
Maranello - MR
MODENA
Soliera
Rubiera
Casalgrande
Formigine
Castelnuovo Rangone
Castelfranco Emilia
SASSUOLO
Castelvetro di Modena
Spilamberto
VIGNOLA
NONANTOLA

Figure 1



Boundary layer depht (m)
3000
2500
2000
1500
1000
500
0
Boundary layer depth Modena
Boundary layer depth L'Alcora
January
February
March
April
May
June
July
August
September
October
November
December

Figure 2

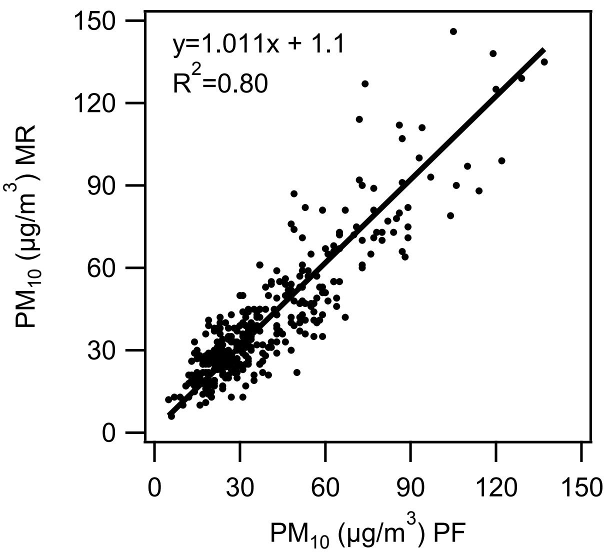


Figure 3

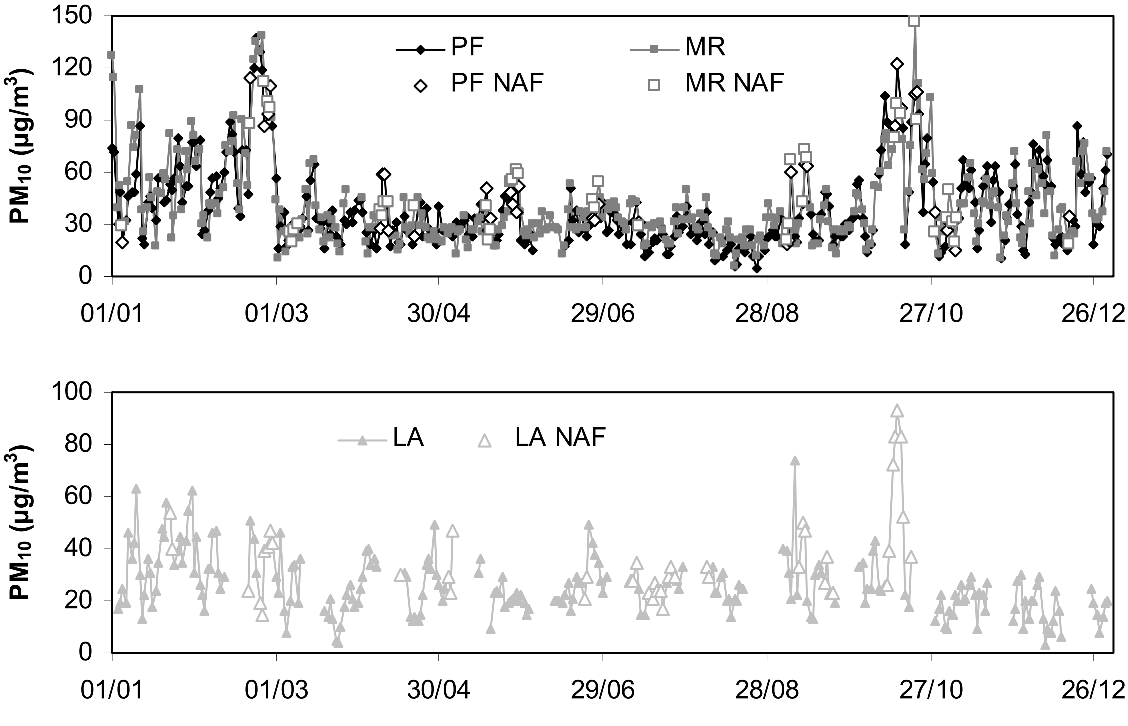


Figure 4

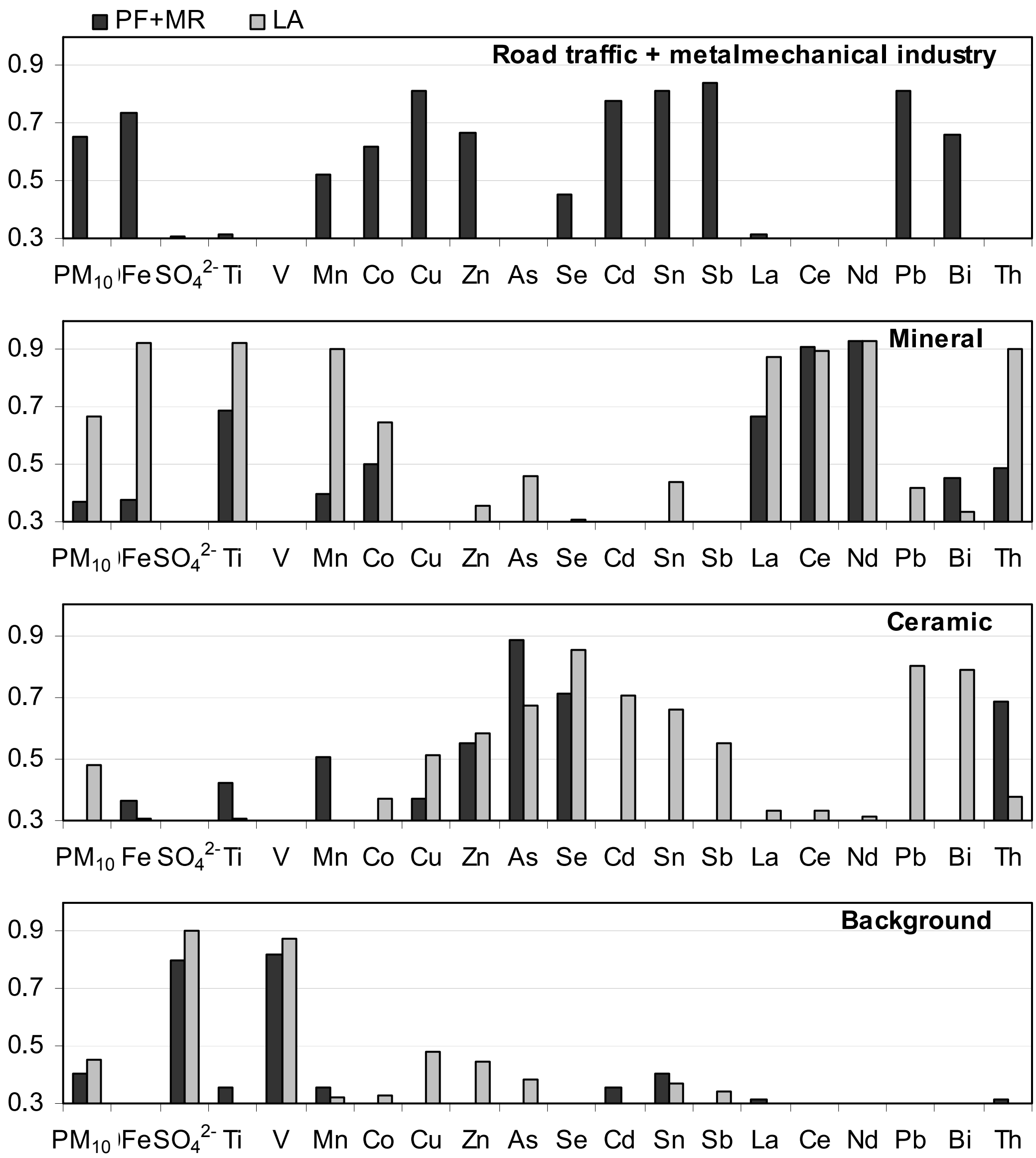

PF+MR
LA
Road traffic + metalmechanical industry
Mineral
Ceramic
Background
0.9
0.7
0.5
0.3
PM10 Fe SO4 2- Ti V Mn Co Cu Zn As Se Cd Sn Sb La Ce Nd Pb Bi Th

Figure 5

SUPPLEMENTARY MATERIAL

AIR QUALITY COMPARISON BETWEEN TWO EUROPEAN CERAMIC TILE CLUSTERS

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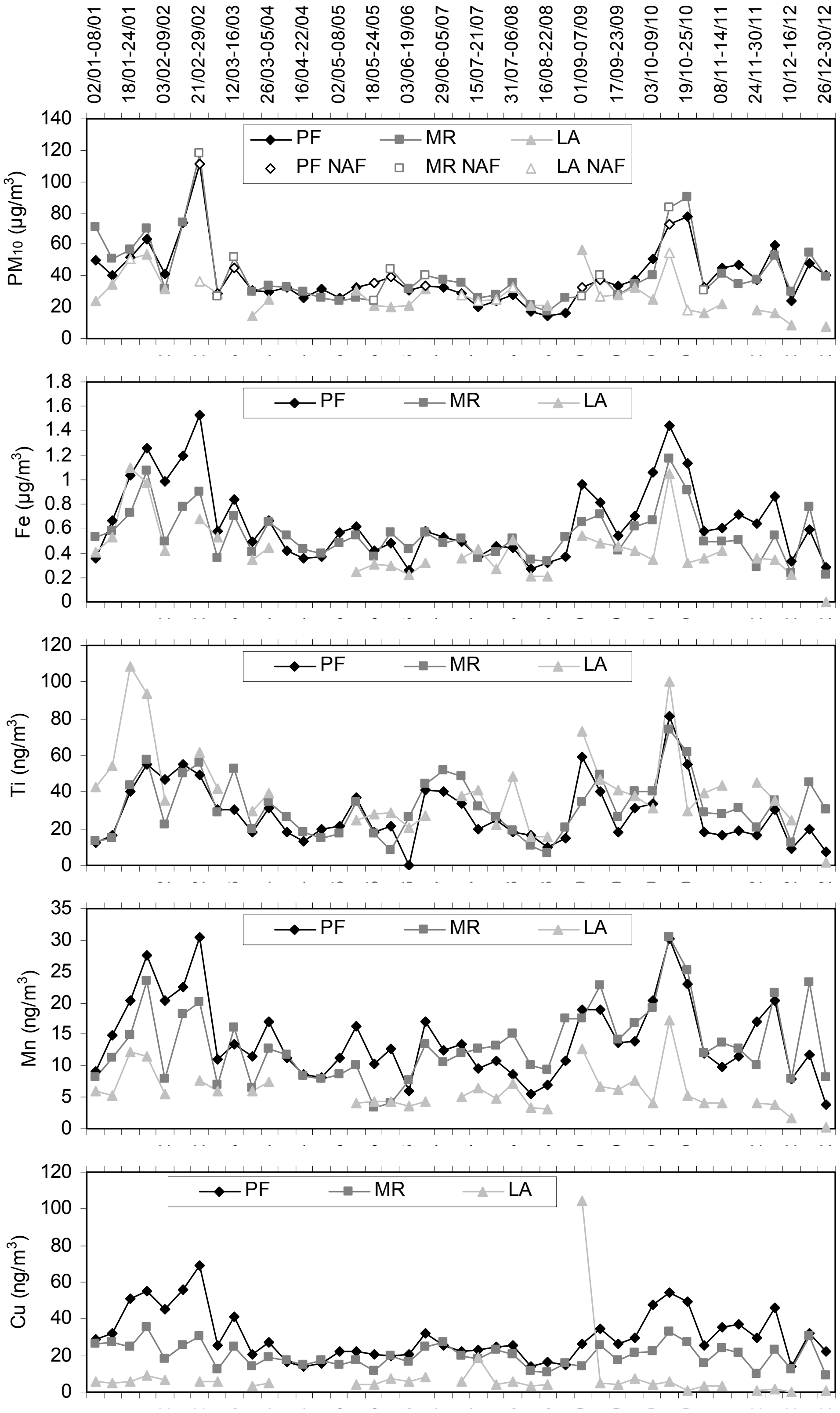
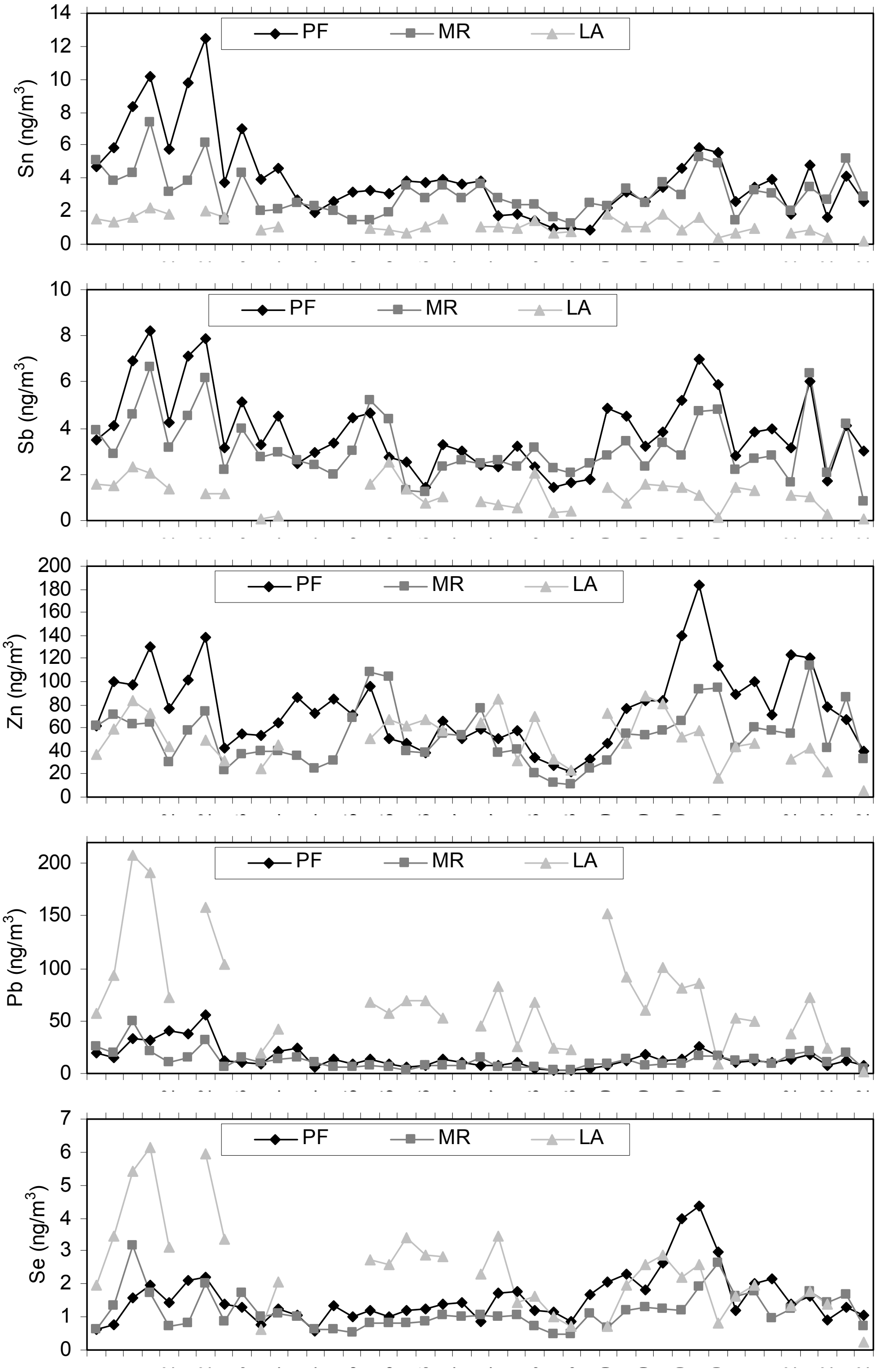
SECTION S1. LEGISLATION

European standards (Directive 2008/50/EC) regulate the levels of PM_{10} (particles with diameter ≤10 µm) and $PM_{2.5}$ (≤2.5 µm), setting annual limits of 40 and 25 µg/m^3 of PM_{10} and $PM_{2.5}$, respectively, the latter to be met in 2015, and a daily limit of 50 µg/m^3 of PM_{10} not to be exceeded more than 35 times per year. Concentrations of Pb, Cd, As and Ni are also regulated (Directive 2008/50/EC, Directive 2004/107/EC), with an annual limit of 500 ng/m^3 of Pb (in force since 2005), and annual target values of 5 ng/m^3 of Cd, 6 ng/m^3 of As and 20 ng/m^3 of Ni (to be met in 2013).

SECTION S2. TIME TRENDS OF PM_{10} AND SOME SPECIES

Figure S1 shows PM_{10} and some elements concentrations for composite samples at PF and MR. Average concentrations matching the composite samples periods were calculated for LA for comparison purposes and they are also included in Figure S1. Empty symbols were used in the PM_{10} plot to indicate the influence of African dust outbreaks. Note that since the composite samples correspond to 6-8 days period, some samples classified as influenced by African dust outbreaks may include days without this influence and the other way around.


02/01-08/01
18/01-24/01
03/02-09/02
21/02-29/02
12/03-16/03
26/03-05/04
16/04-22/04
02/05-08/05
18/05-24/05
03/06-19/06
29/06-05/07
15/07-21/07
31/07-06/08
16/08-22/08
01/09-07/09
17/09-23/09
03/10-09/10
19/10-25/10
08/11-14/11
24/11-30/11
10/12-16/12
26/12-30/12
PM10 (µg/m3)
PF
MR
LA
PF NAF
MR NAF
LA NAF
Fe (µg/m3)
Ti (ng/m3)
Mn (ng/m3)
Cu (ng/m3)


PF
MR
LA
Sn (ng/m3)
Sb (ng/m3)
Zn (ng/m3)
Pb (ng/m3)
Se (ng/m3)

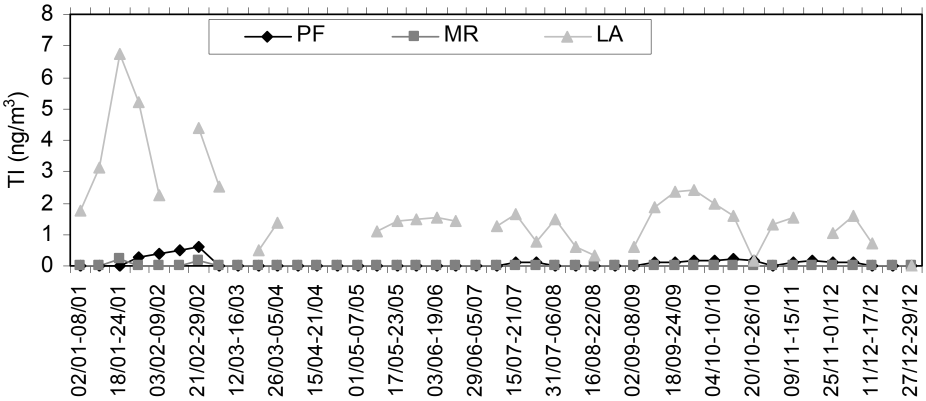


Figure S1. PM_{10} and some elements concentrations of the composite samples at PF and MR. Average of PM_{10} and elements matching the sampling period of the composite samples is shown for LA. Date format: dd/mm-dd/mm.