Variations in atmospheric PM trace metal content in Spanish towns: Illustrating the chemical complexity of the inorganic urban aerosol cocktail

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Abstract

The majority of the Spanish urban population breathes air containing inhalable ambient airborne particles at average concentrations of 30-46 µg m^{-3} (PM$_{10}$) and 20-30 µg m^{-3} (PM$_{2.5}$). Even though the average weight of inhaled urban aerosol is commonly similar, however, there can be large chemical differences between the ambient dusts from different towns, including the more bioreactive elements such as some metals. In this context we compare the source apportioned trace metal content of airborne PM$_{10}$ and PM$_{2.5}$ collected daily over a one-year period from six population centres in Spain: Barcelona, Alcobendas, Llodio, Huelva, Tarragona, and Las Palmas de Gran Canaria. Total average trace metal (ΣTM) PM$_{10}$ and PM$_{2.5}$ contents vary by up to a factor of around 3, reaching a maximum of ΣTM$_{10}$ 811 ng m^{-3} and ΣTM$_{2.5}$ 503 ng m^{-3} at Llodio, an industrial but humid site with the lowest PM$_{10}$ mass levels but high contamination by Zn, Pb, Mn, Sn, Ni and Cr. In contrast, pollution at Huelva, although another

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industrially influenced site, instead emphasises Cu and As, whereas Barcelona, where traffic emissions and resuspension contribute to some of the highest average PM_{10} levels in Spain, has unusually raised levels of Ti, V and Ba. Such variations in both daily and annual average PM bulk chemistry, particularly in potentially toxic trace metals concentrated in the finer aerosols (such as Cd, As, Pb, Hg, and Ni) predict that PM health effects on resident populations from different towns are unlikely to be the same.

1. Introduction

Papers on PM pollution levels usually begin with a reminder of the health hazard associated with inhaling increased particle mass: "*The proven epidemiological link between enhanced levels of breathable particulate matter (PM$_{10}$: particles with aerodynamic size <10 µm) and poorer human health … has led directly to environmental legislation designed to reduce anthropogenic dust*" (Moreno et al., 2005a). However, generalised epidemiological correlations between particle mass and health effects obscure the fact that the air we breathe as individuals contains a complex and highly variable mixture of different chemical elements and compounds from different sources. This becomes important if health problems can be shown to be related to specific components in the particulate matter rather than just simple increases in mass (e.g. Adamson et al., 2000). Differences in aerosol toxicity are likely to be linked not only to increasing particle mass, but also to variations in particle size (Schwartz and Meas, 2000), shape and chemistry (Richards, 1997; Adamson et al., 2000), and the presence of small amounts of highly toxic elements such as cadmium (Nawrot et al.,

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2006), especially if these are soluble (Fernández-Espinosa et al., 2002; Birmili et al., 2006). In this context trace metals, although usually very low in mass, are thought to play a role in human health problems because they are commonly highly bioreactive. Furthermore many trace metals in airborne particles occur in the very fine (<1 µm) and ultrafine (<0.1 µm) size fraction (Milford and Davidson, 1985; Utsunomiya et al., 2004; Birmili et al., 2006), and therefore are able to reach alveolar regions in the lungs (Schaumann et al., 2004).

While some trace metal emissions are due to natural processes (e.g. volcanic eruptions, dust storms, rock weathering, forest fires), many are of anthropogenic origin. For example V, Co, Mo, Ni, Sb, Cr, Fe, Mn and Sn are emitted during combustion of fossil hydrocarbons (e.g. Pacyna, 1986; Lin et al., 2005), As, Cr, Cu, Mn and Zn are released into the atmosphere by metallurgical industries (Pacyna, 1986; Querol et al., 2002; Alastuey et al., 2006), and traffic pollution involves a wide range of trace element emissions which include Fe, Ba, Pb, Cu, Zn and Cd (Pacyna, 1986; Birmili et al., 2006). Because of the possible health hazards linked to the more toxic trace elements (especially when carcinogenic effects are suspected or proven e.g. Blot and Fraumeni, 1975; Sorahan and Waterhouse, 1985; Nawrot et al., 2006), the World Health Organization (WHO) has established air quality guidelines (WHO, 2000). Similarly, the European Union has set annual limits on selected trace elements such as 500 ng m^{-3} for Pb (1999/30/CE), and has established target values for As (6 ng m^{-3}), Ni (20 ng m^{-3}) and Cd (5 ng m^{-3}) (2004/107/CE).

In this paper we present data on trace metal concentrations and source origins in airborne particles at a range of urban sites in Spain, each registering "normal" levels of urban air pollution which, in the case of Spain, means average concentrations of 30-46 µg m^{-3} (PM$_{10}$) and 20-30 µg m^{-3} (PM$_{2.5}$) (Querol et al., 2004). We show that the

chemical mixture of trace elements breathed at these sites varies enormously, and confirm that the most toxic metals are usually concentrated in the finer particle fraction.

2. Methodology

2.1. Site descriptions

Six sites were chosen from the monitoring network across Spain run by the different Autonomous Governments, all situated in the built environment but reflecting a wide range of urban settings. The sites are, from north to south, Llodio, Barcelona, Tarragona, Alcobendas, Huelva and Las Palmas de Gran Canaria (Fig. 1). Two of these sites (Llodio and Huelva) are strongly impacted by heavy industry, one (Barcelona) is in the centre of a major city, one (Las Palmas) is on an island regularly visited by dust outbreaks from African deserts, and the remaining two (Alcobendas and Tarragona) lie within medium sized towns, the first north of Madrid in the centre of the Iberian Peninsula with low industrial development, and the other on the Mediterranean coast close to major petrochemical and chemical industries. Each site is considered below in more detail.

The industrial town of **Llodio** (20 000 inhabitants) is located in a valley 20 km away from the city of Bilbao in the far north of Spain (Fig. 1), with a humid climate that suppresses air pollution levels (the PM_{10} average of 31 $\mu g\ m^{-3}$ is the lowest of the six). The area is hilly with maximum heights (>700 m) in the west and east inducing canalisation of air masses through the Nervión valley. The station is located in a park in the city centre surrounded by a residential area and 15 m away from a low traffic road. The monitoring station shows a strong industrial influence from factories involving pigment manufacture (mostly chromates and Pb molybdenates, iron oxides and anticorrosives), glass, and siderometallurgic (steel tubes) production. Despite the

relatively low PM_{10} values, the $PM_{2.5/10}$ ratio is unusually high (78%), due to low resuspension given the humid environment and probably to the emission of fine industrial particles in the form of condensates. The **Barcelona** site is located in a local park within a metropolitan area of 3 million inhabitants and 150 m away from a busy road. The park substrate is mainly sandy, favouring the resuspension of crustal particles as a local effect frequently reinforced by arrival of sand and clay particles during African dust intrusions. Industrial activity in the Barcelona metropolitan area includes two power stations (gas and fuel oil), two urban residues incinerators, and an active port, although these are all sited some distance from the monitoring station which is in the city centre where traffic is by far the dominant anthropogenic pollutant emission source. The combination of strong traffic pollution, industrial emissions, exotic dust intrusions, resuspension and local climatic conditions produces high average PM_{10} loadings (41 µg m^{-3}) and a higher than average $PM_{2.5/10}$ ratio (0.67). The port city of **Tarragona** (115 000 inhabitants) is located 98 km southwest of Barcelona and also on the Mediterranean coast. The station is located on the top of a seven storey building and records the combined influences of the urban environment, port and industrial (mainly petrochemical and chemical) emissions, with an annual PM_{10} average of 37 µg m^{-3}. The **Alcobendas** (100 000 inhabitants) collection site is an urban background station with low industrial influence, located in a park in a residential area with relatively low volumes of local traffic, and so has one of the lowest PM_{10} averages (32 µg m^{-3}). The most significant pollution source is a motorway (< 1 km) east of the station that links Madrid with the north of the country and helps to maintain a higher than average $PM_{2.5/10}$ ratio (79%). Industrial activities nearby include a Zn smelting plant. The collecting site in **Huelva**, in the south of Spain, is located in the city centre (150, 000 inhabitants) and is located in an open area more than 15 m away from light traffic, but

prone to receiving the plume from the two industrial areas of Punta del Sebo (3 km south) and Nuevo Puerto (7 km southeast) which raise annual PM_{10} averages to 37 µg m^{-3}. The main industrial activities include chemical (phosphates), petrochemical and metallurgical factories. Finally, the Atlantic island site in **Las Palmas de Gran Canaria** (361 000 inhabitants) has important port activity (third largest in the country) and traffic-related emissions. The monitoring site is located on the roof of the town market (20 m high) more than 50 m away from main roads, registering annual PM_{10} average values of 37 µg m^{-3}. Like the other Canary Islands, Gran Canaria is often reached by African dust outbreaks (Viana et al., 2002) which can enormously increase particulate matter concentrations, especially in the coarse PM_{10} fraction, which results in the lowest average $PM_{2.5/10}$ ratio of our sample group (0.5).

One other sometimes important contribution to particle matter concentrations is related to sea spray particles. This source has a much higher influence on PM_{10} levels in the Canary Islands than in the other sites within the Iberian Peninsula, accounting for up to 12 µgPM_{10} m^{-3} in the Canaries, compared to 2–3 µg m^{-3} in the coastal areas, and only 0.5–1.0 µg m^{-3} in the central locations such as Madrid (Querol et al., 2004).

2.2. Sample collection and data

Periods of 24h sampling were carried out at each station over an entire year (2001) using a PM_{10} Graseby–Andersen high volume sampler (68 m^3 h^{-1}, EN12341 reference instrument), and a MCV high volume sampler (30 m^3 h^{-1}) equipped with a $PM_{2.5}$ inlet and quartz fibre filters (QF20 Schleicher and Schuell). Three PM_{10} and two $PM_{2.5}$ 24 h monitoring samples were collected per week at the six sampling stations, from which two PM_{10} and one $PM_{2.5}$ samples were selected for chemical analysis. Trace element concentrations were obtained by ICP-MS and ICP-AES following the procedure

described by Querol et al. (2002). Blank field filters were used for every stock purchased for sampling (at least five blank filters for each 50 filter stock). Fractions of the blank filters were analyzed in the same batches as their respective filter samples. For analysis control, 3-5 mg of the reference material NIST 1633b was added to a fraction of a blank filter to check the accuracy of the analysis of the acidic digestions. For most elements, relative analytical errors were <10%. This methodology was successfully tested for the analysis of city dust in an IEA round robin exercise (Bleise and Smodiš, 2002).

Source apportionment analysis was applied to all six collection sites in order to quantify the contribution of different sources to the ambient PM levels. Receptor modelling techniques are based on the evaluation of data acquired at receptor sites, and most of them do not require previously identified emission sources (Henry et al., 1984). Two main stages are distinguished in the multivariable receptor models: source identification and calculation of source contribution. During the source identification process, a number of groups of chemical species of PM are differentiated on the basis of the degree of association or correlation between the analysed PM components, with each chemical group identified being associated with one or more PM sources. Chemical species of known origin are frequently used as source tracers. Principal Component Analysis (PCA) was applied to obtain such emission sources (factors), in our analyses accounting for at least 75% of the variance of the dataset. The quantitative determinations of the source contributions were based on multilinear regression analysis (MLRA), in which the bulk PM concentration was used as a dependent variable, and the absolute factor score matrix contained the independent variables. The mean daily and annual contributions of the different sources to PM levels were thus calculated, as well as the contributions of the sources to specific PM components (e.g. trace elements). The

lower number of PM$_{2.5}$ samples and the narrower range of sources which contribute to this fraction prevented the analysis from being sufficiently accurate to quantify the PM$_{2.5}$ sources. Therefore, multilinear regression was only applied to PM$_{10}$ samples.

3. Results

3.1. Trace metal concentrations

The highest average annual PM$_{10}$ concentrations of all trace metals (total average trace metal: ΣTM$_{10}$) were registered at the Llodio (ΣTM$_{10}$ 811 ng m^{-3}) and Barcelona (ΣTM$_{10}$ 418 ng m^{-3}) sites, followed by Huelva (ΣTM$_{10}$ 281 ng m^{-3}), Alcobendas (ΣTM$_{10}$ 243 ng m^{-3}), Tarragona (ΣTM$_{10}$ 175 ng m^{-3}) and Canaries (ΣTM$_{10}$ 170 ng m^{-3}). In the fine fraction (ΣTM$_{2.5}$) the same pattern continued, with once again the highest concentrations being recorded at Llodio (ΣTM$_{2.5}$ 503 ng m^{-3}) and Barcelona (ΣTM$_{2.5}$ 210 ng m^{-3}), whereas the minimum values were registered at Tarragona (ΣTM$_{2.5}$ 103 ng/m^3) and the Canaries (ΣTM$_{2.5}$ 84 ng m^{-3}) sites. In detail, however, these average ΣTM figures disguise large variations in specific elements. Thus, the highest levels of Sn, Zn, Mn, Ni, Cr, Pb and Mo were recorded at Llodio (2–20 times higher than at the other sites) (Table 1), whereas Huelva presented the highest levels of Cu and As (2–5 times higher than at the other sites). The most abundant trace element metals in absolute terms are Zn, Cu, Ti, Mn, Pb and Ba.

Regarding preferential fractionation of trace elements into the fine or coarse fraction, Ti, Mn, Sr, Sb and Ce are always preferentially concentrated in the coarser sample in all sites, whereas V, Ni, Co, As, Se, Cd, Sn, Yb, Lu, Tl, Pb, Bi and Th are more enriched in the PM$_{2.5}$. Similarly, Li, Rb, Nb, Cs, Ba and La-Nd tend to be concentrated in the coarser fraction, whereas Cr, Hg, Cu, Zn, Mo, Sm-Tm and U are more likely to prefer the finer fraction.

3.2. Source apportionment

Source apportionment analysis using PCA-MLRA has identified crustal, industrial, marine and traffic as common PM$_{10}$ aerosol sources at the six sites (Querol et al., 2004). Some sites show additional influences such as a "combustion" factor related to local emissions from power plants (present only in Barcelona and Canaries), and an "external" factor characterized by the presence of ammonium sulphate which is a tracer of regional and long-range transport (found in Llodio and Canaries). Given the fact that with regard to trace elements it is primarily the metals that are potentially of health concern, and that trace metals are mostly sourced from traffic, industry and "crustal" (i.e. geological rock forming minerals), the following section focuses on these three sources, excluding marine and other contributions.

Table 2 shows the trace elements and the percentages attributed by source apportionment to the traffic, industry and crustal components. The **traffic** component shows high correlations between the levels of Pb, Zn, Cd, As and Cu, with other trace elements present including Sb, Ba, Mn, V, Ni, Sr, Ti and Rb. Most of these elements can be linked to motor combustion processes (Pb, Zn, Sb, Cd, V), brake-linings (Sb, Cu) and tyre abrasion (Ba, Mn) (e.g. Morawska and Zhang, 2002; López et al., 2005; Birmili et al., 2006). The rest of the elements (As, Sr, Ti, Rb) are more related to the resuspension of crustal material, especially at the Barcelona site. The **industrial** component includes a wide list of metals depending on the type of industry present in each area. Combustion processes and petrochemical works emit variable amounts of V, Pb, Ni, Zn, Cr and Co (identified at the Canaries, Alcobendas, Barcelona, Tarragona and Huelva sites). Some of these metals are also emitted by other industrial activities, the pollution from which can be highly specific in its chemistry: metallurgical activities

in Huelva are responsible for emissions of As, Cu, Pb and Zn, whereas in Llodio As, Cr, Mo, Ni, Cu and Co are linked to the pigment industry, and mixtures of Pb, Zn, Mn, Cd and As emanate from the steelworks. Finally the **crustal** component includes a wide range of naturally occurring trace elements, notably Ti (present in all six sites), Sr, Rb, Li, As, Co, Mn, V, Ba and/or Cr. Elevated concentrations of some of these (Co, As, Cr, V and Ni) have been in part linked to intrusions of masses of air laden with African dust (Viana et al., 2002), although local activities, including both industrial and resuspension processes due to wind and traffic activity, also have a role to play.

Regarding mass contents, calculated by MLRA using element concentrations as dependant variables, although ranges in values are very wide (Table 2) the contribution from traffic is highest at Barcelona, with an average ΣTM_{10} mass of 217 ng m^{-3}. In contrast, heavy industry is the major contributor to ΣTM_{10} mass in Llodio and Huelva, accounting for an average of 658 (mostly Zn, Pb, Mn and Cr) and 190 ng m^{-3} (mostly Cu, Zn and Pb) respectively. PM_{10} originating from rock forming minerals in weathered crustal materials shows highest average mass values at the Canaries and Barcelona sites (85 and 143 ng m^{-3} respectively), mainly due to African dust outbreaks, traffic resuspension, and, in the case of Barcelona possibly the sandy nature of the surroundings of the monitoring site.

We illustrate the differences between source apportioned PM_{10} masses of trace elements (Table 2) by introducing a 3-component "TIC" (Traffic-Industrial-Crustal) triangle (Fig. 2). This figure displays how the source apportionment method predicts the dominance of industrial anthropogenic sources at Huelva and Llodio, the strong traffic influence at Alcobendas and Barcelona, and the prominent crustal component registered in the Canaries. Barcelona shows a tight linear clustering of compositions extending from the traffic to crustal sub-triangles. In contrast, the data from Alcobendas,

Tarragona and, especially, the Canaries show a broader scatter as the main source shifts compositions from more traffic-dominated into the crustal sub-triangle. Figure 2 also shows both the average ΣPM_{10} and ΣTM_{10} adjacent to each triangle. Although all sites fall in a relatively low range of average PM_{10} concentrations, varying from 31.3-41.0 µg m^{-3}, note the differences in average total trace metal contents. Thus Huelva and Llodio, both classified as essentially "urban industrial" by source apportionment, have radically different trace element levels. Even though Llodio has nearly 20% less average PM_{10} mass, it not only shows a nearly three times higher concentration of metals than Huelva but also a much higher $PM_{2.5/10}$ ratio. Furthermore, whereas the two most abundant metals (in terms of mass) at Huelva are Cu and Ti (and As is comparatively exceptionally high), at Llodio the two most abundant metals are Zn and Pb, and Mn, Cr, Ni, Mo, and Sn are all also especially enriched. Similarly, the two sites most linked to traffic pollution, Alcobendas and Barcelona, show large differences in trace metal concentrations, with the Barcelona site not only having higher overall PM_{10} levels but almost double the trace element concentrations, with notable enrichments in Ti, V, Ba (and, to a lesser extent, Zr and Sb) due to intense traffic emissions, tyre wear and resuspension of crustal particles.

3.3. Enrichment factors

Another method commonly used to help identify the influence of anthropogenic sources on the levels of a specific element in airborne particles is the element Enrichment Factor (EF). To obtain such factors it is necessary to compare the concentration of the element in a sample to its concentration in the Upper Continental Crust (UCC), calculated with the formula EF=(El$_{sample}$/X$_{sample}$)/(El$_{UCC}$/X$_{UCC}$) (e.g. Chester et al., 1999), where El is the concentration of the element under consideration,

both in the sample and in the UCC (Taylor and McLennan, 1995), and X is a reference element that is typically crustal such as Al, Fe, Li, Ti, etc. Thus, an EF close to 1 will suggest a natural origin for a certain element whereas higher values will indicate an anthropogenic source to be more likely. However, while low EF indicate "crustal" composition they cannot exclude the involvement of anthropogenic processes: resuspension of rock forming mineral dust by traffic, while a purely anthropogenic phenomenon, will not enhance EF. Several authors indicate an arbitrary value of 10 as indicative of anthropogenic influence (e.g. Chester et al., 1999; Veyseeyre et al., 2000), however it is important to recognise that variables such as weather patterns (e.g. humidity) and the local geology of each collecting site will influence the concentration of specific elements in the filter samples, especially the soluble ones, thus emphasising the artificial nature of establishing a universal cut-off value (Reimann and Caritat, 2005). We would always advise caution when defining EF for airborne samples, only using them jointly with other sources of information. For this study Li was chosen as the reference element for comparison, because it was the only one linked specifically and uniquely to the crustal component when calculating source apportionment, as opposed to other characteristically crustal elements such as Ti, Sr, Rb that in some cases were also linked to industrial and/or traffic sources.

Converting trace element concentrations measured as ng m^{-3} into µg g^{-1} (Table 1) emphasises from a geological perspective just how anthropogenically enriched many of these trace elements are compared to their "geological" averages in crustal rocks. The highest EF for all samples are found in the fine fraction of Barcelona, with EF>500 for Cu, Zn, As, Se, Cd, Sn, Sb and Pb (Sb and Se as well in the PM$_{10}$ fraction). In the Canarian site fine Se, Cd, Sb and Pb particles are the most clearly anthropogenic in origin, similar both to Alcobendas (Se, Mo, Cd, and Sb), and Tarragona (Cu, Se, Mo,

Cd, Sb and Pb) in the fine fraction. Cu, As, Se, Cd and Sb show high EF in Huelva for both size fractions, whereas the highest EF were observed in Llodio for Zn, Se, Mo, Cd, Sn, Sb and Pb (the latter only in the fine fraction). Thus all sites have collected aerosols strongly anthropogenically enriched in Cd, Se and Sb, with Cu, Pb, Zn, As, Sn and Mo commonly also prominently enhanced to well above "natural" levels. In contrast, very low EF (<6) are observed for Ti, Mn and Ba at almost all sites. Ti is usually found in clay minerals (as well as detrital titanite and ilmenite) and is a useful tracer of African dust intrusions. The only unusual enrichment in Ti occurs in the finer aerosols analysed at the Barcelona site, this being tentatively attributed to a contribution from traffic because levels of Ba are also high. Mn is similarly enriched in the Barcelona $PM_{2.5}$, but is also anthropogenically enhanced in the industrially influenced Llodio samples.

4. Discussion and Conclusions

The primary objective of this paper is, using collection sites across Spain as an example, to provide a demonstration of how the trace metal contents of urban aerosols vary greatly depending on the environmental setting, irrespective of the average PM mass measured at a given site. The observed chemical variations in trace metal compositions are controlled by the relative contributions from traffic *versus* industry, the type of industry, the prevalence of resuspension processes, and the frequency of exotic dust intrusions (e.g. Querol et al., 1998; Sternbeck, et al., 2002; Sun et al., 2004; Moreno et al., 2005a, 2006). Such differences are illustrated by our study of six locations in Spain by combining the use of source apportionment methods, TIC triangles, and Enrichment Factors, focusing on the trace metals. As shown by Figure 2, urban sites in Spain with similar PM_{10} mass concentrations can and do have great differences in their trace metal contents. To illustrate this further, Figure 3 plots PM_{10}

and PM$_{2.5}$ compositional variations in mixtures of metals which can be ranked in terms of their relative toxicity as high (Pb, As, Cd), medium (Ni, Cu, Zn), and low (Ti, Ba, Sr). On this figure, most samples scatter across the Ni, Cu, Zn sub-triangle, reflecting the relatively high levels of Zn and Cu in all samples except those from the Canaries. Compositions also spread towards the right-hand apex, this being mainly attributable to the "crustal" component, with Ti residing in iron oxides and materials weathered from mafic silicates, and Ba present in feldspars and carbonates. The strongly crustal signature of the Canaries sample is particularly well demonstrated.

In our study trace metals are used as a surrogate for variations in general PM bulk chemistry because several of them are good indicators for industrial and traffic pollution, and because these elements are of especial environmental concern. Many publications have by now created a compelling argument for the involvement of the more toxic trace metals in human disease (e.g. Adamson et al., 2000; Pope et al., 2002; Schaumann et al., 2004; Nawrot et al., 2006), and enhanced levels of inhalable atmospheric aerosols bearing elements such as As, Cd, Hg, Pb and Se are clearly undesirable. The U.S. Agency for Toxic Substances and Disease Registry (ATSDR) lists the top 20 hazardous substances according to a combination of their frequency, toxicity, and potential for human exposure. In this list As, Pb, Hg and Cd appear as the most toxic metals for human health, being first, second, third and eighth in the list. The EU (Directives 2004/107/EC and 199/30/CE) has correspondingly established annual "target value" desirable threshold limits on concentrations of As (6 ng m^{-3}), Cd (5 ng m^{-3}), and for Ni (20 ng m^{-3}), and a limit value for Pb (500 ng m^{-3}). Although none of our six sites exceeded the *annual* average PM$_{10}$ concentration target value limits established by the EU for Pb, As or Cd, and only the Llodio site exceeded the 20 ng m^{-3} limit for

Ni, several *daily* averages exceeded desirable threshold limits, with the worst pollution episodes being associated with the highly industrial sites.

Perhaps the aspect of our study of most interest to epidemiologists is the fact that most samples show higher than average $PM_{2.5/10}$ ratios in the most toxic metals (Fig. 3), reinforcing a similar observation made by other studies on trace metals size fractionation (e.g. Milford and Davidson 1985; Allen et al., 2001; Utsunomiya et al., 2004; Lin et al., 2005; Moreno et al., 2005b; Birmili et al., 2006). The study by Lin et al. (2005) on traffic-derived aerosols in southern Taiwan, showed much higher levels of Pb, Ni, and Cd in the finer ($PM_{<2.5}$) particles as compared to $PM_{2.5-10}$. In fact, many of these metals are especially concentrated as abundant tiny particles within the very fine and ultrafine size fractions: for example, Cd, Pb, and Zn are strongly preferentially present in aerosol sizes below 0.5 μm in urban dusts from Birmingham, UK, with both Cd and Zn being among the most soluble of the metals (Birmili et al., 2006). Such studies indicate that if the chemistry of only the finer PM fractions is considered then concentrations of metals such as Cd will frequently exceed the WHO threshold limits applied for PM_{10}, due to the preference of those metals for finer aerosol fractions. The preference of the finer particles in our samples (represented by the open circles on Fig. 3) for the Ni-Cu-Zn and, to a lesser extent, Pb-As-Cd apices is clear in most cases. Only Llodio, overwhelmed by high concentrations of Zn in both PM_{10} and $PM_{2.5}$, shows no obvious preference for Pb-As-Cd in the finer size range. The best examples of metal enrichment of the finer fraction are provided by the Huelva and, especially, the Canaries samples. Thus, although the Canaries samples contain the least amounts of the more toxic metals, those that are present occur mainly in the finer sized aerosols.

As indicated above, very many of these metalliferous particles will be ultrafine (<0.1 μm): a study of Californian PM showed dust samples with particles in the size

range 0.056-0.1 μm aerodynamic diameter contained up to 26% metals (average 14%: Cass et al., 2000). Together with primary and secondary carbonaceous particles from combustion processes, such ultrafine particles will form the vast majority of atmospheric particulates in terms of numbers, although their total mass will be small. The surface area available for biochemical reaction is around 10^5 times greater in ultrafine particles than those between 10-2.5 μm (Harrison et al., 2000). Therefore, rather than simply concentrating on particle mass levels in urban PM, a consideration of particle number and potential bioreactivity would place a much higher emphasis on the toxicity of the finer fraction, and inevitably on the role of trace metals in air pollution health effects. As emphasised by our study, and is already clear from other published work, the chemical complexity and variability of the inorganic urban aerosol cocktail is such that the air pollution signature for each town needs to be individually characterised, especially if there are nearby sources of industrial metalliferous emissions.

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Figure captions

Fig. 1. Geographical location of the six PM collection sites described in the text.

Fig. 2. Traffic-Industrial-Crustal (TIC) source apportionment triangles for trace elements in the PM_{10} fraction from all six sites, showing for comparison the average annual concentrations at each site of both PM_{10} and trace metals (TM).

Fig. 3. Comparison between concentrations of selected trace metals at all six sites grouped according to their potential health concern, varying from most (Pb+As+Cd) to least (Ti+Ba+Sr) toxic. Average annual levels of PM_{10}, $PM_{2.5}$ and $PM_{2.5}/PM_{10}$ ratio (*) for the three metal groups are shown.

Table captions

Table 1. Average annual concentrations of some of the main trace metals in ng m^{-3} and µg g^{-1}, as well as enrichment factor *vs* Li (EF) and Upper Continental Crust (UCC) ppm values (from Taylor and McLennan, 1995) in both coarse (PM_{10}) and fine ($PM_{2.5}$) fractions of all six sites.

Table 2. Trace element proportions and factor loadings attributed by source apportionment analysis to traffic, industrial and crustal factors, showing calculated average total mass, range and variance for each source. Factor loadings < 0.30 not considered.
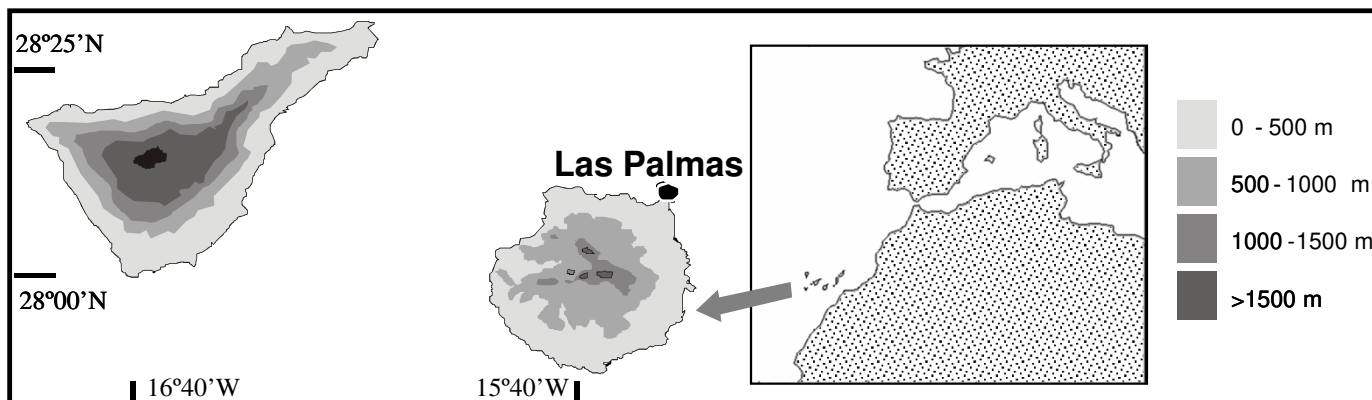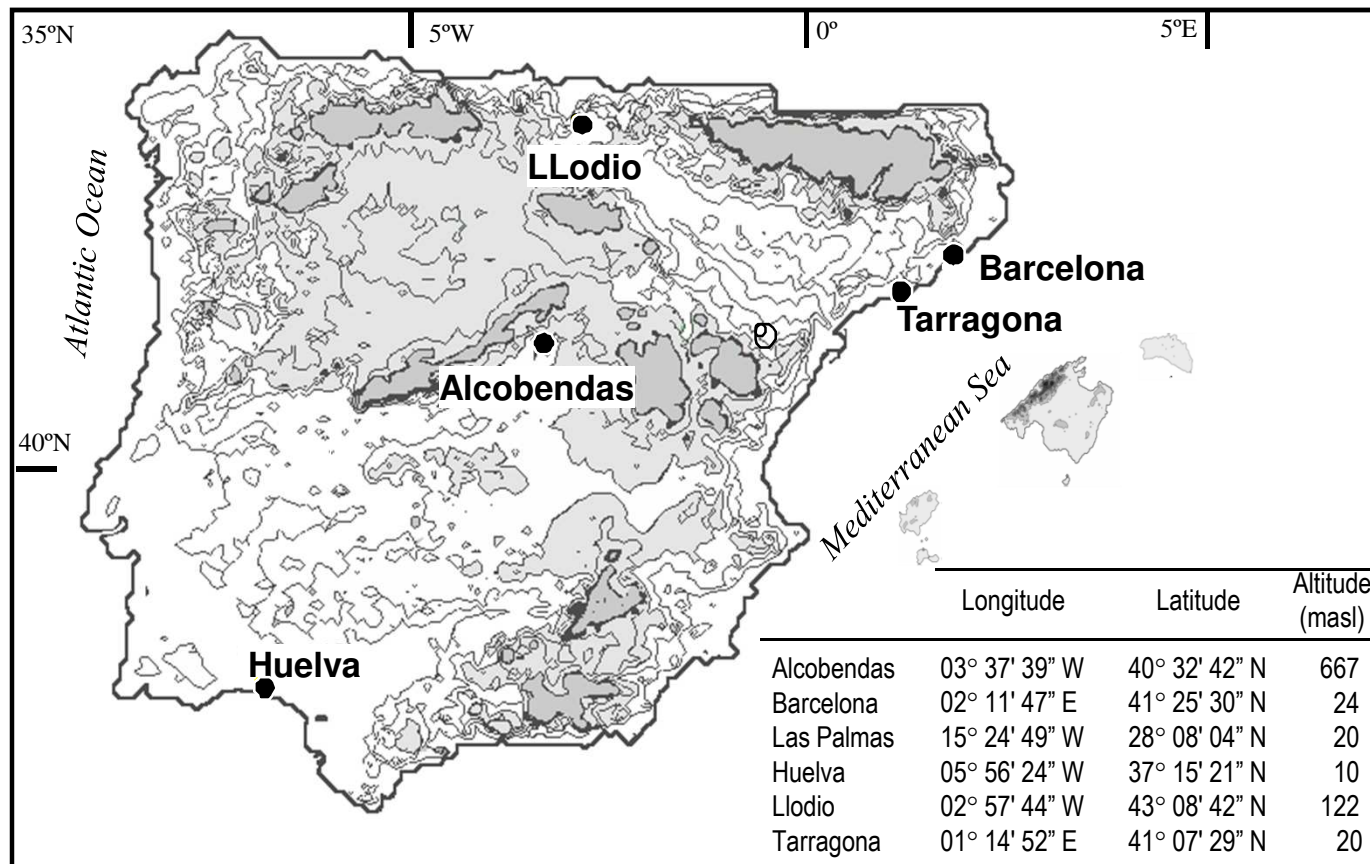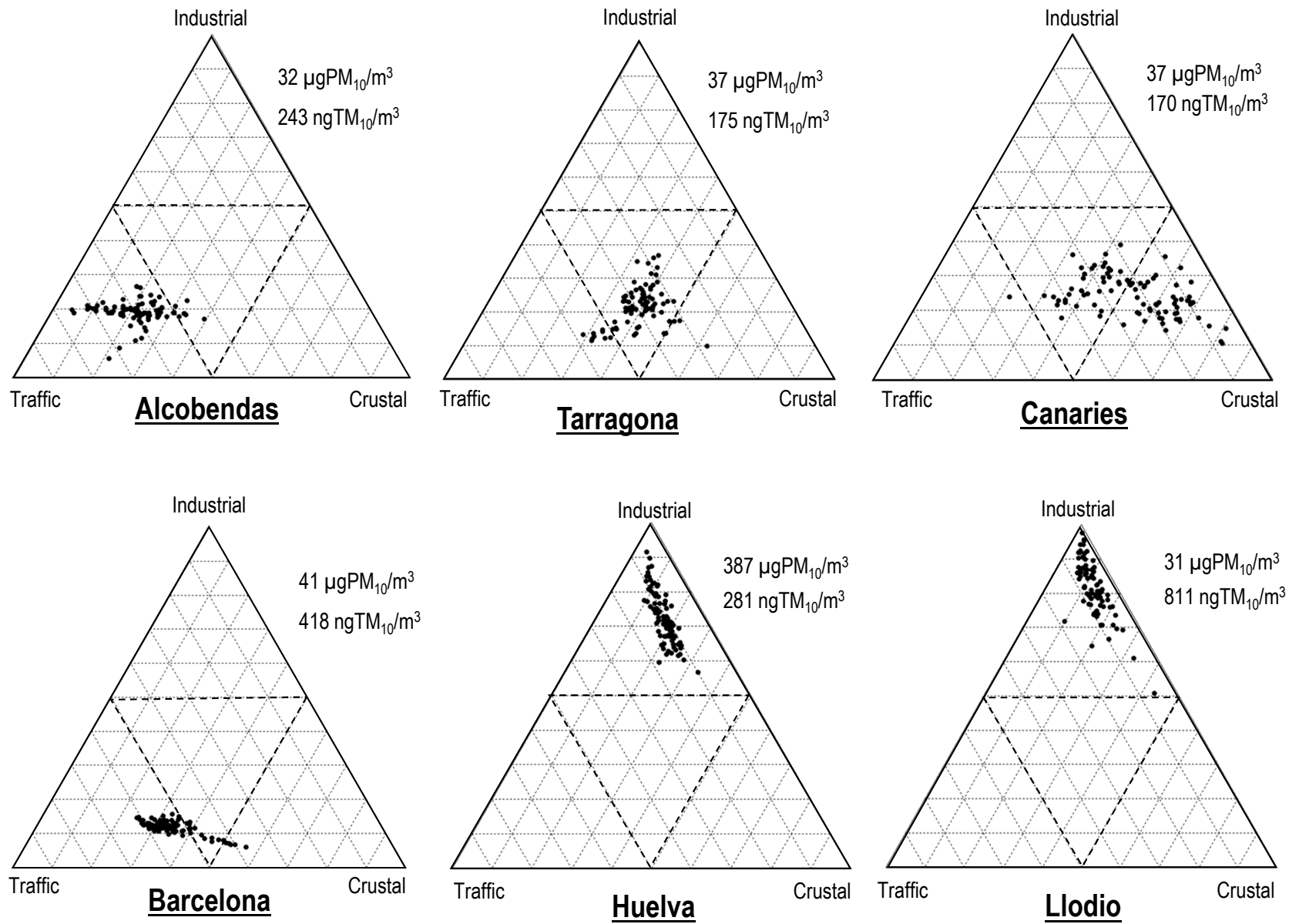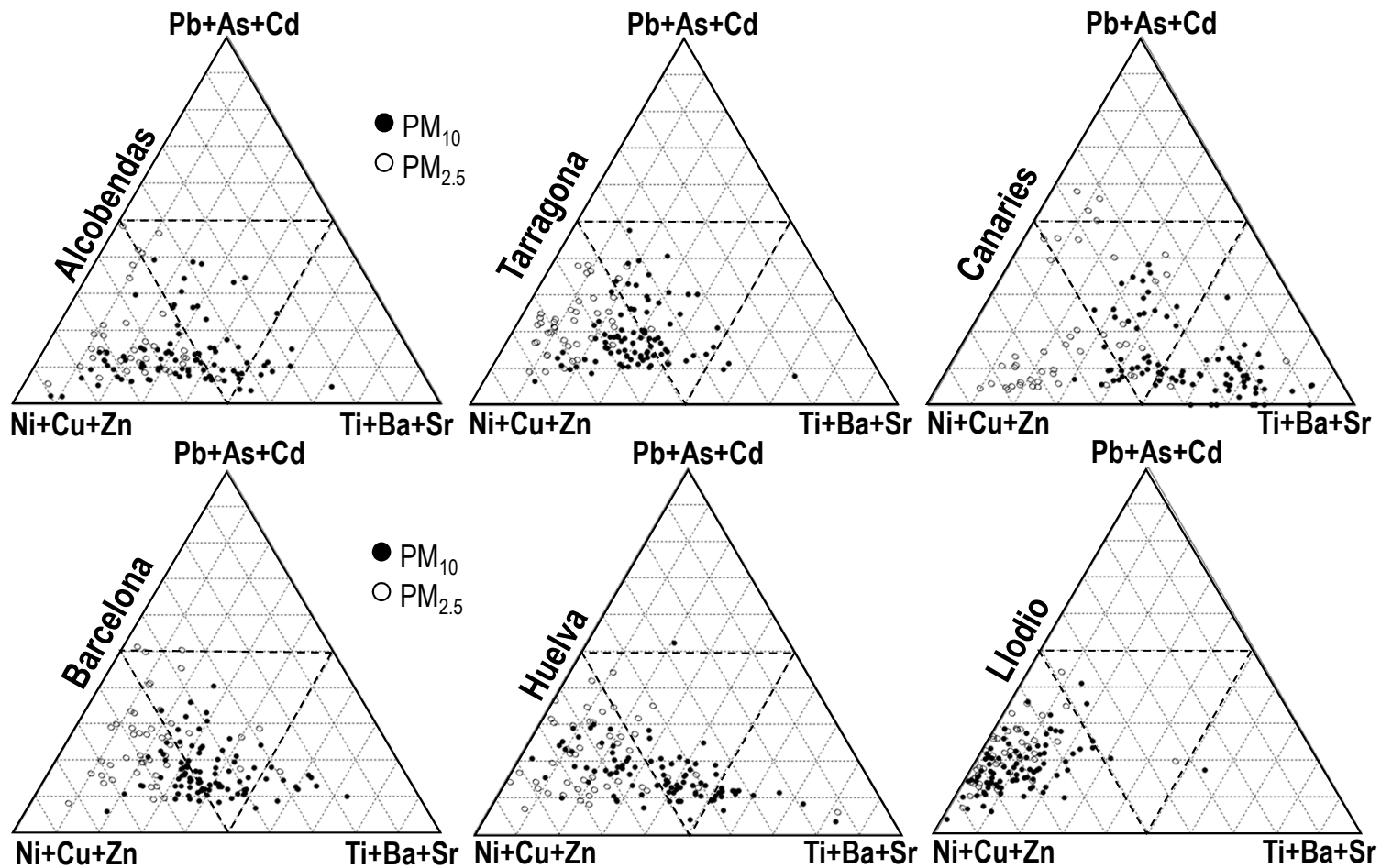
	Longitude	Latitude	Altitude (masl)
Alcobendas	03° 37' 39" W	40° 32' 42" N	667
Barcelona	02° 11' 47" E	41° 25' 30" N	24
Las Palmas	15° 24' 49" W	28° 08' 04" N	20
Huelva	05° 56' 24" W	37° 15' 21" N	10
Llodio	02° 57' 44" W	43° 08' 42" N	122
Tarragona	01° 14' 52" E	41° 07' 29" N	20

0 - 500 m
500 - 1000 m
1000 - 1500 m
>1500 m

Fig.1

Alcobendas

32 µgPM$_{10}$/m^3
243 ngTM$_{10}$/m^3

Tarragona

37 µgPM$_{10}$/m^3
175 ngTM$_{10}$/m^3

Canaries

37 µgPM$_{10}$/m^3
170 ngTM$_{10}$/m^3

Barcelona

41 µgPM$_{10}$/m^3
418 ngTM$_{10}$/m^3

Huelva

387 µgPM$_{10}$/m^3
281 ngTM$_{10}$/m^3

Llodio

31 µgPM$_{10}$/m^3
811 ngTM$_{10}$/m^3

Fig.2

Average		Alcobend.		Tarrag.		Canaries		Barcelona		Huelva		Llodio	
PM_{10}	$\mu g/m^3$	**31.9**		**37.4**		**37.3**		**41.0**		**37.5**		**31.3**	
Pb-As-Cd		23		26		16		59		43		105	
Ni-Cu-Zn	ng/m^3	126		72		41		153		124		483	
Ti-Ba-Sr		57		39		77		130		80		41	
$PM_{2.5}$	$\mu g/m^3$	25.3	0.79*	22.2	0.59*	18.6	0.50*	27.7	0.67*	19.3	0.51*	24.5	0.78*
Pb-As-Cd		20	0.87*	18	0.69*	13	0.81*	42	0.71*	32	0.74*	79	0.75*
Ni-Cu-Zn	ng/m^3	61	0.48*	55	0.76*	35	0.85*	92	0.60*	79	0.64*	289	0.60*
Ti-Ba-Sr		17	0.30*	11	0.28*	20	0.26*	37	0.28*	26	0.32*	17	0.42*

Fig.3

Table 1

Alcobendas / Tarragona / Canaries

	UCC	Alcobendas PM10			Alcobendas PM2.5			Tarragona PM10			Tarragona PM2.5			Canaries PM10			Canaries PM2.5		
	µg/g	ng/m³	µg/g	EF	ng/m³	µg/g	EF	ng/m³	µg/g	EF	ng/m³	µg/g	EF	ng/m³	µg/g	EF	ng/m³	µg/g	EF
Ti	3117	30.2	859	1	10.6	447	1	22.5	599	1	6.1	335	1	52.3	1003	2	12.3	517	1
V	60	3.6	103	8	2.3	83	7	7.7	199	11	5.3	222	45	7.5	174	22	6.1	317	45
Cr	35	2.5	87	12	1.1	63	8	2.9	76	7	2.2	107	22	1.9	43	9	1.0	65	11
Mn	600	9.7	271	2	4.3	179	2	9.2	240	1	2.8	143	2	11.0	224	3	3.2	156	2
Ni	20	2.3	78	20	2.2	106	30	4.2	112	21	3.5	162	76	3.8	90	32	3.7	200	70
Cu	25	28.1	837	142	23.7	988	254	32.9	895	125	31.7	1541	552	22.9	581	245	17.3	974	445
Zn	71	95.7	2444	163	34.9	1474	102	35.0	921	48	19.3	910	103	14.5	352	43	14.0	870	73
As	1.5	0.6	18	49	0.5	17	56	0.8	19	44	0.5	21	142	0.3	6	32	0.3	16	97
Se	50	0.4	14	560	0.4	23	3638	0.5	13	622	0.2	15	1663	0.3	7	1033	0.3	21	3470
Sr	350	4.0	111	1	1.4	66	1	4.8	132	1	1.2	58	1	6.5	124	3	1.6	69	3
Mo	1.5	3.9	161	666	2.9	133	572	2.2	64	139	2.6	124	524	2.2	52	268	0.7	32	85
Cd	0.098	0.3	8	339	0.3	15	714	0.3	8	237	0.2	10	1174	0.2	4	429	0.1	8	702
Sn	5.5	1.5	42	19	1.3	55	65	1.7	47	34	0.9	43	85	0.5	11	17	0.5	26	87
Sb	0.2	8.2	295	4819	2.8	117	3128	6.9	199	2765	2.6	125	3814	7.3	202	5294	0.8	41	1930
Ba	550	23.4	573	5	4.6	201	2	12.1	335	2	3.2	166	3	17.8	398	6	5.6	340	4
Pb	20	22.2	632	194	19.0	745	152	25.5	671	177	17.5	842	415	15.3	394	201	12.5	739	511

Barcelona / Huelva / Llodio

	UCC	Barcelona PM10			Barcelona PM2.5			Huelva PM10			Huelva PM2.5			Llodio PM10			Llodio PM2.5		
	µg/g	ng/m³	µg/g	EF	ng/m³	µg/g	EF	ng/m³	µg/g	EF	ng/m³	µg/g	EF	ng/m³	µg/g	EF	ng/m³	µg/g	EF
Ti	3117	82.9	1862	1	26.3	902	14	59.7	1484	4	21.8	1029	1	24.2	762	1	8.6	365	1
V	60	15.3	315	10	9.5	329	190	6.8	175	30	3.6	176	23	8.3	228	10	7.0	259	16
Cr	35	8.2	180	10	2.9	111	81	1.9	53	11	0.9	52	6	24.6	796	92	15.8	658	92
Mn	600	22.8	500	2	9.6	346	18	10.7	282	4	3.2	155	2	86.5	2881	11	39.2	1630	15
Ni	20	7.3	156	15	5.2	191	434	3.3	83	32	3.0	150	57	33.0	1046	197	20.8	866	218
Cu	25	48.5	1093	84	31.7	1236	1247	70.1	1825	494	32.9	1709	461	32.6	1065	124	29.1	1251	262
Zn	71	97.3	2227	61	55.5	2113	1120	50.5	1315	126	42.6	2066	164	417.4	12319	439	239.0	9744	839
As	1.5	1.5	34	46	1.1	37	1008	5.4	134	628	4.2	174	744	1.8	59	115	1.5	62	195
Se	50	1.1	22	691	0.8	35	1712	1.5	39	6399	1.1	69	9121	2.8	92	5426	2.8	125	7861
Sr	350	6.2	134	1	1.9	69	1	4.4	112	2	1.0	54	1	2.9	92	1	0.9	40	1
Mo	1.5	4.0	101	127	1.7	65	205	1.9	60	152	1.4	89	290	15.5	515	1266	12.3	521	1573
Cd	0.098	0.7	17	353	0.6	22	7234	0.8	19	1273	0.8	35	2164	1.2	36	1031	1.0	37	2413
Sn	5.5	4.4	91	30	3.7	140	648	2.2	58	73	1.9	97	122	37.5	1139	511	37.0	1451	1207
Sb	0.2	10.8	258	2398	4.3	165	23010	2.7	72	2529	1.0	61	1623	3.6	139	1602	1.2	45	1244
Ba	550	40.8	936	3	9.3	356	23	15.8	450	5	2.5	145	1	14.1	453	2	7.2	295	5
Pb	20	57.1	1311	133	40.3	1496	2063	36.8	927	285	26.9	1242	418	101.7	3072	376	76.5	2975	987

	Traffic		Industrial		Crustal	
Alcobendas n= 86	$Zn_{0.82}+Sb_{0.8}+Pb_{0.74}+Cd_{0.63}+As_{0.58}+Ba_{0.57}+Cu_{0.54}+Mn_{0.38}$		$Cr_{0.56}+Pb_{0.3}$		$Li_{0.8}+Ti_{0.73}+Sr_{0.66}+Co_{0.65}+Rb_{0.58}+Mn_{0.57}+V_{0.5}+Ba_{0.45}$	
	Average Total mass: 140 ng/m^3 Variance: 24%	Range: 1609-16	Average Total mass: 40 ng/m^3 Variance: 13%	Range: 402-8	Average Total mass: 38 ng/m^3 Variance: 38%	Range: 149-6
Tarragona n= 88	$Pb_{0.8}+Zn_{0.61}+As_{0.58}+Cd_{0.35}$		$V_{0.82}+Ni_{0.75}+Co_{0.46}+Cu_{0.43}+Cd_{0.34}+Sb_{0.3}$		$Ti_{0.88}+Sr_{0.8}+Rb_{0.79}+Ba_{0.56}+Co_{0.42}+Cu_{0.33}+As_{0.3}$	
	Average Total mass: 60 ng/m^3 Variance: 10%	Range: 158-23	Average Total mass: 33 ng/m^3 Variance: 15%	Range: 106-11	Average Total mass: 58 ng/m^3 Variance: 45%	Range: 152-22
Canarias n= 90	$Cd_1+Pb_{0.94}+Sb_{0.75}+As_{0.51}+Cu_{0.5}$		$Zn_{0.67}+Ni_{0.65}+V_{0.65}+Sn_{0.59}+Cr_{0.57}+Ba_{0.49}$		$Ti_1+Sr_{0.72}+As_{0.55}+Co_{0.51}+Ba_{0.46}+Cr_{0.41}$	
	Average Total mass: 35 ng/m^3 Variance: 13%	Range: 208-4	Average Total mass: 36 ng/m^3 Variance: 4%	Range: 180-7	Average Total mass: 85 ng/m^3 Variance: 50%	Range: 986-19
Barcelona n= 92	$Cd_{0.84}+Sb_{0.74}+Zn_{0.71}+Pb_{0.71}+Cu_{0.69}+Ba_{0.61}+Cr_{0.48}+Ni_{0.4}+V_{0.33}+Mn_{0.3}$		$V_{0.54}+As_{0.52}+Ni_{0.49}+Cr_{0.31}$		$Rb_{0.9}+Ti_{0.83}+Mn_{0.71}+Co_{0.49}+Sr_{0.47}+As_{0.36}+Ba_{0.33}$	
	Average Total mass: 217 ng/m^3 Variance: 18%	Range: 544-67	Average Total mass: 46 ng/m^3 Variance: 14%	Range: 109-17	Average Total mass: 143 ng/m^3 Variance: 42%	Range: 579-36
Huelva n= 91	$Cr_{0.81}+V_{0.52}$		$As_1+Cu_{0.89}+Ni_{0.87}+Pb_{0.87}+Zn_{0.86}+Ti_{0.64}+V_{0.41}$		- - - -	
	Average Total mass: 26 ng/m^3 Variance: 7%	Range: 88-5	Average Total mass: 190 ng/m^3 Variance: 28%	Range: 713-41	Average Total mass: 38 ng/m^3 Variance: 31%	Range: 151-7
Llodio n= 87	$Sb_{0.36}$		$Pb_{0.91}+Cr_{0.87}+Mo_{0.87}+Zn_{0.85}+Ni_{0.82}+Cu_{0.71}+Mn_{0.67}+Cd_{0.61}+Co_{0.55}+As_{0.54}+Sb_{0.3}$		$Ti_{0.94}+Sr_{0.79}+Li_{0.74}+Ba_{0.6}+V_{0.34}+Co_{0.33}+Sn_{0.3}$	
	Average Total mass: 40 ng/m^3 Variance: 4%	Range: 162-7	Average Total mass: 658 ng/m^3 Variance: 41%	Range: 3799-70	Average Total mass: 65 ng/m^3 Variance: 8%	Range: 193-15

Table 2