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Spatial and temporal variations of trace elements distribution in soils and street dust of an industrial town in NW Spain: 15 years of study

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ABSTRACT

Extensive spatial and temporal surveys, over 15 years, have been conducted of soil in urban parks and street dusts in one of the most polluted cities in western Europe, Avilés (NW Spain). The first survey was carried out in 1996, and since then monitoring has been undertaken every five years. Whilst the sampling site is a relatively small town, industrial activities (mainly the steel industry and Zn and Al metallurgy) and other less significant urban sources, such as traffic, strongly affect the load of heavy metals in the urban aerosol. Elemental tracers have been used to characterise the influence of these sources on the composition of soil and dust. Although PM₁₀ has decreased over these years as a result of environmental measures undertaken in the city, some of the “industrial” elements still remain in concentrations of concern for example, up to 4.6% and 0.5% of Zn in dust and soil, respectively. Spatial trends in metals such as Zn and Cd clearly reflect sources from the processing industries. The concentrations of these elements across Europe have reduced over time, however the most recent results from Avilés revealed an upward trend in concentration for Zn, Cd, Hg and As. A risk assessment of the soil highlighted As as an element of concern since its cancer risk in adults was more than double the value above which regulatory agencies deem it to be unacceptable. If children were considered to be the receptors, then the risk nearly doubles from this element.

Key words: Street dust; urban soil; urban geochemistry; risk assessment; metals

1. INTRODUCTION

The negative effects of urbanization and industrialisation on the urban environment are well known (Sancini et al., 2011; Wang et al. 2012), due to the many geochemical studies of street dusts, road deposits and soils that have been undertaken eg Charlesworth et al., 2003; Charlesworth et al., 2011; De Miguel et al., 2007; Loredó et al., 2003; Tositti et al., 2014. These studies found that one of the most important heavy metal sources in urban environments are vehicle emissions. Whilst the gradual shift from leaded to unleaded petrol has significantly reduced vehicular emissions of this element, its persistence in the urban environment has been noted by authors such as Charlesworth et al., 2003 and De Miguel et al., 1997, particularly near heavily trafficked areas. Traffic also contributes significant amounts of Zn, Cu, Ba, Cd and Ni (Charlesworth et al., 2011).

However, the urban environment is exposed to varying concentrations of heavy metals from other anthropogenic sources such as fossil fuel combustion, mining, metallurgical and other industrial activities, as well as from natural geochemical processes, e.g. the resuspension of soil particles. Industrial sources of pollution are obviously specifically site related depending on the activity. The spatial distribution of pollutants in urban areas largely reflects the impact of current and past industrial activities, as well as traffic movements (Zierock, 1994). Due to rapid urbanisation and scarcity of land, most of the parks and recreational areas in cities are often located close to major roads or industrial areas, where they are subject to many potential pollution sources (Li and Liu, 2001). The typology and density of industries, together with local factors such as weather conditions and wind patterns cause considerable variation in the concentrations of heavy metals found in urban environments, as was found in Ordóñez et al., 2003. This latter study was carried out in an industrial city in Northern Spain: Avilés, and was based on the collection and analysis of street dusts and soils. The study found that there were concerning levels of elements such as Zn, Cd, Hg and Pb in the street dusts related to industrial activities and exhaust emissions, with similar distributions but lower concentrations in the soil samples. Such metal concentrations have the potential to have significantly negative impacts on the health of those living in such industrialised cities.

Trends with time across Europe appear to reflect the declining economic situation, with metals exhibiting a general decline in their deposition (sampled in mosses across Europe) in recent decades. For example, between 1990 and 2005, the average concentrations of As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn declined by values ranging from 11% (Cu) to 77% (Pb) (Harmens et al., 2013). This particular study reported on concentrations of a variety of metals as well as nitrogen from 3 regions in northern Spain (La Rioja and Navarra in the NE, and Galicia to the NW) but not Asturias.

Many studies on street dust have focused on elemental concentrations and source identification (Charlesworth et al., 2011; De Miguel et al. 1997; Ferguson and Kim, 1991). Heavy metals in urbanized areas can accumulate on topsoil from atmospheric deposition by sedimentation, impaction and interception (Sezgin et al. 2004), with lengthy persistence (Alloway, 1990; Kelly et al., 1996). Inhalation of suspended particles and ingestion of dust particles and soils (especially in the case of children) are among the possible routes through which people can be exposed to these elevated levels of trace elements. If children and the elderly are exposed to an environment with high metal contamination, their health may be affected (Charlesworth et al., 2011; Li and Liu, 2001). Consequently, the geochemical investigation of pollution in soils and street dust particles is an important contribution to the characterisation of the urban environment and associated potential health risks.

The aim of this research was to carry out a comprehensive urban geochemical study focussing on urban parks and roadside dusts in a traditionally industrial Spanish town. It assesses, both spatially and temporally, heavy metal contamination over a 15 year period (1996-2011), investigating possible sources of the metals and also the potential implications of elevated levels on human health.

2. AREA OF STUDY

Avilés is a city located on the coast of Asturias, NW Spain (Fig. 1). It used to be a markedly industrial area, including the steel industry and non-ferrous metal production (mainly Zn and Al), glass production, fertilizer manufacturing, etc., but some of these activities have declined over the last few years. Factories related to Zn, Al and steel production and processing are located to the N, NE and E of the city, respectively. Due to industrial growth in the city the population quadrupled from 1950 to 1970, but recently decreased, currently standing at 83,000 inhabitants (SADEI, 2014).

Environmental guideline values for several substances have been dramatically exceeded in the past. For example, during December 1979, the level of total suspended solids was 300 times the maximum allowed value. This led to Avilés being declared a Polluted Atmosphere Area in January 1981, the most polluted city in Spain, and one of the most polluted European cities (Gobierno del Principado de Asturias, 2014). Suspended particulate matter was of particular concern, leading to high incidences of asthma. Industrial restructuring began in 1990: several factories closed or introduced more conservative environmental measures and monitoring plans. Also, a series of actions undertaken by local authorities over the last 30 years have helped to meet air quality objectives, resulting in regeneration of the urban environment. Currently, only one monitoring station (located in the N of the city) revealed that the allowed levels of PM₁₀ had been exceeded, due to its proximity to an area of storage and handling of bulk ore from the port. Analysis of the particles retained on the filter from that monitoring station had high concentrations of Zn and S (up to 90%), but this was not found at the other stations (Gobierno del Principado de Asturias, 2014). Fig. 2 shows the general downward trend in average PM₁₀ values registered across the city's monitoring network during 1996-2013. The same figure shows the Industrial Production Index (IPI) of metal industries in Asturias which increased until recently, when it was affected by the economic crisis.

Major roads with high vehicular traffic density cross the city reach up to 20,000 light vehicles/day (Ordóñez et al., 2003); however, away from these major roads the rest of the city is rather quiet. 50% of the houses were built before 1960 and 81% before 1980, with the built environment in total occupying an area of more than 5 million m², which increases on average about 1.4% per year (SADEI, 2014).

The local bedrock geology consists mainly of clastic rocks (conglomerates), red clays, carbonates (limestones and dolostones) and marls of Mesozoic age (López and Flor, 2008), covered by recent deposits near the estuary, which has been partly filled up artificially. Consequently, the terrain is basically flat, with an elevation ranging from 0 to 140 m above sea level (SADEI, 2014).

According to the Agencia Estatal de Meteorología, the climate is humid, with an average yearly precipitation over the last 45 years of 1100 mm (effective rainfall of 410 mm per year) and a mean temperature of 13°C. The wind direction is predominantly west, (55%), although wind velocities are generally low (average of 3-4 m s⁻¹). The wind direction explains maximum PM₁₀ values registered at some of the city's monitoring stations (Gobierno del Principado de Asturias, 2014).

3. METHODS

Street dust, the particulate matter deposited onto urban roads and pavements, has high spatial variability, so it is essential to select the appropriate sampling design. Therefore, the urban area was divided into seven mapping squares of 1 km² each, designated A to G (Fig. 1). Sixteen sampling points were randomly distributed in each mapping unit, yielding a total of 112 sub samples in both residential and industrial sectors. Sampling was always carried out one week after the last precipitation event. Sampling was performed using a small broom and a dustpan, collecting dust deposited mainly on the road, close to the pavement. The approximately 150 g of street dust collected at each sampling point was combined to represent one whole mapping unit. This sampling design was maintained in all four sampling campaigns, although the location of the 16 sub samples could

not be maintained, due to the variability in dust deposition. As an example, the location of the 16 sub samples taken in unit B in the 1996 campaign are shown in Fig. 1. As detailed in Ordóñez et al. (2003), Visman methodology (Visman, 1947) was applied in order to evaluate precision in terms of estimating the sampling unit's mean value.

In urban soils it is not possible to apply a systematic sampling design as their location depends on there being open areas such as parks, yards, roads, roadsides, private gardens, undeveloped land, etc., from which to sample, and these are not evenly distributed across the city. Samples were collected from public parks and other green areas to cover the different districts of the city and assess possible influences from traffic or industry as a function of distance from their potential source. Sampling points were located at about 15 m from the nearest major road or street with high traffic density. Soils collected were not necessarily restricted to the urban area, unlike the street dust campaign, and therefore covered a larger area (10 km²) including soils surrounding the city. As far as the authors know, the areas where soils were collected are not fertilized and the potential contribution of compost to the trace element load was therefore considered negligible.

Soil samples were composites of five sub samples (of about 0.5 kg each), which were taken according to a cross pattern (center and extremes), with 5 m distance between sub samples. These were taken using garden tools (a small pick to make a surface hole and a plastic shovel to collect the samples). In 1996, 40 samples in total were collected (Ordóñez et al., 2003), whereas in campaigns which followed, only 17 samples were taken from the same sites (designated nos. 1 to 17), chosen from the locations identified in 1996 (Fig. 1); these locations were selected as the most visited green spaces in the centre of the city, some associated with residential blocks and some with the city outskirts. In 1996 and 2006, samples were collected from the upper 15 cm of the soil profile, whereas in 2001 they were collected from the upper 25 cm; in the last campaign (2011), samples were taken at both depths (15 and 25 cm) every time in order to evaluate the vertical mobility of trace elements in the soil profile and how this translocation may affect the concentrations reported for different depths.

In order to avoid metal contamination, only plastic tools were used for dust and soil sampling. All the samples were kept in plastic bags and taken to the laboratory. After drying for 72 h at 45°C, each sample was sieved through a 2 mm non-metallic mesh to remove large particles, and then carefully homogenised and sieved to obtain the <147 µm fraction (particles that can be easily resuspended). After reduction by repeated quartering, 0.5 g sub samples were digested using 3 ml of 3:1:2 HCl: HNO₃: H₂O at 95°C for 1 h and diluted to 10 ml with water. Multielemental analyses of all samples from all campaigns were determined by ICP-MS at accredited ACME Analytical Laboratories, in Vancouver (Canada). Quality controls involved routine analyses of standards and duplicates. Approximately 5% of the samples were analysed as internal and external control samples; the variability was found to be < 10% for all elements analysed.

Descriptive statistics of the analytical data, as well as multivariate analysis techniques, i.e. Cluster Analysis, were performed to describe and interpret the results.

In order to identify metal-enriched particles and whether they had combined with other elements, two samples from the 2011 campaign (street dust from grid A and soil from superficial sample no. 16) were observed by means of scanning electron spectroscopy. SEM-EDAX studies were carried out at the Oviedo University facilities, using a JEOL 6610LV Scanning Electron Microscope (30 kV, 3 nm of theoretical resolution) with a silicon-drift detector type X-max 50 (125 eV to 60 keV). Secondary electrons were used to obtain the images and backscattered electrons were used to identify particles with elements of high molecular weight. Elemental analyses were developed with an EDAX module. This technique enabled the characterization of size, morphology, and chemical composition of metal-bearing particles (Miler and Gosar, 2015, 2013, 2012).

The mineral composition of the same samples used for SEM was determined by X-Ray Diffraction (XRD), utilising the powder method, and a Bruker D8 Discover diffractometer, working with K_{α} Cu radiation and an Ni filter. The applied voltage and anodic current were 45 kV and 40 mA, respectively.

The methodology used by Wang et al. (2012) when defining the concept of “urban environmental entropy” to investigate the effect of urbanization on the overlying atmosphere, was applied to this case. Urban growth is a necessary condition for the urban system to prevail but as it is irreversible, it may decrease the quality of the system. Entropy is a commonly used way to address urban sprawl; it must be kept within a range in which the system is sustainable. Environmental pollution generates excess entropy; the greater the entropy, the greater the effect on the environment (Cabral et al., 2013; Ouyang et al., 2008). The relationship between the development of urbanization and street dust quality in Avilés between 1996–2011 has therefore been studied through the determination of urban environmental entropy in the 7 square sampling units, based on statistical analysis of the main metals (Al, Ba, Fe, Pb and Zn) present in the samples.

Lastly, the potential health effects on the urban population of the exposure to trace elements in dust and soil was derived from a risk assessment following the USEPA methodology. To characterize the systemic and carcinogenic risk, a Hazard Index (eq. 1) and a Cancer Risk (eq. 2), respectively, were determined. The chronic average daily dose (CADD) or concentration in air (C_{air}) was divided by the corresponding reference dose (RfD) or reference concentration (RfC), and the lifetime average daily dose (LADD) or concentration in air was multiplied by the corresponding slope factor (SF) or unit risk (UR). Additivity of adverse health effects was assumed for mixtures of elements and multiple exposure routes.

$$HI = \sum_i HQ_i \quad HQ = \frac{CADD [C_{air}]}{RfD [RfC]} \quad (\text{eq. 1})$$

$$RISK = \sum_i RISK_i \quad RISK_i = LADD [C_{air}] \cdot SF [UR] \quad (\text{eq. 2})$$

Chronic and lifetime average doses through ingestion, inhalation and absorption through the skin were calculated using USEPA’s default exposure parameters for a residential scenario. Toxicity values were retrieved from the US Department of Energy’s Risk Assessment Information System (USDoE, 2014), except the oral reference dose for Pb, which was derived from the World Health Organization’s Guidelines for Drinking Water Quality. Dermal toxicity values have been determined from oral values, multiplying reference doses and dividing slope factors by the corresponding gastrointestinal absorption factor. The concentration term used in the estimate of reasonable maximum exposure was the upper limit of the 95% confidence interval for the arithmetic mean (calculated with ProUCL 5.0 software (USEPA, 2014)).

4. RESULTS AND DISCUSSION

Street dust

A statistical summary of the analytical results of the 1996, 2001, 2006 and 2011 sampling campaigns is shown in Table 1. The coefficient of variation (standard deviation/mean) is low for Ca, Mg, Sr, V, La and Th. The concentrations of these geogenic elements (Ordóñez et al., 2003) show little variation in the area due to their natural origin. In contrast, Zn, Cd, Hg, Ag, Pb and As (in the 2011 sampling campaign), have high coefficients of variation and heterogeneous distribution, corresponding to anthropogenic origins. The concentrations of the latter elements in every square unit for the four sampling campaigns are shown in Fig. 3. The highest concentrations of these elements were found in the northern sampling square unit (A), related to the raw materials used in the Zn metallurgical industry, located in the northern section of the city. The concentrations of some metals found in some sampling units were noticeably high. For example, elevated concentrations of Zn (4.6%), Pb (0.15%) or Cd (139 mg kg⁻¹) were

found in unit A in 2011. To the best knowledge of the authors, such values have not been exceeded in street dust in other cities in the world (Charlesworth et al., 2011).

Cluster Analysis (Fig. 4) revealed several groups of highly correlated elements, suggesting common origins. There was a distinct separation between elements with a clear anthropogenic origin (first cluster) and those with a natural or mixed origin (second cluster). The first sub-group of elements (Hg, Zn, Pb, Tl, Cu, S, Cd, Ag, As and Sb) within the first cluster can be linked to the Zn processing industry, which uses sphalerite (ZnS) as a raw material, in which Fe, Cd and Pb are frequently found and less so Mn, Hg, In, Tl, Ga, Ge, Sb, Sn, Ag, Ba, Au, Bi and Cu (Mindat, 2014). Anju and Banerjee (2011) found high, correlated concentrations of heavy metals including Pb, Zn, Mn, and Cd in the soils surrounding historical Pb-Zn mining and smelting areas in India, and Xu et al. (2013) found high As contents in the street dust of a Zn smelting district in China.

Another subgroup in the first cluster was composed of Co, Ga, P, Al and Sc. These are related to aluminium processing by the Bayer process, using bauxite as the raw material. The main impurities in bauxite are SiO₂, Fe, Ti, Be, Ca, Cr, Ga, Mn, V, P, K, S, Na, B, Ba, Cd, Co, Pb and Sc, depending on the initial composition of the ore and also processing conditions. Most bauxites contain between 0.001-0.05% of Ga₂O₃, and are the main source of Ga (RACI, 2011). Ga and Al are in the same column of the periodic table and therefore have similar chemical properties, reflected in their similar distribution in the present study. The second main cluster included the alkali elements Na-K and Ca-Sr, whose origins are basically geogenic/natural. Fe, Ti, Cr, V, Mn and Mg, most likely have mixed origins, i.e. natural and related to steel production and processing in coke ovens. The emissions from such facilities can be very broad, including organic compounds, as well as As, Cd, Be, Cr, Pb, Ni, Mn, Hg, Se, V, Cu and Zn (Graham and Holtgrave, 1990). Trace elements found in the coke are directly related to those present in raw coal and are highly variable, depending on its origin. The steel industry in the study area recently measured atmospheric annual emissions consistently above 60 kg As, Hg and Cd, 160 kg Cr, 500 kg Cu, 190 kg Ni, 2 t Pb, 580 kg Zn and 88 t of PM₁₀ (MAGRAMA, 2014).

Sampling grids A and B, located to the north of the study area were clearly different from the rest, with a higher industrial influence, and higher concentrations of Zn, Cd and Hg. Some of the metals discussed here can have typically urban origins such as traffic or heating emissions, construction, urban degradation of metal surfaces, etc. (Charlesworth et al., 2011). However, in this case, the industrial influence is so prevalent that its contribution masks any other potential sources.

Fig. 5A shows contour maps of Zn concentrations found in the four sampling campaigns; although the range was variable, the spatial distribution of this element was similar in the four maps; it tended to steadily increase in a northerly direction. The spatial distributions of Cd and Pb are shown in Fig. 5B and have the same tendency of increasing concentration towards the site where the Zn smelter is located. In contrast, elements such as Fe and Cr (Fig. 5B) showed a different distribution, with maximum contents in square E, close to the steel industry.

Over time, the concentrations of Zn, Cd, Hg, Ag and As in street dust decreased from 1996 to 2001, then either remained stable or further decreased from 2001 to 2006, and then rose to maximum values in 2011. These reductions in concentrations between the first and second sampling campaigns are in agreement with the European trend found in the study carried out by Harmens et al. (2013), leaving methodological differences aside (Table 2). In the case of Avilés, they can be related to changes in the method of transport of the Zn ore from the harbour to the factory which occurred in 1998. A covered conveyor belt replaced the lorries previously used to transport the dusty ore by road, moving the ore directly from the harbour to the factory, potentially reducing the release of particulate material and thus its incorporation in the street dust. A second important factor was that in 2004 the Spanish mine supplying the mineral to the Zn smelter closed, and the ore had to be imported, principally from Canada and Alaska. Due to climatic conditions in these countries, mines are only able to open half of the year, so the mineral is delivered to the N of Aviles in summer and

autumn. It is then stored in uncovered heaps and there is great potential for it to be incorporated in street dust. For the rest of the year (winter and spring), mineral particles will only make a significant contribution to the trace element load of street dust if they are resuspended from the heaps by NW winds which are infrequent during these months. This fact would explain the increased concentrations of elements associated with the Zn ore in the 2011 campaign (carried out in the summer) relative to the 2006 one (undertaken at the end of the year). The change of origin – and composition – of the ore in 2004 is most likely also the explanation of the higher concentrations of Ag and As in street dust after that date (although the latter can be also related to the steel industry).

In spite of its increase in concentration in the northern grids in 2011, Pb was generally lower in comparison with the first campaign. This is because not all of the Pb found in the street dust was necessarily associated with the Zn metallurgical industry since one major source of this element at the time that the first sampling was undertaken was traffic. This was highlighted by Ordóñez et al. (2003) due to the enrichment of Pb along busy roads, but the shift to unleaded petrol has since reduced the emissions of this metal. The concentration of Ba, for example, usually linked to diesel vehicle emissions, has remained steady during monitoring. Concentrations of Al in street dust have not undergone substantial changes during this period. Despite the gradual substitution of coal for gas in the heating systems of the city, which could lead to a reduction of Cu concentration, the potential input of this metal from other sources such as coke production and traffic, have probably caused it to slightly increase.

The entropy results reinforce the geochemical discussion on temporal and spatial variability (Table 3). The total values of entropy are negative for four units (B, C, D and G) which implies that urbanization has not been negatively affected by the presence of metals in the street dust in these areas, in contrast to units A, E and F. The fact that the concentration of Fe and Zn increased in sampling units E and A respectively, is also reflected in an increase in urban entropy; this means a negative effect over these units, which is related to industrial emissions. By analysing the absolute value of entropy, urban activities over time have not significantly affected street dust Al content, although unit E has clearly improved in relation to this element. The same can be said for Ba, as the entropy values are low for all the units; relating this metal to vehicular emissions, the central units (C, D, E and F, where most traffic concentrates) register less improvement (entropy > 0), as traffic increases urban entropy in these neighbourhoods. In contrast, Pb emissions are now more related to industry (northern units: A and B) than traffic. It is noticeable that the entropy results for Zn are negative in only one unit (D); this metal is the main input to the total entropy of the city.

Some examples of the SEM-EDAX analyses of street dusts are shown in Fig. 6. In the sample from the N of the city, this shows that particles essentially contain O, C, Fe, Si, Al and Ca with concentrations of metals such as Zn, Pb or Hg high enough to be detected in some of the particles. Particles of sulphides such as sphalerite and Zn carbonates were clearly identifiable in Fig. 6A, with an Hg-rich particle (probably cinnabar) in Fig. 6B. XRD analysis indicated quartz as the major crystalline mineral, and moderate quantities of calcite and sphalerite were also found.

Soils

The analytical results obtained for soils in the four sampling campaigns are summarised in Table 4. As expected, the concentrations of anthropogenic trace elements, which are deposited on the surface of the soil as resuspended street dust and particulate atmospheric aerosol, decrease with depth. Concentrations of Zn, Cd, Ag, Pb and Ba are 6.2, 5.9, 3.2, 1.6 and 1.3 times higher in the shallower samples.

Comparing campaigns with the same sampling depth, elements of anthropogenic origin generally increase with time in the soil. In 15 years, average contents of Zn, Cd, Ba and Pb have increased by 275%, 210%, 74% and 17%, respectively. Contents of these elements have particularly increased to the N of the city, close to the Zn industry and the main routes of ore transport, and downwind from the industrial area. Thus, Zn concentrations in sample nos. 5, 16 and 1 have increased 14, 8 and 5

times, respectively in 15 years and concentrations of Zn and Cd in sample no. 16 reached values up to 5,458 and 28.6 mg kg⁻¹, respectively, in 2011, whereas samples taken in the residential southern area, such as nos. 10, 11 or 12 had relatively little variation in concentration. However, elements such as Fe and Al, which have both industrial and natural origins, reflect the reduction in their industrial emissions over time, in decreased mean concentrations in superficial soils. A 65% increase in P concentration over time is probably related to the fertilizer industry.

Compared to values in the surrounding street dust, average metal contents in soil are appreciably lower. Mean contents of Zn, Cd, Ag and Pb in the street dust sampled in 2011 were 7.8, 5.8, 5.2 and 2.7 times higher than those found in superficial soils. Non anthropogenic elements, such as K, Mg, Th or La, had similar or slightly higher average concentrations in soils and street dust, as the latter is fed from soil particle resuspension. In the most recent campaign, elements such as Al and Ga were lower in the street dust in comparison with the soils. This may again be due to the reduction in industrial emissions affecting dust, whereas soil acts as a pool that accumulates elements deposited over time; also, Al is present in the natural composition of soil (phyllosilicates). Despite these differences in absolute values, cluster analysis of the soil data essentially replicated the results previously found for street dust (Fig. 4): groupings reflecting elements related to typical emissions from Zn and Al metallurgy, the steel industry and those of natural origin.

Fig. 7 shows some images and analyses of soil sample 16 by SEM-EDAX. The observed particles essentially comprised O, Si, Al, Fe, Ca and K; phyllosilicate sheets could also be clearly identified. In Fig. 7A, particles of Fe carbonate and weathered Pb-rich sphalerite were observed and Fig. 7B shows Fe-As carbonate. According to XRD analysis, the soil sample contained quartz, muscovite and kaolinite as major mineral crystalline phases. Other metallic mineral phases could not be clearly distinguished by XRD analysis, since they were present in concentrations below 2%. These techniques will be further explored in future research.

The soil was mostly sampled in parks and undeveloped land, not used to grow vegetables. The Regional Soil Guideline Levels for As, Cd, Co, Cu, Mn, Pb and Zn defined in Asturias for residential soils (40, 20, 25, 400, 2135, 400 and 4550 mg kg⁻¹, respectively) were exceeded in a total of 26 of the samples, mostly in the most recent sampling campaign. In order to assess the potential adverse health effects of exposure to these trace elements, a risk assessment was carried out, using the results of the 2011 superficial sampling campaign. The output of the risk assessment (Table 5) indicated that the highest risk was associated with ingestion of soil particles and that the trace element of most concern was As. The exposure to As resulted in a cancer risk value for an adult individual of $2.6 \cdot 10^{-5}$, above the $1 \cdot 10^{-5}$ probability level deemed unacceptable by most regulatory agencies. Regarding non-cancer effects, exposure to the urban soils yielded an aggregate hazard index (HI) below the threshold value of 1. For children, HI>1, with As and Pb as main contributors, and the value of cancer risk almost doubles.

Although the main conclusions of this risk assessment in terms of the elements and exposure pathways of main concern are perfectly valid, the quantitative results must be interpreted with caution because they are affected by three important sources of uncertainty: Firstly, the default exposure factors taken from the USEPA may not accurately reflect the characteristics and habits of the population in Aviles. In particular, contact rates and exposure frequency used in the model probably overestimate the actual values for Aviles, where climatic conditions restrict the amount of time spent outdoors, and the percentage of houses with gardens is lower than in the United States. Secondly, the use of the default Particulate Emission Factor suggested by the USEPA may not correctly extrapolate the concentration in air from the concentration in soil for the climatic conditions and surface soil characteristics of Avilés. Thirdly, the concentration term has been calculated using pseudo-total (i.e. aqua regia extractable) concentrations. For elements whose oral toxicity reference values have been derived from studies in which the hazardous element was administered in a soluble form (for example, As), the use of pseudo-total, instead of bioavailable, concentrations could lead to an over estimate of risk. Elements present in the soil are bound to particles in a variety of ways, depending on which, the element will be released in

the gastrointestinal tract to a lesser extent than that corresponding to the soluble form on which the toxicity value is based.

5. CONCLUSIONS

A geochemical study of street dust and urban soils of an industrial city was performed in four campaigns over a 15 year period. In both milieus, the industrial influence was clearly identified. Elements such as Zn, Cd, Hg, Ag, Pb or As were found in high concentrations (up to 4.6% and 0.5% of Zn in dust and soil, respectively), particularly in the N of the city. These elements appear to be correlated in their distribution and can be related to the Zn ore, sphalerite, and its associated trace elements, used in the Zn industry (particles of this sulphide were identified in soil and street dust by SEM-EDAX and XRD analyses). The spatial and temporal distribution of these elements is a function of the distance to the storage area of the ore, the intensity and method of transport from the port, and the prevailing wind direction. The elemental concentrations in the particulate matter, characterised by short residence times, shows high variability depending on the time of the year that the sampling was done; they are more stable in the soils, as they retain the input of particles deposited over time. In both cases, the average concentrations of these elements have generally increased over the monitored period. In agreement with this, the entropy model used to analyse the relationship between the development of urbanization in the period 1996-2011 and the street dust geochemistry shows that urban development has been negatively affected by the presence of metals in the street dust, particularly in the north of the city, with Fe and particularly Zn the main metals responsible.

Other groups of elements included those related to bauxite and its impurities, used in the Al industry (Al, Ga, etc.), those related to the steel industry (Fe, Cr, V, Mn, etc.) or those with natural/geogenic origin, not linked to anthropogenic activity (La, Th, Ca, Na, etc.). Many of the elements cannot be classified with certainty, as they have more than one possible industrial or urban source. In this case, typical urban geochemical fingerprints, such as traffic, are masked by the widespread and considerable industrial influence.

In comparison with temporal trends across Europe in general, it was found that until the present sampling campaign, concentrations of pollutants in the street dusts appeared to mainly decrease in common with European values. However, whilst European values continue in their downward trend, those from Aviles mainly increased in concentration, reflecting industrial activity in the area in spite of various actions having been taken to reduce its impact.

Metal reference values established for soils with the characteristics of those sampled were exceeded at times. Although the assumptions in the model may result in an overestimate of the quantitative results arrived at, a risk assessment applied to the urban soils reveals that the concentrations of some elements, such as As and Pb, could result in unacceptable levels of risk for residential receptors, with ingestion of soil the exposure pathway with the largest contribution. However, samples with the highest concentrations were taken in industrial, rather than in residential areas. Some environmental measures, such as a new isolated warehouse and a new conveyor belt associated with the Zn industry, which will come into use shortly, will reduce particle emissions associated with ore transport and storage, and should have positive environmental and human health benefits.

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Table 1. Descriptive statistics of the analytical data found in street dust from the four sampling campaigns (n=7 at each campaign)

	MIN.				MAX.				ARITH. MEAN				MEDIAN				COEF. VARIATION			
	1996	2001	2006	2011	1996	2001	2006	2011	1996	2001	2006	2011	1996	2001	2006	2011	1996	2001	2006	2011
Ag (mg kg ⁻¹)	0.40	0.30	0.40	1.10	4.55	3.20	2.90	10.9	1.73	1.20	0.97	3.76	1.75	0.40	0.80	3.20	0.81	0.97	0.90	0.89
Al (%)	0.72	0.61	0.46	0.71	1.12	0.81	0.72	1.07	0.86	0.70	0.62	0.84	0.86	0.70	0.67	0.78	0.17	0.09	0.17	0.16
As (mg kg ⁻¹)	11.0	10.9	9.70	16.4	26.0	29.8	29.4	110.1	18.2	18.7	22.1	37.6	18.0	18.8	24.0	28.7	0.30	0.32	0.33	0.86
Ba (mg kg ⁻¹)	244	303	248	185	489	446	407	640	369	386	326	400	375	378	327	405	0.21	0.14	0.19	0.38
Ca (%)	9.08	7.96	5.75	9.90	12.0	10.1	11.0	14.1	10.2	9.11	8.05	12.0	9.7	9.17	7.21	12.3	0.11	0.08	0.25	0.12
Cd (mg kg ⁻¹)	9.60	6.70	4.00	11.0	104	82.6	41.3	139	31.2	26.0	15.4	45.1	15.7	11.1	11.2	26.1	1.07	1.16	0.82	1.01
Co (mg kg ⁻¹)	5.00	3.4	3.7	6.4	11.50	8.9	6.5	19.2	7.36	5.44	5.24	10.9	6.50	4.70	5.20	10.7	0.33	0.36	0.17	0.41
Cr (mg kg ⁻¹)	32.0	46.2	29.0	57.0	54.5	73.4	67.0	214	42.4	55.7	50.6	109	44.5	55.2	52.0	102	0.20	0.16	0.25	0.49
Cu (mg kg ⁻¹)	104	159	102	167	374	222	319	966	203	189	212	370	171	189	189	265	0.51	0.12	0.38	0.75
Fe (%)	3.24	2.14	1.47	2.36	5.74	3.30	3.58	6.56	4.30	2.63	2.51	3.87	4.60	2.59	2.45	3.82	0.21	0.18	0.30	0.37
Ga (mg kg ⁻¹)		1.00	1.00	2.00		3.00	2.00	6.00		1.57	1.57	3.00		1.00	2.00	3.00		0.50	0.34	0.47
Hg (mg kg ⁻¹)	1.20	0.31	0.18	0.90	10.8	4.03	1.08	10.3	3.40	1.40	0.60	2.93	1.95	0.61	0.61	1.53	0.99	1.09	0.49	1.14
K (%)	0.09	0.07	0.06	0.10	0.24	0.18	0.17	0.18	0.14	0.11	0.11	0.13	0.15	0.09	0.10	0.13	0.33	0.38	0.32	0.21
La (mg kg ⁻¹)	8.0	9.0	6.0	8.0	11.5	31.0	8.0	11.0	10.4	16.4	7.57	9.14	11.0	11.0	8.00	9.00	0.13	0.57	0.10	0.12
Mg (%)	0.94	1.01	0.73	0.83	1.29	1.84	1.20	1.23	1.10	1.47	0.85	0.98	1.06	1.44	0.77	0.90	0.12	0.21	0.20	0.17
Mn (mg kg ⁻¹)	1,194	1,301	604	1,074	3,149	2,415	1,467	4,761	1,770	1,793	1,095	2,522	1,446	1,766	1,106	2,362	0.41	0.21	0.24	0.56
Mo (mg kg ⁻¹)	3.0	3.5	2.9	3.6	5.0	6.9	7.2	10.3	4.2	4.7	5.2	6.9	4.0	4.5	5.3	7.2	0.17	0.22	0.30	0.35
Na (%)	0.03	0.02	0.02	0.03	0.05	0.04	0.11	0.09	0.04	0.03	0.04	0.05	0.04	0.03	0.03	0.04	0.21	0.25	0.71	0.51
Ni (mg kg ⁻¹)	18.0	15.0	16.0	22.4	50.0	25.8	27.1	69.3	28.9	21.3	21.8	43.3	28.5	21.3	24.9	33.8	0.36	0.18	0.23	0.50
P (%)	0.04	0.05	0.07	0.06	0.23	0.32	0.13	0.28	0.11	0.13	0.10	0.14	0.07	0.08	0.08	0.12	0.69	0.78	0.24	0.48
Pb (mg kg ⁻¹)	330	162	157	208	964	919	705	1,482	559	400	289	496	484	278	207	320	0.46	0.69	0.67	0.92
Sb (mg kg ⁻¹)	7.0	4.8	5.4	5.7	9.0	8.9	15	20	8.0	6.9	8.3	10.4	8.0	7.2	7.6	8.8	0.08	0.23	0.40	0.46
Sr (mg kg ⁻¹)	222	208	159	255	310	422	242	362	266	277	201	315	271	226	192	324	0.13	0.34	0.16	0.11
Th (mg kg ⁻¹)	4.00	1.70	1.10	1.60	8.00	2.00	1.90	2.30	6.50	1.90	1.50	1.96	6.50	1.90	1.50	2.00	0.21	0.06	0.19	0.13
Ti (%)	0.02	0.02	0.01	0.02	0.03	0.03	0.02	0.04	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.21	0.12	0.19	0.31
V (mg kg ⁻¹)	25	22	18	29	35	29	28	76	28	26	23	44	28	25	22	39	0.12	0.11	0.15	0.36
W (mg kg ⁻¹)	<2	0.7	0.4	0.7	4.0	1.5	1.9	6.5	3.5	1.0	0.9	2.7	3.5	0.9	0.7	2.2	0.20	0.30	0.59	0.69
Zn (mg kg ⁻¹)	2,422	1,359	813	3,015	23,400	10,966	3,037	45,675	6,904	4,018	1,833	12,036	3,112	2,091	1,641	5,682	1.09	0.95	0.41	1.27

Table 2. Reduction (%) of concentrations of pollutants in the Avilés street dusts compared with trends across Europe, according to Harmens et al., 2013 (¹); (-ve = reduction in concentration, +ve = increase in concentration)

Element	Europe ¹	Avilés	Europe ¹	Avilés	Avilés net change
	1990-2005	1996-2006	2005-2010	2006-2011	1996-2011
Al	na	-28	-28	35	-2
As	-26	21	-25	70	107
Cd	-51	-51	-7	193	45
Cr	-43	19	-23	115	157
Cu	-11	4	-6	75	82
Fe	-52	-42	-15	54	-10
Hg	-23	-82	-20	388	-14
Ni	-33	-25	-12	99	50
Pb	-77	-48	-36	72	-11
V	-57	-18	-27	91	57
Zn	-34	-73	-7	557	74

Table 3. Urban environmental entropy calculated in terms of metal content in street dust of the 7 sampling units between 1996 and 2011, according to the methodology defined by Wang et al. (2012)

Sampling unit	Al	Ba	Fe	Pb	Zn	Total
A	-0.007	-0.001	-0.054	0.009	0.318	0.130
B	0.020	-0.002	-0.170	0.002	0.122	-0.017
C	0.034	0.001	-0.447	-0.006	0.017	-0.192
D	0.006	0.001	-0.081	-0.002	-0.001	-0.037
E	-0.150	0.001	0.820	-0.053	0.251	0.485
F	-0.004	0.007	0.148	-0.001	0.051	0.092
G	-0.026	-0.001	-0.044	-0.001	0.021	-0.011

Table 4. Descriptive statistics of the results for urban soils in the four sampling campaigns (n=17, same sample locations in all four campaigns)

	MIN.					MAX.					ARITH. MEAN					MEDIAN					COEF. VARIATION				
	1996	2001	2006	2011		1996	2001	2006	2011		1996	2001	2006	2011		1996	2001	2006	2011		1996	2001	2006	2011	
Sampling depth (m)	0.15	0.25	0.15	0.15	0.25	0.15	0.25	0.15	0.15	0.25	0.15	0.25	0.15	0.15	0.25	0.15	0.25	0.15	0.15	0.25	0.15	0.25	0.15	0.15	0.25
Ag (mg kg ⁻¹)	<0.3	0.10	0.20	<0.1	<0.1	1.20	0.50	1.30	1.90	0.60	0.69	0.19	0.62	0.72	0.22	0.7	0.1	0.5	0.55	0.2	0.41	0.65	0.52	0.84	0.62
Al (%)	0.60	0.59	0.76	0.69	0.73	2.49	1.67	1.58	2.95	2.31	1.55	1.19	1.14	1.39	1.53	1.52	1.18	1.2	1.26	1.51	0.36	0.30	0.20	0.40	0.32
As (mg kg ⁻¹)	8.00	6.40	5.30	7.70	9.00	117	39.0	30.7	39.8	61.1	30.8	16.3	15	19.3	24.3	19	14.1	12.8	16.8	23.4	0.96	0.51	0.44	0.43	0.54
Ba (mg kg ⁻¹)	77.0	67.0	40.0	88.0	70.0	401	399	550	921	674	185	201	199	321	249	177	153	161	220	223	0.45	0.55	0.67	0.72	0.68
Ca (%)	0.24	0.19	0.21	0.23	0.24	10.9	8.46	13.5	9.48	6.56	1.69	1.36	2.35	4.12	2.06	0.64	0.58	1.56	3.25	1.13	1.64	1.43	1.33	0.75	1.09
Cd (mg kg ⁻¹)	0.80	0.20	0.40	1.10	0.30	7.30	6.20	15.6	28.6	6.20	2.53	1.58	3.79	7.84	1.32	2.1	1.2	2.1	2.8	0.8	0.67	0.90	1.14	1.13	1.10
Co (mg kg ⁻¹)	2.00	1.90	1.90	0.90	2.60	30.0	10.2	10.4	11.4	14.1	9.59	5.36	5.45	7.28	7.04	8	5.5	5.1	7	6.7	0.78	0.39	0.41	0.39	0.46
Cr (mg kg ⁻¹)	9.00	9.70	11.0	12.0	12.0	40.0	107	91.0	75.0	38	22.5	23	24.5	32.8	20.9	21	17	20	27	22	0.37	0.97	0.76	0.47	0.32
Cu (mg kg ⁻¹)	21.0	13.0	9.20	8.00	10.5	243	67.0	138	435	89.1	70.9	30.9	45.5	95.5	28.9	46	26.7	29.8	53.3	23.2	0.84	0.55	0.74	1.10	0.71
Fe (%)	1.80	1.32	1.40	1.40	1.47	9.83	9.89	7.35	6.77	4.18	4.03	2.62	2.6	2.92	2.58	3.23	1.91	2.28	2.62	2.6	0.57	0.77	0.53	0.45	0.29
Ga (mg kg ⁻¹)		2.00	2.00	2.00	2.00		5.00	4.00	8.00	7.00		4.00	3.53	4.59	4.53		4.00	4.00	5.00	5.00		0.25	0.18	0.31	0.31
Hg (mg kg ⁻¹)	0.21	0.06	0.07	0.24	0.25	2.18	1.32	3.62	3.02	1.40	0.72	0.42	0.62	0.92	0.74	0.51	0.28	0.39	0.74	0.68	0.79	0.76	1.33	0.87	0.50
K (%)	0.07	0.07	0.08	0.07	0.07	0.42	0.34	0.29	0.49	0.57	0.21	0.16	0.17	0.2	0.19	0.19	0.13	0.17	0.17	0.15	0.53	0.52	0.35	0.50	0.66
La (mg kg ⁻¹)	8.00	6.00	8.00	7.00	9.00	36.0	16.0	19.0	21.0	26.0	16.8	11.9	11.2	12.4	14.9	16.0	13.0	11.0	13.0	14.0	0.40	0.24	0.25	0.28	0.29
Mg (%)	0.09	0.11	0.14	0.05	0.12	3.53	1.55	1.53	2.93	2.57	0.6	0.53	0.6	0.9	0.85	0.34	0.4	0.48	0.62	0.54	1.32	0.78	0.63	0.85	0.84
Mn (mg kg ⁻¹)	246	191	148	53.0	112	4,261	6,821	2,388	2,257	3,099	1190	822	721	958	658	601	405	492	745	493	1.08	1.90	0.90	0.68	1.02
Mo (mg kg ⁻¹)	<0.1	0.40	0.20	0.60	0.30	3.00	3.90	1.80	6.10	2.10	1.43	1.12	0.92	1.89	0.84	1	0.7	0.8	1.4	0.6	0.60	0.91	0.43	0.74	0.64
Na (%)	0.01	0.004	0.008	0.007	0.003	0.04	0.06	0.04	0.04	0.05	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.58	1.03	0.46	0.47	1.14
Ni (mg kg ⁻¹)	5.00	4.70	5.60	4.30	5.70	35.0	27.6	21.7	31.7	23.8	16.9	13.4	12.9	17.9	15.8	15	11.8	12.4	16.4	16.7	0.53	0.48	0.33	0.38	0.35
P (%)	0.04	0.03	0.02	0.05	0.03	0.20	0.22	0.21	0.62	0.10	0.07	0.07	0.09	0.22	0.05	0.06	0.06	0.09	0.17	0.05	0.60	0.60	0.58	0.75	0.39
Pb (mg kg ⁻¹)	54.0	46.1	23.0	37.2	27.6	353	259	793	462	471	154	107	194	181	114	155	79.3	125	141	74.1	0.54	0.65	0.95	0.69	1.00
Sb (mg kg ⁻¹)	<1	1.10	1.70	0.80	0.20	15.0	6.10	4.90	8.70	2.30	6.6	2.67	3.07	3.48	1.11	6	2.5	2.6	2.7	0.8	0.67	0.49	0.38	0.66	0.63
Sr (mg kg ⁻¹)	10.0	9.00	11.0	14.0	8.00	381	200	204	230	115	45.6	36.8	56.6	106	45.2	24	19	37	98	28	1.92	1.24	0.86	0.65	0.77
Th (mg kg ⁻¹)	<1	1.60	1.40	0.20	2.00	7.00	4.20	6.70	4.90	7.80	5.08	3.18	2.68	1.66	3.52	5	3.5	2.6	1.1	3.3	0.31	0.24	0.45	0.78	0.45
Ti (%)	0.01	0.002	0.004	0.002	0.002	0.02	0.05	0.02	0.03	0.01	0.01	0.008	0.009	0.009	0.004	0.01	0.005	0.006	0.007	0.004	0.25	1.50	0.70	0.67	0.55
V (mg kg ⁻¹)	22.0	13.0	19.0	20.0	19.0	55.0	92.0	43.0	54.0	45.0	34.8	27.0	27.3	33.2	28.4	32	22.0	25	32	29	0.28	0.66	0.25	0.25	0.26
W (mg kg ⁻¹)	<0.1	<0.1	0.10	<0.1	<0.1	<0.1	1.20	0.60	0.80	0.20	<0.1	0.44	0.18	0.36	0.13	<0.1	0.3	0.1	0.3	0.1		0.83	0.73	0.52	0.43
Zn (mg kg ⁻¹)	110	95.0	85.0	148	86.0	1,024	1,528	1,599	5,458	636	412	376	604	1545	249	356	238	478	848	218	0.68	0.95	0.72	1.07	0.58

Table 5. Element concentration (C, mg kg⁻¹), reference dose (RfD, mg kg⁻¹ day⁻¹), slope factor (Sf (mg kg⁻¹ day⁻¹)⁻¹), hazard quotient (HQ, unitless) and cancer risk (unitless) for an adult individual from exposure to urban soils. HI=ΣHQ, RISK=ΣRisk. In bold: values of risk > 1 10⁻⁵

	Non carcinogenic															Carcinogenic			
	Al	As	Ba	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Sr	V	Zn	As	Cd	Ni	Pb
C	16,182	22,8	432	17,2	39,3	145	1,3	1,342	2,5	20,8	247	4,5	135	36,8	2,413	22,8	17,2	20,8	247
RfD_{ing}	1,0E+00	3,0E-04	2,0E-01	1,0E-03	1,5E+00	4,0E-02	3,0E-04	1,4E-01	5,0E-03	2,0E-02	3,5E-03	4,0E-04	6,0E-01	7,0E-03	3,0E-01	Sf_{ing}	1,5E+00		8,5E-03
RfC_{inh}	5,0E-03	1,5E-05	5,0E-04	1,0E-05			3,0E-04	5,0E-05		2,0E-05				7,0E-06		UR_{inh}	1,5E+01	6,3E+00	8,4E-01
RfD_{der}	1,0E-01	1,2E-04	1,4E-02	1,0E-05	7,5E-03	1,2E-02	2,1E-05	5,6E-03	1,9E-03	5,4E-03	5,3E-04	8,0E-06	1,2E-01	7,0E-05	6,0E-02	Sf_{der}	3,7E+00		8,5E-03
HQ_{ing}	2,2E-02	1,0E-01	3,0E-03	2,4E-02	3,6E-05	5,0E-03	5,9E-03	1,3E-02	6,9E-04	1,4E-03	9,7E-02	1,5E-02	3,1E-04	7,2E-03	1,1E-02	Risk_{ing}	2,0E-05		1,2E-06
HQ_{inh}	2,4E-03	1,1E-03	6,4E-04	1,3E-03			3,2E-06	2,0E-02		7,6E-04				3,9E-03		Risk_{inh}	7,2E-08	2,3E-08	2,2E-09
HQ_{der}	8,8E-04	3,0E-02	1,7E-04	9,4E-03	2,9E-05	6,6E-05	3,4E-04	1,3E-03	7,3E-06	2,1E-05	2,6E-03	3,0E-03	6,1E-06	2,9E-03	2,2E-04	Risk_{der}	5,9E-06		4,9E-09
HI	2,5E-02	1,4E-01	3,8E-03	3,4E-02	6,5E-05	5,0E-03	6,3E-03	3,4E-02	7,0E-04	2,2E-03	9,9E-02	1,8E-02	3,1E-04	1,4E-02	1,1E-02	RISK	2,6E-05	2,3E-08	0,0E+00

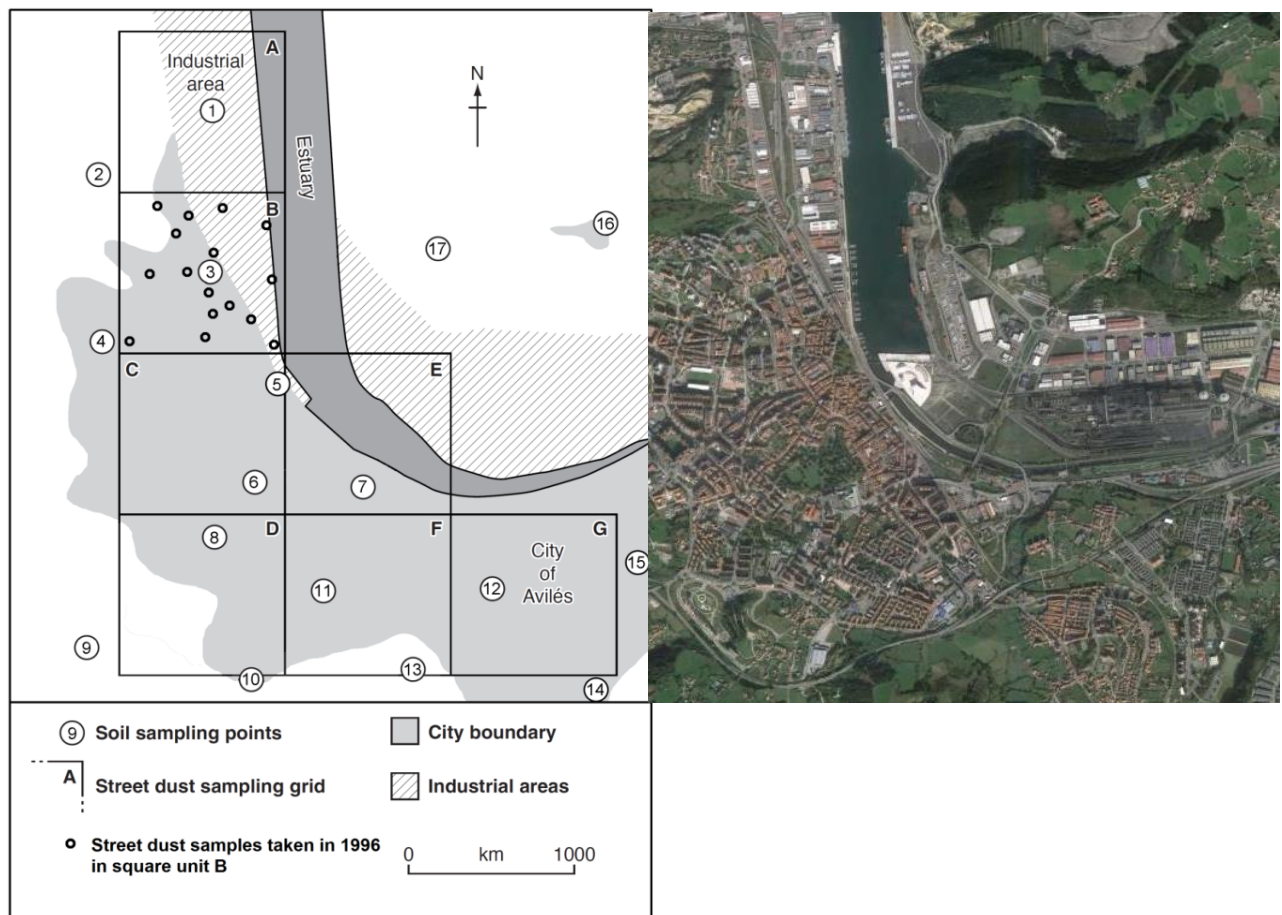


Fig. 1. Study area: Soil sampling points and street dust sampling grid

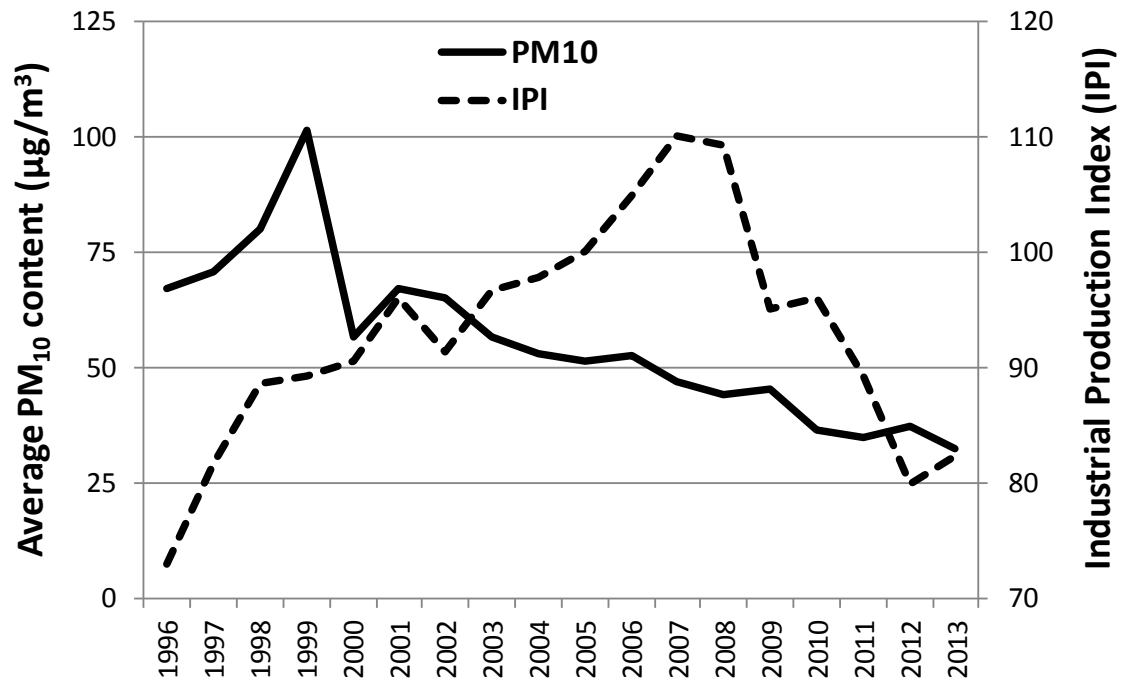


Fig. 2. Average PM₁₀ content in Avilés and the Industrial Production Index of metal industries in Asturias (2005 referenced) from 1996-2013

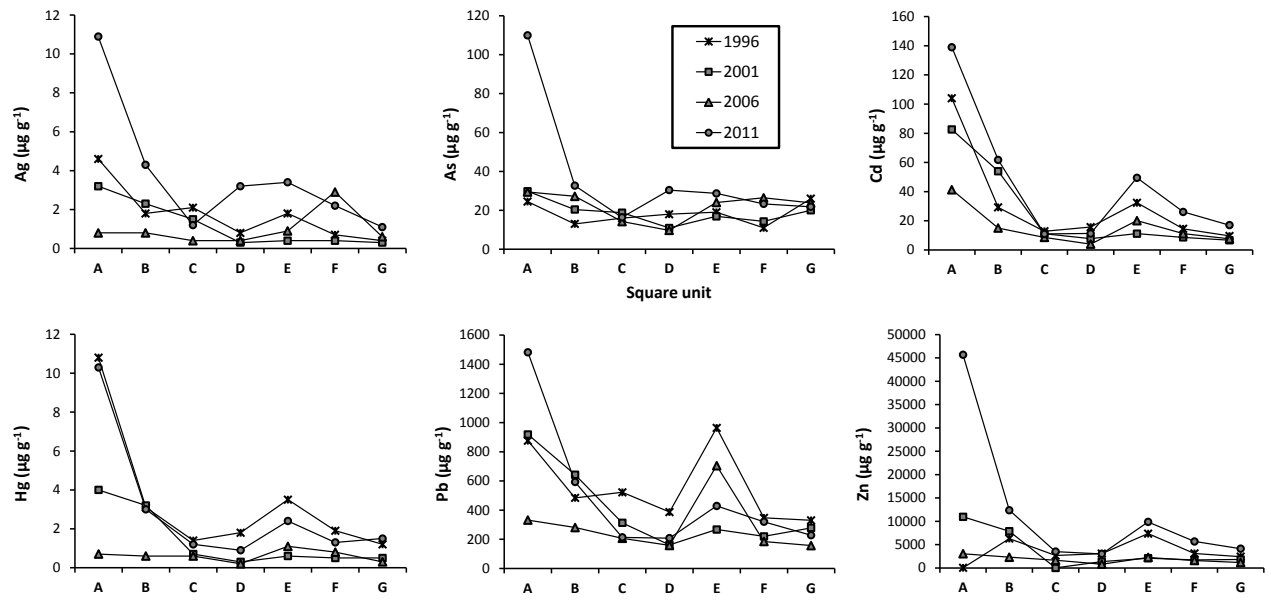


Fig. 3. Metal contents found in the square units sampled for street dust

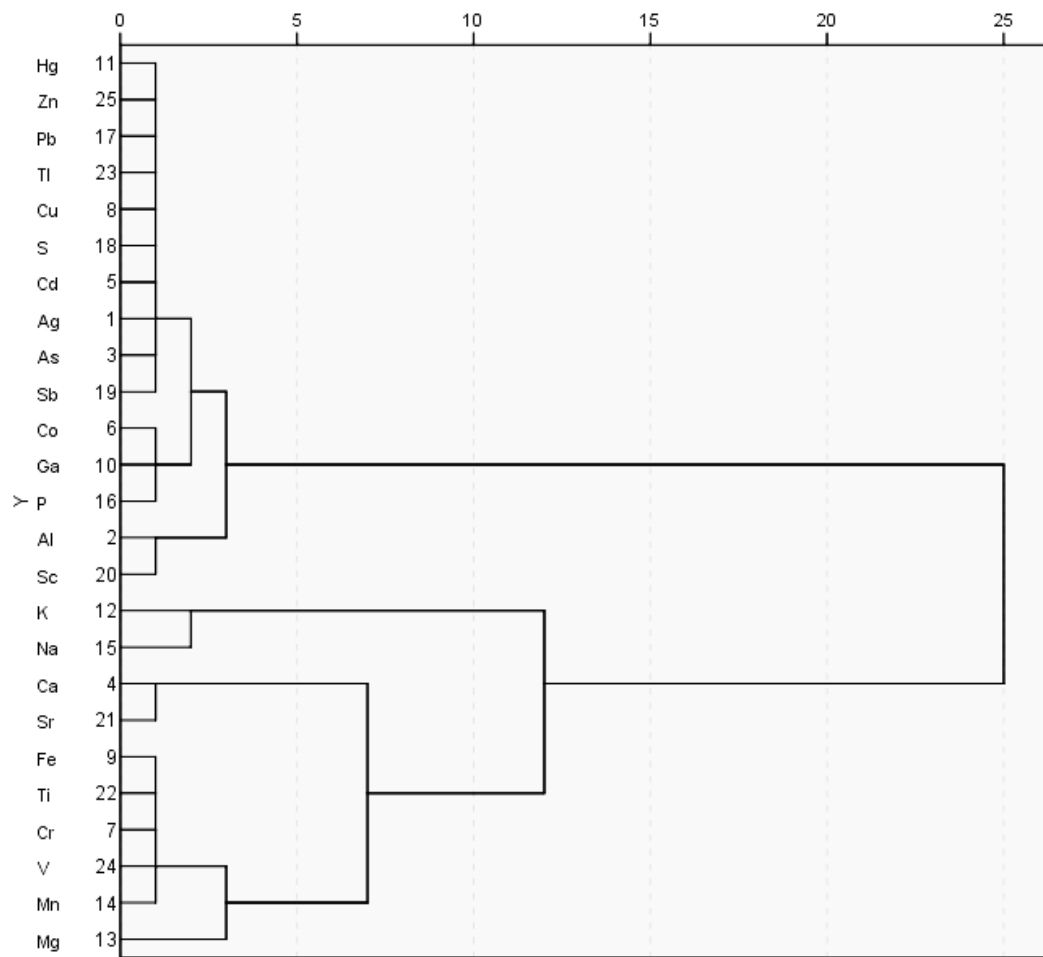


Fig. 4. Clustering of variables analysed for street dust in 2011 (Linkage method: Ward; squared Euclidian distance).

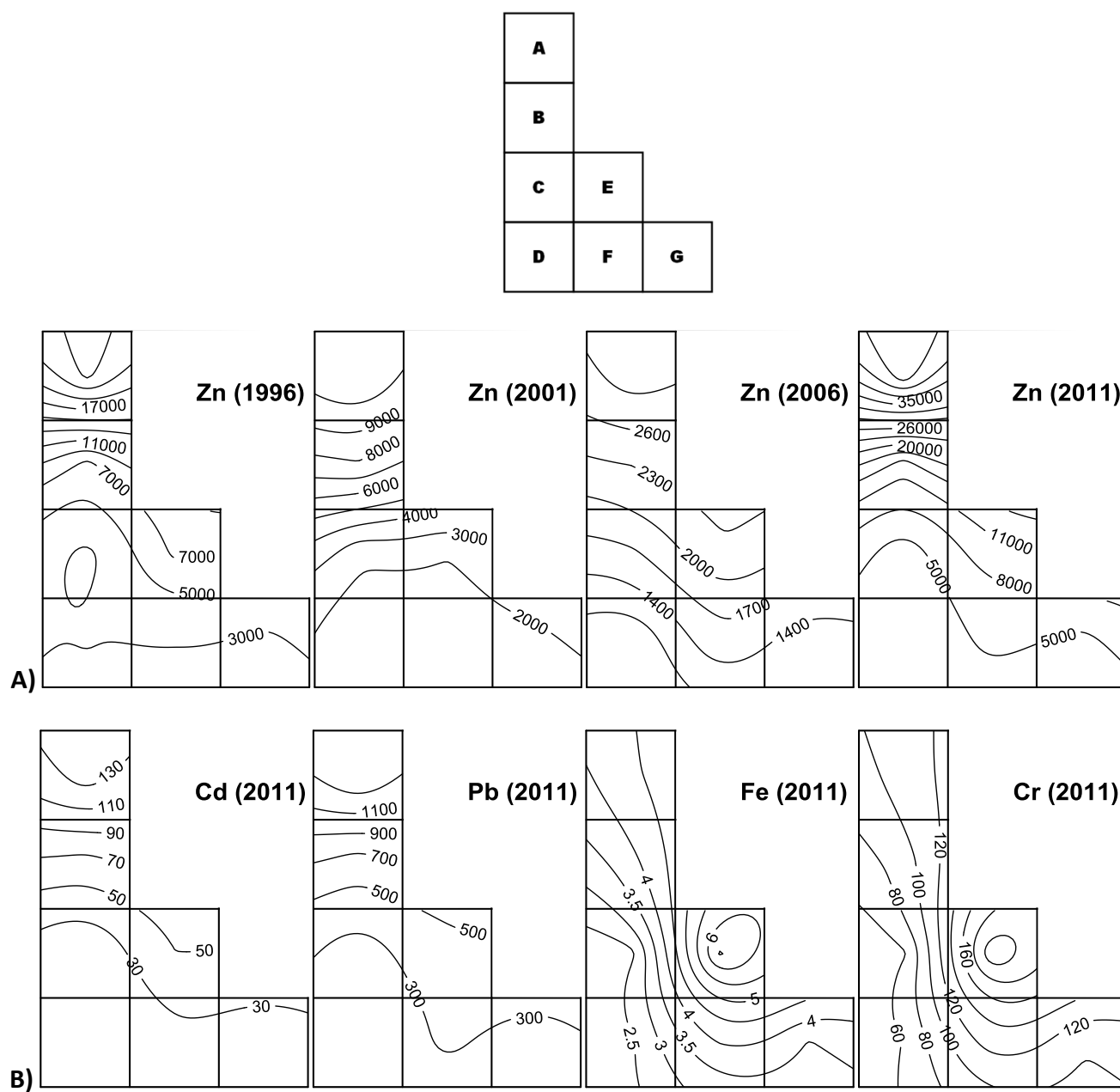
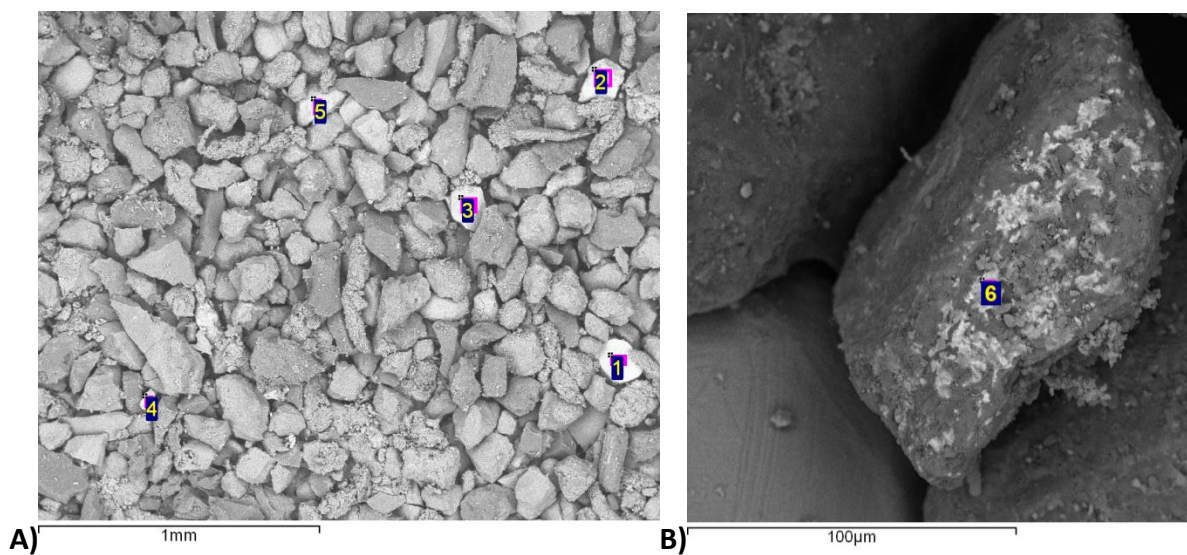
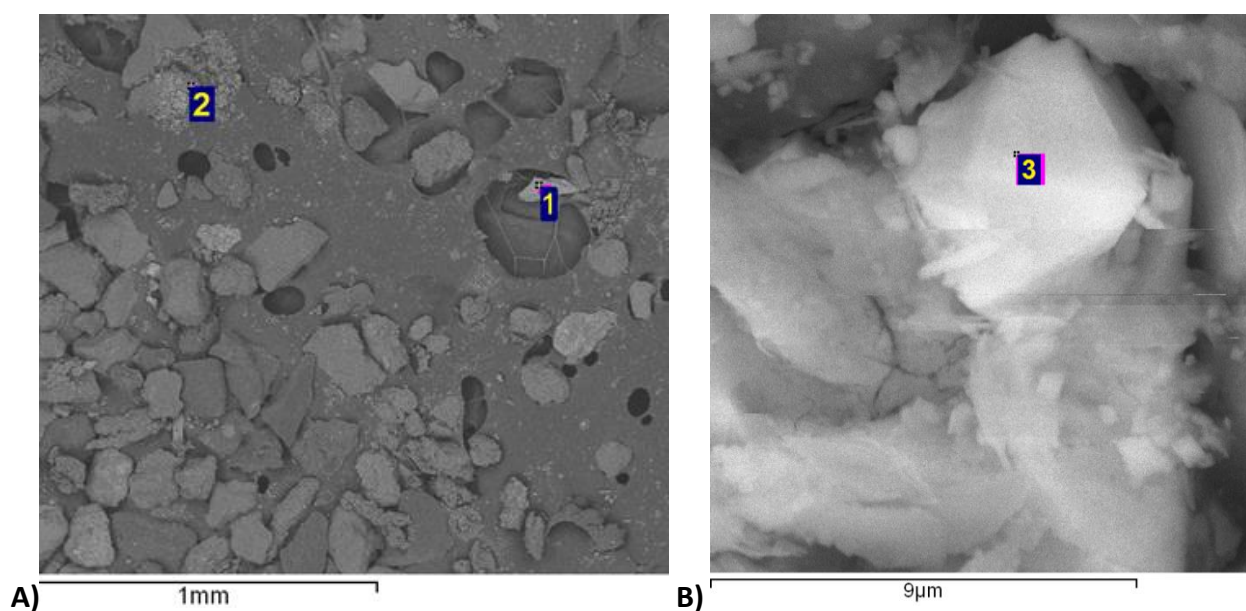


Fig. 5. Contour maps of metal concentrations found in street dust: A) Zn in the four sampling campaigns; B) Cd, Pb, Fe and Cr in the most recent campaign.
All concentrations in mg kg^{-1} , except Fe (in %)



Point	C	O	Al	Si	S	Ca	Mn	Fe	Zn	Pb	Hg
1					22.3				77.7		
2	24.2	30.0	1.6	6.1		0.8		2.78	28.5	6.1	
3	23.9	30.3	1.0	1.6		2.9		40.3			
4	27.0	18.0		1.0	0.54	0.5		0.90	52.1		
5	17.3	35.1	2.2	2.2		0.8		42.4			
6	22.5	25.8		0.8	6.02	2.1	0.87		1.72		40.2

Fig. 6. SEM-EDAX images and composition of analysed points in street dust sample A (all results in weight %)



Point	C	O	Al	Si	S	Ca	K	Fe	Zn	Pb	As
1	18.8	32.7						48.5			
2	26.2	20.2		2.4	11.6	1.31		8.78	21.6	7.91	
3	10.4	48.8	1.9	1.8			2.25	20.0			13.9

Fig. 7. SEM-EDAX images and composition of analysed points in soil sample 16 (all results in weight %)