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RESEARCH ARTICLE

Enrichment factors to assess the anthropogenic influence on PM_{10} in Gijón (Spain)

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Abstract Thirty-two chemical species were determined in Q1 PM_{10} sampled at a suburban site on the north coast of Spain. Enrichment factors were applied to infer their soil/non-soil origin. The geochemical ratios were calculated using two databases: soil composition from locations in the surroundings of the sampling station and the Earth's average upper-crust composition. In the present study, dissimilarities were found between the enrichment factors obtained using these two databases. Al, Ti, La and Ce were taken as the reference elements to normalise the data, reaching analogous conclusions. Bi, Cd, Cu, Sb, Se, Sn and Zn were associated with predominantly non-soil apportionments. As the relevance of soil/non-soil sources for the other analysed elements was found to be variable, they were probably of mixed origin. Furthermore, pairs of elements showed strong relationships, thus pointing to a common origin. Na–Mg and Co–Ni, with Pearson correlation coefficients above 0.9, were respectively related to marine and industrial apportionments. Enrichment factors have proved to be a useful tool to distinguish the soil/non-soil origin of chemical species present in airborne particulate matter. However, the choice of the reference database for soil composition considerably determined the accuracy of the conclusions.

Keywords Air quality · Crustal origin · Enrichment factor · Geochemistry · Particulate matter · Soil dust · UCC

Introduction

Soil is a major contributor of particulate matter (PM) to the atmosphere (Aleksandropoulou et al. 2015; Paraskevopoulou et al. 2015; Perrino et al. 2015). Mineral dust (13 % in mass) is one of the major natural sources of PM on the global scale. On a local scale, however, this value depends on the region under study, as it is highly affected by broad spatial variability (Viana et al. 2014). The contribution of PM may be due to natural processes such as erosion and windblown transport, but also to human activity, e.g., traffic causes the resuspension of soil dust. Non-crustal sources make a significant contribution to certain elements in PM (Salma and Maenhaut 2006; Adgate et al. 2007; Jiang et al. 2015). The difficulty lies in identifying the natural sources of PM and differentiating them from anthropogenic apportionments.

Non-dimensional crustal enrichment factors (EF) are commonly used to assess the anthropogenic influence on PM (Zhang et al. 2014; Silva et al. 2015). An EF is a ratio of two chemical species present in the atmosphere (E/R, where E is the element of interest and R is the reference element) divided by the corresponding ratio in crustal material. R is used to normalise the data and hence it should be mainly influenced by crustal sources. Although Al, Si and Fe have normally been used as R in the literature given their high concentrations in soil, other less abundant chemical species

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have also been used, such as Mn, Sr, Zr and Ti (Reimann and de Caritat 2000; Cesari et al. 2012 and references therein; Rashki et al. 2013; Bouhila et al. 2015). Zoller et al. (1974) used EFs to analyse the chemical composition of airborne PM collected at the South Pole. They chose Al as R and were able to infer the weathering or oceanic nature of a wide range of elements (Sc, Th, Sm, V, Mn, Eu, Fe, La, Ce, Co, Cr, Na, K, Mg and Ca), given that the EFs were close to 1. Zn, Cu, Sb, Se, Pb and Br, however, were thought to be derived from other sources.

Not all authors have considered the same value as a reference threshold for reading the EFs. In fact, Cesari et al. (2012) proposed a two-threshold scheme in order to unify the variety of criteria used in the literature. These authors differentiated between elements likely to be of predominantly crustal, mixed or anthropogenic origin. However, other researchers have preferred to use a simpler criterion, employing one cut-off value. Rogula-Kozlowska et al. (2015) used Ca as R and considered that the closer EFs are to 1, the weaker the anthropogenic contribution. They found mineral matter to be a source of K, Ni, Sr and Ba. In contrast, Alghamdi et al. (2015) considered five to be an acceptable value below which they confirmed the crustal origin of Na, Mg, Si, K, Ca, Ti, Cr, Mn, Fe, Rb and Sr. Some of these soil-related elements may also have significant apportionments from other sources depending on location. In fact, Na is considered a tracer for sea spray, which may be one of the major natural sources affecting air quality (Perrino et al. 2014; Viana et al. 2014; Budhavant et al. 2015).

The Earth's crust has been studied over the years differentiating between three layers, namely the upper, middle and lower crust. The first is the most accessible and its composition has been estimated employing either weighted averages of surface samples or inferring it through concentrations of insoluble to moderately soluble trace elements obtained in studies of shales and loess (Rudnick and Gao 2003). Due to the heterogeneity of soil, its influence on PM is likely to vary depending on the geochemical characteristics of the sampling site. Consequently, another point of disagreement among EF studies found in the literature comprises the data on the soil ratio (i.e., $(E/R)_{SOIL}$). Although the best approach would be to determine EFs by means of the composition of local soil, the Earth's average upper-crust composition (UCC) has been used when no other database was available (Rushdi et al. 2013; Wang et al. 2014; Budhavant et al. 2015).

The primary aim of this study was to distinguish soil and anthropogenic apportionments to PM_{10} by means of enrichment factors. Fifty-two daily samples were collected at a suburban station on the north coast of Spain and subsequently chemically analysed to determine 32 species. Furthermore, a comprehensive study was performed to reduce the uncertainties due to the variability of two factors that greatly affect EFs (Reimann and de Caritat 2005): the reference element and the geochemical composition of soil. A range of chemical species mainly present in soil were considered as R, including both abundant and trace elements. Two databases were used to calculate the geochemical ratios: the soil composition from seven locations in the surroundings of the sampling station and the Earth's average UCC. The results obtained using the two databases and other EF studies from the literature were compared.

Materials and methods

Sampling area

Samples of airborne particulate matter, i.e., PM_{10}, were obtained at a suburban station on the university campus of Gijón, in northern Spain (43° 31′ 23″ N 5° 37′ 16″ W). This city is located in the shoreline of the Cantabrian Sea, over Mesozoic materials. The soil surrounding the sampling area was characterised by a variety of rocks (Fig. 1), comprising limestone, clay, sandstone, dolomite, loam and siliceous conglomerate (IGME 1974).

The origin of air masses reaching the sampling site was determined as in Megido et al. (2016a). For this purpose, five-day back trajectories were calculated with the HYSPLIT model developed at the NOAA (Stein et al. 2015) and catalogued in eight sectors: northern Atlantic, north-western Atlantic, western Atlantic, south-western Atlantic, northern African, Mediterranean, European and regional. Meteorological data were provided by the Spanish Meteorology Agency (AEMET) at the sampling site since October 2013 and by another meteorological station located at a distance of 1.7 km. Wind speeds up to 13 m/s were detected from July 2013 to July 2014. In general, the weather in Gijón is influenced by its low altitude, seasonal winds and land-sea breezes. It is characterised by an annual accumulated rainfall around 1000 mm and annual temperatures with minimum and maximum mean values of about 10 and 18 °C, respectively (Government of the Principality of Asturias 2009).

The sampling location was near several industrial facilities (<10 km), including harbour activities handling around 19 million of tons of goods (Port of Gijón 2014), a steelmaking industry (Almeida et al. 2015), a 903 MW thermal power plant, a coalfield and a cement plant that operates a dry-process furnace with a production capacity of 2750 t/day (PRTR-Spain[1]). According to the respective Integrated Environmental Authorizations,[1] the thermal power plant near the sampling station used coal, siderurgical gases from the nearby steelmaking industry and fuel-oil and gas-oil as support fuels for ignition; the cement plant consumed mainly

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[1] Information available at The Spanish Register of Emissions and Pollutant Sources (PRTR-Spain)

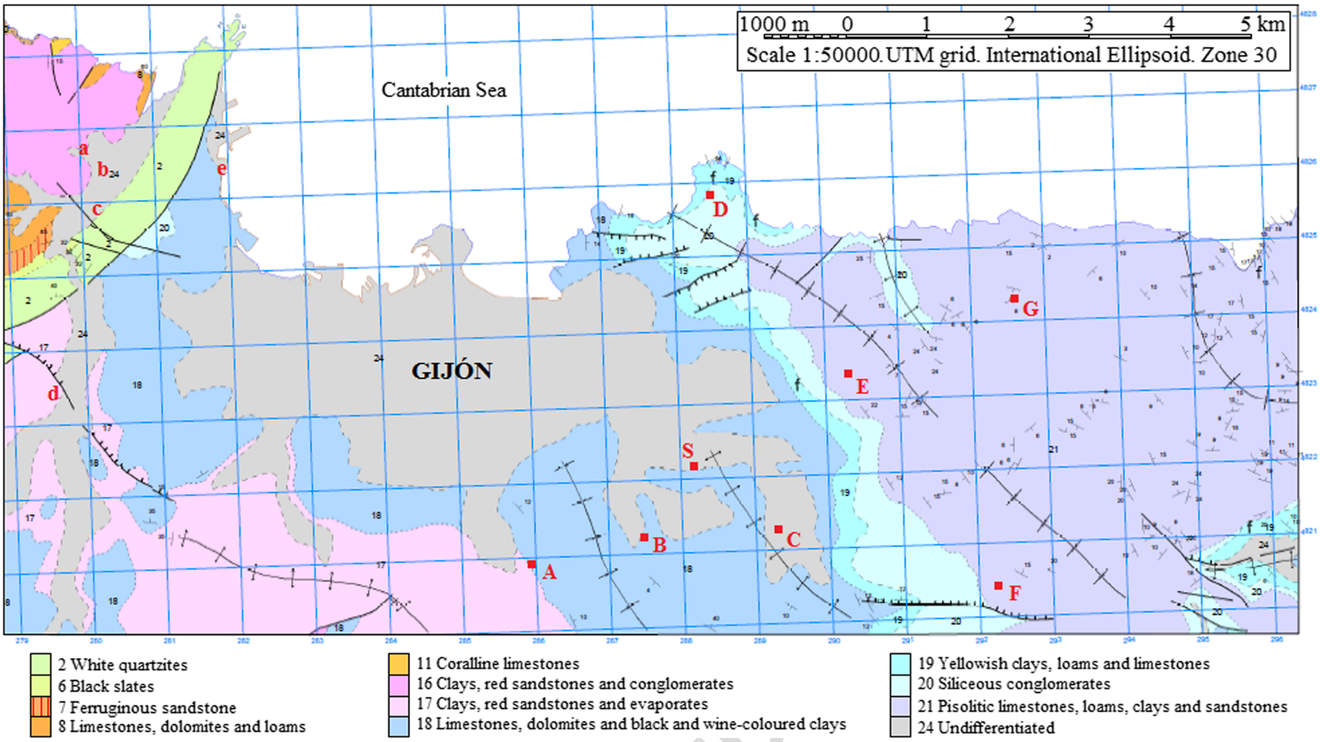

Fig. 1 Geological map of the surroundings of the sampling station (S), with the situation of the seven soil locations (*a*–*g*) whose composition was used to calculate the geochemical ratios, and the main industrial activities: cement plant (*a*), coalfield (*b*), coal-fired power station (*c*), steel plant (*d*) and port facilities (*e*). Geological map from the IGME

petroleum coke, but also wood, fuel-oil and occasionally coal, while the steelmaking industry primarily used natural gas, rich gas (gas from batteries), steel mill gas, lean gas (blast furnace gas), mixed gas (mixture of the above), coke and anthracite (these last two in the sinter facility) and, to a lesser extent, fuel-oil and propane.

The sampling was affected by irregular traffic from a nearby trunk road and a motorway. A hospital (covering a population of over 255,000 inhabitants), three educational centres (over 6000 people including teaching and research staff, students, administrative and service staff) and Gijón Science and Technology Park (130 companies with over 3600 workers) were located in the vicinity and attracted many local residents. Figure 1 shows the location of the sampling site and the main industrial activities.

PM_{10} sampling and chemical analysis

A sequential high-volume sampler MCV CAV-A/MSb (MCV SA, Barcelona, Spain) was used to collect one 24-h PM_{10} sample per week from July 2013 to July 2014. The matrix employed comprised quartz microfiber filters (Pallflex-Tissue Quartz 2500QAT-UP). A total of 52 PM_{10} samples were processed to extract metals using the methodology described in Negral et al. (2008). Thirty-two chemical species were analysed by inductively coupled plasma mass spectrometry (ICP-MS): Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ta, Ti, Tl, V, Zn and Zr. The same procedure was applied to treat and analyse a control sample using Standard Reference Material® 1648a (Urban Particulate Matter) from the National Institute of Standards & Technology (NIST). Further details concerning the chemical analysis methodology have been reported in a previous paper (Megido et al. 2016b).

Enrichment factor analysis

EFs were calculated for each chemical species analysed in every PM_{10} sample, applying the following expression:

$$EF_{X,Y} = \frac{\left({}^{X}/_{R}\right)_{PM10}}{\left({}^{X}/_{R}\right)}Y$$

where X refers to the chemical species considered in each case, R is the reference element and Y represents the geochemical composition database used in the calculation, i.e., “SOIL” or “UCC”. For instance, $EF_{Ti,SOIL}$ indicates that the EFs for Ti were obtained using local soil composition to estimate the geochemical ratio. The Earth’s average UCC was taken from Rudnick and Gao (2003), who reviewed relevant research studies in this respect, providing an updated estimation. The Geological and Mining Institute of Spain (IGME) studied the chemical composition of residual soils at two depths (0–25 cm and 25–50 cm) during their 2012 geochemical survey.[2] Seven samples of soil were available within a 5-km radius around the sampling station (Fig. 1). Those denominated A–B were taken at points where the bedrock was quite similar (clay, limestone and dolomites); the same applies for samples E–G (clay, limestone, sandstone and loam). C was taken in an undifferentiated area and D was the only sample that comprised siliceous conglomerates (IGME[3]). Table 1 presents the concentration of 31 of the abovementioned elements that were available in the IGME dataset; Al, Ca, Fe, K, Mg, Na and Ti being the most abundant. Additionally, $EF_{X,Y}$ were calculated using an average local soil composition (Table 1). In this case, Y refers to "average soil". To get a more statistically significant value, the average geochemical composition was estimated from 113 local soil samples analysed by IGME within a 25-km radius around the sampling station (Online Resource 1, Table S1). According to the IGME website,[2] the soil samples were sieved (2 mm) and several elements were extracted using aqua regia and chemically analysed by ICP-MS, ICP-AES (inductively coupled plasma atomic emission spectroscopy) and INAA (instrumental neutron activation analysis).

The element chosen as R was Al due to its abundance in soil. Nevertheless, other elements frequently associated with crustal origins, i.e., Ti, La and Ce (Cao et al. 2009; Mariet et al. 2001; Avino et al. 2014; Grigoratos et al. 2014), were also used for this purpose. Despite being frequently employed as R, Si was not considered in the present study given its presence in the matrix used to collect the PM_{10} samples.

In the current study, three main sources of PM_{10} were distinguished, namely soil, non-soil and mixed origin. Table 2 shows the two cut-off values considered in each case (Cesari et al. 2012). An element was defined as being of predominantly soil/non-soil origin when at least 95 % of the total PM_{10} samples satisfied the established criteria; otherwise, the element was considered of mixed origin. It should be noted that when the conclusions drawn from EFs calculated using local soil and UCC were different, the former calculation was considered more reliable.

Results and discussion

This section has been divided in two subsections. In the first, Al is used as R for the calculation of EFs in order to distinguish the origin of each element determined in PM_{10}. In the second subsection, other chemical species were used as R.

It is worth noting that the elemental composition of the 52 PM_{10} samples was highly variable, with the relative standard deviation (RSD) ranging from 52 % for Bi to 226 % for Ni. Moreover, as the geochemical composition of the seven soil locations in the area surrounding the sampling station was also variable, the average geochemical composition of these locations was not used. Figure 2 shows a contour graph in which Fe/Al and Ca/Al ratios can be seen for each location (Fig. 2a, b, respectively). Although these elements are abundant in the local soil, there are substantial differences between relatively close sites, especially in the case of Ca, which presented the highest RSD (210 %). As previously mentioned in the "Enrichment factor analysis" section, the average chemical composition of the local soil was calculated using 113 samples, a more statistically significant average being obtained for some elements. Nevertheless, other species reached RSD up to 257 % (Online Resource 1, Table S2). The results of $EF_{X,\text{AVERAGE SOIL}}$ are described in the "Other elements as the reference element" section.

Aluminium as the reference element

The content of aluminium at the seven soil locations ranged between 3.3 and 7.4 % in terms of mass (Table 1). This scattering was expected to have some influence on $EF_{X,\text{SOIL}}$. The variability was found to be higher or lower depending on the element. In the case of R = Al, Ba was the element whose $EF_{\text{Ba,SOIL}}$ showed the lowest variability between the seven locations (14.8 %) and Mn, the highest (105.9 %).

The EFs obtained for all the elements using Al as R are available in the Online Resource 1.

Non-soil origin elements

Throughout the entire sampling period, a few elements presented an enrichment in PM_{10} with respect to soil, regardless of the soil location. These elements were Bi, Cd, Cu, Na, Sb, Se, Sn and Zn. Table 3 shows their minimum and maximum $EF_{X,\text{SOIL}}$. Considering all soil locations, Table 4 shows the percentage of samples that exceeded the upper threshold ($EF_{X,\text{SOIL}} > 10$). As more than 95 % of the samples were above this cut-off value, these elements were defined as being of non-soil origin.

The minimum and maximum $EF_{X,\text{UCC}}$ for the aforementioned elements are also shown in Table 3. These $EF_{X,\text{UCC}}$ were greater than those from $EF_{X,\text{SOIL}}$. The exception was Na. $(\text{Na/Al})_{\text{SOIL}}$ was an order of magnitude greater than $(\text{Na/Al})_{\text{UCC}}$. Thus, $EF_{\text{Na,SOIL}}$ and $EF_{\text{Na,UCC}}$ differed 78–91 % depending on the soil location. Results from the current study were in agreement with those reported by Cesari et al. (2012), who collected soil samples in the Salentum Peninsula (Italy) that were then re-suspended in the laboratory to obtain PM_{10}. These researchers calculated EFs using UCC, local soil composition and the re-suspended PM_{10}. They obtained higher EFs for Na and lower EFs for Cu, Zn and Sb using local soil

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[2] Information available at the Geological and Mining Institute of Spain (http://info.igme.es/Geoquimica/)

[3] Information available at the Geological and Mining Institute of Spain (http://info.igme.es/cartografiadigital/geologica/Magna50.aspx)

Q2 **Table 1** Chemical composition of local soil samples A–G analysed by the IGME and the average estimated using 113 local soil samples

Soil sample	A	B	C	D	E	F	G	Average soil (n = 113) *
IGME identification	5-19-4-14T17	5-19-4-14T18	5-19-4-14T19	5-19-4-14T16	5-19-4-14T20	5-19-4-14T22	5-19-4-14T23	
Al (%)	7.39	5.3	5.5	3.3	4.64	4.16	4.79	5.2
Ba (ppm)	358	222	277	160	227	254	314	368
Be (ppm)	3.6	1.8	1.8	0.8	1.6	1.2	1.6	2.0
Bi (ppm)	0.5	0.3	0.4	0.3	0.3	0.2	0.5	0.3
Ca (%)	0.35	8.51	0.25	0.42	0.25	0.34	0.23	1.03
Cd (ppm)	0.7	0.6	0.4	0.7	0.6	0.4	0.3	0.5
Ce (ppm)	123	68.5	98.4	78.1	85.3	85.7	79.7	90.9
Co (ppm)	29	11.6	19	4.6	2.6	2.2	3.5	9.7
Cr (ppm)	74	44	63	40	49	55	47	57
Cu (ppm)	31	28.4	25.7	13.6	6.7	25.4	13.1	20
Fe (%)	3.93	2.44	3.58	1.4	1.64	1.62	1.71	2.87
K (%)	2.84	2.61	1.72	0.79	1.21	1.38	2.4	1.70
La (ppm)	43.1	29.6	40.1	34.3	39.4	38.7	36.7	38.9
Li (ppm)	118	66.5	69.9	24.9	45.4	50.1	40.7	55.9
Mg (%)	1.1	5.22	0.4	0.19	0.24	0.22	0.35	0.85
Mn (ppm)	1400	630	2010	109	53	110	210	584
Mo (ppm)	1	1	3	1	2	2	1	1
Na (%)	0.11	0.09	0.18	0.07	0.09	0.1	0.11	0.12
Ni (ppm)	46.5	38.2	26.4	21.9	13.4	9.9	14.2	22.8
Pb (ppm)	101	49.8	66.5	71.1	44	46	43.6	43.2
Rb (ppm)	181	135	111	74	80.8	91.8	138	115
Sb (ppm)	2.4	1	2	2.3	2.5	2	1.9	3.9
Se (ppm)	1.2	1.3	2.3	1.3	1.5	2	1.5	1.6
Sn (ppm)	2	2	3	2	2	3	3	2.3
Sr (ppm)	71.5	73.6	65.4	57.9	59.9	58.5	55.4	73.4
Ta (ppm)	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2
Ti (%)	0.21	0.31	0.47	0.26	0.35	0.51	0.29	0.33
Tl (ppm)	2.02	1.52	1.11	0.41	0.75	0.68	0.87	0.72
V (ppm)	66	75	91	41	70	79	53	71
Zn	222	80.7	112	77.9	51	80.1	73	101
Zr	72	87	130	112	102	138	108	73

*Information given in Online Resource 1 (Table S1)

Table 2 Classification of predominant sources of an element X on the basis of enrichment factors (EF) calculated using local soil composition ($EF_{X,SOIL}$) and the Earth's average upper-crust composition ($EF_{X,UCC}$)

Predominant origin	Criteria	
Soil	$EF_{X,SOIL} < 5$	$EF_{X,UCC} < 10$
Mixed	$5 < EF_{X,SOIL} < 10$	$10 < EF_{X,UCC} < 20$
Non-soil	$EF_{X,SOIL} > 10$	$EF_{X,UCC} > 20$

composition than using UCC. $EF_{Na,UCC}$ showed values above the upper threshold ($EF_{X,UCC} > 20$) in 81 % of the samples (Table 4), pointing to a source other than soil to explain the Na levels determined in PM_{10}. Owing to the proximity of the sampling station to the Cantabrian Sea, sea spray was likely to be one of the main sources of Na.

The geochemical analysis of the seven soil locations did not include arsenic. As this element presented $EF_{As,UCC} > 20$ in more than 95 % of the PM_{10} samples, non-soil contributions seemed to have been predominant. $EF_{As,UCC}$ fell within the 20–850 range.

The high EFs of Zn, Sn, Sb, Bi and Cu may be due to the influence of traffic in the sampling area. These chemical species have been related to non-exhaust emissions due to the degradation of tyres, brakes and pavement abrasion (Minguillón et al. 2012; Rogula-Kozlowska et al. 2015). In fact, Sn, Sb and Bi correlated with Cu with Pearson correlation coefficients (r) above 0.80. In a previous study (Megido et al. 2016a), these four elements were related to a certain extent to brake wear.

Adamo et al. (2008) calculated EFs using R = Al and the average concentration in surface soils of an urban area in Naples (Italy). The highest EFs found by these authors were for Cd (256), Pb (120), Ni (80) and Zn (50), which were associated with traffic and other anthropogenic sources such as fossil fuel combustion. In the present study, the strongest relationship for Zn was found for Pb ($r = 0.80$) and Cd ($r = 0.73$). Moreover, the highest correlation for Cd was with Pb ($r = 0.62$). Zn correlated slightly with other metals, namely Bi ($r = 0.60$), Fe ($r = 0.64$) and Mn ($r = 0.55$). Mn, Fe, Zn and Pb are tracers of iron and steel production (Dai et al. 2015), associated with basic oxygen steelmaking and sinter plants (Almeida et al. 2015). Other elements frequently emitted by the latter source are Cu, Cd, Se, As, Cr and Ni (Querol et al. 2007; Almeida et al. 2015; Dai et al. 2015). Arsenic presented $0.50 < r < 0.65$ with Cu, Sn, Sb, Ba, Pb and Bi. However, the strongest relationship was found with K ($r = 0.79$), Co ($r = 0.78$) and Ni ($r = 0.70$). According to the literature, Se could be emitted from coal and heavy oil combustion appliances (Hueglin et al. 2005; Gianini et al. 2012). However, Se did not show any important correlation with V or Ni, tracers of the latter source (Flores-Rangel et al. 2015), or any other analysed element. Lage et al. (2016) studied the surface soils in the surroundings of Gijón (including the nearby area of the sampling site of the present study). These authors concluded that the surface soils presented high levels of contamination for Zn, Sb, As and Br, and pointed to atmospheric deposition.

Mixed-origin elements

Mn, Fe In the case of Mn, the $EF_{Mn,SOIL}$ were dissimilar for the seven soil locations, with those calculated for location E reaching the highest values, up to 468. This was because location E had lower concentrations of Mn (by one or two orders of magnitude) than the other locations (Table 1). Therefore, this location presented the lowest $(Mn/Al)_{SOIL}$ factor. However, no location should be excluded, as they were all near the sampling station. The conclusions drawn will be more reliable if they can be inferred from all the locations.

Locations A, B and C presented the lowest $EF_{Mn,SOIL}$ (0.3–45) throughout the whole sampling period. This was due to the greater abundance of Mn at these points (Table 1), with an average $EF_{Mn,SOIL}$ of 6.0, 9.6 and 3.1, respectively. Notwithstanding the differences, some PM_{10} samples (e.g., those collected on 21 October 2013 and 12 February 2014) presented a clear enrichment in Mn (Fig. 3), pointing to non-soil emission sources. However, inconsistent conclusions were reached for other PM_{10} samples, e.g., sample collected

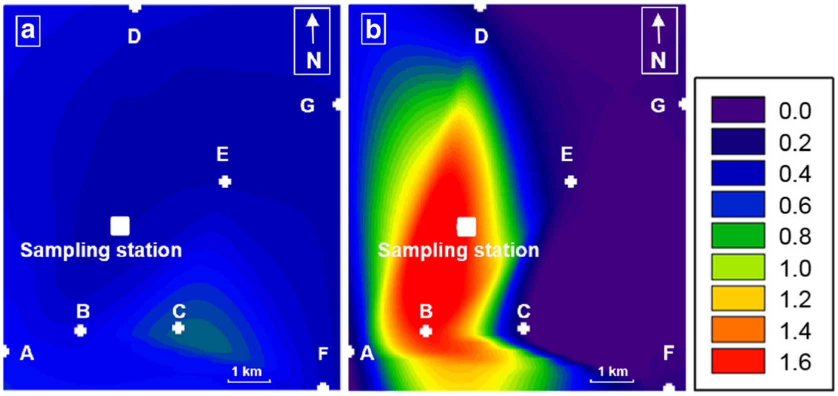

Fig. 2 Contour graphs of **a** $(Fe/Al)_{SOIL}$ and **b** $(Ca/Al)_{SOIL}$ using the geochemical composition of seven soil locations (*a*–*g*) in the surroundings of the sampling station

Table 3 Minimum and maximum $EF_{X,SOIL}$ for soil locations (A–G) and $EF_{X,UCC}$ ($n = 52$), using Al as the reference element

Element	Min–Max $EF_{X,SOIL}$							Min–Max $EF_{X,UCC}$
	A	B	C	D	E	F	G	
Bi	28–737	33–880	26–685	21–548	29–771	39–1037	18–477	190–5077
Cd	1–2810	1–2351	2–3660	1–1255	1–2058	1–2768	2–4250	24–48,212
Cu	13–837	10–655	11–751	13–852	37–2431	9–575	19–1283	31–2043
Na	44–6888	38–6038	20–3133	31–4834	34–5286	27–4265	28–4465	4–689
Sb	30–1705	51–2935	27–1523	14–794	18–1028	20–1152	24–1396	395–22,564
Sn	52–2819	37–2022	26–1399	23–1259	32–1770	19–1058	22–1218	108–5923
Se	12–1506	8–997	5–585	5–621	6–757	4–509	6–781	358–44,302
Zn	15–677	30–1337	22–999	19–862	41–1852	24–1057	30–1335	110–4952

on 1 July 2013 (Fig. 3). If only locations A, B and C were considered in this sample, soil could be revealed as the predominant source of emission, given $EF_{Mn,SOIL} < 5$ for these locations. Conversely, the opposite assumption could be made for locations D–G, given that $EF_{Mn,SOIL}$ exceeded the threshold of 10. This highlighted the ease with which conclusions could be totally different, even using local soil composition.

Location C (in the southern sector) gave the highest number of PM_{10} samples with $EF_{Mn,SOIL} < 5$ (88 %). $EF_{Mn,UCC}$ presented comparable results to those obtained for location G (in the eastern sector). Therefore, while 81 % of $EF_{Mn,SOIL}$ obtained for location G were above 10, only 40 % of $EF_{Mn,UCC}$ exceeded the threshold of 20. No PM_{10} sample had an $EF_{Mn,SOIL}$ that reflected a strong soil origin, although some of them (e.g., samples collected on 18 and 26 January 2013 and 4 February 2014 (Fig. 3)) presented values below 5 at almost every location. Bearing in mind all the gathered information, Mn was likely to be of mixed origin. The contribution of non-soil sources to the Mn determined in airborne PM varied in relevance depending on the sampling day. Although a possible anthropogenic source of Mn to PM_{10} is traffic (Poulakis et al. 2015), Mn did not show a strong correlation with Cu ($r = 0.36$) or Sb ($r = 0.35$), both of which are tracers of traffic, as stated in the "Non-soil origin elements" section. Moreover, Mn has also been related to industrial sources (Almeida et al. 2015; Flores-Rangel et al. 2015).

Table 4 Percentage of PM_{10} samples ($n = 52$) with $EF_{X,SOIL} > 10$, considering seven soil locations, and $EF_{X,UCC} > 20$, using Al as the reference element

Element	% of $EF_{X,SOIL} > 10$	% of $EF_{X,UCC} > 20$
Bi	100	100
Cd	96	100
Cu	98	100
Sb	100	100
Se	96	100
Sn	100	100
Na	100	81
Zn	100	100

$EF_{Fe,SOIL}$ (Fig. 4) was above 10 in more than 23 % of the PM_{10} samples taking into account all soil locations, while $EF_{Fe,UCC} > 20$ in 31 % of samples. The differences between the EFs calculated using local soil composition and UCC for Fe (Fig. 4) differed from those reported by Cesari et al. (2012), who found comparable values between both databases for Fe, K and Mn. As the ratio $(Fe/Al)_{SOIL}$ varied differently depending on the seven locations (Fig. 2a), differences in $EF_{Fe,SOIL}$ were not as large as those found for other elements (e.g., Mn). Fe in PM_{10} may be of mixed origin, although there were days on which it was of predominantly non-soil origin. For the latter, the $EF_{Fe,SOIL}$ ranged between 10 and 65. Possible anthropogenic sources of Fe are traffic and iron-related industrial activities. Gianini et al. (2012) related Fe to non-exhaust road traffic emissions (brake wear) and re-suspension of road dust. The average concentration of Fe determined over the sampling period (467 ± 344 ng Fe/m^3) was similar to the levels reported by these authors in an urban background site in Zurich (Switzerland) and exceeded those found in European cities such as London (UK), Zabre (Poland), Debrecen (Hungary) and Augsburg (Germany) (Rogula-Kozłowska et al. 2015 and references therein). In the present study, however, the ironmaking industry near the sampling station was also likely to have played an important role. Almeida et al. (2015) conducted a study of the PM_{10} emitted by this steelmaking factory. These researchers associated 21 % of the Fe and Mn they found with the factory's blast furnaces. In the present study, Mn and Fe were highly related ($r = 0.75$). Thus, metallurgical activities close to the sampling station, in the western sector (Fig. 1) may have a relevant contribution to PM_{10}. In fact, three PM_{10} samples coincided with $EF_{Fe,SOIL}$ and $EF_{Mn,SOIL}$ above 10 for the seven locations. The study of 5-day air-mass back trajectories revealed that those days were under western Atlantic and regional episodes. As stated in the

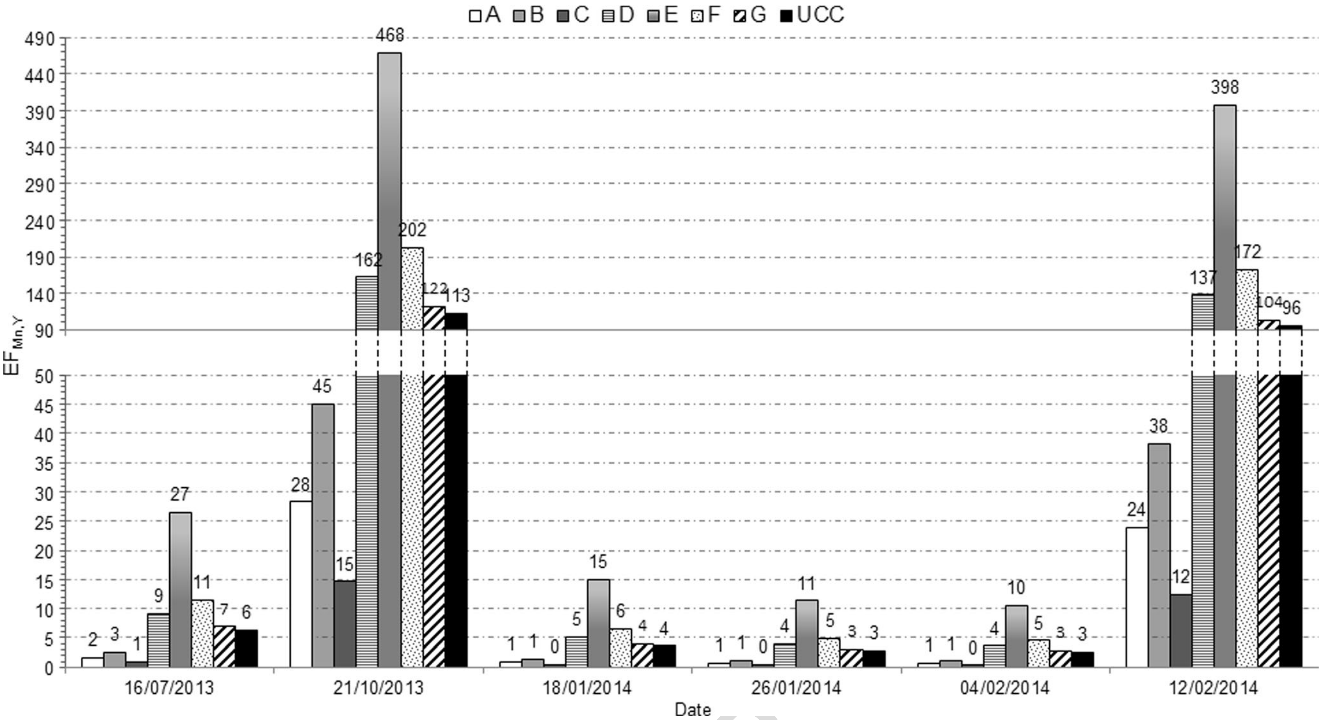

Fig. 3 EF$_{Mn,SOIL}$ for locations *a*–*g* and EF$_{Mn,UCC}$ of samples collected on 1/07/2013, 21/10/2013, 18/01/2014, 26/01/2014, 04/02/2014 and 12/02/2014, using Al as the reference element

"Introduction" section, Fe was widely used as R in EF studies. Nevertheless, in light in all the above, in this sampling area using R = Fe could lead to inaccurate conclusions.

K, Rb, Tl In this study, location E (in the eastern sector) gave similar results for EF$_{K,SOIL}$ and EF$_{K,UCC}$. Moreover, 42–77 % of PM$_{10}$ samples provided EF$_{K,SOIL}$ < 5 depending on the soil location, thus revealing the soil origin of K (83 % considering EF$_{K,UCC}$ < 10). Possible sources of K were soil dust re-suspension and combustion of fuel, biomass and wood (Hueglin et al. 2005; Cao et al., 2009; Rogula-Kozłowska et al. 2015.). In this sampling location, Megido et al. (2016b) found C-rich particles in PM$_{10}$ that carried K and whose shapes pointed to combustion processes. The arithmetic mean K concentration during the cold period (October–March) was 195 ± 110 ng K/m^3 ($n = 26$ samples), decreasing in the warm period (April–September) to 132 ± 67 ng K/m^3 ($n = 26$ samples). Given that the data of both periods were not normally distributed, the Mann-Whitney U test was applied to compare these values; a statistically significant difference ($P = 0.032$) being found. The coldest month of the sampling period was December 2013 with arithmetic mean temperatures of 9.0 ± 2.0 °C. The highest arithmetic mean K concentrations were determined (328 ± 186 ng K/m^3) during this

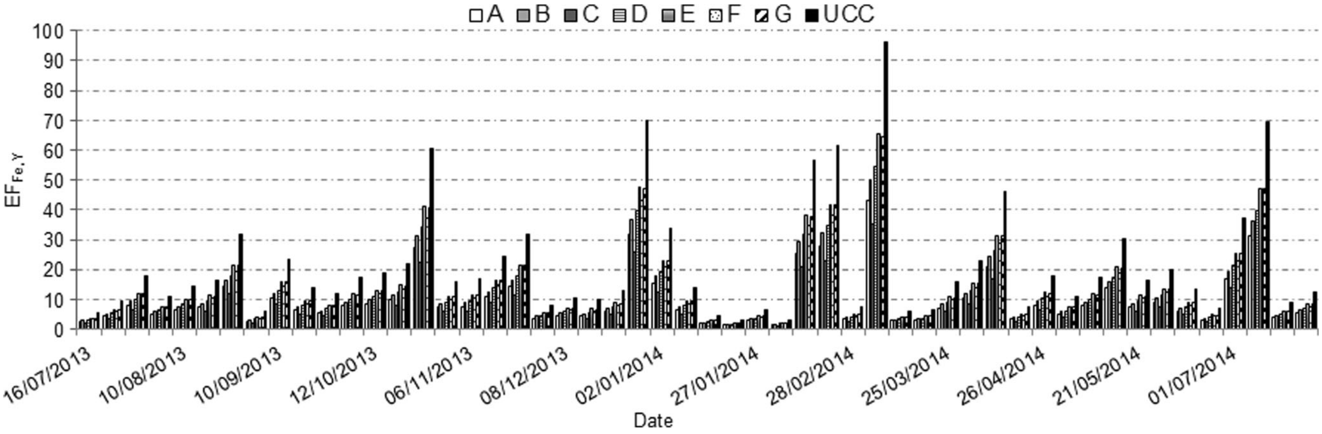

Fig. 4 EF$_{Fe,SOIL}$ for locations *a*–*g* and EF$_{Fe,UCC}$, using Al as the reference element ($n = 52$)

month, followed by March 2014 (250 ± 68 ng K/m^3). According to Tsai et al. (2015), this seasonal pattern points to wood combustion as a potential source.

Crustal origin played an important role in airborne Rb, given that 83–92 % of the PM_{10} samples had $EF_{Rb,SOIL} < 5$. In contrast, only 63 % had $EF_{Rb,UCC} < 10$. The maximum $EF_{Rb,SOIL}$ was 25, whereas the maximum was found to be 83 when using the UCC database. Rb is another tracer of emissions from wood and biomass combustion (Gianini et al. 2012). In fact, K and Rb reasonably correlated ($r = 0.69$). Of PM_{10} samples, 92 % presented an $EF_{Tl,SOIL}$ above 10, reaching values of up to 1078, while 96 % of $EF_{Tl,UCC}$ were above 20. The maximum $EF_{Tl,UCC}$ was 2427. In this study, Tl was found to be linked somehow to K and Rb ($r = 0.77$ and $r = 0.86$, respectively).

Cr, Pb Cr and Pb had a high percentage of PM_{10} samples with $EF_{X,SOIL} > 10$ (83 and 88 %, respectively) reaching values of up to 384 (Pb) and 566 (Cr). The $EF_{X,UCC}$ for these elements were much higher than the $EF_{X,SOIL}$, with maximums of 3351 and 833, respectively. In fact, if only $EF_{Pb,UCC}$ were considered, a non-soil origin would be proposed for this element. The minimum value of $EF_{Pb,UCC}$ was 45. However, as stated in the "Enrichment factor analysis" section, when $EF_{X,SOIL}$ and $EF_{X,UCC}$ were in disagreement, $EF_{X,SOIL}$ was considered the more reliable value. Therefore, given that less than 95 % of the PM_{10} samples fulfilled $EF_{X,SOIL} > 10$ for the seven locations, Cr and Pb were concluded to be of mixed origin. Pb has been related to the combustion of petrochemicals used in industrial processes (Campos-Ramos et al. 2009). Song et al. (2015) linked Pb and Cr, among others, with coal industries given EFs above 10. Cr has also been associated with emissions from cement plants (Gupta et al. 2012).

Co, Ni A similar pattern as previously reported for Mn was found for the $EF_{Co,SOIL}$ and $EF_{Ni,SOIL}$ obtained for the seven soil locations. In the case of Co, even greater differences were obtained. For this element, similar results were found between locations A, B and C, and between E and F. Less than 95 % of the PM_{10} samples had $EF_{Co,SOIL} < 5$ (up to 94 % for location A). Regardless of the soil sample considered, $EF_{Co,SOIL} > 10$ were obtained in up to 65 % of the samples for location F. An example of a PM_{10} sample that exceeded the threshold of 10 was that obtained on 09/12/2013, when the Co concentration (0.57 ng Co/m^3) was found to be well above the average for the sampling period (0.08 ± 0.08 ng Co/m^3). Higher PM_{10} levels (42.6 μg PM_{10}/m^3) than the arithmetic mean for the 52 samples (23.4 ± 10.3 μg PM_{10}/m^3) were also obtained on this day, coinciding with regional air masses that hinder the dispersion of pollutants and without rainfall either on this particular day or the previous days. Of the $EF_{Co,UCC}$, 90 % remained below 10 and only 6 % of the samples exceeded the threshold of 20. $EF_{Ni,SOIL}$ varied between 0.2 and 623 throughout the sampling period, although less than 85 % of the samples could be defined as being of non-soil origin. Similar results were found using the UCC database. Of the PM_{10}, 69 % presented $EF_{Ni,UCC} > 20$. Ni and Co have been related to industrial combustion processes (Viana et al. 2008; Alharbi et al. 2015). In the present study, these two elements correlated highly ($r = 0.91$), suggesting a common source for both which may be related to the nearby industry given the fuels employed there (see section 2.1).

Mg Location B had the highest $(Mg/Al)_{SOIL}$, which was close to 1, whereas the other six soil locations had values in the 0.05–0.15 range. Therefore, for location B, only 4 % of the PM_{10} samples exceeded the threshold of 10, while for the others, more than 54 % of the samples exceeded this value. Using the UCC database, 48 % of the samples gave $EF_{Mg,UCC} > 20$. Excluding location B, $EF_{Mg,UCC}$ were below the analogous $EF_{Mg,SOIL}$, as was the case with Na mentioned previously. In fact, concentrations of these two elements considerably correlated ($r = 0.93$), indicating a common source. Two PM_{10} samples (25 December 2013 and 25 March 2014) coincided with $EF_{Mg,SOIL}$ and $EF_{Na,SOIL}$ above 10 and were collected during north-western Atlantic episodes. On 25 March 2014, the EFs reached their maximums for Na and Mg. This day, western winds were predominant (Online Resource 1, Fig. S2), the maximum wind speed being 95 km/h (wind direction: 290°) according to AEMET. Apart from being present in soil, Mg is the characteristic of marine origin (e.g., $MgSO_4$ and $MgCl_2$). Marine aerosols are emitted due to wind stress at the ocean surface, i.e., via bubble bursting processes (EEA 2012). This source could explain the EF_{Mg} values.

Ca, Sr, Zr, V, Ba As occurred with Mg, the $(Ca/Al)_{SOIL}$ factor of location B (1.61) was in discordance with the rest of the soil locations ($(Ca/Al)_{SOIL}$ in the 0.05–0.13 range) and with the UCC ratio ($(Ca/Al)_{UCC} = 0.16$). It thus provided the most conservative $EF_{Ca,SOIL}$, the highest value being 7.3. However, more than 75 % of the samples $EF_{Ca,SOIL}$ reached values above 10 for the other soil locations. It may thus have a different source which contributes to Ca in PM_{10}, e.g., sea spray (Adamo et al. 2008), although no correlations with Na or Mg were found pointing to such a source. Its origin could also lie in regional transport from urban zones (e.g., building, construction, demolition, road dust re-suspension) and cement industries (Campos-Ramos et al. 2009; Alharbi et al. 2015). In fact, there was a cement plant near the sampling station (at a distance of over 10 km).

Sr, Zr, V and Ba also showed a mixed origin throughout the sampling period, with $EF_{X,SOIL} > 10$ in 40–69, 62–92, 31–79 and 29–56 % of the PM_{10} samples, respectively. $EF_{X,UCC}$ for these elements also pointed to a mixed origin. Sr has been related to soil re-suspension and other anthropogenic sources; V is usually associated with coal and oil combustion and long-range transport, while Ba is related to soil and road traffic

(Hueglin et al. 2005; Adamo et al. 2008; Campos-Ramos et al. 2009; Minguillón et al. 2012; Rogula-Kozlowska et al. 2015).

In a previous study, Ba was related to traffic given its connection to Cu, Bi, Sn and Sb (Megido et al. 2016a). However, other origins were not ruled out. In view of the EFs, soil may provide important apportionments to Ba in PM_{10}. Barite ore is the major natural source of Ba. It is mainly composed of barium sulphate ($BaSO_4$) and is found in beds or masses in limestone, dolomite, shales and other sedimentary formations (ATSDR 2007). Limestone was present at five of the soil locations and dolomite in locations A and B (Fig. 1).

Mo, Ta, Be, Li, La, Ce Mo presented over 30 % of the $EF_{Mo,SOIL} > 10$ and $EF_{Mo,UCC} > 20$. Ta provided less than 69 % of the $EF_{Ta,SOIL}$ below 5, ranging from 0.1 to 148. However, $EF_{Ta,UCC}$ varied between 0.1 and 36, with 83 % of the samples indicating a soil origin. Likewise, $EF_{Be,SOIL} < 5$ in up to 87 % of the PM_{10} samples depending on the soil location and $EF_{Be,UCC} < 10$ in 63 % of them. For Li, more than 96 % of the samples at five soil locations pointed to a soil origin (90 and 92 % for the other two locations), the percentage being 54 % when with respect to $EF_{Li,UCC}$.

Lage et al. (2016) related the local bedrock geochemistry of the region of Gijón with some elements determined in surface soil samples (i.e., Hf, K, La, Rb, Sc and Sm). In the present study, La and Ce correlated highly ($r = 0.91$). The $EF_{X,SOIL}$ for these elements were below 5 in more than 90 % of the samples, except on isolated days when they even took values of above 10. Soil re-suspension may explain those values. Hueglin et al. (2005) studied PM_{10} and PM2.5 in Switzerland, finding road traffic to be a major emission source for La and Ce and for Ba, Cu, Mn, Sb, Ca, Fe and Pb. Bouhila et al. (2015) suggested a soil re-suspension origin for Mn, Hf, Sc, Cr, and Ce given the low EF_{UCC} and $r > 0.5$.

Elements of soil origin

The criterion established to distinguish the soil/non-soil origin of the elements analysed in the 52 PM_{10} samples was very restrictive. Therefore, the majority of the elements were considered as being of mixed origin. Only Ti pointed to soil origin with the condition that more than 95 % of the samples having $EF_{Ti,SOIL} < 5$ and 98 % of the cases with $EF_{Ti,UCC} < 10$. Moreover, Ti and Al correlated with $r = 0.81$.

Elements in the atmospheric aerosol are brought to the Earth's surface or the sea via dry or wet deposition after a different residence time (Siegel 2002; Nordberg et al. 2015). Chemical species with a lower residence time in the atmosphere and/or a more difficult path to enter the atmosphere than Al will present EFs < 1. These two factors will depend on the physical and chemical properties of the element. EFs below 1 will indicate that $(X/\mathrm{Al})_{PM10}$ was below $(X/\mathrm{Al})_{SOIL}$. In other words, the element X in PM_{10} was not found in the same proportion with Al as it was in soil. Depending on the soil location considered, between 10 (location A) and 92 % (location F) of the PM_{10} samples presented $EF_{Ti,SOIL}$ within the 0.1–1 range. For La and Ce, this was the case in 27–88 and 46–85 % of the samples, respectively. In view of these dissimilarities between soil locations, further research is needed regarding the residence time of the elements in PM_{10} as well as their path to enter the atmosphere. Given that the present study only addresses the PM_{10} fraction, the size distribution of these elements in PM should also be addressed accordingly.

Other elements as the reference element

Ti could be another reliable element to use as R according to the present EF study and the literature (Cao et al. 2009; Dai et al. 2015). Other elements such as La and Ce may also be used, though bearing in mind that they can have sporadic non-soil contributions, e.g., Moreno et al. (2010) found that high values of the ratio La/Ce may indicate La emissions from refineries, whereas low values could point to Ce-emissions from the ceramic industry. Fe and Mn, which have been classically used as R, are not recommended, as they may have a significant anthropogenic influence. Lyu et al. (2015) used Fe as R to indicate substantial contributions of coal combustion to PM1 based on high EFs for Cd, Se and Pb. Using Ca and Mg as reference elements, Paulino et al. (2014) concluded that Fe and Cu may originate from brake linings and associated Zn and Ca with tyre wear.

Using Ti, La and Ce as reference elements, the $EF_{Al,UCC}$ pointed to a soil origin given that 100 % of the PM_{10} samples satisfied $EF_{Al,UCC} > 20$. $EF_{Al,SOIL}$ fell within the 0.1–9.4 range for R = Ti. The arithmetic mean $(\mathrm{Al/Ti})_{PM10}$ of the 52 PM_{10} samples was 19 ± 14. The highest levels of $EF_{Al,SOIL}$ found with R = Ti were shown by those PM_{10} samples with $(\mathrm{Al/Ti})_{PM10}$ substantially above the aforementioned mean. The maximum $(\mathrm{Al/Ti})_{PM10}$ was 77, due to a low concentration of Ti in PM_{10}. Using R = Ti, 94 and 92 % of the samples were found to have $EF_{Al,SOIL} < 5$ for locations C and F, respectively. In the case of La and Ce as R, the maximum values of $EF_{Al,SOIL}$ (0.1–14.2 and 0.1–11.9, respectively) were obtained for location D for days with high $(\mathrm{Al/La})_{PM10}$ and $(\mathrm{Al/Ce})_{PM10}$. With R = Ti, the elements La and Ce satisfied the established criteria to be considered of soil origin. Using Ce as R, Ti and La were found to be of this origin. Similarly, with R = La, the elements found to be of soil origin were Ti and Ce.

Those elements found to be of non-soil origin with R = Al in the "Non-soil origin elements" section (i.e., Bi, Cd, Cu, Na, Sb, Se, Sn and Zn) were also included in this group using Ti, La and Ce as the reference elements. Cu was the exception. With R = La, one soil location (location B) provided 94 % of the PM_{10} samples with $EF_{Cu,SOIL} > 10$.

As previously seen, using R = Al, $EF_{X,SOIL}$ and $EF_{X,UCC}$ presented important discrepancies for some elements. Table 5

Table 5 Predominantly, soil/non-soil origin for chemical species in PM_{10} according to EFs calculated using Al, Ti, La and Ce as reference elements

Reference element	Geochemical database	Soil origin	Non-soil origin
Al	Local soil average local soil UCC	Ti Ce, La, Li, Ti Ti	Bi, Cd, Cu, Na, Sb, Se, Sn, Zn Bi, Cd, Cu, Na, Pb, Sb, Se, Sn, Tl, Zn As, Bi, Cd, Cu, Pb, Sb, Se, Sn, Tl, Zn
Ti	Local soil average local soil UCC	Ce, La Al, Ce, La, Li Al, Ba, Be, Ce, Co, K, La, Rb, Sr, Ta	Bi, Cd, Cu, Mo, Na, Sb, Se, Sn, Zn Bi, Cd, Cu, Mo, Na, Pb, Sb, Se, Sn, Tl, Zn As, Bi, Cu, Cd, Mo, Pb, Sb, Se, Sn, Zn
La	Local soil average local soil UCC	Ce, Ti Al, Ce, Li, Ti Al, Ba, Ce, Co, K, Li, Rb, Sr, Ta, Ti	Bi, Cd, Cu, Mo, Na, Sb, Se, Sn, Zn Bi, Cd, Cu, Mo, Na, Pb, Sb, Se, Sn, Zn Bi, Cd, Cu, Mo, Pb, Sb, Se, Sn, Zn
Ce	Local soil average local soil UCC	La, Ti Al, La, Ti Al, Ba, Co, K, La, Li, Rb, Sr, Ta, Ti	Bi, Cd, Cu, Mo, Na, Sb, Se, Sn, Zn Bi, Cd, Cu, Mo, Na, Pb, Sb, Se, Sn, Tl, Zn Bi, Cd, Cu, Mo, Pb, Sb, Se, Sn, Zn

summarises the conclusions drawn for the 32 elements present in PM_{10} depending on the reference element considered and the geochemical database employed. Major differences were found in the conclusions drawn for some elements. With the four elements used as R (i.e., Al, Ti, La and Ce), $EF_{Na,UCC}$ pointed to a mixed origin, whereas $EF_{Na,SOIL}$ clearly revealed non-soil apportionments.

The conclusions reached from the EFs calculated using an average soil composition based on 113 local soil samples within 25 km around the sampling site are presented in Table 5. It should bear in mind that the standard deviation was high for some elements (Online Resource 1, Table S2). Using this database and R = Al, the elements Ce, La, Li and Ti were associated with soil origin. Li was also found from soil origin using La and Ti as R, but not for R = Ce. Bi, Cd, Cu, Na, Pb, Sb, Se, Sn and Zn were associated with non-soil origin regardless of the R. Additionally, Mo and Tl seemed to have predominantly non-soil origin with three of the R used.

Conclusions

EFs have allowed us to distinguish the soil/non-soil origin of 32 chemical species determined in the airborne particulate matter collected at a suburban station situated in the coastal city of Gijón (north of Spain). Two databases of soil geochemical composition were used for this purpose: local soil composition from seven locations in the surroundings of the sampling station and the Earth's average upper-crust composition, which has been frequently used for this purpose. Furthermore, Al, Ti, La and Ce were considered as reference elements.

The main conclusions drawn from this study are summarised below:

- Large differences were found between EFs calculated using the seven soil locations, especially for elements like Mn and Co. This highlights how easily results may differ even when using local soil composition. The right choice of the reference database for soil composition is highly important in order to obtain accurate results.
- In general, the Earth's average upper-crust composition gave comparable results to those obtained with the local soil database. However, the conclusions could differ in some cases (i.e., Na and Pb).
- Aluminium, an element widely used as the reference in EF calculations, pointed to predominantly non-soil apportionments for As, Bi, Cd, Cu, Na, Sb, Se, Sn and Zn.
- Ti was the only element found to be exclusively of soil origin using Al as R.
- The other chemical species analysed were considered of mixed origin, although soil or non-soil sources may occasionally provide large apportionments.
- La and Ce presented a strong relationship ($r = 0.91$), with a non-soil origin being predominant on only a few days.
- Despite being commonly used for this purpose, Fe and Mn were ruled out as possible R given the relevance of non-crustal apportionments. Ti, La and Ce were considered reliable reference elements, leading to similar conclusions to Al.
- Regardless of the reference element considered (i.e., Al, Ti, La and Ce) or the database used in the EF calculation (i.e., surrounding soil locations and UCC), the following elements were found to be of non-soil origin: Bi, Cd, Cu, Sb, Se, Sn and Zn.

Although being widely applied in the past, EFs are still very present in the current studies. The way in which this methodology is applied may affect the conclusions of the findings. The comparisons of the results from the EF using several elements as R and geochemical databases constituted a reliable basis for overall conclusions regarding the soil/non-soil origins of each analysed chemical species in PM_{10}.

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