



Contribution of micro-PIXE to the characterization of settled dust events in an urban area affected by industrial activities

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Abstract

This study aimed to identify possible sources of settled dust events that occurred in an urban area nearby an industrial park, which alarmed the local population. Settled dust was collected in January 2019 and its chemical characterization was assessed by micro-PIXE, focusing on a total of 29 elements. Comparison with chemical profiles of particulate matter from different types of environment was conducted, along with the assessment of crustal enrichment factors and Spearman correlations, allowing to understand which sources were contributing to this settled dust event. A nearby industrial area's influence was identified due to the contents of Fe, Cr and Mn, which are typical tracers of iron and steel industries.

Keywords Air pollution · Industrial environments · Pollution sources · Settled dust · Micro-PIXE

Introduction

Air quality has become a worldwide concern for governments and society in general, due to a strong scientific research investment in the last decades, where the impact of natural and anthropogenic emissions on the air that people breathe was assessed, along with its potential health impact on the citizens [1, 2]. Among the several air pollutants that are studied and legislated, particulate matter (PM) is of

particular interest since a wide evidence of its impact on human mortality [3, 4] and morbidity [5, 6], along with a wide range of different implications (such as visibility [7] and climate change [8, 9]), has been arising.

In 2013, the fine fraction of PM (PM_{2.5}, i.e., particulate matter with an aerodynamic diameter below 2.5 μm) was classified as carcinogenic to human beings by the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) [10, 11]. Around 5500 deaths are attributable to PM_{2.5} exposure in Portugal with an annual mean concentration of 9.8 μg m⁻³ (which is below both European and WHO's guidelines, namely, of 25 μg m⁻³ and 10 μg m⁻³), regarding 2015 [12]. As stated by WHO, there is no evidence of a safe level of PM exposure or a concentration value below which no adverse effects occur [13].

Despite the risk perception of air pollution has not always been a reality for citizens [14, 15], environmental health literacy has been increasing in order to empower the populations with knowledge about sources, adverse impacts (in terms of environment, health and climate) and potential mitigation measures [16, 17]. This strategy may be a powerful tool in order to change individual behaviors and to promote societal pressure for implementation of actions that may mitigate air pollution and its harmful effects [18].

Due to a higher awareness of citizens towards air pollution, the population of an urban area in Portugal, located nearby an industrial park, noticed occasional settled dust events and promoted some pressure over the authorities in

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order to understand its sources and potential health hazards. With the purpose of assessing the population exposure and associated health risks regarding these events, along with corresponding with the population's needs, the local council promoted a set of actions, such as, assess the chemical composition of the settled dust in order to understand its source. Therefore, the present study aims to reach this goal, namely, perform the chemical characterization of the settled dust, using the micro-PIXE technique, and assess the potential pollution sources, through the analysis of their chemical tracers and comparison with chemical profiles of different types of environments.

Experimental

Study site

This study was carried out in the municipality of Seixal (Portugal), which is located in the peninsula of Setúbal and nearby the Tagus river. The area pertaining this study has

a high influence of industries, having in the vicinity a shipyard, a steelwork and other metallurgic activities, as well as the residential area of Seixal containing 165 547 inhabitants in 95.5 km² [19]. Figure 1 shows the location of the study site, which was in the parish of “União das Freguesias do Seixal, Arrentela e Aldeia de Paio Pires” within Seixal municipality. The sampling site was the cemetery of Aldeia de Paio Pires (38°37'35.72"N, 9°4'51.69"W), which is adjacent to a steelwork (200 m away), 150 m away of national roads, 3 km away of the highway and with a distance of 2.5 km from a shipyard.

Sampling and treatment

In order to evaluate the recent events of dust deposition identified by the local population, the samples were collected from the surface of recently washed (previous or same day that the sampling occurred) graves of the cemetery of Aldeia de Paio Pires. This strategy allowed to sample only the dust material that deposited due to these events, while the choose of the graves was due to their horizontal surface

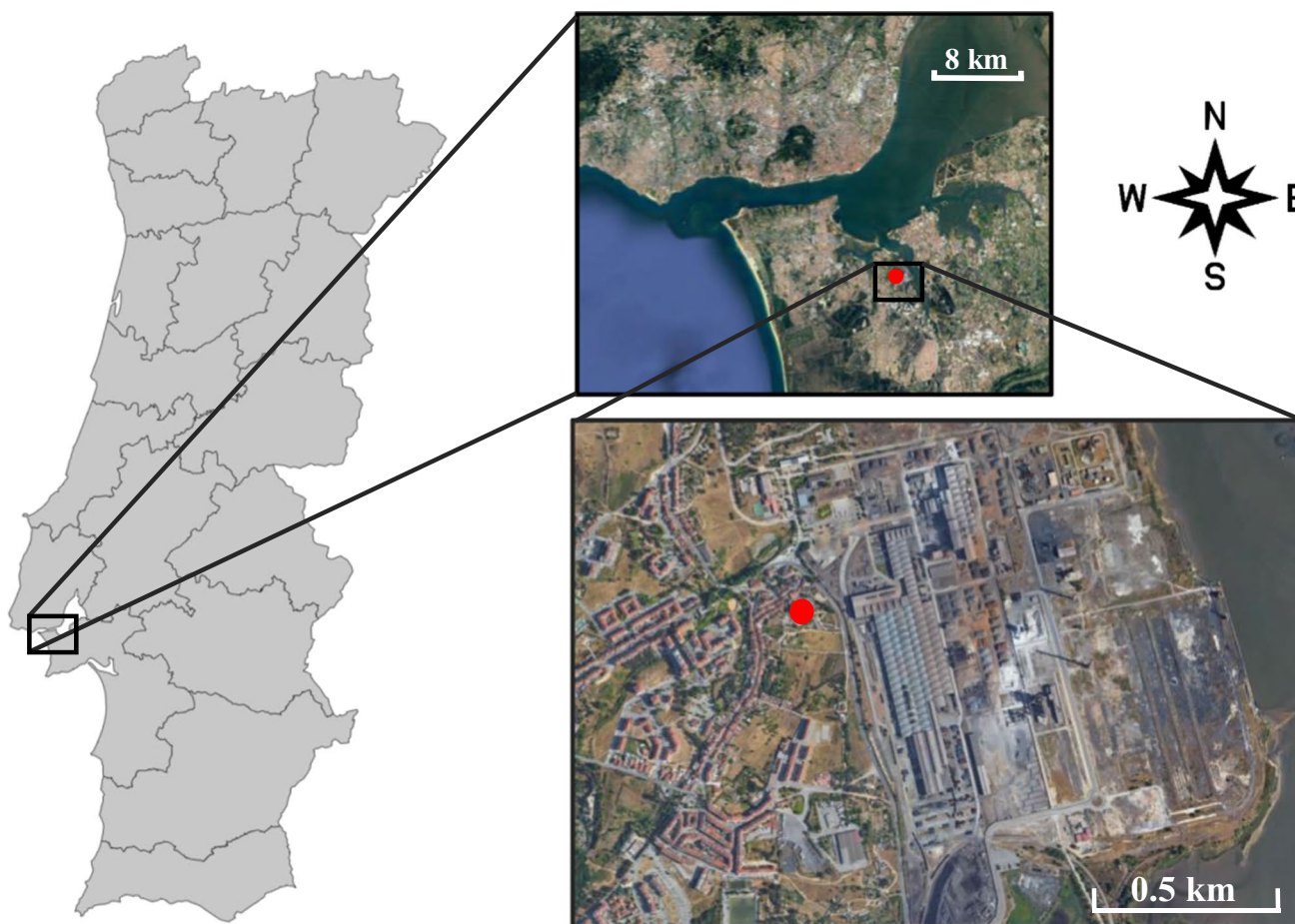


Fig. 1 Location of the study site within Seixal municipality (Portugal). Red dot identifies the sampling location (cemetery of Aldeia de Paio Pires). (Color figure online)

with knowledge that the dust deposited on them was recent since they were washed, at the maximum, 24 h before. The sampling was performed on 15th January 2019.

The dust was collected with the help of brush and the assistance of a card frame to standardize the sampling area and, afterwards, stored in polyethylene containers (as shown in Fig. 2. A total of 7 samples were collected from five different graves (from A to E), whereas three samples (A1, A2 and A3) were sampled from the same grave.

At the laboratory, it was found that the collected settled dust had magnetic properties by testing with a magnet, as shown in Fig. 3.

Micro-PIXE analysis

Micro-Particle Induced X-ray Emission (micro-PIXE) was used to determine the quantitative elemental composition of the seven dust samples, using the scanning nuclear microprobe installed at the 0° beamline of the 5MV Van de Graaff accelerator at the Institute for Nuclear Research of the Hungarian Academy of Sciences, Debrecen, Hungary [20]. The samples were irradiated with a focused H⁺ beam with 2.5 MeV energy and of 200–300 nA. The beam size was 3 μm × 3 μm.

For each sample, one pellet with 5 mm diameter was prepared from the collected dust by using a stainless-steel press without adding any aggregate. The pellets were fixed on a sample holder, which was placed in the vacuum chamber

of the nuclear microprobe. Regarding the measurement, on each sample two randomly selected areas of 1 mm × 1 mm were measured, with an accumulated charge on each measurement point between 120 and 150 nC.

Samples were positioned in the focus point of the chamber with the help of two lasers. PIXE spectra and elemental maps were recorded from all measured areas. Two X-ray detectors placed at 135° geometry to the incidence beam were applied to collect the emitted characteristic X-rays. A SDD detector with AP3.3 ultra-thin polymer window (SGX Sensortech) with 30 mm² active surface area was used to measure low and medium energy X-rays (0.2–12 keV, Z > 5). A permanent magnet protected the detector from the scattered protons. A Gresham type Be windowed Si(Li) X-ray detector with 30 mm² active surface area equipped with an additional kapton filter of 125 μm thickness was applied to detect the medium and high energy X-rays (3–30 keV, Z > 19). The beam dose was measured with a beam chopper. Full description of the setup can be found elsewhere [21].

The obtained PIXE spectra were evaluated with the GUPIXWIN program code [22]. The samples were treated as thick samples and the trace elements mode was used for the evaluation. A total of 29 elements were fitted, namely, Al, Ba, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Ga, Ge, Hf, K, Mg, Mn, Na, Nb, Ni, P, Pb, S, Se, Si, Sr, Ti, V, Zn and Zr.

The uncertainty of the PIXE measurement for the main components was between 2% and 5%, while for the trace

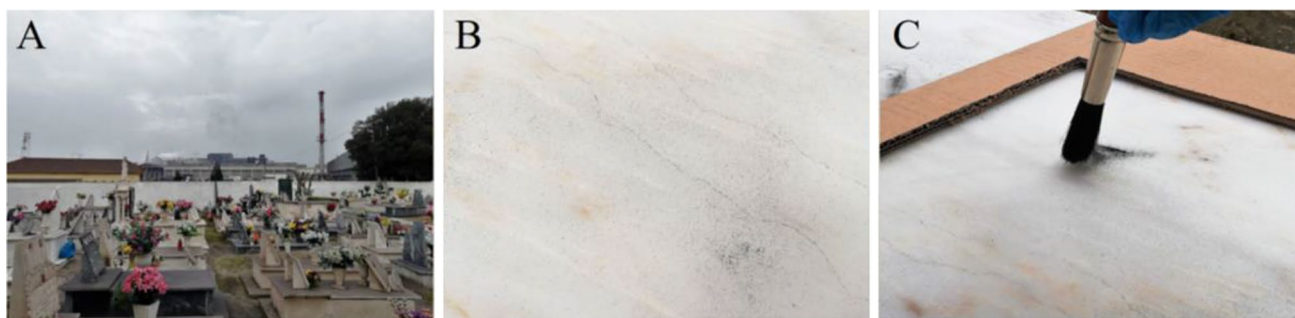


Fig. 2 **a** Cemetery with the industrial area in the background; **b** detail of settled dust on the marble of a gravestone; **c** collection of the settled dust using a brush and a card frame

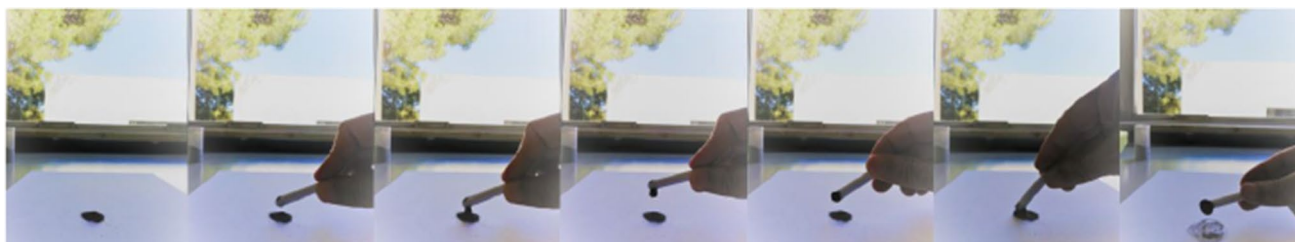


Fig. 3 Magnetic properties of the settled dust by using a magnet

elements it was between 10% and 15%. The uncertainty originated from the fitting process was added to it. Carbon could not be fitted with GUPIX, therefore it was treated as matrix elements with an average of 7 wt% concentration. The composition of the samples is given in weight % for elements present in samples with more than 1% and in mg/kg for the trace elements.

In order to check the quality and accuracy of the dose measurement and of the determination of the concentrations, measurements on standard reference materials were carried out, namely, NIST 610 glass, a series of pure metals (Pb, Zn, Fe, Sn) and a layered sample (6 μm thick Ti foil on 50 μm Ni). The calibration of the beam chopper was also done at the beginning of the campaign. These measurements were used for the determination of the exact measurement conditions (e.g., solid angles of detectors).

Crustal enrichment factor

The crustal enrichment factor method has been widely used to identify the contribution of the crustal and non-crustal origin of elements [23, 24], i.e., the degree of enrichment of a certain element compared to the relative abundance of it in crustal material [25]. In this study, crustal enrichment factor (EF) was calculated using Si as a crustal reference element [26] and the reference values of soil composition defined by Mason and Moore [27]. The EFs were calculated based in Eq. (1):

$$EF_X = \frac{\left(\frac{[X]}{[Si]}\right)_{\text{Settled Dust}}}{\left(\frac{[X]}{[Si]}\right)_{\text{Crustal}}} \quad (1)$$

Statistical analysis

Statistical analysis was performed using STATISTICA software version 13. To perform an analysis of variance of the results, non-parametric statistics at a significance level of 0.050 were selected. Spearman correlations were used to understand the associations between parameters.

Results and discussion

Chemical composition

As an example, Fig. 4 presents the elemental maps recorded for sample A1 during a measurement (with a scan size of 1 mm \times 1 mm). Overall, all analyzed samples had a similar aspect and it was found that Zn and K particles had, generally, the greatest sizes, namely between 50 μm and 100 μm . Moreover, Zn appeared often together with Cl and Na.

Taking in account that all samples referred to the settled dust into the graves in the last 24 h prior the sampling, the elemental characterization of the settled dust was done by considering the mean of all the analyzed samples.

Table 1 presents the mass fractions of major and trace elements of the settled dust.

The major elements (> 1%) found in the settled dust were, by decreasing order, Fe (32.4%), Ca (26.2%), Si (14.9%), Al (9.7%), Mg (6.3%), Mn (4.6%) e Cr (1.7%).

Understanding the origin of the settled dust

In order to understand the type of sources that could be promoting and influencing the dust event under study, a literature review was conducted to gather mean values of the chemical composition of PM₁₀ for different types of environments in different countries, for comparison purposes. Three different settings were analyzed: urban areas (Greece [28], Italy [28], Portugal [28, 29], Spain [28, 30, 31] and Switzerland [32]), rural areas (Spain [30, 31] and Switzerland [32]) and industrial areas with steel works nearby (Australia [33], France [34, 35], Germany [36], Greece [37], Poland [38], Spain [31, 39] and Turkey [40]). It is noteworthy to highlight that the 13 studies considered above refer to atmospheric particles with an aerodynamic diameter below 10 μm , whereas the samples of settled dust considered in the present study are of a much higher granulometric dimension.

The mean values found for each type of environment were compared with the ones obtained from the present study in order to identify potential common sources of the settled dust collected. Table S 1 (in section “Supplementary Information”) presents the mean values of the elemental mass fractions for the different three settings, based in the above literature.

Figure 5 shows the comparison of the elemental mass fractions between the different types of environments and the studied settled dust. Taking into account the major seven elements, industrial setting with steelworks presented the following decreasing order: S > Ca > Fe > Cl > Zn > Si > K, while urban environment presented a different decreasing mass fractions order, namely, S > Cl > Si > Fe > Ca > Na > K; and the rural environment presented the following decreasing order: Ca > Na > Cl > Fe > K > Al > Mg. For major elements found in the settled dust, only the industrial environment with steelworks presented elements with similar mass fractions (with a variability of 30%), namely, Fe and Ca, as noted by Fig. 5. Sr and Ga levels in industrial environments with steelworks were also found to have similar mass fractions (variability of 30%) with the ones found in the studied settled dust. In other types of environments, similar variability (30%) was found for Ba, Zr, Ni and Se for urban environments, and for P, Ba, Cu, Zr, Ni and Se for rural environments.

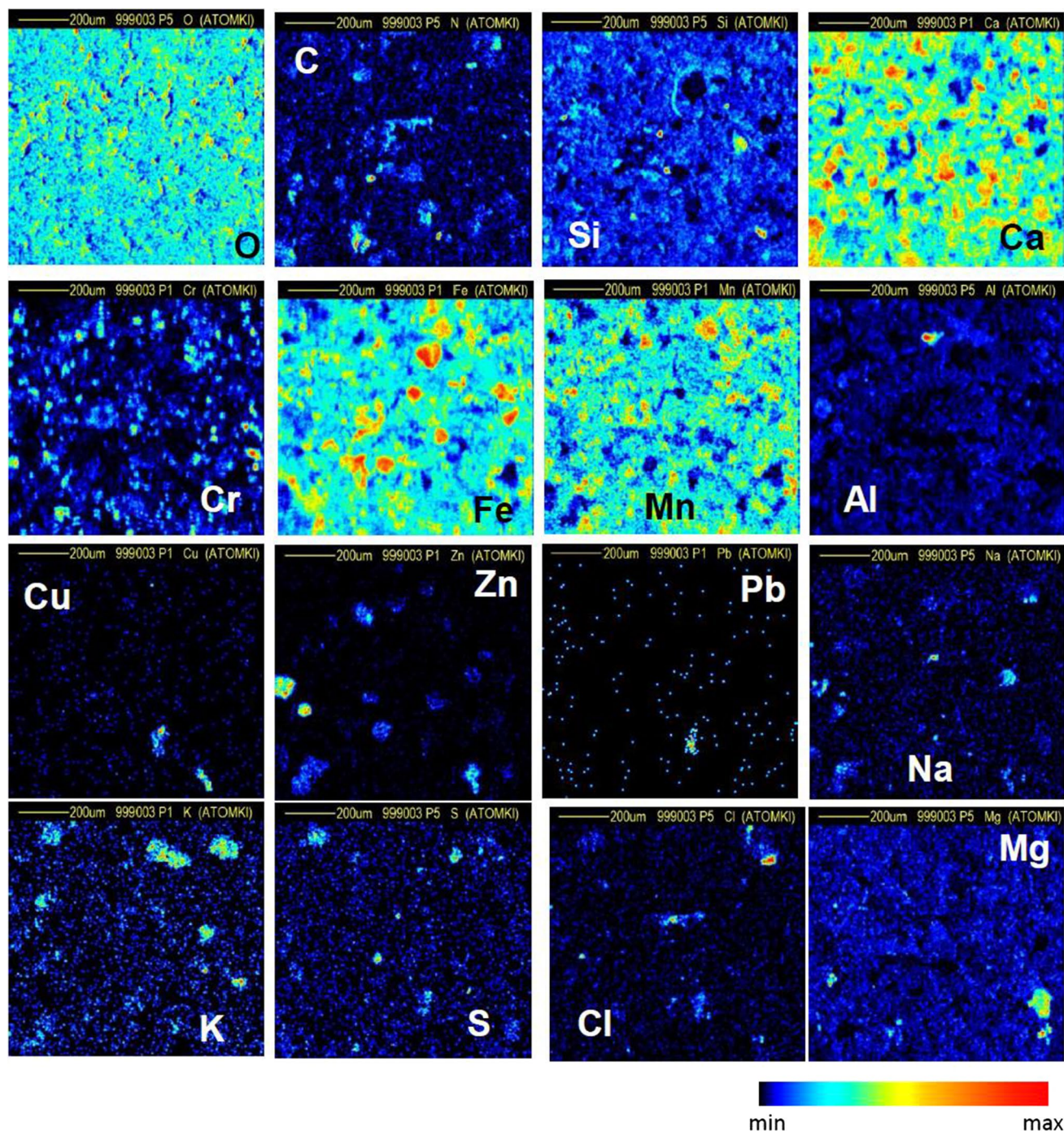


Fig. 4 Elemental maps recorded on sample A1, for the second measurement area with the scan size of 1 mm × 1 mm

Table 2 presents the variability, in %, between the elemental mass fractions found in the studied settled dust and the different types of environments. For comparison purposes, it was added results from studies on road settled dust, one in Czech Republic [41] and other in Portugal [42], whose mass fractions can be found in Table S 2 (Supplementary Information section).

Based on Table 2, it is possible to assess that the levels of Fe and Ca found in the studied settled dust are in agreement (below 30% of variability) to the ones found in industrial environments with steelworks. In fact, the possible anthropogenic sources for these elements may be iron and steel industries for Fe and the cement industry or from fugitive emissions from the sinter plant for Ca [26, 43], respectively.

Table 1 Elemental mass fractions of the settled dust, whereas n stands for the number of replicates

Type	Element	n	Mass fractions ($\mu\text{g g}^{-1}$)			%
			Mean \pm SD	Min	Max	
Major	Fe	14	183,000 \pm 14,000	158,600	208,800	32.4
	Ca	14	148,000 \pm 13,000	132,900	172,900	26.2
	Si	14	83,900 \pm 5400	79,100	98,500	14.9
	Al	14	54,600 \pm 6000	45,500	67,900	9.67
	Mg	14	35,700 \pm 2900	31,000	40,700	6.33
	Mn	14	26,100 \pm 1600	22,300	28,300	4.62
	Cr	14	9460 \pm 680	8100	10,500	1.68
Trace	Ba	13	801 \pm 155	570	1130	0.14
	Br	7	46.4 \pm 8.5	40	60	0.01
	Cd	10	375 \pm 82	245	540	0.07
	Cl	14	2520 \pm 1910	460	6580	0.45
	Co	14	682 \pm 101	530	910	0.12
	Cu	14	310 \pm 55	220	420	0.06
	Ga	12	32.1 \pm 9.9	15	45	0.01
	Ge	8	49.4 \pm 15.2	35	85	0.01
	Hf	7	153 \pm 51	85	230	0.03
	K	14	1180 \pm 660	350	2420	0.21
	Na	13	5360 \pm 6740	950	25,000	0.95
	Nb	14	223 \pm 86	135	375	0.04
	Ni	14	105 \pm 46	45	220	0.02
	P	14	2010 \pm 320	1150	2400	0.36
	Pb	8	238 \pm 163	120	620	0.04
	S	14	2680 \pm 630	1940	3915	0.47
	Se	5	24.0 \pm 9.6	10	35	< 0.01
	Sr	14	263 \pm 56	150	360	0.05
	Ti	14	3230 \pm 340	2720	4000	0.57
	V	14	740 \pm 92	560	850	0.13
	Zn	14	2620 \pm 1100	955	4950	0.46
	Zr	13	188 \pm 32	110	390	0.03

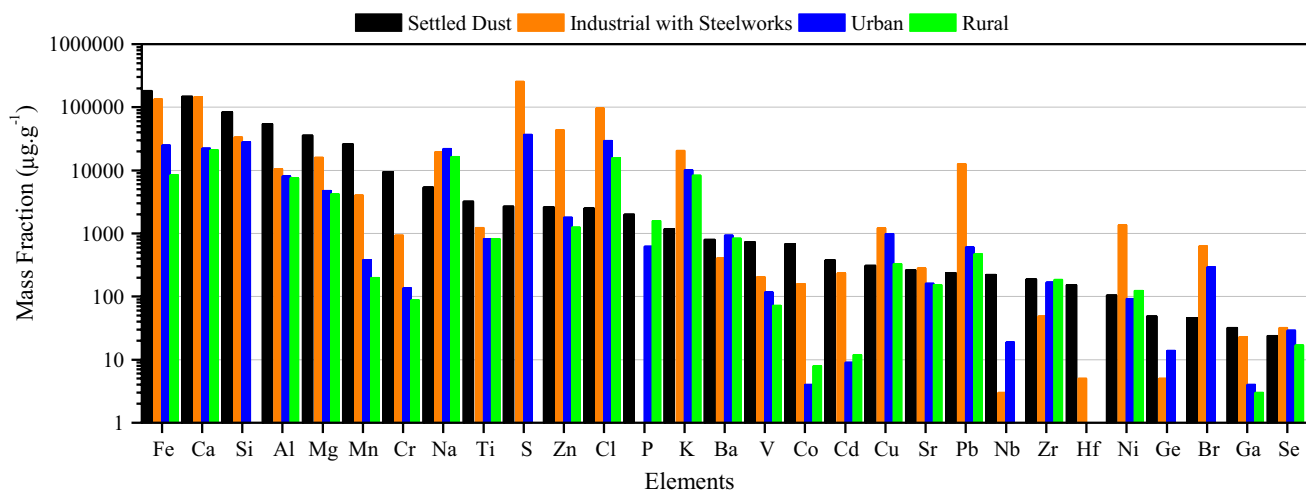
**Fig. 5** Comparison of elemental mass fractions in the studied settled dust and in PM₁₀ studies available in the literature for different type of environments

Table 2 Variability of elemental mass fractions between the studied settled dust and different types of environments, in %. Ind. w/SW refers to “Industrial with steelworks” and RSD stands for road settled dust

Elements	Variability between Settled Dust with the different environments (%)					Possible Sources [26]	
	Urban	Rural	Ind. w/SW	RSD [1]	RSD [2]	Natural	Anthropogenic
Fe	86	95	27	76	79	Soil	Oil burning and iron and steel industries
Ca	85	86	1.1	n/a	77	Soil	Cement industry
Si	66	n/a	60	-232	n/a	Soil	
Al	85	86	81	n/a	40	Soil	Coal burning and non-ferrous metal industries
Mg	87	88	55	n/a	93	Sea salt	
Mn	99	99	85	94	99		Oil burning and iron and steel industries
Cr	99	99	90	94	99		Steel industry, heavy industry, oil burning, iron and steel industries and non-ferrous metal industries
Na	-310	-210	-270	n/a	-31	Sea salt	
Ti	74	74	62	7	56		Heavy industry and coal burning
S	-1300	n/a	-9400	n/a	-16		Oil burning, coal burning and automobile diesel
Zn	31	52	-1600	90	47		Heavy industry, iron and steel industries, non-ferrous metal industries, refuse incineration, vehicle tailpipe and mechanical abrasion of tires
Cl	-1100	-530	-3700	n/a	n/a	Sea salt	
P	69	22	n/a	n/a	67	Sea salt, mineral dust [49], primary biogenic sources, volcanic eruptions [47]	Agricultural fertilizers [48], biomass burning [48] and fossil fuel combustion [47]
K	-760	-600	-1600	n/a	-1100	Soil	Refuse incineration, biomass burning and firework combustion
Ba	-17	-4.8	50	n/a	-15	Soil	Firework combustion and mechanical abrasion of brakes
V	84	90	73	91	97		Heavy industry, petrochemical industry and oil burning
Co	99	99	77	n/a	99		Heavy industry and coal burning
Cd	98	97	38	n/a	n/a		
Cu	-220	-5.5	-290	67	-290		Copper metallurgy, non-ferrous metal industries and mechanical abrasion of brakes
Sr	39	42	-7.2	n/a	80	Soil	Firework combustion and coal combustion [44]
Pb	-150	-99	-5200	87	4.5		Ceramic industries, coal burning, non-ferrous metal industries, refuse incineration and firework combustion
Nb	91	n/a	99	n/a	91		
Zr	11	1.2	74	n/a	47		Ceramic industries
Hf	n/a	n/a	97	n/a	97		
Ni	12	-18	-1200	72	95		Steel industry, heavy industry, petrochemical industry and oil burning
Ge	72	n/a	90	n/a	91		
Br	-530	n/a	-1300	n/a	n/a	Sea salt	Biomass burning
Ga	86	91	30	n/a	25		Coal combustion [45]
Se	-23	30	-33	n/a	n/a		Coal burning

variability ≤ -75 %
 -75 % < variability ≤ -30 %
 -30 % < variability ≤ 30 %
 30 % < variability ≤ 75 %
 variability > 75 %

Regarding the industrial environment with steelworks nearby, a good agreement between elemental mass fractions were also found for Ga and Sr (also below 30% of variability). Although these elements are not typically associated with industry activities, some studies have already found an association with coal combustion [44, 45]. When comparing with elemental levels in urban environments, Ba, Zr, Ni and Se showed the lowest variability with the levels found in the studied settled dust. Barium is a tracer of mechanical abrasion of brakes [26] and, together with Zn (that reported a variability of 31% and it is associated with mechanical abrasion of tires [24, 46]), can indicate the contribution of

a local traffic source to the settled dust. The remaining elements, namely, Ni, Se and Zr, are usually associated with industrial activities (steel, heavy, petrochemical industries and oil burning, coal burning and ceramic industries, respectively [26]).

The rural environments presented a similar elemental variability (below 30%) regarding P, Ba, Cu, Zr, Ni and Se. As the possible sources identified for urban environments, Ba and Cu may be originated from the mechanical abrasion of brakes [26] and Ni, Se and Zr may be originated by industrial activities. In this environment, P also had a similar variability. Phosphorous may have natural (sea salt,

mineral dust, primary biogenic sources, volcanic eruptions) and anthropogenic sources (agricultural fertilizers, biomass burning and fossil fuel combustion) [47]. The similar P levels in the settled dust to the rural environments may indicate an anthropogenic contribution from, for instance, fertilizers [48].

When comparing the studied settled dust with other studies regarding to road settled dust, for example, in Czech Republic (Ostrava) [41] and in Portugal (Oporto) [42], other elements presented similar levels. For instance, in Czech Republic, Ti levels presented a similar variability (7%), which may indicate an industrial source, namely, heavy industry and coal burning [26]. In Portugal, Ba, S, Pb, Ga presented similar levels and their provenience may come from traffic, coal burning or industrial activities [26].

Crustal enrichment factors

Figure 6 presents the enrichment factors (EF) for the studied settled dust. Elements with EF values that approach unit can be considered predominantly from crustal source [46], while elements with EF values higher than 10 indicate that their source is associated with other natural or anthropogenic sources due to local, regional and/or long transportation phenomena. Several elements presented EF values above the threshold of 10, which indicates their non-crustal origin, namely, Ba, Fe, Ca, Cu, V, S, Ge, Cl, Nb, Pb, Zn, Mn, Br, Co, Hf, Cr, Se and Cd.

Some of the possible anthropogenic sources [26] may be heavy industry, usually characterized by elemental fingerprints of V, Cr, Co, Zn and Pb; cement industry identified by Ca contribution; iron and steel industries due to the contribution of Mn, Cr, Fe and Zn; coal burning identified by the

contribution of elements such as Co, Pb and Se; or traffic due to contribution of mechanical abrasion of tires (Zn), automobile diesel (S) and mechanical abrasion of brakes (Cu and Ba). This mixture of different anthropogenic sources that contribute to the studied settled dust, namely, from industrial activity to traffic influence, agrees with the location where the sampling was conducted, taking into account that it is characterized by an urban area with an industrial area with strong activity nearby.

Spearman correlations

Table 3 presents the Spearman correlations between the assessed elements for the studied settled dust. From the total dataset, the elements Ba, Br, Cd, Ga, Ge, Hf, Na, Pb and Se were not considered, along with two replicas, due to missing values. Therefore, the analysis of Spearman correlations considered only 12 replicas with a characterization of 20 elements.

Significant positive correlations were found for: (1) Ba with Ni ($r=0.65$) and Sr ($r=0.59$); (2) Cl and Na ($r=0.76$), which indicates their sea salt source [26]; (3) Cr and Fe ($r=0.59$) and Mn ($r=0.85$), indicating their common source as iron and steel industries [26]; (4) Ni and S ($r=0.65$) that are usually associated with oil burning [26]; Nb and Sr ($p=0.59$); and P and Ti ($p=0.63$) that may indicate fuel combustion [26, 42].

Considerations

The chemical characterization of the settled dust is crucial to understand its sources. The present work aimed to perform its elemental characterization by micro-PIXE,

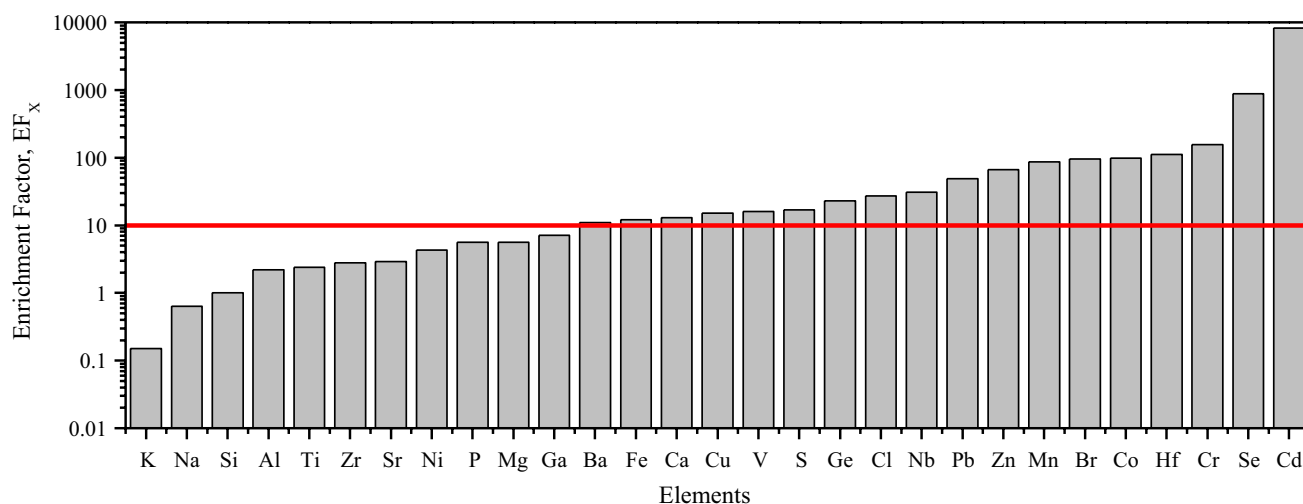


Fig. 6 Crustal enrichment factors for the studied settled dust. Red line stands for the threshold of 10 regarding a non-crustal source. (Color figure online)

Table 3 Spearman correlations between elements of the studied settled dust. Values in bold and italics are significant (p value below 0.050)

Elements	Al	Ba	Ca	Cl	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Nb	Ni	P	S	Si	Sr	Ti
Al	1.00	-0.11	0.23	0.42	-0.46	0.15	-0.25	-0.54	-0.19	-0.09	0.44	0.54	0.29	-0.59	0.17	-0.89	0.15	0.21	0.42
Ba	1.00	1.00	0.10	-0.49	-0.20	0.06	0.24	-0.06	-0.33	-0.24	-0.06	-0.26	0.32	0.65	0.18	0.21	0.02	0.59	0.06
Ca	1.00	1.00	1.00	-0.08	-0.49	-0.47	-0.56	-0.62	0.13	-0.17	-0.20	-0.42	-0.02	0.06	0.31	0.06	0.52	0.09	-0.10
Cl	1.00	1.00	1.00	1.00	-0.17	-0.11	-0.22	-0.04	0.52	0.08	0.05	0.76	-0.11	-0.32	0.17	-0.50	0.18	-0.36	0.08
Co	1.00	1.00	1.00	1.00	1.00	0.28	0.09	0.37	0.05	0.42	0.08	-0.18	-0.12	0.17	-0.41	0.46	-0.24	-0.27	-0.44
Cr	1.00	1.00	1.00	1.00	1.00	1.00	0.31	0.59	-0.68	-0.02	0.85	0.09	0.14	-0.17	0.31	-0.35	-0.77	-0.20	0.42
Cu	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.35	-0.29	0.43	0.07	0.00	0.03	0.20	-0.22	0.06	-0.19	0.12	-0.01
Fe	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-0.24	-0.18	0.34	0.06	-0.17	0.15	0.32	0.17	-0.78	-0.53	0.22
K	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.13	-0.75	0.10	-0.57	0.18	-0.30	0.32	0.50	-0.30	-0.43
Mg	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-0.08	-0.15	0.09	0.06	-0.56	0.14	0.36	0.14	-0.62
Mn	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.27	0.44	-0.46	0.41	-0.59	-0.51	-0.16	0.44
Na	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.19	-0.44	0.15	-0.72	-0.10	-0.09	0.40
Nb	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-0.14	-0.01	-0.29	0.19	0.59	-0.08
Ni	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.10	0.65	0.02	0.21	-0.33
P	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-0.34	-0.44	-0.25	0.63
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.17	-0.66
Si	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.32	-0.62
Sr	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-0.03
Ti	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

which allowed to compare it to chemical profiles of particulate matter from different types of environment, in order to understand the origin of the studied settled dust. As already stated, the granulometric fractions between the studies considered were different, since levels of particulate matter are usually assessed focusing on specific granulometric fractions, such as PM_{10} or $PM_{2.5}$, which are regulated by the European directives and national legislation. It is noteworthy to highlight this fact, since the elemental mass fractions in the different granulometric fractions are different taking in account their sources. For instance, some contaminants, including metals, are found at higher concentrations in finer particles than in coarser particles [50], due to the process (such as combustion) that originates them [26]. However, the analysis between elemental mass fractions of different environments and granulometric fractions allows to identify the potential sources that are common between them.

Taking into account that the studied settled dust is characterized by coarse particles, which are heavier and have a short lifetime in the atmosphere (i.e., travel short distances) [51], it is possible to suggest that the emission source of the settled dust event is nearby the sampling location. The analysis of the chemical profile of the studied settled dust indicates a major contribution from the industrial area nearby, along with minor traffic influence. It is possible that the source of this settled dust event is not only the industrial processes conducted in the industrial area, but also due to fugitive emissions of raw materials, for instance [52, 53].

Regarding the potential health risk of this settled dust to the population, it is possible to state that it won't have a significant impact [54], since the health risk increases with the decrease of the particle size [55] and coarser particles will not penetrate in the human respiratory tract, minimizing their health impact. However, it is noteworthy to highlight the possibility of other exposure ways, such as ingestion [56], when the particles deposit in food or water, for instance. Moreover, taking in account that children usually have a more frequently hand-to-mouth contact, this group of the population may be more exposed to the settled dust.

In order to understand exactly which are the settled dust's specific sources and/or from which industrial activity it is being originated (since the industrial area gathers several different types of processes), it would be important to evaluate raw materials stored in the industries' areas, in order to compare them to the studied settled dust. Moreover, for future work, an assessment of PM_{10} and $PM_{2.5}$ levels and their chemical characterization should be conducted in the area, in order to define, by receptor models, what are the contributions of the different emission sources. This information would allow to identify more carefully the health risk for the population regarding the local air pollution, namely, the inhalable fraction of particulate matter in the air.

Conclusions

This study allowed to identify potential sources that contributed to the settled dust event through the analysis of the chemical composition assessed by micro-PIXE and comparison with chemical profiles of particulate matter from different types of environments. A strong contribution of iron and steel industrial sources, based, namely, on Fe, Cr and Mn levels of the samples, along with a known short lifetime of coarse particles, such as the studied settled dust, indicates that the origin of this event may be due to the nearby industrial area.

This preliminary approach allows to identify potential sources and to define future strategies to perform monitoring campaigns to comply with national legislation and to understand the human exposure of the population to local air pollution and its associated health risk.

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Compliance with ethical standards

Conflict of interest The authors declare no conflicts of interest.

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