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Atmospheric Dust Characterisation in the Mining District of Cartagena-La Unión, Spain:

Air Quality and Health Risks Assessment

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ABSTRACT

Nowadays, air pollution has a major impact on the environment and human health. Owen gauges allow the sampling of atmospheric depositions in polluted sites for further characterisation. This paper shows the study of the air particles of an old mining zone in Cartagena-La Unión (South-east of Spain) in order to quantify their potential risk on human health. There were 4 strategic sites monitored: the main mining tailing (Avenque), the urban area (La Unión), an agricultural zone (formerly mining) and a site in the Mediterranean coast. Physico-chemical and mineralogical

characterisation was applied to atmospheric fallouts. The granulometry revealed a dust particle size around 15 µm, with the coarsest particles in the urban area and the thinnest at the tailing site. XRD analyses showed the presence of quartz, carbonates, sulphides and sulphates. Observations with SEM-EDX confirmed chemical spectra and allowed us to classify the particles into well-crystallised minerals and heterogeneous dusts. Total metal content determination was carried out by ICP-MS analyses and results showed Zn, Pb, As and Cd fluxes (respectively 2549, 1275, 68 and 7 µg.m⁻².d⁻¹) exceeding the limit values set by European legislations in the mining area. The fluxes of Zn, Pb and As also exceed these standards in the urban area whereas the coastal zone only exceeds the thresholds in the case of As. Inhalation health risk (defined by US EPA, 1995) was quantified in the sites using total and bioaccessible metal contents of the dusts. Risk calculations using total metal content considering a residential scenario showed acceptable risk for all sites except for the mining tailing which presented non-acceptable cancer and hazard risk mainly due to the total As and Pb contents. When considering the bioaccessible fraction of As and Pb, the risk diminished to acceptable values, demonstrating the overestimation produced when using total metal contents.

Keywords: mining activities, atmospheric fallouts, metal(loid)s, bioaccessible fraction, inhalation pathway, risk assessment.

1. INTRODUCTION

In Europe, more than 3 million sites are listed as polluted areas due to anthropogenic activities and 250,000 of them need to be urgently remedied (Jones et al., 2012). Among human activities, extractive and especially mining ones are important sources of metallic contamination in the environment, particularly due to highly toxic and persistent heavy metal emissions in the different environmental compartments (Boamponsem et al., 2010). The fate of stored mining residues remains a very high concern because the associated risk depends on metal contents but also on the mineral

species in presence. Actually, according to abiotic parameters (such as pH, temperature, redox potential, etc.), metal speciation can change and enhances their bioavailability, and then their toxicity for the environment and the human populations (Goix et al., 2014; Navel et al., 2015).

The “Sierra Minera” of Cartagena-La Unión corresponds to a large zone of mining activities in the south-east of Spain whose first exploitation by the Carthaginians (Murcia county, n.d.) is the oldest in Europe and dates back to the 3rd century BC (Gonzalez-Fernandez et al., 2011). Extractive processes were taken over by the Romans producing about 45,000 tons year⁻¹ of lead during the 1st and 2nd century AD (Moreno-Grau et al., 2002). Neglected until the 19th century, its exploitation was then extended to a larger scale. But now, this region includes nearly 40 abandoned mine tailings on an area of about 160 hectares (Martínez-Orozco et al., 1993), in between the town of La Unión and the Mediterranean Sea.

Mining activity in Sierra Minera historically focused on the extraction of lead (Pb), zinc (Zn) and iron (Fe) as reported by Alcolea-Rubio (2015). Various studies have thus been carried out in this area for assessing the contamination of soils and plants, as well as surface and groundwater (Acosta et al., 2011; Alcolea-Rubio, 2015; Conesa et al., 2006; 2008; 2009; Conesa and Faz, 2010; Garcia et al., 2008; Garcia-Lorenzo et al., 2012; Gonzalez-Fernandez et al., 2010, Martínez-Sánchez et al., 2008; Moreno-Grau et al., 2002; Robles-Arenas et al., 2006). Conesa et al. (2008) estimated that the contents of Zn, Pb and As in the main tailing (Avenque Tailing), near the city of La Unión, are about 9,100, 5,200 and 350 mg kg⁻¹, respectively. Moreover, several investigations (Conesa et al., 2006; 2009; 2010; Gonzalez-Fernandez et al., 2010) on plant species naturally growing on these contaminated soils have reported that Pb and Zn are bioaccumulated in plant shoots, highlighting a global contamination risk. However, except for Sánchez Bisquert et al. (2017) who studied metallic contaminations in soluble and insoluble fractions of atmospheric deposits in the large scale of 50 km² from the plain of Campo de Cartagena to the Mar Menor touristic area, the air quality in this mining district of Cartagena-La Unión remains poorly described (especially in terms of dust physico-chemical characterisation and health risk assessment), even if it becomes a major challenge for human health.

Actually, recent studies have reported that in the last 50 years, atmospheric pollution has become a growing public health concern worldwide and accounts for almost 10% of all deaths according to the Environmental Performance Index (EPI, 2016). Indeed, more than 3.5 billion people live in countries with unsafe levels of air pollution (Yang and Wang, 2017). Air quality and climate change from local to global scales are also influenced by airborne emissions from human activities in urban, industrial and mining areas (Baklanov et al., 2016).

Thus, as the mining wastes are stored near urban, touristic and agricultural areas in this “Sierra Minera” of Cartagena-La Unión, pollution dispersion could involve severe and growing damages for the environment and human health, especially due to these atmospheric fallouts (Csavina et al., 2012). Wind erosion can resuspend and transport metallic-rich particles over long distances from mine tailings to the surrounding urban and agricultural areas (Kulkarni et al., 2011). Resuspension of large quantities of particles from mine waste deposits, whether active or abandoned and mainly associated with wind events, result in “atmospheric dusts”, corresponding to dry and wet depositions (Castillo et al., 2013; Sánchez Bisquert et al., 2017). These depositions from mining sites present severe toxicity due to their high contents of heavy metals (Golomb et al., 1997) and especially the finest particulate matters (PM, with a diameter less than 10 μm , PM_{10} or even 2.5 μm , $\text{PM}_{2.5}$) that can reach the pulmonary alveoli and potentially the blood system (Goix et al., 2011). Many health problems have been already identified (respiratory and cardiovascular diseases, intestinal disorders, keratoses, skin cancers, neurological effects and mutagenic pathologies) during inhalation, contact or ingestion of atmospheric particles (Boamponsem et al, 2010; Wise et al., 2017). Several studies have also reported positive correlations between the effects of atmospheric dusts on human health due to heavy metal contents and the distance between ore extraction and inhabited zones (Munksgaard and Parry, 1998; Navel et al., 2015). However, although there is a difficulty in establishing direct relations of the total amount of metals in the air particles with inhalation effects on human health, exposure assessment methods are commonly used to quantify the potential associated risks. Conventional exposure assessment methods can overestimate the risks associated with these locations as they are based on the total metal(loid) content of the air particles, which cannot be totally bioavailable. Bioavailability is defined as the potential of the metal(loid) to mobilise from the soil matrices to the blood stream;

bioaccessibility is then defined as the potential to reach the human digestive or respiratory systems (Hernández-Pellón et al., 2018). Bioaccessibility by inhalation can then be estimated using *in-vitro* tests, simulating pulmonary fluids and inhalation conditions, and is now considered as a rapid, simple and low-cost method especially useful for rapidly predicting the health risk in these kinds of areas (Guney et al., 2017).

Moreover, in a global context, the current situation of contaminated sites is expected to worsen due to climate change. Actually Alcolea-Rubio (2015) states that, in this semi-arid region, global warming could lead to an increase of aridity indices and enhance atmospheric transport of heavy metals. As an example, the mass balance of metals on the Mar Menor (coastal salty lagoon in the north of the Sierra Minera) shows that metal transfer due to wind erosion represents 81%, while the groundwater contributes to 16% and the runoff to 3% (Alcolea-Rubio, 2015), suggesting a high impact of contaminant dispersion through the air.

Taking into consideration all these statements, it becomes therefore essential to determine the air quality within this mining area of the Cartagena-La Unión district in order to accurately quantify the associated health risks for the local population. This study aims to sample atmospheric dusts in an area of 25 km² on 4 strategic sites (urban, agricultural, coastal and mining areas) in order to carry out a physico-chemical characterisation of the dust deposits, quantify the elemental contents (heavy metals especially) and finally, evaluate the potential health risk for the population considering total content and specific bioaccessibility factors of the metals of concern. For that, a combination of physical and chemical methods (X-ray diffraction, high-resolution scanning electron microscopy: SEM-EDX and laser-granulometry) was applied for the analysis of samples of atmospheric fallout dusts from the selected locations of the contaminated area, and bioaccessible *in vitro* tests were conducted for health risk assessment. This made it possible to determine the pollution distribution, the contaminant fluxes existing from the mining sources to the Mediterranean Sea and the health risks potentially induced in people living in this mining environment, and finally inform the population, as a part of the global SOIL TAKE CARE project (under the Interreg SUDOE Program) which combines several approaches, both scientific and societal.

2. MATERIALS AND METHODS

2.1 Study area

The study area of the mining district of La Unión is located in the Sierra Minera, at 10 km from the city of Cartagena in South-Eastern Spain. The Sierra Minera, with an area of approximately 50 km², is part of the betic chain set up in the Miocene (5.3 to 23 million years, (SIGES, 2017)). At the end of this period, the post-orogenic magmatic activity associated with a hydrothermal circulation allowed for the creation of polymetallic ore deposits (Garcia et al., 2008). The surrounding rocks of the Gorguel mining site, studied here, belong to both the "Alpujarride" geological complexes (limestones, dolomites and phyllites) and the "Nevado-Filabride" complex (micaschists). Exploited ores consisted of silver galena (PbS, Ag), sphalerite (ZnS) and pyrite (FeS) as underlined by Alcolea-Rubio (2015) and Rico et al. (2009). The exploitation of Zn, Pb and Fe in this area has been taking place for 2,000 years, from the 3rd century BC to the industrial era in the 19th century (Moreno-Grau et al., 2002). Peñarroya® (later named Metaleurop®) ceased operations in the 1990s (Troly, 2008). This exploitation led also to the mobilisation of the following elements: As, Cu, Cd, Sb, Sn, Co, Ni and Cr (Alcolea-Rubio, 2015). The soils, located in the area where the mining was deposited, can be considered spolic anthropic regosols enriched with sulphates and iron oxides (Garcia et al., 2008).

The climate of this area is semi-arid with a rainfall of 250 to 400 mm year⁻¹, concentrated in spring and autumn, and an average temperature of 18°C (SIAM, 2017). The hydrogeology of this region, one of the most arid in Europe, is characterised by intermittent watercourses and flash floods (Conesa et al., 2008).

Four strategic sites were selected over an area of 25 km² in the mining district of La Unión to collect the atmospheric dusts: the urban area of La Unión, the main mining tailing zone called "Avenque Tailing", the coastal area corresponding to "Playa del Gorguel" located near the Mediterranean Sea and finally the agricultural area (corresponding to an old mining area) of "Las Matildes mine ". These four sites are in the transect of the prevailing winds as shown in Figure 1. Mean wind force in this area was reported to be about 2.76 ± 0.64 knots during the sampling period

(from May to November 2017), with the greatest value in May (3.77 knots) and the lowest value recorded in October (1.90 knots), in the meteorological station of Las Belones (SIMA, 2017). Even if winds are often blowing in this area near the Mediterranean Sea, their forces are not so high. Only few days per month (7 for the maximum value) with winds > 4.86 knots were reported in the concerning period.

2.2 Dust sampling

Atmospheric depositions (dry and wet) were sampled using Owen gauges corresponding to 5 litre containers made of polypropylene with large entrances (19 cm diameters) and fixed at 1.70 m height (NFX43-014 standard; Schreck et al., 2012a, 2012b; Navel et al., 2015). Sampling campaigns consisted of exposing Owen gauges for 6 months in each site and then collecting particles from the inner surface of the gauges using ultra-pure water. Dust samples were then dried in an oven (40° C) for 48 hours.

Due to very arid climate and the small quantity of particles sampled over 6 months, the two campaigns were performed for different goals. The first sample campaign was performed from May 2017 to November 2017 and the collected samples were used to determine physico-chemical properties, total content of metal(loid)s and evaluate the risk to human health for the inhalation pathway. The second sampling campaign was conducted in the same four sites from November 2017 to May 2018. These samples were used to test the bioaccessibility and perform a better estimation of the inhalation risk assessment. By the way, another study (submitted elsewhere), conducted on epiphyte plants (*Tillandsia usneoides*) as bioindicators of air quality in the same area and during the same periods, has statistically concluded that climate seasons (with rainfall intensity, wind direction and force, etc.) have no influence on atmospheric fallouts (Schreck et al., submitted; SIAM, 2017).

2.3 Determination of dust physico-chemical properties

The characterisation described here was performed for the four samples obtained during the first sampling campaign.

2.3.1 Granulometry

The particle size distribution from the 4 different sites was carried out using a granulometer Laser scattering LA-950V2 from Horiba Partica®. This technique calculates particle size using light scattered off the particle (edge diffraction) and through the particle (secondary scattering refraction), and incorporates the full Mie scattering theory. Hexametaphosphate was used as surfactant to break up the particles. Granulometry determination was performed using a 15 mL microcuvette filled with distilled water and stirred by a magnetic bar, after ultrasonication over 2 minutes (to avoid particles aggregation). Replicas were performed on each sample to test the reproducibility of the analysis. However, it is important to take into consideration that a part of metals could be present in dusts as soluble salts (formed after evaporation process in the Owen gauges) and therefore potentially dissolved when recovering dusts in the device. So, unfortunately this part cannot be assessed by granulometry measurements.

2.3.2 Morphology and mineralogy

Morphology and chemical composition of atmospheric dusts were firstly analysed using scanning electron microscopy with energy dispersive X-ray spectroscopy SEM-EDX. A field emission microscope (FEG) JSM-7800F Prime (from Jeol®) was used for analysis. The atmospheric dust samples were prepared with a silver lacquer to stabilise and fix the sample, then a carbon or platinum lacquer to conduct the electrons.

In addition, particle mineralogy was analysed by X-Ray diffraction (XRD) using a D2 Phaser diffractometer (Bruker®). Due to the small amount of material, ethanol was added to the preparation to improve the sample distribution. Analyses were interpreted using the diffract_EVA software.

2.3.3 Elemental content determination (major and Trace Elements (TE))

Samples were acid-mineralised within the clean room (class ISO 5 and ISO 7 according to the European legislation 14644-1). For each sample, 100 mg of atmospheric dusts were precisely weighed in Teflon vessels. 1 mL of H₂O₂ and 0.5 mL of bidistilled HNO₃ were added to the samples and left at

room temperature for 24 hours. Then, 1 mL of HNO₃ was added and the solutions were warmed at 80°C for 24 h. The solution was then evaporated on a plate at 80°C. 1.2 mL of HF and 1.2 mL of bidistilled HNO₃ are then added for a new warming step at 80°C. After evaporation, 20 drops of bidistilled HCL and 10 drops of bidistilled HNO₃ were added. The acid solution was warmed at 115°C for 24 h and finally evaporated at 80°C. After complete evaporation, the remaining solid residue for each sample was dissolved in 10 mL of a 10% HNO₃ solution. Acid blanks and certified reference material samples (LKSD-03, lake sediment samples and NIST SRM 1648 and Urban Particulate Matter) were also used to ensure the quality of the measures and their traceability.

Metal and metalloid concentrations were measured using ICP-MS (iCAP Q, Thermo Scientific®- Kinetic Energy Discrimination mode using He) at the AETE-ISO platform. Concentrations were determined using Be, Sc, Ge, In and Rh as internal standards to correct potential sensitivity drifts. Analysis accuracy and precision was checked by analysing international certified reference waters (CNRC SLRS-5, NIST SRM 1643e). Accuracy was better than 5%, relative to the certified values, and analytical error (relative standard deviation) was better than 5% for concentrations 10 times higher than the detection limits. Metal(loid) concentrations were expressed in dry weight (mg kg⁻¹, DW).

Moreover, enrichment factors (EF) of atmospheric dusts in the different elements were calculated by comparison to the estimated average contents registered for the upper Earth's crust as described by Taylor and McLennan (1985) and Ng et al. (2012). Thorium (Th) was chosen as an invariant in this context of polluted soils. Enrichment of dusts is also evaluated by comparing elemental contents in atmospheric fallouts to the local geochemical background reported by Martínez-Sánchez and Pérez-Sirvent (2007).

2.4 Inhalation bioaccessibility tests

The atmospheric fallout samples collected in the second sampling campaign were dried at 25°C for 24 h, sieved at 20 µm and finally mixed to create an aggregated sample so as to obtain the

required amount to perform the inhalation bioaccessibility test. Contribution of each sample to the aggregated one was recorded as represented in Table SI-1 (in Supplementary Information).

The total metal concentration of the aggregated sample was determined by ICP-MS (Agilent 7500cx) after microwave assisted acid digestion according to EPA method 3051. Bioaccessibility tests for Zn, As, Pb, Cd, Cr and Sb were conducted based on the method described by Kastury et al. (2017) and Kim et al. (2014). Cu and Sn were not considered here as they do not contribute to the risk for the inhalation pathway. A Phagolysosomal Simulant Fluid (PSF) solution was prepared by combining 142.0 mg sodium phosphate dibasic anhydrous (Na_2HPO_4), 6650.0 mg sodium chloride (NaCl), 71.0 mg sodium sulphate anhydrous (Na_2SO_4), 29.0 mg calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), 450.0 mg glycine ($\text{C}_2\text{H}_5\text{NO}_2$), 4084.6 mg potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{KO}_4$) and 50 mg of alkylbenzyltrimethylammonium chloride (ABDC) with deionised water in a final volume of 1.00 L, as reported by Stefaniak et al. (2005). The pH of the PSF solution was stabilised at 4.5 ± 0.1 . An aliquot of 0.05 g of the sample was added to 5 mL of PSF (solid liquid ratio of 1/100) and placed on an agitator at 170 rpm at 37°C for 24 h. The experiment was performed in triplicate. The solution was then filtered through a VWR 0.45 μm nylon filter and the dissolved metal concentration was measured using ICP-MS (Agilent 7500cx). The bioaccessible fraction (BAF) was calculated as the ratio of the dissolved metal concentration in the extraction solution over the total metal concentration in the sample.

2.5 Risk assessment methodology

For the calculation of the risk, considering the total metal(loid)s content of atmospheric fallouts, the metal(loid) concentration in air dusts (C_{air} , in mg m^{-3}) was calculated considering the total metal(loid) content in the Owen gauge particles (C_{sample} , in mg kg^{-1}) and an estimation of the air particles in the study region ($C_{\text{particles}}$, in mg m^{-3}) as shown in Table SI-2 (Equation 1). When calculating the risk considering the bioaccessible fraction of the metal(loid)s, the metal(loid) the accessible concentration in air particles (C_{air} , in mg m^{-3}) was calculated as shown in Table SI-2 (Equation 2). Air particle concentration was considered to be $20.4 \mu\text{g m}^{-3}$ N PM_{10} particles (average

value from 2017–2018). It was obtained from yearly PM_{10} measurements in the weather station of Alumbres (close to the studied area).

Risk assessment was conducted following the methodology indicated by USEPA (2009) considering the metals and metalloids having toxicity data for the inhalation pathway (Zn, Pb, As, Cr(III), Sb, Cd, Ni, and Co). For each metal(loid), exposure concentration for assessing cancer risk (EC_{CR}) was estimated using Equation 3, and exposure concentration for assessing the hazard quotient (EC_{HQ}) was estimated using Equation 4 (Table SI-2). A residential scenario of a child becoming an adult (with 6 years as child + 26 years as adult) was considered. Exposure parameters are shown in Table SI-3.

Cancer risk and a hazard quotient for each metal was estimated using toxicity values as shown in the equations of Table SI-2. For cancer risk, inhalation unit risk (IUR) values from literature were used (Table SI-2). For the hazard quotients, chronic inhalation reference concentration (CIR) for adults and subchronic inhalation reference concentration (sCIR) for children were used based on literature data (Table SI-4).

Total cancer risk and total hazard quotient were estimated by adding the individual risks and quotients calculated for each metal(loid) selected for the study. Non-acceptable risk was considered when either total cancer risk was over $1E-5$ or total hazard quotient was above 1 as defined in the Spanish law (RD 9/2005).

3. RESULTS

3.1 Total dust deposition

The Owen gauges placed for 6 months at the 4 strategic sites raised an average of $39 \text{ g m}^{-2} \text{ year}^{-1}$ of dusts (corresponding to dry and wet deposits) for the first sampling campaign. The mining (Avenque tailing) and the urban (La Unión) sites had the highest sampled masses with respectively 60 and $51 \text{ g m}^{-2} \text{ year}^{-1}$. The coastal zone near the Mediterranean Sea showed a deposition of $31 \text{ g m}^{-2} \text{ year}^{-1}$. Finally, the agricultural (and formerly mining) area of Las Matildes had the lowest atmospheric

particle deposition rate of $16 \text{ g m}^{-2} \text{ year}^{-1}$. The cumulative rainfall over the sampling period (from May to November 2017) was 63 mm.

3.2 Granulometry

Figure 2 represents the particle size distribution of the atmospheric dusts recovered from the Owen gauges as curves corresponding to the mine tailing, the Gorguel beach and the urban and agricultural zones. As explained before, only the insoluble fractions (excluding thus the soluble metallic salts) can be assessed here in the granulometry determination.

As particle size distribution follow for each sampling site a non-symmetric distribution, the mode visualized in the graph (Figure 2) as the highest peak seen in the distribution corresponding to the peak of the frequency distribution was followed and compared for each sampling condition. This mode value represents the particle size range most commonly found in the distribution. Granulometries of coastal and agricultural zones were quite similar to mode peaks at 15 and 17 μm , respectively. However, the sites of La Unión city and Avenque tailing showed two peaks. The urban site (La Unión) was composed of a fine fraction at 20 μm and a coarser one at 51 μm . The mining dump site (Avenque Tailing) had two fine fractions with peaks at 10 μm and 0.5 μm .

3.3 Dust morphology and mineralogy

Figure SI-1 (in Supplementary Information) presents different SEM-EDX observations of samples from mining, urban and coastal areas, along with the associated spectra. SEM-EDX analyses reveal the presence of well-crystallised minerals on one hand and residue clumps on the other. By the way, as previously underlined, the presence of metal salts is supposed but Owen gauges technique and experimental set-up don't allow their recovery nor their analysis.

XRD analyses (Table 1) also helped identify possible minerals previously highlighted by SEM chemical spectra. The gypsum ($\text{CaSO}_4 \cdot 2 (\text{H}_2\text{O})$) was clearly identifiable by the peaks of Ca, S and O. Clays were found with the peaks of K, Al, Mg, Fe, Si and O. The halite (NaCl) was preponderant in the atmospheric fallouts of the Playa del Gorguel site (near the beach). Anglesite (PbSO_4), possibly

encountered on XRD analyses, could also be represented in the chemical spectra by the peaks of Pb, S and O (Figure SI-1).

Table 1 presents the minerals assumed to be identified by XRD analyses of atmospheric deposition collected in Owen gauges. Quartz was omnipresent in the samples, through the evaporites group (gypsum and sometimes anhydrite, halite and sylvite), the carbonate group (calcite and sometimes smithsonite) and the group of clay minerals (illite and sometimes kaolinite and smectite). Sulphur minerals (silver galena, pyrite, pyrrhotite and sphalerite) were identified as possibly present in the two studied sites of agricultural and urban areas. Anglesite was found in the mine tailing area and the agricultural zone. Jarosite (potassium and iron sulphate) was suspected in the agricultural zone. Note that the presence of jarosite, silver galena, pyrite, pyrrhotite, sphalerite and smithsonite cannot be ruled out at Avenque tailing.

3.4 Elemental contents in atmospheric dusts

The total elemental contents in atmospheric dusts and the fluxes are reported in Table 2 for each studied site. According to Table 2, the mine site showed Zn, Pb, As and Cd fluxes exceeding the limit values set by Switzerland (Opair, 1985) and Germany (TA LUFT, 2002). The fluxes of Zn, Pb and As also exceeded these standards in the urban area. The coastal zone only exceeded the thresholds in the case of As. The agricultural zone, meanwhile, did not reach any limit value.

3.5 Bioaccessibility fraction

The inhalation bioaccessible fraction (BAF), measured as the average metal released from the samples to the PSF fluid over the total metal content, can be found in Table 3. As can be seen, Cd, Zn and Sb were the compounds which presented a higher percentage of weight released into the PSF fluid (90–29%), whereas Pb, As and Cr presented the lower percentage of release (10–0.9%) and therefore, the lower BAF.

3.6 Health risk assessment

3.6.1 Using total metal(loid) content

Health risk assessment was first conducted on the total metal(loid) content obtained from the dust samples collected in the first sampling campaign. The different elements considered for the assessment were Zn, Pb, As, Cr (III), Sb, Cd, Ni and Co. Results are presented in Table 4 and show acceptable risks in all cases except for the site of Avenque tailing where the total cancer risk and total hazard quotient were above the non-acceptable thresholds. The main contributor to cancer risk in Avenque tailing was arsenic (87% of contribution), followed by cobalt (8%) and lead (5%). For the hazard quotient, the main contributors were lead (59%) and arsenic (32%), followed by cadmium (5%) and cobalt (3%).

Taking these results into account, a health risk assessment was conducted on the new samples collected in the second campaign (the aggregated sample – i.e. the mixture previously described in the 2.4 section – contained 46% of dusts from Avenque tailing). Using total metal(loid) content, the aggregated sample presented unacceptable cancer risk, mainly due to arsenic (95%), lead (3%) and cadmium (2%); the hazard quotient was also unacceptable, coming from lead (55%), arsenic (42%) and cadmium (3%). Therefore, results from both sampling campaigns were consistent and presented similar trends when indicating the main contributors to risk.

3.6.2 Using the bioaccessible fraction (BAF)

Using the bioaccessible fraction instead of the total metal content, the estimated risk diminished significantly and no risk above the threshold was observed in the aggregated sample (Table 4). Arsenic and lead which were the main contributors to risk, resulted in low bioaccessibility. Cadmium, which was seen as very bioaccessible, did not present sufficient amount in the sample to generate non-acceptable risk.

4. DISCUSSION

4.1 Physico-chemical description of dusts

The atmospheric dusts collected near the mining tailing were those with the finest grain size, suggesting a potential impact on the environment near the Avenque tailing. Indeed, two characteristic peaks were found at 0.5 and 10 μm , but the finest particles, with diameters less than 10 μm (PM_{10}) or even thinner $\text{PM}_{2.5}$, are reported to be the most dangerous because they could reach, after inhalation, the pulmonary alveoli and potentially the blood system (Goix et al., 2011). The fine grain size found at the mine tailing zone could be explained by the mineral processing phase carried out since the Roman exploitation period, already described by Rico et al. (2009). Actually, the aim of this operation was to evacuate the lighter particles of the ore, previously crushed, using successive washings, and thus recover the heaviest minerals (Rico et al., 2009). Alcolea-Rubio (2015) also described two other processes used over time: firstly, the particle size separation, performed using sieves following the grinding of the ores and then the froth flotation (grinding and washing with surfactants). All these operations have been able to lead over time to form a fine fraction, subject to subsequent dusting.

In contrast, the atmospheric dusts collected in the city were the coarsest, with a peak at 51 μm . This observation confirms what had already been observed in the case of the mining town of Oruro in Bolivia (Goix, 2012) where it has been found that the urban particles were coarser (53% of coarse sand of 200–2000 μm granulometry) than those from smelters and neighbouring mines (20 to 23% coarse sand). The coarser dusts are usually reported to come from urban anthropogenic activity such as combustions, resuspension by road traffic, industrial activities, etc. (Widory et al., 2002; Rodríguez et al., 2004), certainly not negligible in this urban part of the studied area.

The agricultural zone (Las Matildes mine) and the beach site (Playa del Gorguel) had approximately the same particle size (around 15–17 μm); the urban area also showed a peak around 20 μm . According to Rodríguez et al. (2004), marine aerosols are often contained in the size fraction between 2.5 and 10 μm , which is smaller than in our experiment. But, in our case, the influence of mining and urban activities near the Mediterranean was not neglected and dusts were widely spread in this coastal area by wind erosion.

From a mineralogical point of view, the XRD analyses showed the presence of sulphides (silver galena, pyrite, pyrrhotite and sphalerite) and sulphates (jarosite and baryte) in the atmospheric

dusts of the agricultural zone (Las Matildes mine). These minerals, and especially the highly dense minerals pyrite and silver galena (already cited by Rico et al. (2009) as the main ore mined in the Sierra Minera region) come from the former mining activity of this agricultural area and their presence in the atmospheric fallouts suggests a possible risk following the ingestion of the crops of the area. In addition, some sulphides (pyrite and pyrrhotite) are also likely to be found in the atmospheric deposition in the urban area and could be directly related to the transport of particles following the main wind direction (Figure 1) from the very adjacent old mine (Las Matildes), but not from the main tailing (Avenque) which doesn't show any sulphides. The results of XRD analyses are also consistent with the two parageneses described by Alcolea-Rubio (2015). Chlorides (halite and sylvite) present in atmospheric dusts were not mentioned by Alcolea-Rubio (2015) but come from the Mediterranean Sea vicinity.

In addition, some of the compounds found in this study could also come from exhaust fumes due to vehicle traffic (Pb, Cu, Zn, Cl and K), brakes (Cu, Zn and Cr), tires (Zn) and road dust (Ca, Ti, Fe, P, K, Cr, V and Mn), as evidenced by the study by Rodríguez et al. (2004). These elements could be resuspended by vehicles, at the urban area level, and incorporate the Owen gauges after re-flight.

4.2 High elemental contents in atmospheric dusts and air quality assessment

The relationship between the elemental contents in atmospheric dusts collected by Owen gauges and the estimated average contents registered for the upper Earth's crust (Taylor and McLennan, 1985; Ng et al., 2012) are shown in Figure 3. This Figure 3 allows us to visualise the enrichment of atmospheric dusts in various elements with respect to the upper crust (with normalisation by Th as invariant). Significant concentrations in relation to the earth's crust are recorded for Cd (ratio between 29 and 444), Pb (ratio between 49 and 387), Sb (ratio between 55 and 297), Zn (ratio between 13 and 218) and As (ratio between 8 and 87).

Diagram observations on atmospheric dusts show an accumulation of Zn, As, Cd, Sb and Pb (with enrichment factors greater than 10); these enrichments could be related to the high content of spolic technosols (from mining and metallurgical wastes) described by Alcolea-Rubio (2015) for the

Sierra Minera [Zn (993 to 14,720 ppm), As ($\leq 1,930$ ppm), Cd (≤ 65 ppm), Sb (≤ 220 ppm) and Pb (75 to 27,780 ppm)]. Actually, these values are largely higher than those of the geochemical background in the region of Murcia [Zn (16 to 55 ppm), As (5 to 8 ppm), Cd (0.1 to 0.4 ppm), Sb (0.5 to 1.6 ppm) and Pb (3 to 10 ppm)] reported by Martínez-Sánchez and Pérez-Sirvent (2007) from the “Grupo de Investigación en Contaminación de Suelos - Universidad de Murcia”.

In addition, the total atmospheric dust fluxes collected by Owen gauges were between 12 and 60 g m⁻² year⁻¹, with an average of 39 g m⁻² year⁻¹ for the 4 sites. This value is comparable to the flux (42 g m⁻² year⁻¹) previously determined near the same mining area of the south of the Mar Menor by Sánchez Bisquert et al. (2017). The elementary fluxes (expressed in $\mu\text{g m}^{-2} \text{d}^{-1}$), calculated in the atmospheric deposition, (Table 2) exceed the standards set by the OPAIR and TA LUFT, respectively corresponding to the Swiss and German regulations in the mine area (Zn, Pb, As and Cd), urban area (Zn, Pb, As) and coastal zone (As).

These fluxes can be compared to those of the Viviez site in the Decazeville basin (Aveyron, SW France), also studied in the global SOIL TAKE CARE project from Interreg SUDOE Program, and that was largely affected by heavy metal pollution due to a former (1842–1987) industrial Zn-ore treatment plant and many mining waste as tailings located in the area (Sivry et al., 2008). In comparison, a higher air flux in As ($11.6 < 68 \mu\text{g m}^{-2} \text{d}^{-1}$), Cd ($3.7 < 7 \mu\text{g m}^{-2} \text{d}^{-1}$), Pb ($71 < 1275 \mu\text{g m}^{-2} \text{d}^{-1}$) and Zn ($808 < 2,549 \mu\text{g m}^{-2} \text{d}^{-1}$) was observed at the site of the Avenque Tailing (ORAMIP, 2012).

Similarly, by comparing the fluxes of atmospheric deposition acquired on the former mining town of Saint-Laurent-Le-Minier in France (Navel et al., 2015) to that of the La Unión mining district, the atmospheric contamination is higher at the La Unión urban area for As ($12 \text{ vs } < 1 \mu\text{g.m}^{-2}.\text{d}^{-1}$) and Pb ($185 \text{ vs } < 5 \mu\text{g.m}^{-2}.\text{d}^{-1}$), suggesting a worst air quality for inhabitants in the city of La Unión. But the ore processing site of Saint-Laurent-Le-Minier is more contaminated than the Avenque tailing site in the Cartagena-La Unión district: The fallout fluxes of As, Cd, Zn and Pb are respectively 948, 158, 245 and 3,547 $\mu\text{g m}^{-2} \text{d}^{-1}$ in Saint-Laurent-Le-Minier (Navel et al., 2015) *versus* 68, 7.2, 2,549 and 1,275 $\mu\text{g m}^{-2} \text{d}^{-1}$ for the Avenque tailing in Cartagena-La Unión district.

4.3 Bioaccessibility by inhalation and health risk assessment

Results of *in-vitro* tests performed have shown that Cd, Zn and Sb are the most bioaccessible elements (90–29%) by inhalation, whereas Pb, As and Cr presented the lower percentage of release in biological fluids (10–0.9%). These results are in accordance with the literature: for example, Hernández-Pellón et al. (2018) highlighted that at the Vidriera site, largely impacted by nearby industrial activities in the Cantabrian region (Northern Spain), the average metal(loid) bioaccessibility in Gamble's solution followed the order Sb (47.3%) > Zn (45.5%) > Cd (39.3%) > Mn (34.1%) > Cu (18.8%) > Pb (14.8%) > Fe (4.0%). These values are also in accordance with those reported for Fe, Mn, Zn, Cd and Pb by Mbengue et al. (2015) in Gamble's solution for PM_{2.5} samples collected 800 m from a FeMn smelter.

Actually, due to the acidity of soils (Schneider, 2016) and the speciation of the solid phases, some elements are very mobile, soluble and then bioavailable, such as Cd or Zn and can quickly disperse into the environment and enter organisms. In soils, according to the mineralogy, different constituents of the solid phase are potentially able to fix metal elements: clays, iron and manganese oxides, carbonates, organic matter and sulphides (Ge et al., 2000, Plassard et al., 2000). Their interactions with the metal(loid)s govern their speciation, their mobility and therefore their transfer into the soil solution and can modulate their bioavailability and potentially lead to severe consequences for the environment and human health (Fernandez-Cornudet, 2006). The study of mining sites has already shown that Cd has the highest mobility in soils and dusts, followed by Zn, Ni, Cr, Pb and Cu (Sauvé et al., 2000, Degryse et al., 2009).

Thus, the bioaccessibility fraction in atmospheric dusts (mobilised after wind erosion) highly depends on the soil properties (pH, redox state, organic matter content, etc.) and the particle size but also metal(loid) concentrations and their speciation (soluble forms, complexed, adsorbed, etc.). This experiment had then highlighted that metal bearing-phases collected by Owen gauges devices are also reactive (in addition to soluble compounds), and susceptible to release toxic elements for human

health. Therefore, measurements of inhalation bioaccessibility must be specifically determined site-by-site and cannot be easily extrapolated to other situations.

Moreover, even if bioaccessibility testing is now becoming a popular assay for health risk assessment, the methodology needs to be more standardised to widespread its use and prove its reliability vs *in vivo* tests. Actually, there is a lack of agreement in the protocol concerning synthetic fluid composition and what is more important, an absence of strong *in vivo* correlations to standardise the method and consider it totally accepted (Kastury et al., 2017). Although *in vivo* tests are often considered valid methods for exposure assessment, translation of animal data to human effects presents several difficulties. Correlation between *in vivo* and *in vitro* tests has only been conducted for a few selected metals such as uranium (Ansoborlo et al. 1999) and platinum (Artelt et al. 1999) and should be extended to other compounds in order to tune the exposure assessment and extend the use of bioaccessibility by inhalation for the risk estimation.

Nevertheless, *in vitro* tests could be considered a conservative approach, and the bioaccessible fraction measured by the metal(loid) and dissolved in the synthetic fluid should be usually higher than what could be actually absorbed into a blood stream. As it has been demonstrated in the case of Cartagena-La Unión, health risk estimated with total metal(loid) content can be largely overestimated and then induce non-acceptable risk in some samples that are considered acceptable when examining their bioaccessibility. This observation can suggest that the bioaccessible fraction of metal(loid)s should be systematically introduced in health risk assessment proposed by international institutions after a process of standardisation, in order to better take into account, the biochemical processes involved and better fit to reality.

Moreover, for the complete risk assessment of human health in Cartagena-La Unión, other pathways should be considered together with inhalation, such as ingestion and dermal contact; however, this was out of the scope of this paper.

Finally, some critics could also be evidenced for the health risk assessment method. Actually, this method is based on precise calculations of human exposure to toxic compounds, but various medical and epidemiological uncertainties still exist and the social dynamics are not already really

taken into account in this kind of evaluation (Turner et al., 2003; Barraza et al., 2018). For example, at the individual or community scale, the knowledge of risks incurred by living near a former mining site, the usage of natural resources, the social perception, the consumption habits or protection strategies and the knowledge of environmental issues are the main factors that control population behaviour when the population is faced with the potential risk of the contamination of their atmosphere (Fraser et al., 2003). And unfortunately for the moment, these social parameters are not really taken into account in health risk assessment (Becerra et al., 2016a & 2016b).

5. CONCLUSIONS

The atmospheric dusts collected in the Owen gauges had a mean particle size around 15 μm with, not surprisingly, the finest particles present at the mine tailing area—probably due to ore treatments of the long past mining activity. The urban area showed coarser grain size (with a peak at 50 μm), possibly related to human activity in the city. These atmospheric dusts included, among others, sulphides (iron, zinc and lead), sulphates and carbonates, found in particular in urban and agricultural areas. The atmospheric fallouts were particularly enriched in Zn, As, Cd, Sb and Pb with respect to the upper crust of the Earth and the local geochemical background. Fluxes (expressed in $\mu\text{g m}^{-2} \text{d}^{-1}$) of atmospheric deposition exceeded threshold values (OPAIR, 1985, TA LUFT, 2002) for Zn, Pb, As and Cd in the mine tailing area; Zn, Pb and As in the urban area and As near the beach of Gorguel. Despite this, the health risk estimated via inhalation was considered as acceptable in all sites studied except for the area of Avenque tailing where the high content of arsenic and lead found in the atmospheric dusts could cause a non-acceptable hazard and cancer risk. However, this risk was overestimated as it is calculated using the total metal(loid) content of the sample. When considering the bioaccessible metal(loid) content of the sample related to the fraction that could actually reach the organism measured through *in vitro* tests, the risk drastically diminished as arsenic and lead presented quite low bioaccessibility; the estimated risk was then considered as acceptable. *In-vitro* tests appeared to be useful methodology for rapid and accurate health risk-assessment in a specific site, but the

methodology needs to be standardised and better correlated to *in-vivo* tests to generalise their use and prove their reliability. Further studies should be conducted in Cartagena-La Unión to characterise the health risk, taking into account the global context in this area of prolonged exposure on site, other routes like ingestion and skin contact of these contaminated particles and all metals present in the air.

Finally, this kind of methodology appears as really rapid to perform and allows the determination of various parameters of atmospheric dusts (from dry and wet deposits), even if the use of air impactors for PM₁₀ and PM_{2.5} quantification remains essential for a better health risk assessment. This method could then be applied to various mining sites around the world as the use of Owen gauges is very easy and not expensive. However, the present conclusions cannot be generalised to all the sites and high precautions must be taken, especially when studies involve populations living in potentially impacted areas. Considering all these parameters, it becomes difficult to provide the right management of dust dispersion and deposition but it appears as highly necessary to better constrain the environmental and health risks.

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FIGURES AND TABLES

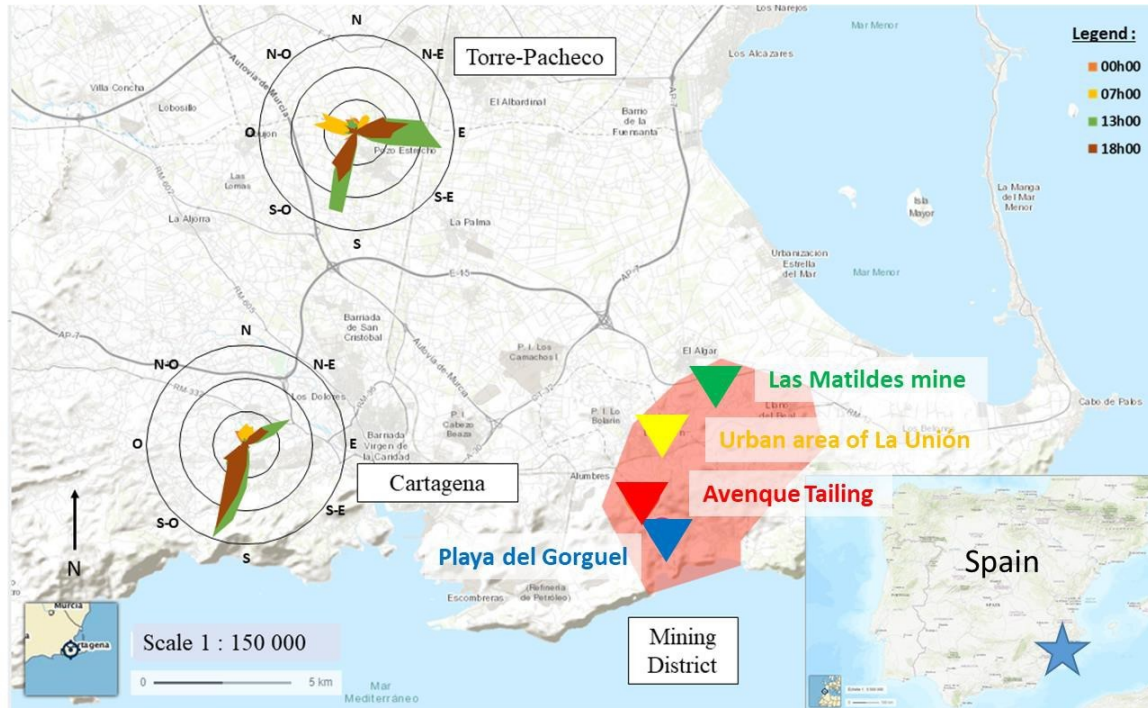


Figure 1. Sampling sites localisation (Avenque tailing, Rayadel Gorguel, Urban area and Las Matildes mine agricultural zone) and prevailing winds in the mining region between 2000 and 2016 (Geportal, 2017; SIAM, 2018)

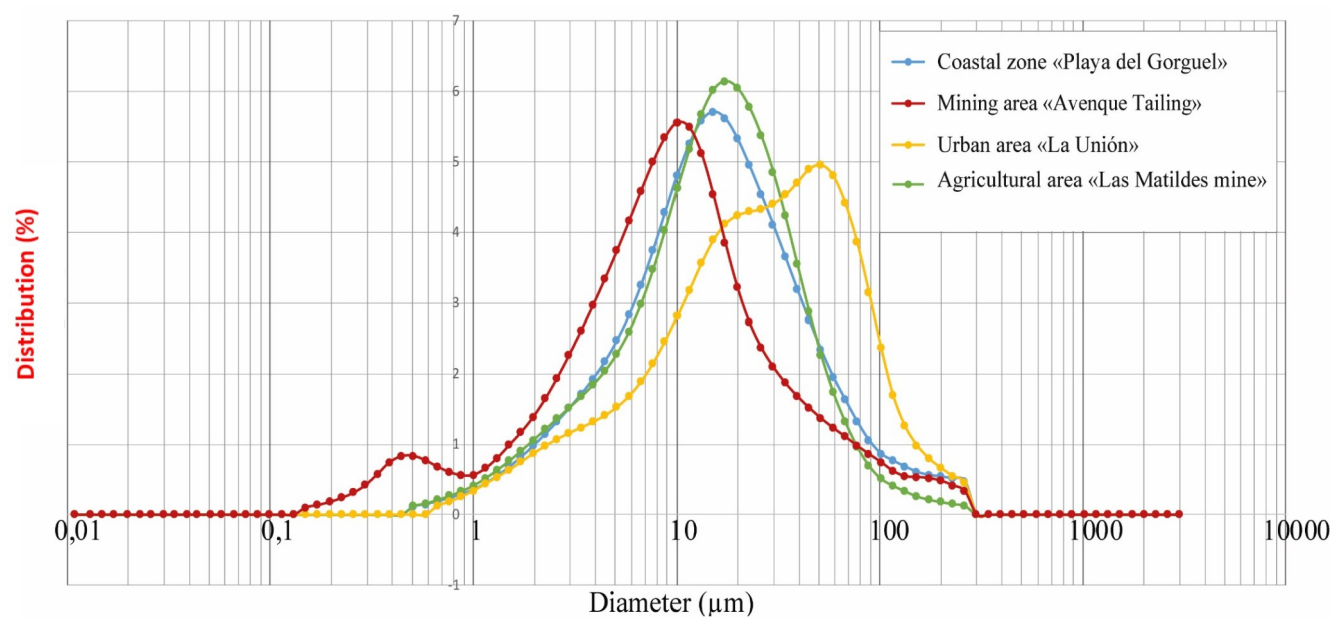


Figure 2. Particlesizedistribution of the atmospheric deposition at the different sites samples

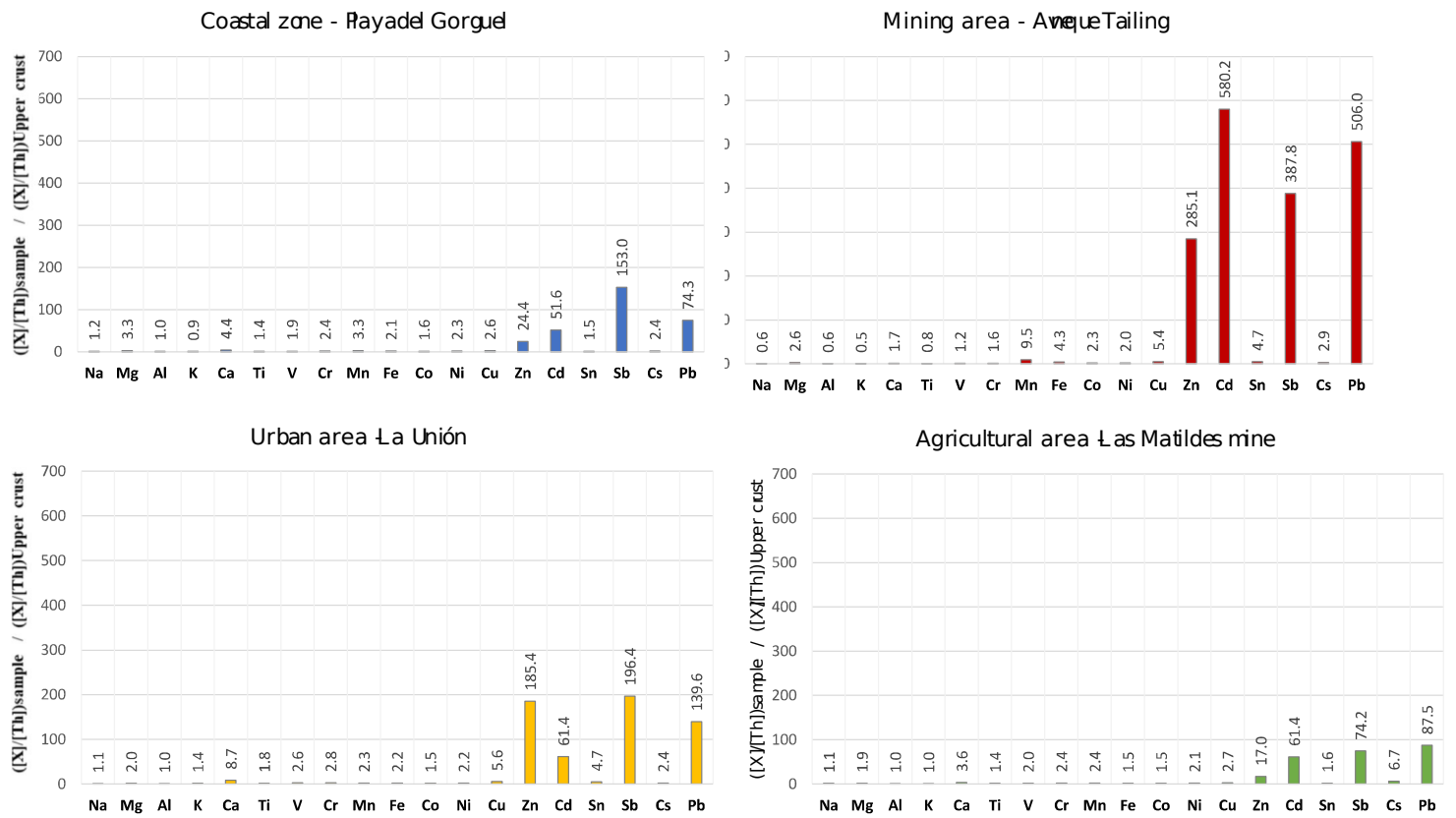


Figure 3. Enrichment factors (EF) of atmospheric dusts relative to the upper Earth's crust. The same scale is used to better assess variation between sites.

Table 1. Mineral composition of atmospheric fallouts, determined by X-Ray diffraction

		Coastal zone « Playadel Gorguel »	Mining area « Avenue Tailing »	Urban area « La Unión »	Agricultural area « Las Matildes mine »
Quartz	SiO ₂	+	+	+	+
Gypsum	CaSO ₄ ·2(H ₂ O)	+	+	+	+
Kadinite	Al ₂ Si ₂ O ₅ (OH) ₄	+	+	Suspected	+
Calcite	CaCO ₃	+	+	+	+
Illite	(K,H ₃ O)(Al,Mg,Fe ₃ ,Al) ₂ O ₁₀ [(OH) ₂ ·(H ₂ O)]	+	+	+	+
Baryte	BaSO ₄	Suspected	+	-	Suspected
Barium sulfide	BaS	Suspected	Suspected	-	-
Anglesite	PbSO ₄	-	Suspected	-	Suspected
Anhydrite	CaSO ₄	Suspected	-	-	-
Halite	NaCl	+	-	+	+
Sylvite	KCl	-	-	Suspected	-
Jarosite	KFe ³⁺ (SO ₄) ₂ (OH) ₆	-	-	-	Suspected
Smectite	(Na,Ca) _{0.3} (Al,Mg)Si ₄ O ₁₀ (OH) ₂ ·nH ₂ O	-	-	-	Suspected
Silver glena	PbS, Ag	-	-	-	Suspected
Pyrite	FeS ₂	-	-	Suspected	Suspected
Pyrrhotite	Fe(1-x)S (x=0-0.17)	-	-	+	Suspected
Sphalerite	(Zn,Fe)S	-	-	-	Suspected
Smithsonite	ZnCO ₃	-	-	-	Suspected
Hydrophilite	CaCl ₂	-	-	Suspected	-

Table 2. Comparative data on trace elements (TE) contents (mg kg^{-1}) and flux ($\mu\text{g m}^{-2} \text{d}^{-1}$) in atmospheric fallouts from the first sample campaign (May 2017 to November 2017) with limit values from Opair (2018) and TA LUFT (2002).

Locaton	Fe	Zn	Pb	As	Cu	Cr	Sb	Cd	Ni	Sn	Co
TE CONTENTS (mg kg ⁻¹)											
Coastal zone "Playadel Gorguel"	48308 ± 1052	1151 ± 20	989 ± 14	168 ± 1.2	43 ± 0.4	56 ± 0.6	20 ± 0.2	3 ± 0.04	30 ± 0.2	6 ± 0.1	11 ± 0.1
Mining area "AvenqueTailing"	115243 ± 760	5484 ± 198	742 ± 26	516 ± 0.9	102 ± 0.7	43 ± 1	59 ± 0.9	43 ± 0.5	31 ± 0.2	20 ± 0.5	17 ± 0.1
Urban area "La Unión"	36031 ± 722	6269 ± 67	1329 ± 61	85 ± 1.3	67 ± 1.1	46 ± 1	19 ± 0.2	3 ± 0.1	21 ± 0.4	12 ± 0.5	7 ± 0.1
Agricultural area "Las Matildes mine"	39888 ± 80	892 ± 5	1289 ± 37	39 ± 0.1	51 ± 0.4	62 ± 0.5	11 ± 0.1	4 ± 0.04	31 ± 0.2	6 ± 0.04	11 ± 0.1
TE FLUX (µg m ² d ⁻¹)											
Coastal zone "Playadel Gorguel"	4050	97	83	14	4	5	2	0	3	0	1
Mining area "AvenqueTailing"	18973	2549	1275	68	17	7	10	7	5	3	3
Urban area "La Unión"	5020	873	185	12	9	6	3	0	3	2	1
Agricultural area "Las Matildes mine"	1743	39	56	2	2	3	0	0	1	0	0
Limit values (Opair. 2018TA LUFT. 2002)											
		400	100	4				2	15		

Table 3. Average metal released from samples during inhalation bioaccessibility tests over the total metal content (Bioaccessible Fraction=BAF)

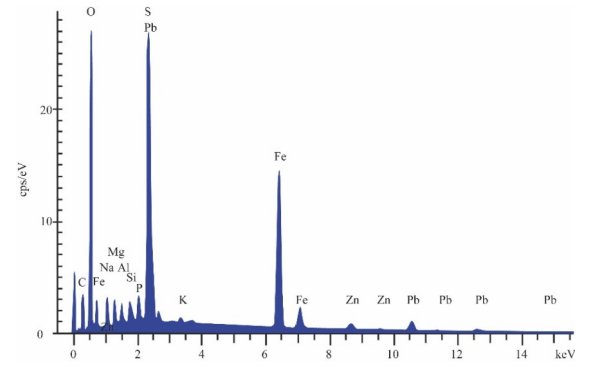
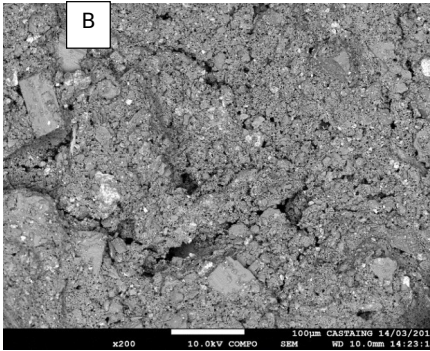
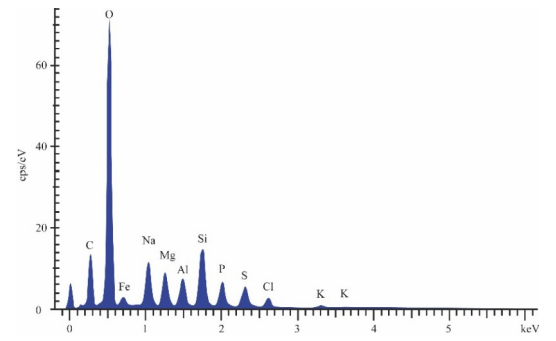
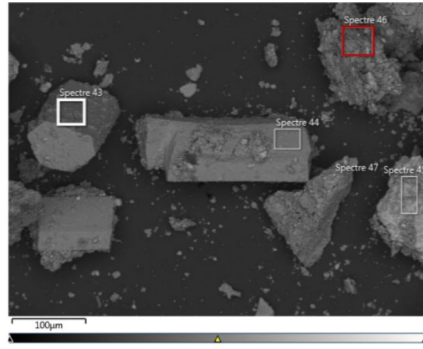
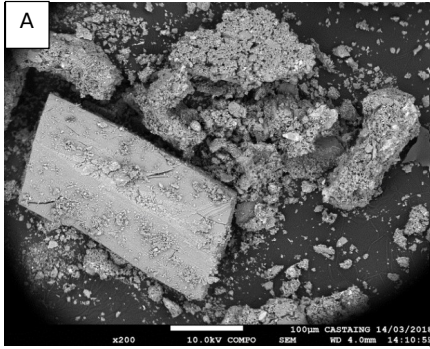
Metal	Average Released (BAF %)	Average Released (mgkg ⁻¹ of sampled dry basis)
Cd	79.7	1.9E+01
Zn	47.6	5.0E+03
Sb	29.5	2.8E+00
Pb	10.0	7.4E+02
As	5.3	3.0E+01
Cr	0.9	9.0E+02

Table 4. Risk assessment conducted on the samples taken in 2017 and the aggregated sample produced from the samplings in 2018. In red, unacceptable risk (>1 for hazard quotient and >1E⁻⁵ for cancer risk) is highlighted. - indicates that cancer risk cannot be calculated due to lack of reference concentration values.

	Coastal zone "Playa del Gorguel"		Mining area "Avenque Tailing"		Urban area "La Unión"		Agricultural area "Las Matildes mine"		Aggregated sample (total metal content)		Aggregated sample (bioaccessible fraction)	
	Hazard quotient	Cancer risk	Hazard quotient	Cancer risk	Hazard quotient	Cancer risk	Hazard quotient	Cancer risk	Hazard quotient	Cancer risk	Hazard quotient	Cancer risk
Zinc	4.50E-06	-	6.06E-05	-	2.45E-05	-	3.49E-06	-	4.15E-05	-	1.97E-05	-
Lead	1.29E-01	9.06E-08	1.01E+00	7.09E-07	1.73E-01	1.22E-07	1.68E-01	1.18E-07	9.63E-01	6.76E-07	9.61E-02	6.75E-08
Arsenic	2.19E-01	5.51E-06	5.43E-01	1.37E-05	1.11E-01	2.79E-06	5.09E-02	1.28E-06	7.36E-01	1.85E-05	3.91E-02	9.84E-07
Chromium (III)*	1.10E-02	-	8.41E-03	-	0.00E+00	-	9.00E-03	-	1.94E-02	-	1.76E-04	-
Antimony	1.30E-03	-	3.85E-03	-	1.24E-03	-	7.17E-04	-	6.29E-04	-	1.86E-04	-
Cadmium	5.87E-03	2.29E-09	8.41E-02	3.28E-08	5.87E-03	2.29E-09	7.82E-03	3.05E-09	4.59E-02	3.22E-07	3.66E-02	2.57E-07
Nickel	6.52E-03	5.95E-08	6.74E-03	6.15E-08	4.56E-03	4.17E-08	6.74E-03	6.15E-08				
Cobalt	3.59E-02	7.56E-07	5.54E-02	1.17E-06	2.28E-02	4.81E-07	3.59E-02	7.56E-07				
TOTAL RISK	3.98E-01	6.42E-06	1.70E+00	1.56E-05	3.19E-01	3.44E-06	2.70E-01	2.22E-06	1.75E+00	1.95E-05	1.72E-01	1.31E-06

*For hazard quotient calculation of Chromium, subchronic inhalation reference concentration has been considered for a conservative approach.

SUPPLEMENTARY INFORMATION



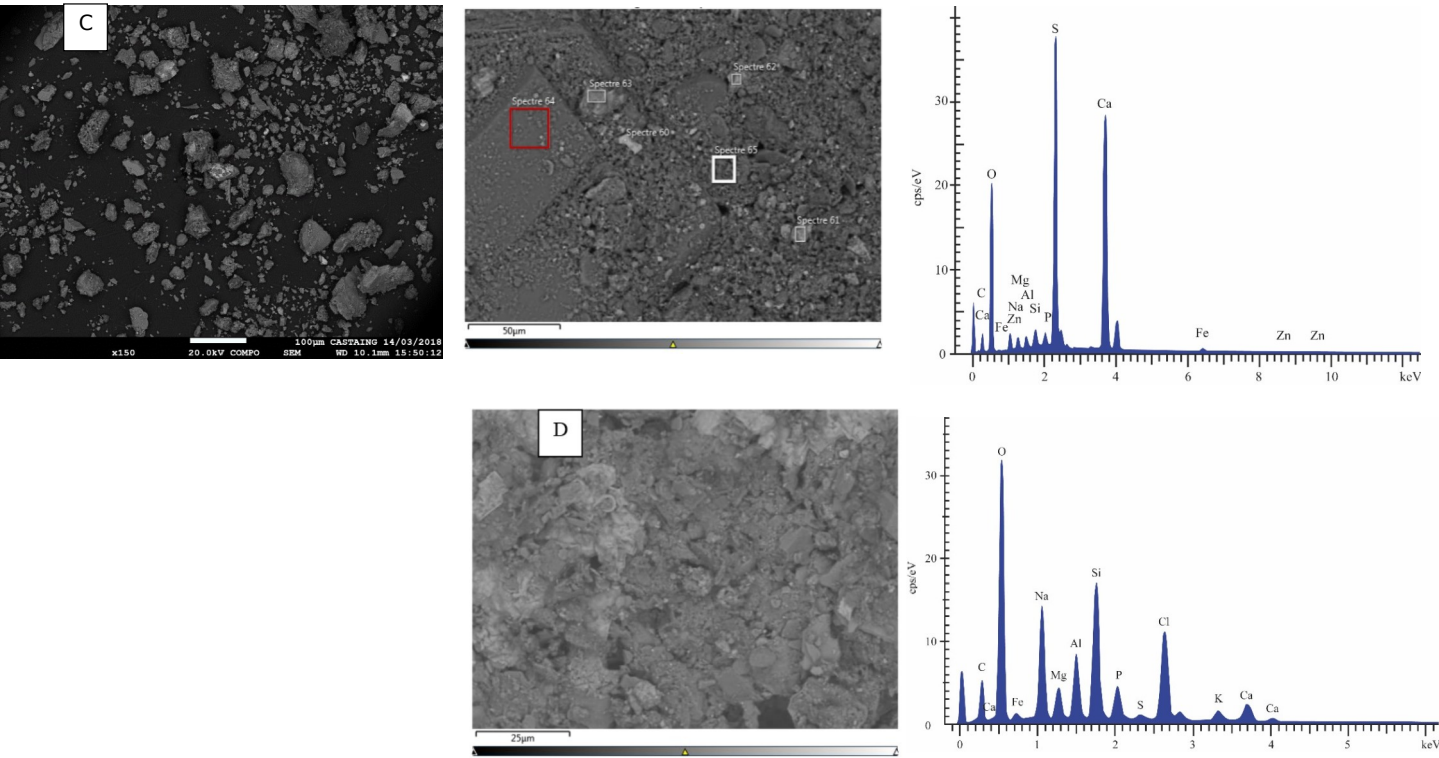


Figure SI-1. Morphology of atmospheric deposition and associated chemical spectra, analysed by SEM-EDX: A) Mining area and day mineral spectra (ex: ~~K~~adinite); B) Mining area and lead sulphate spectra (ex: ~~M~~gnesite); C) Urban area and calcium sulphate (ex: ~~G~~ypsum); D) Coastal zone and halite spectra.

TableSI-1. Dust weight collected in each sampling point and contribution to the total aggregated sample used for bioaccessible tests

Sampling site	Weight (g)	Contribution
Total	0.2849	100%
Coastal zone Playa de Gorguê	0.0762	27%
Mining area "Avenquedão"	0.1301	46%
Urban area "Laiólm"	0.0201	7%
Agricultural area "IsMatilde mine"	0.0585	21%

TableSI-2. Equations used for health risk assessment after inhalation

For risk assessment considering total metal content: $C_{air} = C_{sample} \cdot C_{particles}$ (Eq. 1)

For risk assessment considering bioaccessible fraction: $C_{air} = C_{sample} \cdot BAF \cdot C_{particles}$ (Eq. 2)

For cancer risk	For hazard quotient
$EC_{CR} = \frac{C_{air} \cdot ET \cdot EF \cdot ED}{T_{CR} \cdot 365d/year \cdot 24h/day}$ (Eq 3)	$EC_{HQ} = \frac{C_{air} \cdot ET \cdot EF \cdot ED}{T_{HQ} \cdot 365d/year \cdot 24h/day}$ (Eq 4)
Cancer risk	Hazard index
$IUR \cdot EC_{CR}$ (Eq. 5)	$\frac{CE_{HQ}}{CIR}$ or $\frac{CE_{HQ}}{sCIR}$ (Eq. 6)

Table SI-3. Exposure parameters considered for a residential scenario

Parameter	Symbol	Units	Considered value	Reference
Exposition time	ET	h/day	24	(MMA, 2007)
Exposition frequency	EF	d/year	350	(MMA, 2007)
Exposition duration	ED	Years	Child/adult: 6 + 26	(MMA, 2007)
Average time considered for hazard quotient estimation	T _{HQ}	Years	Child/adult: 6 + 26	(MMA, 2007)
Average time considered for cancer risk	T _{CR}	Years	82	WHO, 2016

Table SI-4. Reference values for chronic and subchronic inhalation reference concentration and inhalation unit risk

	Chemical Abstracts Registry Service CAS	Chronic Inhalation Reference Concentration, CIR (mg m ⁻³)	Chronic Inhalation Reference Concentration Reference	Subchronic Inhalation Reference Concentration, sCIR (mg m ⁻³)	Subchronic Inhalation Reference Concentration Reference	Inhalation Unit Risk, IUR (µg m ⁻³) ⁻¹	Inhalation Unit Risk Reference
Zinc and Compounds	744066-6	5.0E+00	ATSDR				
Lead and Compounds	743992-1	1.5E-04	CALEPA			1.2E-05	CALEPA
Arsenic, Inorganic	744038-2	1.5E-05	CALEPA			4.3E-03	IRIS
Chromium (III)	1606583-1			1.0E-04	ATSDR Final		
Antimony metallic	744036-0	3.0E-04	ATSDR	1.0E-03	PPRTV Archive		
Cadmium	744043-9	1.0E-05	ATSDR	9.0E-04	PPRTV Archive	1.8E-03	IRIS
Nickel soluble salts	744002-0	9.0E-05	ATSDR Final	2.0E-04	ATSDR Final	2.6E-04	CALEPA
Cobalt	744048-4	6.0E-06	PPRTV	2.0E-05	PPRTV	9.0E-03	PPRTV

Notes:

- ATSDR The Agency for Toxic Substances and Disease Registry (ATSDR) minimal risk levels (MRLs).
- CALEPA The California Environmental Protection Agency (CALEPA) Office of Environmental Health Hazard Assessment (OEHH) Chronic Reference Exposure Levels (RELs) and the Cancer Potency Factors (CPF).
- IRIS U.S. EPA Integrated Risk Information System (IRIS).
- PPRTV U.S. EPA Provisional Peer Reviewed Toxicity Values (PPRTVs).

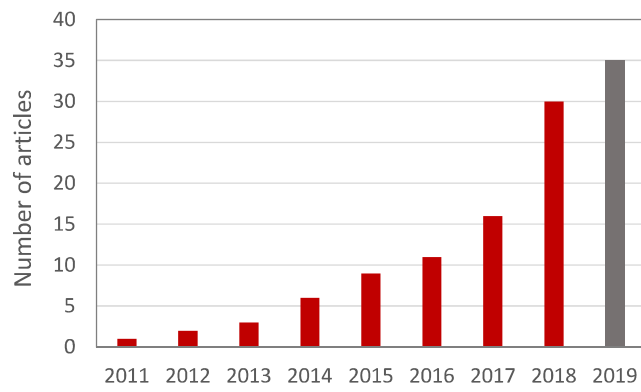


Figure 1: Cumulated publication history for the adaptation and uses of the o-DGT (for 2019, the deadline considered is March 2019).

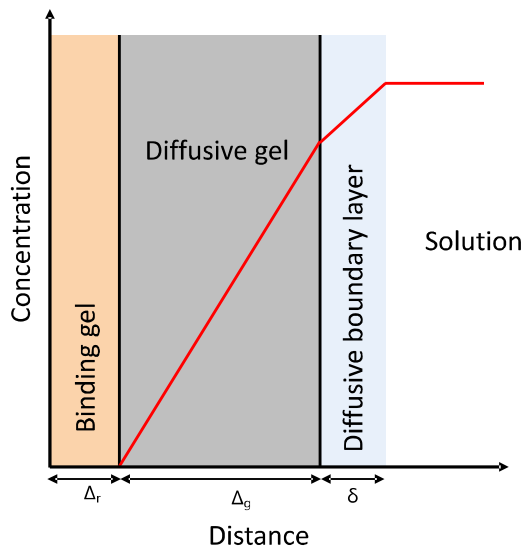


Figure 2: Concentration gradient into o-DGT (Δ_r the thickness of the binding gel, Δ_g the thickness of the diffusive gel and δ the thickness of diffusive boundary layer).



Figure 3: Picture of a diffusion cell device.