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***Tillandsia usneoides* as Biomonitors of Trace Elements Contents in the Atmosphere of the Mining District of Cartagena-La Unión (Spain): New Insights for Element Transfer and Pollution Source Tracing**

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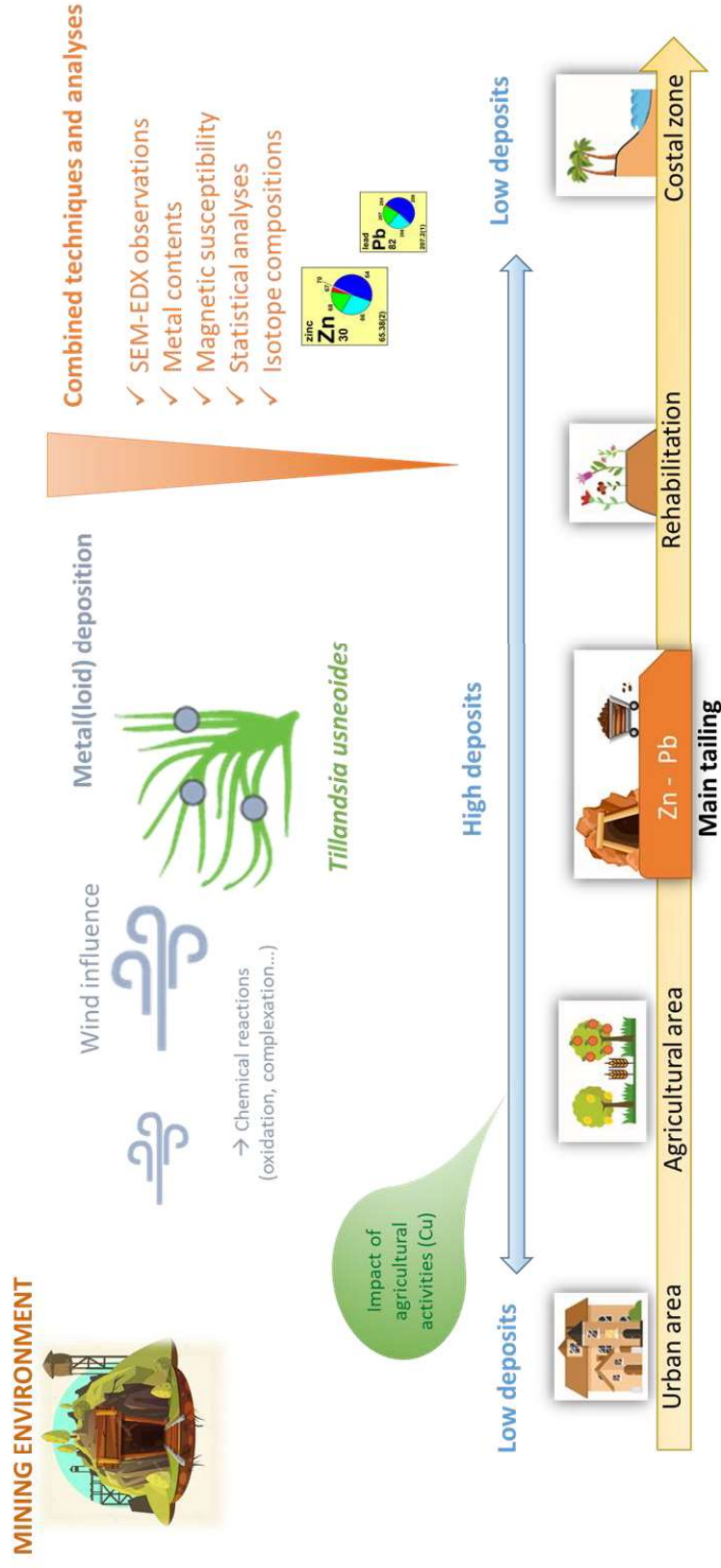
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**GRAPHICAL ABSTRACT**



**Exposure to metal(loid)s in 5 characteristic areas**

→ *T. usneoides* = biomonitors of air quality

→ Chemical form of metal(loid)s mainly governs uptake and bioaccumulation in plants

→ Zn & Pb isotopes : good tools to trace sources in mining areas

***Tillandsia usneoides* as Biomonitors of Air Quality in the Mining District of Cartagena-La Unión  
(Spain): New Insights for Element Transfer and Pollution Source Tracing**

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Grégory Dufrechou, Jérôme Chmeleff, José Darrozes

### **Highlights**

- *T. usneoides* are significantly enriched in As, Cd, Pb, Sb and Zn in the mining district.
- Dust deposition is slower in urban and coastal sites compared to mining zones.
- Chemical form of metal in the air seems to govern its uptake and bioaccumulation.
- *T. usneoides* could be a powerful tool to trace element sources in the atmosphere.

1 ***Tillandsia usneoides* as Biomonitors of Trace Elements Contents in the Atmosphere of the Mining**  
2 **District of Cartagena-La Unión (Spain): New Insights for Element Transfer and Pollution Source**  
3 **Tracing**

4 Eva Schreck<sup>1</sup>, Jérôme Viers<sup>1</sup>, Isalyne Blondet<sup>1</sup>, Yves Auda<sup>1</sup>, Mélina Macouin<sup>1</sup>, Cyril Zouiten<sup>1</sup>, Rémi  
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11

12 **Abstract**

13 Nowadays, atmospheric pollution has a major impact on the human health and the  
14 environment, encouraging the development of biomonitors of the air quality over a wide zone.

15 In this study, the relevance of the epiphyte plants *Tillandsia usneoides* is studied to estimate  
16 the transfer of metal(loid)s from a former Zn and Pb mining zone in the Southeast of Spain  
17 (Cartagena-La Unión) to the local atmosphere. Biomonitoring was performed by installing plants in 5  
18 sites along a transect from the main mining area to the urban and the coastal zones. An aliquot of  
19 plants was collected in every site every 2 months over 1 year. The *Tillandsia usneoides* have been  
20 observed with SEM-EDX, and analysed by ICP-MS to determine trace element concentrations,  
21 magnetic susceptibility signals and Zn and Pb isotopes ratios.

22 Results show that atmospheric particles are distributed homogeneously at the plant surface.  
23 By comparing elemental contents in *Tillandsia usneoides* with regard to the values of the

24 geochemical background of the region of Murcia, significant enrichments are observed in the  
25 epiphyte plants for Sb, As, Cd, Zn and Pb.

26 The statistical analyses (decentred PCA and PLS) also suggest that the kinetics of dust  
27 deposition is slower for the urban and coastal sites compared to the mining sites and highlight an  
28 influence of agricultural activities in Cu deposition. The similarity of isotopic compositions (Zn and Pb)  
29 between *Tillandsia usneoides*, soils and atmospheric particles also put in evidence that these plants  
30 could be a powerful tool to trace the source of matter in the atmosphere. Finally, this experiment  
31 provides new insight to better understand the foliar absorption mechanisms.

32

33 **Keywords:** *Tillandsia usneoides*; air quality biomonitoring; mining activities; isotopes; source tracing;  
34 magnetic susceptibility.

35

## 36 1. Introduction

37 Mining activities are still an important source of contamination by trace elements (TE)  
38 worldwide, involving severe damages in the different environmental compartments (Bes et al.,  
39 2014). Trace metals are highly toxic and persistent in the environment, and both heavy metals and  
40 metalloids pose a very serious and significant threat to the ecosystem health and nearby habitats,  
41 including soil, surface water and atmosphere (Boamponsem et al., 2010; Gu et al., 2018).

42 Among these damaged places, the Cartagena-La Unión mining district (Murcia region, SE  
43 Spain) is one of the most notable sites of geochemical pollution and geotechnical instability in Spain's  
44 abandoned mining heritage (IGME, 2002, Rodríguez et al., 2011). Metal extraction has been carried  
45 out since ancient (Roman) times, with a peak of activities in the 1980s (Navarro et al., 2008). A  
46 number of research papers have been published in the last decade regarding soil contamination in  
47 this area (Conesa et al., 2006, Conesa et al., 2008) and possible strategies for the remediation or the  
48 alleviation of the TE toxicity of these soils (Pardo et al., 2017; Zornoza et al., 2012).

49 But, there is a notable lack of knowledge concerning air quality in this old mining site and its  
50 surroundings, whereas air pollution was reported to be one of the most important environmental  
51 problems in the developing countries (Serbula et al., 2017). Sánchez Bisquert et al. (2017) studied  
52 metallic contaminations in soluble and insoluble fractions of atmospheric deposits in a large scale of  
53 50 km<sup>2</sup> from the plain of Campo de Cartagena to the Mar Menor touristic area. Our research team  
54 had recently recorded and analysed atmospheric dusts using Owen gauges in the mining district of  
55 Cartagena-La Unión, and first results reported high contents of Zn, Pb, As, Cd and Sb (Blondet et al.,  
56 2019). Also, only Querol et al. (2008) have really taken this area into consideration for modelling  
57 spatial and temporal variations in airborne particulate matter across Spain during the 1999–2005  
58 period. However, the monitoring of air quality in mining sites has now become really important  
59 because TE emitted through mining activities in the atmosphere can inter in the pulmonary system  
60 and cause severe damages or chronic inflammatory and respiratory diseases (Boamponsem et al,  
61 2010; Goix et al., 2011; Wise et al., 2017).

62 So, this study aims to develop a biomonitoring of metals and metalloids present in the air in  
63 the mining district of La Unión-Cartagena, using epiphyte plants in order to propose efficient but  
64 easy-to-perform and not expensive tools to follow contamination dispersion in the atmosphere and  
65 later develop the right remediation techniques. In several sites, standard techniques for air  
66 monitoring were prohibitive in terms of cost (Carnevale et al., 2012; Schreck et al., 2016; Xing et al.,  
67 2019). Thus, biomonitoring methods using mosses, lichens and epiphytic bromeliads (i.e., *Tillandsia*  
68 *spp.*) have been largely developed (Ares et al., 2012, Bermudez et al., 2009, Szczepaniak and Biziuk,  
69 2003, Grangeon et al., 2012; Schreck et al., 2016). Among these plants, *Tillandsia spp.* are reported to  
70 be efficient due to their epidermal trichomes allowing the uptake of atmospheric water, minerals  
71 and organic nutrients (Martin et al., 2013; Schreck et al., 2016) and are therefore independent of the  
72 soil (Rodriguez et al., 2011; Martínez-Reséndiz et al., 2015).

73           The epiphyte *T. usneoides* has largely been studied as a good bioindicator of metallic  
74 contamination in several areas (Martínez-Carrillo et al., 2010; Pellegrini et al., 2014; Zheng et al.,  
75 2016). These *Bromeliaceae* plants are mainly found in the neotropic ecotone (from southern North  
76 America to southern South America, Techato et al. 2014). Their particularity comes from the fact that  
77 they adapt to arid and semi-arid climates (such as the Cartagena zone) and are resistant to water  
78 stress. Zheng et al. (2016) demonstrated that *Tillandsia usneoides* are excellent bioindicators that can  
79 deal with the abiotic stress associated with a long period of exposure to strontium. In addition, *T.*  
80 *usneoides* are recognised as indicators of effective atmospheric contamination for elements such as  
81 As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn and Zn (Zheng et al., 2016), suggesting their promising role in  
82 mining environments. Moreover, Pellegrini et al. (2014) also approve the use of *T. usneoides* as  
83 biomonitor of TE in urban areas of the Mediterranean basin, particularly in Italy.

84           However, even if the biomonitoring role of *Tillandsia usneoides* has been relatively well  
85 studied, to our knowledge, nothing has been reported concerning their use as tools for sources  
86 tracing and pollution dispersion through the air. In environmental studies, metal pollution is often  
87 assessed by comparing stable metal isotope ratios as signatures of point sources (Rosca et al., 2019).  
88 Their use allows us to improve our understanding of contaminant sources and pathways in the  
89 environment and especially in anthropogenic emissions from mines, industries, metallurgy (Cloquet  
90 et al., 2006; Araújo et al., 2018). Of special interest are the elements Pb and Zn, since they are  
91 important constituents of several man-made materials and especially extracted in this mining district  
92 of Cartagena-La Unión, and whose cycles are drastically altered by anthropogenic activities (Guéguen  
93 et al., 2012).

94           Thus, focusing on the area of the Cartagena-La Unión mining district, this study aims to  
95 investigate the potential use of *T. usneoides* as new and easy-to-perform tools to monitor  
96 atmospheric contents of metals and metalloids in mining environments. Experimentations will be  
97 performed in an area of 25 km<sup>2</sup> on 5 strategic sites including mining sources (the main tailing and a



98 rehabilitated zone) but also agricultural (Las Matildes) and inhabitant or touristic zones, such as La  
99 Union city or the Gorguel beach, located in the vicinity of the main tailing. We plan to use combined  
100 techniques (microscopic observations using SEM-EDX and elemental content determination by ICP-  
101 MS coupled to magnetic susceptibility measurements) in view of determining the kinetics of the  
102 atmospheric deposition and the potential contribution of abiotic factors such as pluviometry,  
103 agricultural inputs, etc. We also aim to better understand the mechanisms of transfer of TE in the  
104 environmental compartments and later through the plant. Finally, by investigating isotope ratios of  
105 Zn and Pb in epiphyte plants, we propose a source tracing in mining environments and to better  
106 understand the fate of these TE in mining environments and especially in the atmosphere.

107

## 108 **2. Materials and Methods**

### 109 **2.1 Study area description**

110 The investigated area of the mining district of Cartagena-La Unión is located in the Sierra  
111 Minera, an area of approximately 50 km<sup>2</sup> (SIGES, 2017), at 10 km from the city of Cartagena in South-  
112 Eastern Spain. Polymetallic ore deposits were created during the post-orogenic magmatic activity  
113 associated with a hydrothermal circulation (Garcia et al., 2008). Exploited ores consisted of silver  
114 galena (PbS, Ag), sphalerite (ZnS) and pyrite (FeS), as underlined by Alcolea-Rubio (2015) and Rico et  
115 al. (2009). This exploitation led then to the mobilisation of the following elements: As, Cu, Cd, Sb, Sn,  
116 Co, Ni and Cr (Alcolea-Rubio, 2015).

117 Five strategic sites that have been selected for air biomonitoring over an area of 25 km<sup>2</sup> in  
118 the mining district of La Unión (Figure 1 and Blondet et al., 2019): the urban area of La Unión, the  
119 main mining tailing zone called "Avenque Tailing", the coastal area corresponding to "Playa del  
120 Gorguel" and located near the Mediterranean Sea, an area of soil remediation by organic  
121 amendments "Santa Antonieta" and finally the agricultural area (corresponding to an old mining  
122 area) of "Las Matildes".

123 Atmospheric depositions (dry and wet) were also sampled using Owen gauges (NFX43-014  
124 standard, Navel et al., 2015) exposed for 1 year and collected every 6 months (from May 2017 to  
125 April 2018). This experiment was entirely described in Blondet et al. (2019).

126 In this area, climate is reported to be semi-arid, with a pluviometry of about 250 to 400 mm  
127 per year (Los Belones station), essentially concentrated during the spring and autumn seasons, with a  
128 mean annual temperature of 18°C (SIAM, 2017). Prevailing winds are facing South/Southwest  
129 directions, with a 190–200° azimuth (Figure 1).

130

## 131 **2.2 Experimental set-up of biomonitoring by *T. usneoides***

132 Several batches of *T. usneoides* (from the same initial plant) were installed at the 5 sites  
133 (Figure 1) in May 2017, using trunks or palm trees with small plastic cable ties, at 2.5 meters in height  
134 to better catch air pollution (see Figure SI-1 for more details). Each batch corresponds to 3 g of fresh  
135 material, placed in a nylon mesh bag, as already described in Schreck et al. (2016). In May 2017, 3  
136 mesh bags of *T. usneoides* were kept as control (no exposure in the mining district of Cartagena-La  
137 Unión), they were cultivated in a clean greenhouse during all the exposure experiment, and later  
138 analysed as well as the exposed ones. For exposed *T. usneoides*, one batch was taken every 2  
139 months, between July 2017 and April 2018, to follow the kinetics of deposition and potential  
140 absorption of atmospheric particles.

141 A washing procedure was also applied for several plants to determine the effects of the  
142 washing process and remove potential adherent particles present on the plant surfaces (Goix et al.,  
143 2013; Smodiš et al., 2004). Then, each plant was placed in ultrapure water, sonicated for 3 min and  
144 rinsed again. Then plants were dried at 40°C for 48 h and ground in an agate mortar in liquid N<sub>2</sub>.  
145 Ground plant samples were then dried again for 48 h and stored in polyethylene vials (Goix et al.,  
146 2013). The washing procedure allowed us to take off about 20% of the deposited particles (results  
147 not shown).

148

### 149 **2.3 Soil sampling**

150 In parallel to *T. usneoides* exposure, soil samples were collected in the vicinity of  
151 bioindicators installation. A composite sample of topsoil was collected, air-dried and sieved at 2 mm  
152 and ground with an agate bench ring mill.

153

### 154 **2.4 Morphological observations by SEM-EDX**

155 Environmental SEM-EDX measurements using a (FEG) JSM-7800F Prime (Jeol®) instrument  
156 equipped with EDX Detector were carried out to investigate the epiphyte morphology, trichome  
157 conformation and potential elemental distribution of the plant surface. Before observation analysis,  
158 *T. usneoides* plants were dried and fixed on a carbon substrate without any further preparation  
159 before analysis. The apparatus was operated in low-vacuum mode (~133 Pa) at 25 kV. Observations  
160 were performed on plant fragments exposed for 6 months, before and after washing process, to  
161 determine its effect on deposit lost.

162

### 163 **2.5 Elemental contents in plants and soils**

164 Dried samples (0.1 g of soil or plant) were digested using a mixture of bi-distilled and  
165 suprapur quality reagents. A solution of 5 mL bi-distilled HNO<sub>3</sub>, 1 mL H<sub>2</sub>O<sub>2</sub> and 200 µL HF was  
166 prepared and added to each sample and then left overnight. After addition of 5 mL bi-distilled HNO<sub>3</sub>,  
167 acid mineralisation was conducted on a Discover micro-waves apparatus from CEM® using 35 mL  
168 pressure vials in quartz tubes and adapted Teflon PFA liners and caps (during 10 min, 3 cycles until  
169 180°C). Afterwards, solutions were completely evaporated at 60°C on a hotplate and the dry residue  
170 was resuspended by adding 0.5 ml of HNO<sub>3</sub>.

171 After mineralisation, samples were diluted with bi-distilled water and filtered through a  
 172 0.22 µm cellulose acetate membrane. Filter membranes were checked to not have any influence on  
 173 metal contents in samples (results not shown).

174 All diluted samples (HNO<sub>3</sub> 0.37 N) were analysed using Inductively Coupled Plasma-Mass  
 175 Spectrometry (ICP-MS) analyses (Agilent® 7500 CE and iCAP Q Thermo Scientific®) in order to  
 176 determine trace metals concentration. Each batch of samples included a blank acid, a certified  
 177 reference material and some replicates. Limits of detection (LD) and quantification (LQ) were  
 178 calculated as 3 and 10 times the standard deviation (SD) of laboratory blank samples. There were 3  
 179 certified reference materials (from the National Institute of Standards and Technology and Institute  
 180 for Reference Materials and Measurements)—SRM 2709 “San Joaquin soil”, SRM 1515 “Apple  
 181 leaves” and BCR482 “Lichen”—used to validate the mineralisation methods. Recoveries of 79 to  
 182 100% were obtained for the different analysed elements.

183 Finally, enrichment factors (EF) can be calculated for elemental contents in *T. usneoides* from the  
 184 main Avenque Tailing site compared to the values of the geochemical background of the Region of  
 185 Murcia region (Martínez-Sánchez & Pérez-Sirvent, 2007; Alcolea-Rubio, 2015) according to the  
 186 Equation 1:

$$187 \quad \text{Eq (1)} \quad EF = \frac{[TE]_{T.usneoides}}{[TE]_{geochemicalbackgroundoftheRegionofMurcia}}$$

188

189

## 190 **2.6 Magnetic susceptibility**

191 Magnetic susceptibility was measured in the *T. usneoides* samples, as well as in soils collected  
 192 in the same areas, in order to estimate the concentration in magnetic particles. Magnetic  
 193 susceptibility measurements were performed with a KLY5 Kappabridge (AGICO) (400 A/m, 1220 Hz)  
 194 with a sensitivity of 2.10<sup>-8</sup> SI. In parallel of geochemical analyses, samples were put into 30 ml tubes  
 195 and their susceptibility was normalised by mass.

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197

**2.7 Zn and Pb isotopes study**

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**2.7.1 Zn isotopes**

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Zinc and Pb isotopes determination was performed on 4 different samples of *T. usneoides* and the associated atmospheric fallouts, collected from 4 of the investigated areas (Avenque Tailing, Playa del Gorguel, La Unión and Las Matildes) and also on 2 soils from the main tailing (Avenque tailing). All these analysed samples were collected in November 2017 to avoid all interferences due to temporal variations, according to the different environmental compartments. One more sample of *T. usneoides* collected in January 2018 from Avenque Tailing was also analysed to have a first idea of a potential seasonal effect.

To determine isotope fingerprints, Zn must be isolated from the rest of the sample matrix. A chromatography separation was carried out twice on aliquots of digested samples using AG MP-1 resin with Biorad® column and according to the protocol adapted from Maréchal et al. (1999) and Viers et al. (2015). In order to obtain great quality measures, the aliquots containing Zn (collected in the last step of the protocol and diluted in HNO<sub>3</sub> 0.05 N to obtain a final content of 300 µg L<sup>-1</sup>) were analysed by ICP-MS to check that the other elements are missing and that the mineralisation and separation processes were well-performed. Recoveries were between 96 and 106% and then considered as good. Purified solutions were spiked with Cu standard (NIST 976) for measurements on MC-ICP-MS (Neptune plus, Thermo Finnigan® at the Observatoire Midi-Pyrénées in Toulouse). Zn isotope ratios are expressed in δ<sup>66</sup>Zn (‰) relative to NIST 976 Cu standard, according to the Equation (2):

218

Eq (2)

$$\delta^{66}\text{Zn} = \left[ \frac{\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}}\right)_{\text{sample}}}{\left(\frac{^{66}\text{Zn}}{^{64}\text{Zn}}\right)_{\text{NIST976}}} - 1 \right] * 1000$$

219 If the internal precision on one measure is close to 10 ppm, a triplicate analysis of our samples would  
220 give an absolute error of 0.07‰.

221

### 222 **2.7.2 Pb isotopes**

223 Lead isotope ratios were directly measured by Element™ Series HR-ICP-MS from Thermo  
224 Fisher Scientific® at the Observatoire Midi-Pyrénées in Toulouse. Solutions were analysed at the  
225 concentration of 0.5 µg L<sup>-1</sup>. Standard SRM 981 was periodically measured (every 5 samples) to  
226 systematically correct for mass bias and instrument drift with time on both isotope ratios (Goix et al.,  
227 2015). Also, corrections were performed using the following ratios: <sup>208</sup>Pb/<sup>206</sup>Pb = 2.168 ± 0.001 and  
228 <sup>207</sup>Pb/<sup>206</sup>Pb = 0.915 ± 0.001. Standard deviations of 0.12 and 0.08% were then obtained for the ratios  
229 <sup>208</sup>Pb/<sup>206</sup>Pb and <sup>207</sup>Pb/<sup>206</sup>Pb, respectively.

230

### 231 **2.8 Statistical analyses**

232 Two types of statistical analyses were carried out. The first consisted of studying the  
233 temporal evolution of the concentration of chemical elements from the reference point constituted  
234 by the month of May 2017, the date on which the plants were installed. A decentred principal  
235 component analysis was adapted to this type of data (Noy-Meir 1973). The centring was not  
236 performed as in a conventional PCA with respect to the average but with respect to a reference  
237 common to all samples, corresponding in this experiment to the first date. The missing data  
238 encountered for magnetic susceptibility were not completed by the mean of the variables but by its  
239 reference value, i.e. its value taken at the beginning of the experiment.

240 The second analysis compared the chemical element concentrations of plants in April 2018  
241 with the concentrations of elements stored in the soil and accumulated in the air during the  
242 experiment. A PLS2 (Partial Least Square) was used to explain plant chemical element concentrations  
243 from soil concentrations or those accumulated in the air (Geladi and Kowlaski 1986). The missing

244 data (Santa Antonieta station in January 2018 and La Union magnetic susceptibility in September  
245 2017 and January 2018) were replaced by the average of the corresponding variables.

246 Calculations were performed using ADE-4 and plsdepot, CRAN packages (Chessel et al. 2004,  
247 Gaston Sanchez 2012).

248

249

### 250 **3. Results**

#### 251 **3.1 SEM-EDX observations: atmospheric deposits on *T. usneoides***

252 The SEM-EDX observation (Figure 2) of a sample of a washed *Tillandsia usneoides* (collected  
253 in November 2017 in the Avenque Tailing area) has shown the plant morphology and especially the  
254 trichome's structure in shields, in order to better uptake nutrients from the atmosphere (Figure 2-A).  
255 Deposited particles from the mining site are homogenously distributed on the plant surface.  
256 Chemical spectra analyses, combined to our previous results of X-ray diffraction (XRD) on  
257 atmospheric particles collected by Owen gauges (Blondet et al., 2019), suggest that the main  
258 minerals observed are calcite ( $\text{CaCO}_3$ ) and gypsum ( $\text{CaSO}_4$ ), but also halite ( $\text{NaCl}$ ), clay minerals (Al, Si,  
259 K) and quartz ( $\text{SiO}_2$ ). Other spectra, composed by Fe and S peaks, also seem to highlight the presence  
260 of pyrite ( $\text{FeS}_2$ ), also observed in the corresponding atmospheric fallouts (Blondet et al., 2019).  
261 Moreover, some spectra show the presence of particles of Zn, Cu, C and O that could correspond to  
262 smithsonite minerals ( $(\text{Zn, Cu})\text{CO}_3$ ). Finally, traces of Pb and Ti are also observed in other spectra  
263 (not shown), highlighting the contamination by mining deposits.

264

#### 265 **3.2 Elemental contents in soils and plants**

##### 266 **3.2.1 Soils**

267 Elemental contents in soils of the different areas are reported in Table 1. Results showed that  
268 some elements, such as Cr, Co and Ni have concentrations in the mining site that are perfectly in  
269 accordance with the geochemical background of the region (Martínez-Sánchez and Pérez-Sirvent,  
270 2007). By contrast, the other ones can be directly linked to an anthropogenic contamination of the  
271 site, especially Zn, Pb, As, Cd, Sb and Cu that show abnormally high concentrations in the sampled  
272 soils (Table 1). Globally, the 5 investigated sites of the mining district of Cartagena-La Unión are  
273 contaminated in different elements (Cu, Zn, As, Cd, Sn, Sb and Pb), with a level of contamination  
274 following the order: Avenque tailing > Las Matildes  $\approx$  Playa del Gorguel > Santa Antonieta > La Unión  
275 for the main considered elements.

276 High contents of TE are reported in the topsoil of Avenque tailing (the main tailing of this old  
277 mine) that are largely higher than the geochemical background of the Region of Murcia in Spain  
278 (Martínez-Sánchez and Pérez-Sirvent, 2007). For example, in this site, the concentrations of Pb and  
279 Zn reached, respectively,  $14,770.39 \pm 659.23$  and  $10,345.08 \pm 336.68$  ppm, whereas these values are  
280 reported to be about 3–10 and 16–55 ppm for Pb and Zn, respectively, in the geochemical  
281 background of the Region of Murcia (Table 1). Another site that appeared as widely contaminated is  
282 the agricultural zone of Las Matildes showing high contents in Pb, Zn but also Cu (respectively  
283  $36,019.35 \pm 801.12$ ,  $4,352.43 \pm 15.23$  and  $232.78 \pm 4.65$ ). By contrast, in this area, As contents are in  
284 accordance with the geochemical background of the site (Table 1). In the remediated site of Santa  
285 Antonieta, concentrations seemed to be attenuated in comparison with the main tailing but are still  
286 high compared to the geochemical background (Table 1).

287

### 288 **3.2.2 Plants**

289 Figure 3 showed the elemental contents of Zn, Pb, As and Cd in *T. usneoides* from the various  
290 investigated sites. Only these 4 elements were represented here because they were the most  
291 significant in terms of plant contamination, but also because they were the most toxic emitted by



292 mining extraction activities. All the results correspond to the mean value ( $\pm$  standard error SE) of 3  
293 replicates. High concentrations in TE are observed, mainly for the *T. usneoides* from the old mining  
294 sites of Avenque Tailing, Santa Antonieta and Las Matildes. Their concentrations recorded  
295 significantly exceed the geochemical background of soils in the Region of Murcia (Martínez-Sánchez  
296 & Pérez-Sirvent, 2007; Alcolea-Rubio, 2015) and globally increase over time. Results of mean  
297 enrichment factors (EF) for Avenque Tailing show that epiphyte plants are significantly enriched in Sb  
298 (EF=1.7), As (EF=2.4), Cd (EF= 7.9), Zn (EF=20.5) and Pb (EF= 33.6). Only Cu does not exhibit a  
299 significant enrichment factor (EF=0.51). In July 2017, we observed a strong increase in Zn and Cd  
300 contents in *T. usneoides* from Avenque Tailing, maybe in relation with the lack of precipitations (see  
301 *Discussion section for more information*). The sites of Playa del Gorguel and La Unión have  
302 concentrations that are generally constant over time, and very close to the geochemical  
303 backgrounds. The area of Las Matildes, an old mining site with large agricultural zones, showed high  
304 contents in Cu.

305

### 306 **3.3 Magnetic susceptibility of soils and epiphyte plants**

307 Results concerning magnetic susceptibility of soil and *T. usneoides* samples are respectively  
308 reported in Table 1 and Figure 3.

309 In soils, values of magnetic susceptibility range  $5.4283E^{-06}$  to  $4.1046E^{-05} \text{ m}^3 \cdot \text{kg}^{-1}$  for the sites of  
310 Avenque tailing and Playa del Gorguel, respectively. It is interesting to notice that the lowest values  
311 are recorded for the mining site (Avenque Tailing) and the coastal area corresponding to "Playa del  
312 Gorguel", whose magnetic susceptibility values are  $5.4283E^{-06}$  and  $1.6519E^{-05} \text{ m}^3 \cdot \text{kg}^{-1}$ , respectively  
313 (Table 1). By contrast, the highest values were measured in the rehabilitated and agricultural areas  
314 (Santa Antonieta and Las Matildes).

315 The epiphyte plants display magnetic susceptibility values that increase over time, from  
316  $2.6766E^{-08}$  (for playa del Gorguel, in July 2017) to  $2.4902E^{-07} \text{ m}^3 \cdot \text{kg}^{-1}$  (for Santa Antonieta in November

317 2017) (Figure 3). As already observed for soil samples, the highest values are reported for Santa  
318 Antonieta and Las Matildes sites. In these two sites, variations according to time of exposure are not  
319 linear but quite similar, and show a pic in magnetic susceptibility observed in November 2017. For  
320 the 3 other sites (Avenque Tailing, Playa del Gorguel and la Unión), magnetic susceptibility values  
321 increase slowly with time of exposure (Figure 3).

322

### 323 3.4 Zn and Pb isotope ratios in environmental compartments

324 Results of isotope ratios (for Zn and Pb) are reported in Table 2. Figure 4 also showed the  
325 mean value of  $\delta^{66}\text{Zn}$  from various samples of plants (*T. usneoides*), soils and atmospheric fallouts in  
326 relation with Zn concentration. The mean  $\delta^{66}\text{Zn}$  value obtained by Sonke et al. (2008) for the analysis  
327 of 29 sphalerites [(Zn, Fe)S] from 10 different mining sites is also reported in Figure 4. Results  
328 highlighted that the 2 analysed soils show values (-0.35 and -0.40 ‰) far lower than those of Zn  
329 sulphurs. Atmospheric fallouts from Owen gauges evidenced high isotope variability (from -0.23 to -  
330 0.56‰). *Tillandsia usneoides* samples also showed a same variability in  $\delta^{66}\text{Zn}$  value (from -0.25 to -  
331 0.50‰) for the 4 analysed samples.

332 Table 2 clearly shows that  $\delta^{66}\text{Zn}$  values are quite the same between the 2 plants from  
333 Avenque Tailing, collected in November 2017 (-0.25‰) and in January 2018 (-0.21‰). Isotopes ratios  
334 of Pb vary between 2.084 and 2.091 and, 1.187 and 1.192 for the  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios,  
335 respectively (Table 2). Since Pb isotope ratios are not modified by high temperature processes, they  
336 must have the fingerprint of Pb extracted during the industrial history of this mining site of  
337 Cartagena-La Unión.

338

## 339 4. Discussion

340 **4.1 *T. usneoides* as bioindicators of atmospheric contents of TE in the mining district of**  
341 **Cartagena- La Unión**

342 By comparing the metal and metalloid contents in *T. usneoides* for the different investigated  
343 areas, it appears that the urban zone of La Unión and the beach "Playa del Gorguel" shows low  
344 contents in toxic metallic compounds. Their metal content values are closed to the geochemical  
345 background values reported for each element [from Martínez-Sánchez & Pérez-Sirvent (2007) and  
346 Alcolea-Rubio (2015)], suggesting that the atmosphere is not enriched in TE. Moreover, the  
347 distribution of TE among the various studied sites are globally in accordance with the results  
348 previously obtained for atmospheric dust deposition in Owen gauges (Blondet et al., 2019), even if no  
349 strict correlation could be calculated between the results of Owen gauges and those of *T. usneoides*  
350 for TE contents. There are some differences in the involved processes by the 2 methods of  
351 monitoring: gauges collect the general fallouts, whereas plants react with selective accumulation of  
352 cations as highlighted by Impens et al. (1980). By the way, the similitudes in contamination profiles  
353 between the different sites for TE content in *T. usneoides* and TE accumulated in atmospheric dusts  
354 from Owen gauges suggest that *T. usneoides* could be relevant bioindicators of atmospheric contents  
355 of TE in this old mining area. This statement was already highlighted by Techado et al. (2014) for  
356 various contaminated sites over the world. *Tillandsia* spp., and especially *T. usneoides*, has proved to  
357 be an efficient atmospheric accumulator of Hg, Cd, Pb, Ni, Cu, Cr, C and Zn by the mechanism of  
358 phytoremediation, as suggested by Brighigna et al. (1997) in Costa Rica, Vianna et al. (2011) in 2  
359 Brazilian metropolitan areas or Malm et al. (1998) in the gold trade centre city, Amazon, Brazil.

360 The TE enrichment factors calculated in *T. usneoides* from the main Avenque Tailing site are  
361 consistent with those reported in soils of mine tailings, as demonstrated by Alcolea-Rubio (2015) in  
362 this area. Therefore *T. usneoides* records the atmospheric contamination brought by mine tailings in  
363 their vicinity. Only Cu does not exhibit a significant enrichment factor (EF=0.51), and it is also not  
364 highly concentrated in atmospheric dusts collected by Owen gauges. A strong enrichment in Zn, As

365 and Sb is also noted by comparing the concentrations obtained in our *T. usneoides* with those of  
366 Figueiredo et al. (2004) placed in industrial sites and under high traffic in Sao Paulo (Brazil), but also  
367 with those of Sánchez-Chardi (2016) who exposed different *Tillandsia* spp. in the urban environment  
368 of Asunción (Paraguay). Indeed, the concentration in Zn (1024 ppm) of *T. usneoides* collected in  
369 November in Avenque Tailing widely exceeds those from the high traffic zones (54 to 102 ppm) and  
370 industrial sites (58 to 134 ppm) described by Figueiredo et al. (2004). However, those collected at the  
371 same time in La Unión (81 ppm) are in the same order of magnitude. The same observation goes for  
372 Sb (with 0.44 to 0.81, 0.2 to 0.59, 0.51 and 3.24 ppm at high traffic sites, industrial sites, La Unión and  
373 Avenque Tailing, respectively). The concentrations recorded for As in industrial sites and high traffic  
374 areas in Sao Paulo (between 0.11 and 0.28 ppm) are lower than those measured at La Unión (2 ppm)  
375 and Avenque Tailing (22 ppm), suggesting really high contents in As in our studied area. Finally, by  
376 comparing these results with those obtained recently by our research team in the urban mining area  
377 of Oruro in Bolivia (Goix et al., 2013; Schreck et al., 2016), we noticed that the epiphyte plants  
378 exposed in the old mining site of Cartagena-La Unión recorded a high level of TE in their tissues,  
379 especially for Cd, Zn and Pb (that are almost 10 times higher than in Oruro), suggesting a strong  
380 influence of the mining area but also differences bring by plant species. Only As is accumulated in the  
381 plants at quite the same range (Schreck et al., 2016).

382 Figure 5, a graphical summary of the decentred PCA, shows that only the first 2 factors are  
383 interpretable. The first factor is a size factor: When a station has a high concentration for 1 chemical  
384 element, it also has a high concentration for all others. A concentration gradient was observed from  
385 the Avenque Tailing station, the most polluted, to La Union, the least polluted, as already suggested  
386 by TE contents in epiphyte plants.

387 The representation of factor 1 as a time curve (Figure SI-2) clearly summarises the evolution  
388 of concentrations for each station. The factor map of the samples, labelled by station, shows a higher  
389 sensitivity to contamination at the Avenque Amont, Santa Antonieta and Las Matildes stations (sites  
390 of former mining activities) than at the Avenque Aval and La Unión stations. The stations, Avenque

391 Tailing and Santa Antonieta, located on heaps, regularly accumulated chemical elements throughout  
392 the experiment. The Union appears as not polluted by the studied metal(loid)s. Playa del Gorgel is  
393 only slightly so at the end of the experiment. The pollution of Las Matildes is fluctuating. Thus,  
394 contaminant concentration appears to be directly related to wind erosion of slag heaps in the vicinity  
395 of *T. usneoides*. These results confirm that *T. usneoides* correctly records variations in concentrations  
396 due to the remobilisation of dusts in the vicinity of mining tailings, even old ones.

397 Contrary to wind, rainfall seems to add no impact on TE contents in *T. usneoides* as suggested  
398 by statistical analyses (results not shown), even if an influence could be suspected at first sight.  
399 Nevertheless, very low cumulative rainfall (about 185 mm) was observed during all the exposure  
400 period of one year.

401

#### 402 **4.2 From site contamination to air quality: suggested mechanisms of TE transfer in the** 403 **environment and their uptake by *T. usneoides***

404 Environmental magnetism could be an effective tool to monitor a polluted area (see Maher,  
405 2009; Mariyanto et al., 2019; Martin et al., 2018; Petrovsky et al., 2000), being a fast and cost-  
406 effective method. Here, results of magnetic susceptibility in soils and in plants have shown that there  
407 was no correlation between Pb or Fe concentrations and magnetic susceptibility ( $R^2=0.41$  for  
408 magnetic susceptibility = f ([Fe]) in *T. usneoides* of the experiment, Figure SI-3 in Supplementary  
409 Information).

410 In this mining district, exploited ores consisted of silver galena, sphalerite and pyrite (Alcolea-  
411 Rubio, 2015; Rico et al., 2009), suggesting that sulphurs are the main compounds. Fe in the form of  
412 pyrite induces only a weak magnetisation (Dunlop and Ozdemir, 1991). Then, in Avenque Tailing,  
413 magnetic susceptibility is very low in soils due to high contents of pyrite. By contrast, the higher  
414 levels of magnetic susceptibility recorded in the old mining site of Las Matildes (agricultural area) and  
415 the rehabilitated site of Santa Antonieta suggests either a process of mineral re-oxidation of pyrite

416 into magnetite or the presence of primary magnetite in the exploited deposits (Oen et al., 1975;  
417 Manteca Martínez and Ovejero Zapino, 1992). Near the Avenque area, Gómez-García et al. (2015)  
418 have studied the infilling process of the Portman Bay (Murcia, Spain) due to direct mine waste  
419 discharge into the sea. They acquired rock magnetic parameters, including magnetic susceptibility on  
420 both minerals deposits and the sand filling the bay. Magnetic parameters indicated high  
421 concentrations (up to 28%) of magnetite in the sand. Moreover, this sand displayed a direct  
422 relationship between magnetite content and the heavy metals Pb, Cu and As. Samples taken at the  
423 mining site gave lower magnetic susceptibility values between  $-6.64 \times 10^{-7}$  and  $6.35 \times 10^{-5} \text{ m}^3 \cdot \text{kg}^{-1}$ ,  
424 indicating a magnetite concentration significantly lower than in the sand filling the Portman Bay. This  
425 indicates that oxidation affected the primary mineralogy.

426 In the Las Matildes and Santa Antonieta, higher magnetic susceptibility values, hence higher  
427 contents in magnetite could be explained by the rehabilitation of the old tailings in these 2 areas by  
428 the use of organic matter amendments, irrigation, soil alteration and plant culture (Moreno-Barriga  
429 et al., 2017). These processes induce an oxidation of the primary pyrite.

430 Magnetic measurements of *Tillandsia spp.* have already been reported by 2 studies.  
431 Castaneda-Miranda et al. (2016) and Mejía-Echeverry et al. (2018) used *T. recurvata* growing  
432 naturally in trees to monitor air pollution in Mexico and Columbia. On unwashed plants, they  
433 obtained values between  $-6.64 \times 10^{-7}$  and  $372 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$  corresponding to residential and heavy  
434 traffic area, respectively. Since the time integrated is unknown in these studies, it is not possible to  
435 directly compare these values with those obtained here, the time being certainly longer than the 6  
436 months sampled in our case. Moreover, in our study, *T. usneoides* were washed prior the  
437 measurements. Then, we can assume that our values of magnetic susceptibilities up to  $2.49 \times 10^{-7}$ ,  
438 especially after 6 months of exposure, are significant.

439 As for the soil samples, the variability in magnetic susceptibility in epiphyte plants could  
440 certainly be explained by mineral transformations (changes in chemical forms of TE, redox state,

441 organic matter complexation, etc.) when they are transported by soil erosion and dust remobilisation  
442 into the atmosphere. Pyrite is altered and reoxidised into the atmosphere (Blondet et al., 2019). The  
443 high signals of magnetic susceptibility in *T. usneoides* from Las Matildes and Santa Antonieta are  
444 certainly explained by wind erosion of these restored and cultivated environment. In the same way,  
445 the magnetic signal for the site “playa del Gorguel” (very low) show that the main influence is from  
446 Avenque Tailing, due to wind erosion of pyrite, as previously suggested by the wind rose and the  
447 main wind directions shown in the Figure 1. By contrast, the urban area of La Unión seems to be  
448 rather protected from wind erosion from Avenque Tailing, as suggested results of TE concentrations  
449 and magnetic susceptibility of *T. usneoides*, as well as the human risk assessment proposed by  
450 Blondet et al. (2019).

451 Copper pollution mainly affects the Las Matildes station, with a peak of contamination in  
452 November (211 ppm). The presence of citrus fruits that are treated with Cu-based plant protection  
453 products could explain this pollution. Indeed, one of the hypotheses put forward to explain this  
454 observation is that the agricultural site could be subject to a Cu fungicide treatment or land  
455 preparation at this time. Copper is widely applied in the Region of Murcia according to Dqagro (2015)  
456 for the treatment of fruits (e.g. citrus fruits in particular but also peaches, nectarines, plums, melons,  
457 apricots) and vegetables (e.g. zucchinis, onions, olives, artichokes, cauliflower, broccoli and  
458 potatoes). There are 2 treatments applied, in spring and autumn.

459 The time curve of factor 2 shows a pollution of Las Maltides by Cu in November 2017 and  
460 April 2018, in agreement with Dqagro (2015), and a pollution of Playa del Gorguel in April 2018.

461 On figure 6, graphics of the PLS2, the explained percentages of variance, indicate that only  
462 one factor is sufficient to interpret the structure. There is no simple relationship between the  
463 concentrations of chemical elements in plants and those in the soil. On the other hand, plant  
464 concentrations can be explained by those of Owen gauges [also discussed in Blondet et al. (2019)],  
465 with the exception of Cu and Ni. Avenque Tailing plants have the highest concentrations of TE, except

466 for Cu and to a lesser extent Ni, although these 2 elements are present in Owen gauges. Then, we  
467 can ask if these last 2 elements could be subject to preferential accumulation or exclusion, linked to  
468 an active mechanism performed by the epiphyte plants. This hypothesis was already suggested by  
469 Wannaz et al. (2011) highlighting that concentrations obtained in the studied plants (*T. capillaris*) are  
470 higher than those found in comparative passive biomonitoring studies, showing then, a selectivity in  
471 the way of metals accumulation. This phenomenon of high contents in elements such as Cu and Zn  
472 can also result according to Wannaz et al. (2011) in growth inhibition and toxicity symptoms.  
473 Moreover, as previously reported by Shahid et al. (2017), various mechanisms of metal uptake could  
474 occur through the plant, depending on plant species and morphological characteristics (stomatal  
475 index, leaf morphology, cuticular structure, leaf surface area, trichome density) of course (Barber et  
476 al., 2004, Schreck et al., 2012) but also metal chemical form, content, granulometry and solubility  
477 (Natasha et al., 2019; Rossi et al., 2019). Several authors (Schreck et al., 2012; Shahid et al., 2017)  
478 highlight the fact that metals such as Pb, Co, Mn but mostly Cu could cross the cuticle of aerial organs  
479 after dissolution or penetrate by the stomatal pathways in case of small particles, whereas larger  
480 particles (1.1  $\mu\text{m}$ ) were unable to penetrate through stomata openings (Eichert et al., 2008; Rai et al.,  
481 2019). But metal speciation is considered as the main parameter governing biogeochemical  
482 behaviour of metals and metalloids at the plant surface (Shahid et al., 2017). Thus, some  
483 explanations could be given in our study case for Cu uptake and accumulation, which is variable  
484 depending on the different studied sites in the mining district of Cartagena-La Unión. In Avenque  
485 Tailing, an active mechanism of Cu inclusion through the plant by the stomatal pathway could be  
486 envisaged: Cu-enriched particles from mineral ores and tailings are deposited on the leaf surface, as  
487 observed in the SEM-EDX images (Figure 2 C&D). They can enter via the stomata openings. In case of  
488 an arid climate, as in summer and autumn 2017, the *T. usneoides* closes its stomata and Cu  
489 bioaccumulation is limited by this active process. But, by contrast, in the Las Matildes area, Cu  
490 contents in the atmosphere are higher than in the other sites and also relatively high in comparison  
491 to other elements [see results of Cu contents in Owen gauges—Figure 5 and data in Blondet et al.



492 (2019)]. Moreover, its speciation is certainly more soluble due to fungicide application in the  
493 cultivated areas at the vicinity of the *T. usneoides* exposure site. Copper uptake through the plant  
494 could then be envisaged by another mechanism involving metal dissolution and cuticle crossing  
495 (passive mechanism). Finally, our results for Cu could enhance the hypothesis that uptake  
496 mechanism occurring for plants in the atmosphere-plant pathways are highly governed by metal  
497 chemical form, redox state and maybe complexation, and can vary depending on abiotic conditions  
498 and human activities.

499

500

### 501 **4.3 Isotopy and air biomonitoring: new insights for source tracing and mapping**

502 The atmospheric fallouts from Owen gauges were collected after 6 months of deposit (from  
503 05/2017 to 11/2017). We can then assume that they deliver an average value (without granulometric  
504 separation) of this period. In the same way, the values of Zn isotopes ratios for *T. usneoides* come  
505 from the plant samples collected in November 2017 and also exposed over 6 months.

506 Firstly, we can observe that Zn isotopes ratios of the soils from the Avenque main tailing are  
507 significantly more negative than those of the Zn primary ores (Sonke et al., 2008, Gelly et al., 2019).  
508 Due to the history of mining and the industrial processes operated in this site over more than 150  
509 years, it is difficult to provide a direct explanation for this difference in isotope composition.  
510 Nevertheless, it is well known that high temperature metallurgical processes induce Zn isotope  
511 fractionation. Recent works included in the review of Yin et al. (2016) have shown that during these  
512 processes, an enrichment of atmospheric emissions in light isotopes can occur (-0.66 to 0.21 ‰),  
513 whereas smelting and slag residues can report heavier isotope signatures (0.13 to 1.49 ‰). The  
514 negative isotope values obtained for the 2 Avenque tailing soils and their very high concentrations in  
515 Zn suggest that these soils were certainly impacted by the fallouts coming from high temperature  
516 processes. This hypothesis is also supported by the recent work of Gelly et al. (2019) on soils sampled  
517 around the old smelter of Escalette (South-East, France). Topsoils around this site have negative

518 signatures because of the impact of the smelter activity. They show values at  $-0.70 \pm 0.04$  ‰,  
519 whereas the geological background is about  $-0.15 \pm 0.02$  ‰.

520 Another important result is the similarity of Zn isotope compositions existing between  
521 atmospheric particles ( $-0.23$  to  $-0.56$  ‰) and *T. usneoides* ( $-0.25$  to  $-0.50$  ‰). Considering the  
522 analytical errors, we find that Pb isotope ratios are also quite similar for *T. usneoides* and  
523 atmospheric fallouts from Owen gauges (Table 2). Moreover, these observations are consistent with  
524 the literature data for ores from this Cartagena mining area (Stos-Gale et al., 1995, Rosman et al.,  
525 1997). Indeed, this result suggests that the epiphyte plants signature is certainly imposed by  
526 deposition of atmospheric particles on these plants and maybe their assimilation in plant tissues  
527 after soil erosion, mineral lixiviation and oxidation, dust mobilisation (due to wind) and then  
528 atmospheric deposition and contamination. It appears thus that at first order Zn (and Pb in a lesser  
529 extend) isotope signatures of *T. usneoides* are good tracers of the origin of the contamination. This  
530 observation provides then new insights using Zn isotope ratios for a better pollution distribution  
531 characterisation in various and contrasted sites and could also allow a better determination in  
532 priorities for mine rehabilitation (in terms of pollution dispersion and the risks involved for natural  
533 protected zones and obviously for human health, etc.).

534 Finally, to go deeper, some differences can be observed in Zn isotope compositions for the  
535 same exposure area between atmospheric particles and the associated epiphyte plants. Given our  
536 quite limited data, it seems premature to offer solid explanations for these differences. But some  
537 hypotheses can nevertheless be proposed: effect of particles granulometry, metal solubility and  
538 speciation, and also mechanisms of particle uptake within the *Tillandsia usneoides*, as previously  
539 suggested in the section 4.2 for Cu for example and already reported by Schreck et al. (2016).

540

## 541 5. Conclusion

542 Focusing on the area of the Cartagena-La Unión mining district, this study investigated the  
543 role of *T. usneoides* as a new and easy-to-perform tool to monitor TE contents in the air from  
544 environments influenced by anthropogenic activities.

545 Main results highlighted the influence of local and abiotic factors (TE contents and chemical  
546 forms with regards to the geochemical background of the region of Murcia, wind direction,  
547 anthropogenic activities in the vicinity) on kinetic of the atmospheric depositions at the leaf surface.  
548 Isotope ratios of Zn and Pb on epiphyte plants allow us to propose new insights for sources tracing  
549 and help, as well as magnetic susceptibility and statistical analyses, to better understand the TE  
550 uptake by plants through atmospheric pathways.

551 The chemical form of TE in the atmosphere seems to highly govern its uptake and  
552 bioaccumulation in plant tissues, certainly by acting on bioavailability properties. Then it may induce  
553 severe consequences on environment contamination but also risks for human health. Further studies  
554 on TE speciation and isotope composition in the different environmental compartments are in  
555 progress to better understand the biogeochemical transformations and the mechanisms occurring in  
556 mining environments and especially in the epiphyte plants phyllosphere.

557

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**FIGURES**

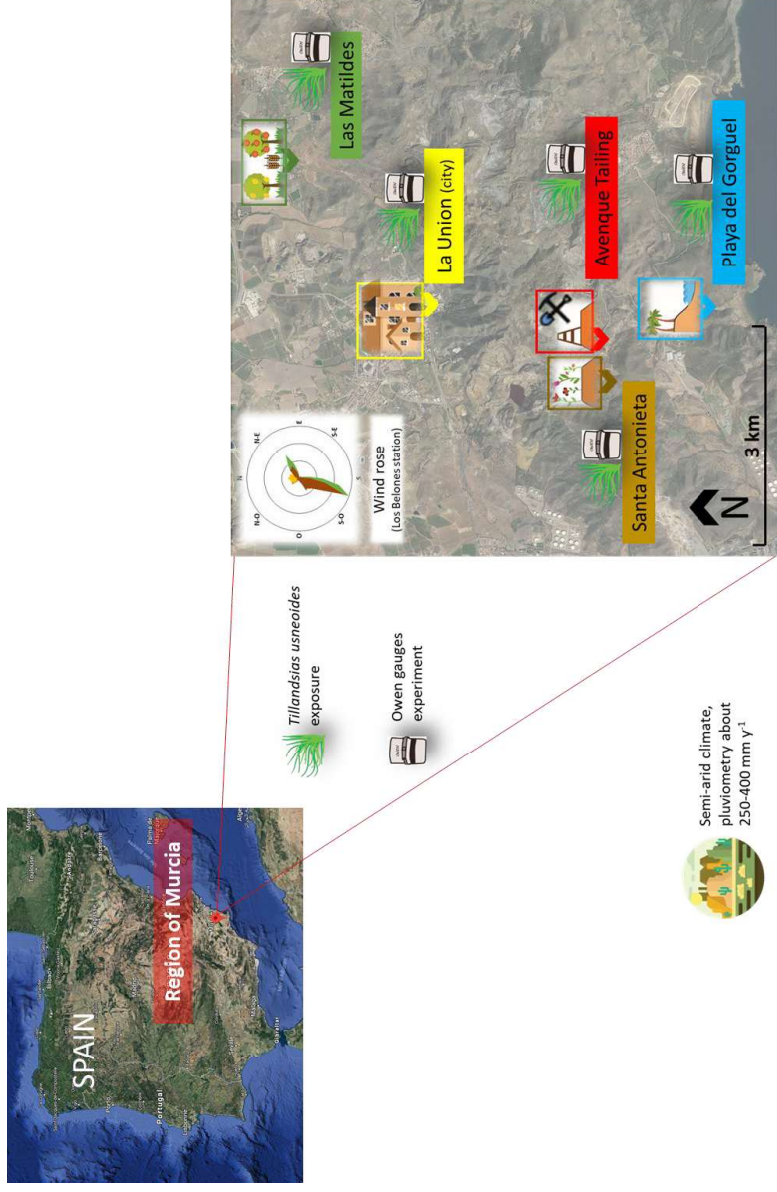


Figure 1. Air quality biomonitoring in 5 strategic sites of the mining district of Cartagena-La Unión (map from Google Earth, 2018)

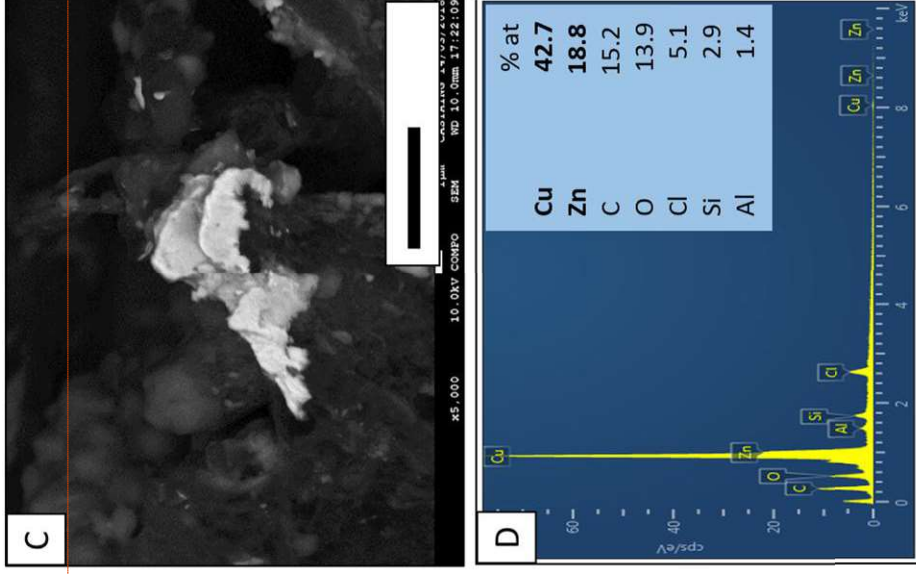
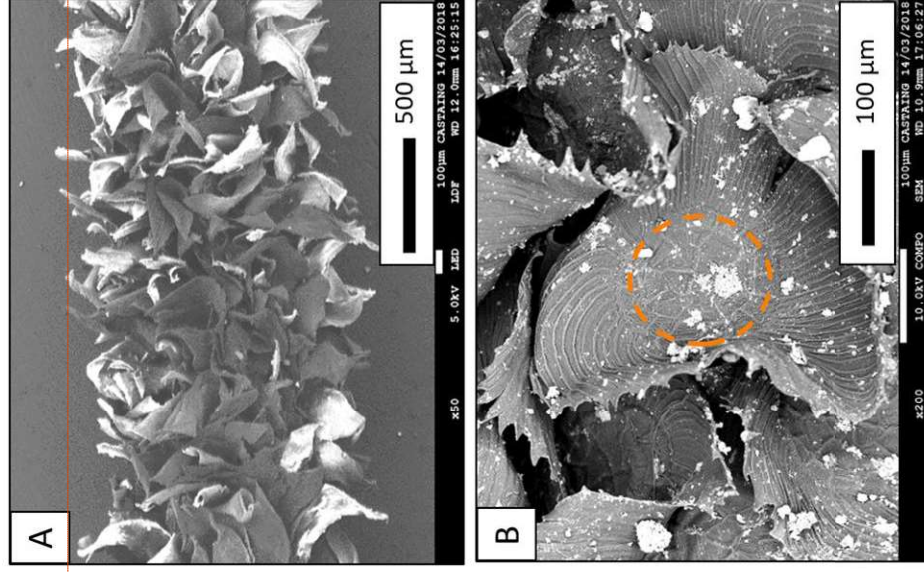


Figure 2. *Tillandsia usneoides* from Avenque tailing area observed by SEM-EDX (after washing).  
A) General observation of the plant structure; B) Atmospheric deposits on *T. usneoides* surface and stomata structure in the middle of a trichome shield (surrounded in orange); C&D) Atmospheric particle (enriched in Zn and Cu) observed in the plant surface and its EDX spectra.

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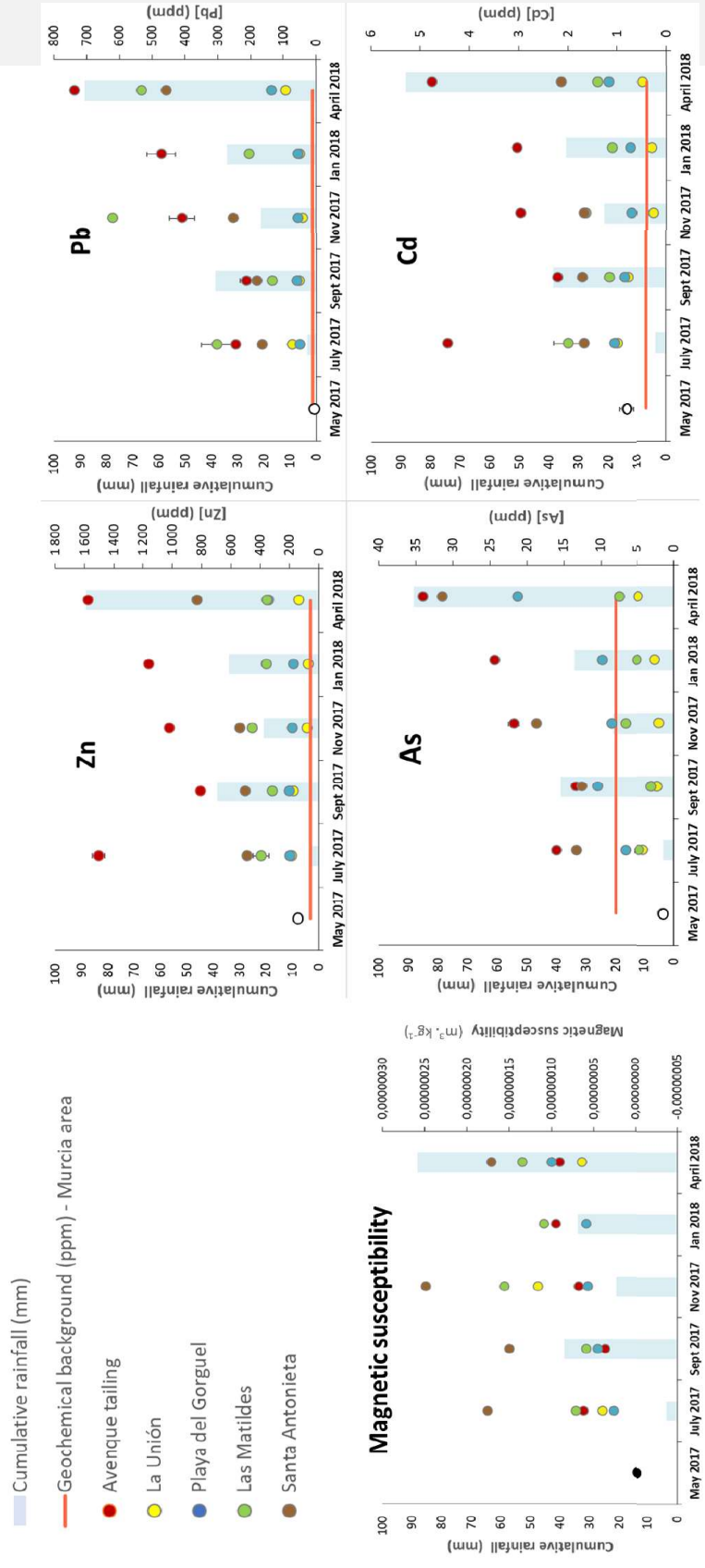


Figure 3. Element (Zn, Pb, As and Cd) contents (ppm) and magnetic susceptibility ( $\text{m}^3 \text{kg}^{-1}$ ) of *T. usneoides* tissues for the five monitored sites and according to cumulative rainfall (mm) during the experiment (may 2017 -in black whatever the site- to April 2018). Geochemical background values are reported for each element (orange line) and come from *Martínez-Sánchez & Pérez-Sirvent (2007)* and *Alcolea (2015)*.

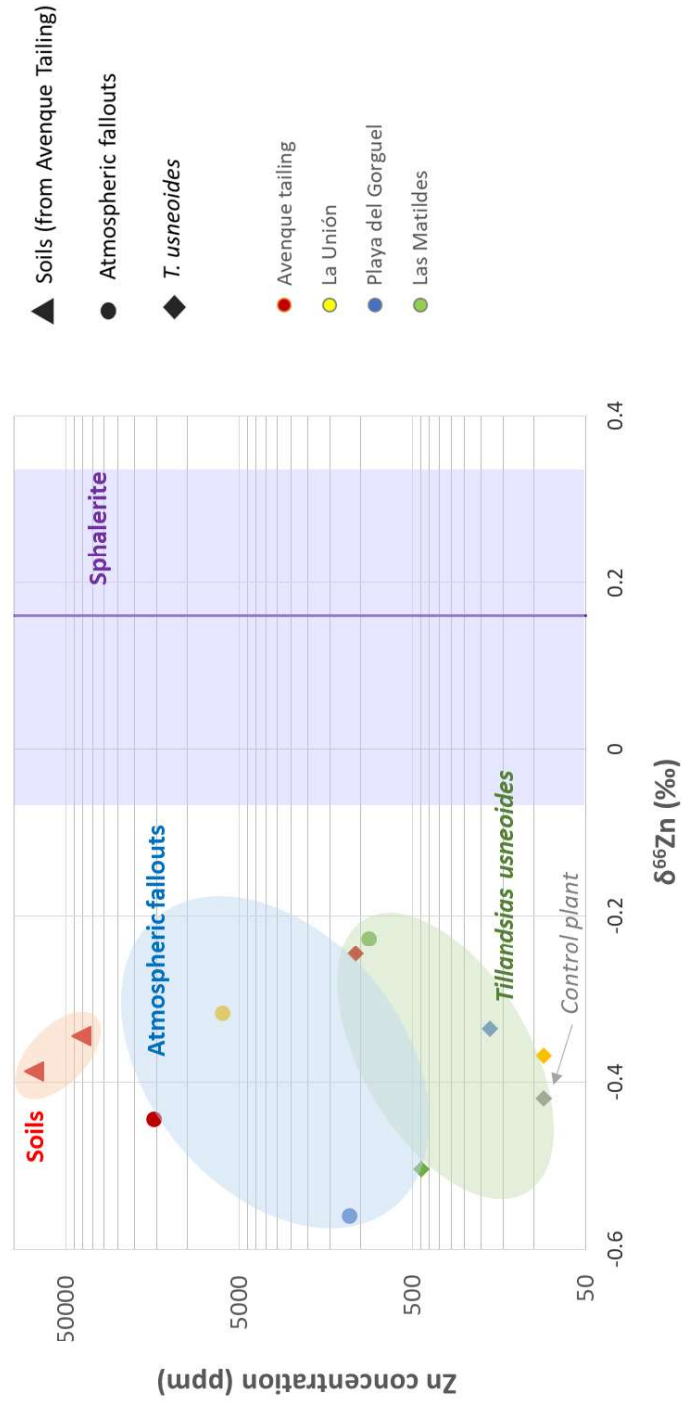


Figure 4. Isotope composition ( $\delta^{66}\text{Zn}$ ) and Zn concentrations of *Tillandsia usneoides*, atmospheric fallouts and soils from the *Avenque Tailing*, compared to 29 sphalerites [(Zn, Fe)S] from 10 different mining sites from Sonke et al. (2008). The control epiphyte plant (from May 2017) is reported in grey in the diagram.

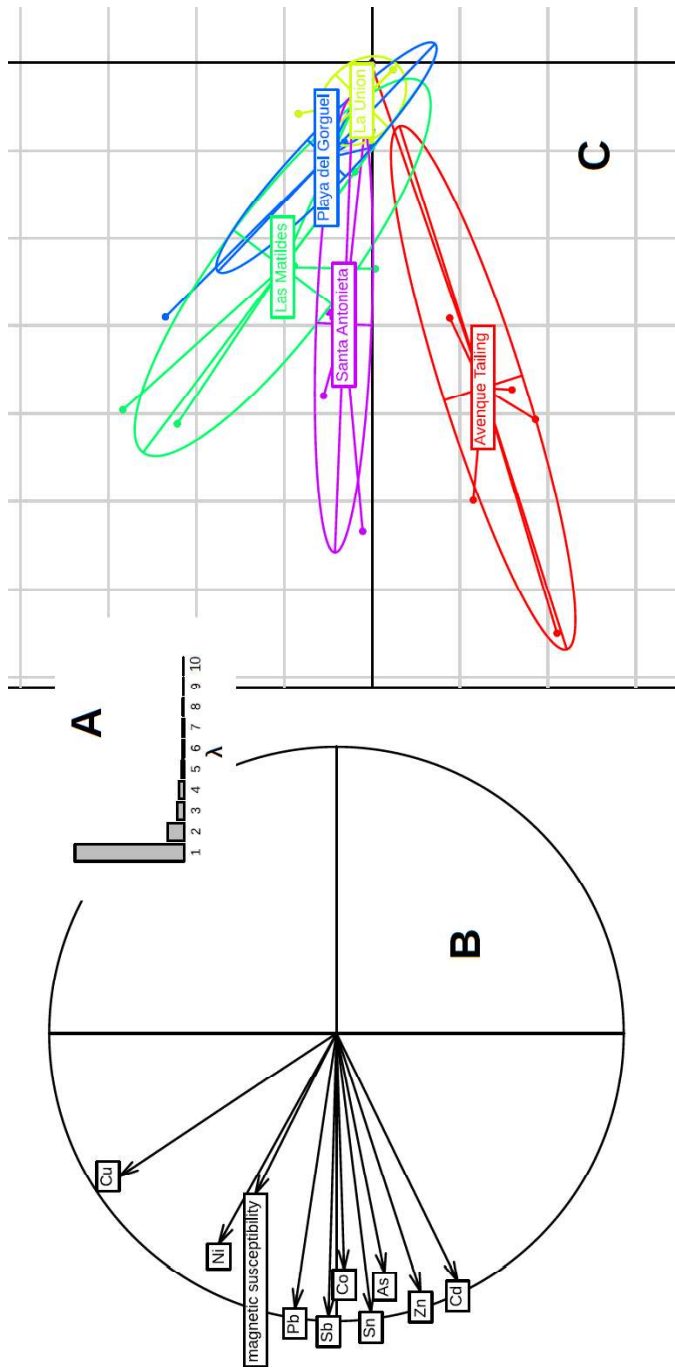


Figure 5. Decentered PCA. A. Eigen values graph. B. Correlation circle. C. Samples factor map. Inertia ellipses group sample by sites.

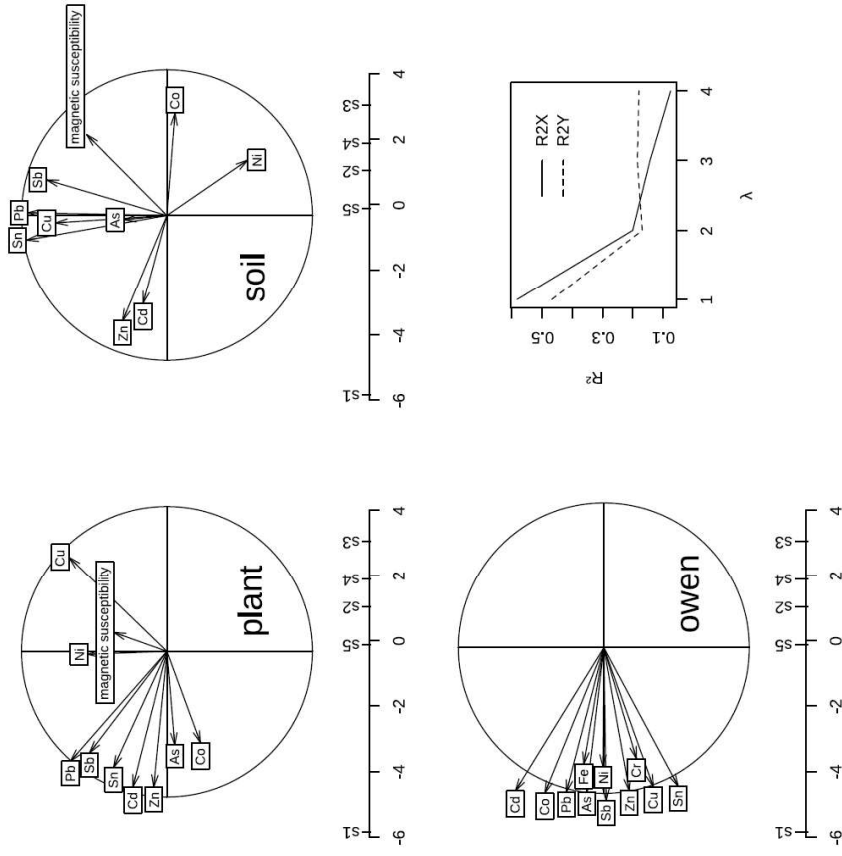


Figure 6. Graph of PLS2. A. Y, dependent variables corresponding to the concentrations measured in plants at the end of the experiment (April 2018). X, explanatory variables grouping the measurements carried out on OWEN gauges and on soil samples.

A. Circle of correlations between Y and scores of X for component 1 and 2.; B, C Circle of correlations between X and scores of X for component 1 and 2, dividing explanatory variables into two groups in different graphs B: OWEN gauge, C: soil samples. At the bottom of A, B, C are represented scores of X. S1, S2, S3, S4, S5 corresponding to Avenque Tailing, La Union, Playa del Gorguel, Las Maitildes, Santa Antonieta. D. R2X explains variance of X by score of X. R2Y explains variance of Y by score of Y.

## TABLES

**Table 1. Trace element concentrations (expressed in ppm – and compared to geochemical background for the Region of Murcia) and magnetic susceptibility for the topsoils (0-20 cm) sampled in the different investigated areas (Avenque tailing, La Unión, Playa del Gorguel, Las Matildes, Santa Antonieta) from the mining district of Cartagena - La Unión, Spain.**

Topsoil (0-20 cm)	Elemental contents (ppm)											Magnetic susceptibility
	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sn	Sb	Pb	
<b>Geochemical background</b> (Martínez-Sánchez & Pérez-Sirvent, 2007)	24-45	n.d.	5-9	17-25	12-23	16-55	5-8	0.1-0.4	n.d.	0.5-1.6	3-10	n.d.
<b>Avenque Tailing</b>	17.79 ± 1.61	1798.13 ± 12.95	6.27 ± 0.23	15.50 ± 1.45	180.70 ± 3.68	10345.08 ± 336.68	973.72 ± 36.79	18.74 ± 6.22	30.07 ± 7.51	120.61 ± 8.59	14770.39 ± 659.23	5.4283E-06
<b>La Unión</b>	18.75 ± 1.33	2133.12 ± 11.62	8.21 ± 0.56	17.12 ± 1.63	125.13 ± 2.99	2833.26 ± 39.69	199.16 ± 27.45	4.65 ± 1.80	17.32 ± 3.66	44.89 ± 1.26	857.63 ± 99.24	n.d.
<b>Playa del Gorguel</b>	18.77 ± 0.07	2434.10 ± 1.78	9.01 ± 2.01	18.65 ± 2.02	146.12 ± 3.02	5835.99 ± 83.56	1389.86 ± 98.65	13.61 ± 1.81	23.73 ± 5.27	175.10 ± 11.81	7066.40 ± 263.41	1.6519E-05
<b>Las Matildes</b>	25.14 ± 1.99	3742.21 ± 21.64	7.64 ± 1.64	14.33 ± 0.12	232.78 ± 4.65	4352.43 ± 15.23	569.20 ± 36.71	6.98 ± 0.36	41.40 ± 6.89	196.72 ± 13.96	36019.35 ± 801.12	4.1046E-05
<b>Santa Antonieta</b>	33.39 ± 1.98	2160.76 ± 9.59	5.80 ± 1.12	15.13 ± 0.98	49.28 ± 2.51	2641.08 ± 55.26	257.33 ± 29.86	5.81 ± 1.29	18.10 ± 2.41	45.80 ± 3.32	1028.05 ± 52.86	2.4623E-05

Notes: n.d.= not determined; Soil geochemical background was determined by the "Grupo de Investigación en Contaminación de Suelos. Universidad de Murcia" and reported in Martínez-Sánchez and Pérez-Sirvent (2007).

**Table 2. Zn and Pb isotope compositions ( $\delta^{66}\text{Zn}$  (‰),  $\delta^{68}\text{Zn}$  (‰),  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$ ) measured in the epiphyte plants, soils and atmospheric fallouts from the mining district of Cartagena - La Unión, Spain.**

	$\delta^{66}\text{Zn}$ (‰)	$\delta^{68}\text{Zn}$ (‰)	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$
	-0.42	-0.76	2.091	1.186
Control (May 2017)				
Avenque Tailing (November 2017)	-0.25	-0.55	2.085	1.190
Avenque Tailing (January 2018)	-0.21	-0.39	2.085	1.189
La Unión (November 2017)	-0.37	-0.64	2.086	1.188
Playa del Gorguel (November 2017)	-0.34	-0.75	2.086	1.190
Las Matildes (November 2017)	-0.50	-0.97	2.088	1.187
Soil (from Avenque Tailing)				
Soil 1	-0.39	-0.69	2.088	1.190
Soil 2	-0.35	-0.67	2.087	1.190
Atmospheric fallouts (from Owen gauge, collected in November 2017)				
Avenque Tailing	-0.44	-0.82	2.084	1.192
La Unión	-0.32	-0.64	2.088	1.187
Playa del Gorguel	-0.56	-1.02	2.084	1.191
Las Matildes	-0.23	-0.39	2.085	1.189