

# Accepted Manuscript

Iron oxide - clay composite vectors on long-distance transport of arsenic and toxic metals in mining-affected areas

Miguel A. Gomez-Gonzalez, Mario Villalobos, Jose Francisco Marco, Javier Garcia-Guinea, Eduardo Bolea, Francisco Laborda, Fernando Garrido



PII: S0045-6535(18)30117-6

DOI: [10.1016/j.chemosphere.2018.01.100](https://doi.org/10.1016/j.chemosphere.2018.01.100)

Reference: CHEM 20681

To appear in: *ECSN*

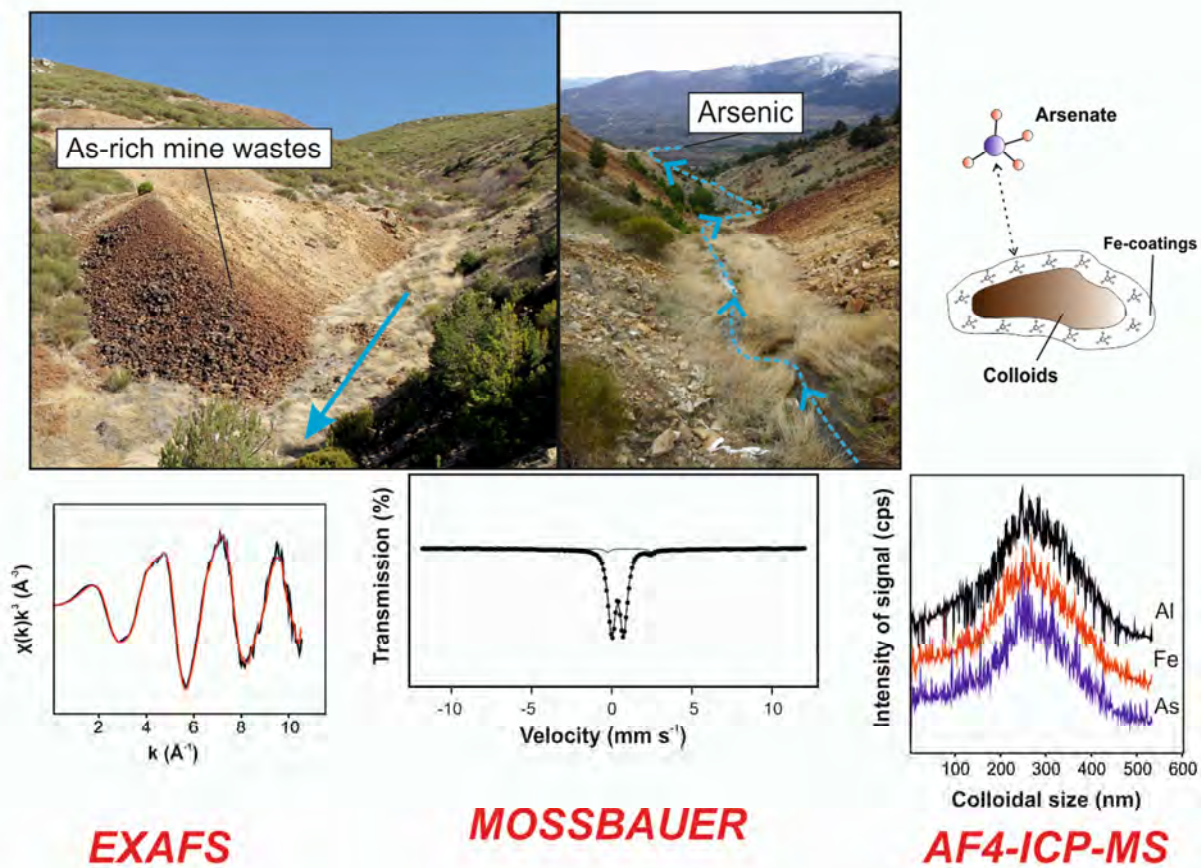
Received Date: 26 October 2017

Revised Date: 15 January 2018

Accepted Date: 22 January 2018

Please cite this article as: Gomez-Gonzalez, M.A., Villalobos, M., Marco, J.F., Garcia-Guinea, J., Bolea, E., Laborda, F., Garrido, F., Iron oxide - clay composite vectors on long-distance transport of arsenic and toxic metals in mining-affected areas, *Chemosphere* (2018), doi: 10.1016/j.chemosphere.2018.01.100.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



1 Iron oxide - clay composite vectors on long-distance transport of arsenic  
2 and toxic metals in mining-affected areas

3

4

5 Miguel A. Gomez-Gonzalez <sup>a,1</sup>, Mario Villalobos <sup>b</sup>, Jose Francisco Marco <sup>c</sup>, Javier

6 Garcia-Guinea <sup>a</sup>, Eduardo Bolea <sup>d</sup>, Francisco Laborda <sup>d</sup>, Fernando Garrido <sup>a\*</sup>

7

8 <sup>a</sup> Museo Nacional de Ciencias Naturales (MNCN, CSIC). C/ Jose Gutierrez Abascal 2,  
9 28006, Madrid, Spain.

10 <sup>b</sup> Instituto de Geología. Universidad Nacional Autónoma de México (UNAM),  
11 Coyoacán, D.F. 04510, Mexico.

12 <sup>c</sup> Instituto de Química Física-Rocasolano (CSIC), C/ Serrano 119, 28006, Madrid,  
13 Spain.

14 <sup>d</sup> Instituto Universitario de Ciencias Ambientales (IUCA), Universidad de Zaragoza. C/  
15 Pedro Cerbuna 12, 50009, Zaragoza, Spain.

16

17

18 Keywords: Arsenic; colloids; XAS; AF4-ICP-MS; mine residues; Fe-coatings

19 Capsule: This study indicates that nano-ferrihydrate may mobilize arsenic as mineral  
20 coatings on the surface of clay minerals. This demonstrates the role of iron coatings as  
21 arsenic scavengers and potential vector.

22 \*corresponding author: fernando.garrido@mncn.csic.es

23 <sup>1</sup>current address: Department of Materials and London Centre for Nanotechnology, Imperial  
24 College London. Exhibition Road. London, SW7 2AZ, UK

25

26

## 27 ABSTRACT

28 Mine wastes from abandoned exploitations are sources of high concentrations of  
29 hazardous metal(oid)s. Although these contaminants can be attenuated by sorbing to  
30 secondary minerals, in this work we identified a mechanism for long-distance  
31 dispersion of arsenic and metals through their association to mobile colloids. We  
32 characterize the colloids and their sorbed contaminants using spectrometric and  
33 physicochemical fractionation techniques. Mechanical action through erosion may  
34 release and transport high concentrations of colloid-associated metal(oid)s towards  
35 nearby stream waters, promoting their dispersion from the contamination source. Poorly  
36 crystalline ferrihydrite acts as the principal As-sorbing mineral, but in this study we find  
37 that this nanomineral does not mobilize As independently, rather, it is transported as  
38 surface coatings bound to mineral particles, perhaps through electrostatic binding  
39 interactions due to opposing surface charges at acidic to circumneutral pH values. This  
40 association is very stable and effective in carrying along metal(oid)s in concentrations  
41 above regulatory levels. The unlimited source of toxic elements in mine residues causes  
42 ongoing, decades-long mobilization of toxic elements into stream waters. The  
43 ferrihydrite-clay colloidal composites and their high mobility limit the attenuating role  
44 that iron oxides alone show through adsorption of metal(oid)s and their immobilization  
45 in situ. This may have important implications for the potential bioavailability of these  
46 contaminants, as well as for the use of this water for human consumption.

47

48

49

50

## 51 1. INTRODUCTION

52 Current mines are typically designed to mitigate potential environmental impacts.  
53 However, waste dumps and tailings are common leftovers from discontinued mines  
54 (Courtin-Nomade et al., 2016). Abandoned mine wastes originally containing high  
55 sulfide concentrations are of particular concern as they become active and harmful point  
56 sources of As and other metals. Chronic exposure to low/moderate inorganic As from  
57 drinking water has been associated with increased cardiovascular mortality (Medrano et  
58 al., 2010). Knowledge of the mechanisms of contaminant release, mobility, and natural  
59 attenuation is crucial to minimize the consequences associated with mine wastes, or to  
60 devise remediation strategies.

61 Although As can be naturally attenuated in mining environments by associating to iron  
62 (hydr)oxides or hydroxy-sulfates, or by precipitating as scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ )  
63 (Courtin-Nomade et al., 2016) and other metal arsenates (Villalobos et al., 2010),  
64 colloidal particles of these minerals may be released from mining wastes and act as As  
65 carriers in surface runoff (Gomez-Gonzalez et al., 2016). Colloid-associated As may be  
66 transported and reach geochemical conditions that are different from those at the source  
67 (e.g., higher pH) thus promoting its release and bioavailability. Accordingly, none of  
68 these natural As scavengers could be considered as completely effective trapping  
69 systems in contact with flowing water because of their small particle sizes (except  
70 perhaps jarosites) (Doucet et al., 2007). This association of As to mineral colloids is  
71 important for the transport of this element in the environment and differs from the  
72 mobility behavior of both dissolved phases and of larger As-containing particles. Co-  
73 transport of contaminants by colloids has been recognized as an efficient mechanism of  
74 trace metal and organic chemical mobility (Kretzschmar et al., 1999), but little attention  
75 has been paid to As speciation in the actual mobile colloidal particles (Bauer and

76 Blodau, 2009) and to the As partitioning between colloids and dissolved fractions  
77 (Serrano et al., 2015).

78 Asymmetric flow field-flow fractionation (AF4) has been used to separate and  
79 characterize mobile colloids from natural samples (Bolea et al., 2010; Laborda et al.,  
80 2011; Baalousha et al. 2011). The mild separation conditions in absence of stationary  
81 phases contribute to the preservation of the original colloid size distribution and it can  
82 be coupled to an ICP-MS to obtain the elemental composition of the colloidal phases  
83 (Neubauer et al., 2013). Direct insight into the speciation of colloidal As and Fe can  
84 additionally be gained using X-ray absorption spectroscopy (XAS), which has been  
85 used to assess the As and Fe speciation in natural samples (O'Day et al., 2004; Voegelin  
86 et al. 2007; Chen et al. 2009) including dispersible soil colloids (Serrano et al., 2015).

87 Recently, Gomez-Gonzalez et al. (2016) combined both techniques to demonstrate that  
88 the mineral nature of the dispersible colloidal fraction obtained after leaching scorodite-  
89 rich mine residues and sediments (Serrano et al., 2015) were similar to those colloids  
90 released by simulated rainfall experiments performed in the field. Both scorodite and  
91 Fe(III)-oxyhydroxides were identified as mineral carriers that can transport As long  
92 distances from the source.

93 Although the role of Fe-oxide nanoparticles as carrier phases has received attention  
94 (Bauer and Blodau, 2009; Kretzschmar et al., 1999), composite mineral colloidal  
95 assemblages may have an important role in the transport of metal(loid)s in the soil-  
96 water system, but they have scarcely been investigated. In this study, we determine the  
97 As solid-phase speciation in the dispersible (i.e., potentially detachable and mobile,  
98 <1000 nm) colloid fraction of soils along the stream that collects drainage from mine  
99 residues. The mineral phases and colloidal vectors involved in the As mobilization have  
100 been characterized and compared to the As-bearing phases present in the bulk

101 (i.e. <2mm) fraction of the soils. We propose a combined approach involving  
102 spectrometric and fractionation techniques to gain information on the size-dependent  
103 elemental composition of colloids, the nature of the colloidal carrier phase, and the  
104 speciation of the associated contaminants.

105

## 106 2. EXPERIMENTAL

### 107 2.1. Site description, sample collection and analyses

108 The experiment was conducted along a stream gorge (NW Madrid, Spain) that collects  
109 water drainage from an abandoned mine in the Guadarrama mountain-range  
110 (40°52'04.48" N - 3°43'48.68" O, 1475 meters altitude), where metal(oid)  
111 contamination had been previously reported (Moreno-Jiménez et al., 2009). Massive  
112 pyritic residues (~500 m<sup>2</sup> of surface, 3 meter-thick, 22 g kg<sup>-1</sup> of As) remain on the soil  
113 surface and are subjected to weathering and erosion. There, 0-15 cm depth bulk samples  
114 were taken from (1) the arsenic-bearing waste-pile (WP), (2) four sampling points  
115 located at 28, 190, 410 and 815 m away from the WP along the gorge downstream (A-  
116 B-C-D, respectively), and (3) adjacent to a semi-permanent water course (Figure S1).  
117 Additional undisturbed soil cores (5-cm diameter, 15-cm depth) were collected from the  
118 downstream locations (A-B-C-D) and kept under anoxic conditions. Stream water  
119 samples were collected from the exit of the abandoned mine (WP) and near the  
120 sampling locations. All samples were processed as described in the Supplementary  
121 Material (SM) where the main physicochemical properties are presented (Tables S1,  
122 S2a-b, S4). Additional observations and analyses were performed through  
123 environmental scanning (ESEM) and transmission electron microscopy (TEM).

124



125 *2.2. Isolation of dispersible colloidal and dissolved fractions*

126 The maximum amount ( $\text{mg kg}^{-1}$  soil) of potentially releasable colloids from the samples  
127 was termed 'dispersible colloidal fraction' (DCF,  $\leq 1000$  nm) (Serrano et al., 2015).

128 Two other fractions were isolated from the DCF upon ultrafiltration through 10 nm  
129 pore-size membranes: (i) the solid colloidal fraction (CF, 1000-10 nm) deposited onto  
130 the ultrafiltration membrane and (ii) the truly water soluble or dissolved fraction (DF,  
131  $<10$  nm) that passed through membranes. The experimental procedure is described in  
132 the SM.

133 DCF aliquots were used for AF4-ICP-MS and TEM analyses, Mössbauer spectroscopy,  
134 and for colloidal mass and element quantification. Aqueous As and metal  
135 concentrations in the dissolved fraction (DF) were quantified by ICP-MS and the  
136 colloidal fraction (CF, 1000-10 nm) obtained upon ultrafiltration was analyzed by As  
137 and Fe K-edge XAS spectroscopy (Figure S2).

138

139 *2.3. Size characterization and element quantification by AF4-ICP-MS*

140 The DCFs from A-B-C-D were analyzed by AF4 (AF2000, *Postnova Analytics*) with a  
141 coupled UV-Vis diode array detector (*Shimadzu*, wavelength range: 200-650 nm). The  
142 AF4-UV-Vis system was coupled to an ICP-MS (ELAN DRC-e *Perkin Elmer*) to  
143 perform an on-line multi-element quantification. The instrumental conditions of the  
144 AF4-UV-Vis-ICP-MS system were previously tested (Serrano et al., 2015) and are  
145 described in the SM.

146

147 *2.4. As and Fe K-edge X-ray absorption spectroscopy (XAS) analyses*

148 Arsenic and Fe XAS measurements were done on bulk ( $<2$  mm) soil samples and on  
149 their CF (1000-10 nm). EXAFS spectra were recorded at the BM25A beamline (ESRF,



150 France) (6 GeV, 100 mA, Si(111) monochromator crystals) at room temperature using a  
151 13-element Ge(Li) solid-state detector. The spectra were obtained by averaging 5-7  
152 replicate scans. Both soil and CFs from A to D sampling points were transported under  
153 anoxic conditions and measured inside a vacuum chamber to preserve the original As  
154 and Fe speciation. Reference and sample spectra were analyzed by linear combination  
155 fitting (LCF) using the code Athena (Ravel and Newville, 2005). Details about the XAS  
156 spectra collected, LCF analyses, and reference spectra are shown in the SM.

157

### 158 *2.5. Mössbauer spectroscopy analyses*

159 Room temperature  $^{57}\text{Fe}$  Mössbauer data of both bulk and colloidal samples were  
160 recorded in transmission mode using a conventional constant acceleration spectrometer  
161 and a  $^{57}\text{Co}(\text{Rh})$  source, analyzing ~200 mg of each sample previously powdered and  
162 capsuled in polyvinyl chloride (PVC) holders which ensures an effective thickness of 5-  
163 10 mg Fe  $\text{cm}^{-2}$  per sample. The velocity scale was calibrated using a 6  $\mu\text{m}$ -thick  $\alpha\text{-Fe}$   
164 foil. The isomer shifts were referred to the centroid of the spectrum of  $\alpha\text{-Fe}$ . The fitting  
165 hyperfine parameters are summarized in Table S7.

166

## 167 3. RESULTS

### 168 *3.1. Bulk soil sample characterization*

#### 169 *3.1.1. Physicochemical properties and metal(oid) concentrations*

170 The WP shows high electrical conductivity (EC, 237  $\mu\text{S cm}^{-1}$ ), low pH (3.5) and total  
171 organic carbon (TOC) (0.2%) in comparison with the downstream samples (A, B, C, D)  
172 which presented circumneutral pH, EC in the range 19-55  $\mu\text{S cm}^{-1}$  and TOC values  
173 from 1.5-5.5% (Table S1).

174 All samples contained quartz and albite as principle minerals in the <2-mm fraction  
175 (Table S2a). Their <2- $\mu$ m fractions (Table S2b) were dominated by montmorillonite  
176 and jarosite in the WP, and by illite, and either kaolinite, or microcline and albite in the  
177 downstream soils.

178 The As, Fe and Pb pseudo-total concentrations were highest in the WP and decreased  
179 with distance from the contamination focus (Table 1). Conversely, Al, Mn and Zn  
180 concentrations were lowest in the WP but they also decreased with distance starting  
181 from point A downstream. This could be the result of the enhanced mineral acidic  
182 dissolution at the WP and the subsequent element enrichment at the closest point (A).

183

#### 184 *3.1.2. Element fractionation in solid phase: Sequential extraction procedure*

185 Common to all samples is the absence of bioavailable, or exchangeable, As (step I)  
186 (Table S4). In the WP, 74% of the total As was extracted in step IV (targeting poorly  
187 crystalline Fe-oxyhydroxides). Riverbed soils showed different As solid phase  
188 distribution than the WP. The fraction of As extracted from step II (strongly adsorbed  
189 complexes) was similar in samples A and B (~22% of total As) but decreased at the  
190 farthest distance from the WP (point D). The As extracted in step III (amorphous Fe  
191 hydroxides, carbonates and volatile sulfurs) represented on average 20% of the total  
192 amount in samples A and C but decreased to 9% in point D. The As fraction extracted  
193 from step IV decreased downstream from 26% to 13% of the total As content.  
194 Conversely, the fraction of As associated to crystalline Fe-oxyhydroxides increased  
195 with distance to the WP from 8% to 33% and 25% in samples C and D, respectively.  
196 The farthest sample from the WP (D) showed a significant contribution of residual  
197 fraction (40%).

198 Iron was mostly extracted in steps III (32%) and IV (24%) (amorphous and weakly  
199 crystalline Fe-oxyhydroxides, respectively) in the WP. The riverbed soils showed a  
200 large residual Fe fraction from 23% (B) to 74% (D). Similarly, Al was mostly extracted  
201 in step III, varying from 20% (WP) to 64% (C). Similar to Fe, sample D stood out for  
202 the amount of Al in the residual fraction (43%), but residual Al was also high in the WP  
203 (61%) (Table S4).

204

### 205 *3.1.3. Observations and analysis through scanning electron microscopy*

206 The WP was characterized by As-Ag-bearing mineralized veins of quartz that also  
207 contained silica and Fe-oxides together with primary sulfide and sulfosalts such as  
208 arsenopyrite, pyrite and scorodite (Figure S3a-b). Large quartz and feldspar grains were  
209 abundant in samples downstream. Arsenic was found associated to Fe-oxyhydroxides  
210 showing low As/Fe concentration ratios by EDX in selected particles (Figure S3c-d-e).  
211 The EDX indicated the highest As/Fe ratio in the WP sample, while downstream  
212 samples presented decreasing As content with distance to the contamination focus. In  
213 sample D (Figure S3f), organic microparticles with important Mn and As content were  
214 detected.

215

### 216 *3.1.4. Speciation of Fe-mineral phases: Mössbauer spectroscopy*

217 All Mössbauer spectra were dominated by an intense paramagnetic doublet whose  
218 parameters can be associated to Fe(III) in octahedral oxygen coordination (Maddock,  
219 1985), and by a less intense second doublet corresponding to Fe(II)-octahedral (Figure  
220 S6).

221 Iron content in the WP was mainly Fe(III), 16% of whose total content corresponded to  
222 goethite and 81% to a Fe(III)-illite/Fe(III)-(hydr)oxides mixture, other than goethite

223 (Table S7). From the WP downstream, the ratio Fe(II)/Fe(III) was lowest in sample A  
224 (0.14), increased to 0.27 in sample B, but decreased to 0.18 in in sample D (Table 2).  
225 Minor presence of hematite was detected in points C and D.

226

### 227 *3.1.5. As speciation of bulk soils: X-ray absorption spectroscopy*

228 Linear combination fitting (LCF) analyses of As spectra, acquired in anoxic conditions,  
229 indicated the adsorption of As on Fe(III)-oxyhydroxides, such as ferrihydrite and  
230 goethite (Table 3, Figure 1). Also, significant contributions of scorodite (26%) and As-  
231 jarosite (17%) were found in the WP.

232

## 233 *3.2. Characterization of the colloidal fraction of contaminated soils*

### 234 *3.2.1. Colloid-mass and metal(loid) quantification*

235 All soil samples released a larger mass of colloids than the WP (Table 4b). Colloidal  
236 mass in the DCF varied little from A (~9200 mg kg<sup>-1</sup>) to D (~7900 mg kg<sup>-1</sup>). The As  
237 colloidal concentration of the samples decreased from ~10000 mg kg<sup>-1</sup> in A to ~1350  
238 mg kg<sup>-1</sup> in D, similar to the WP (1434 mg kg<sup>-1</sup>). The DCF of downstream samples  
239 showed larger concentrations of all metal(oid)s analyzed than the DCF obtained from  
240 the WP (Table 4a). The metal(oid)s contained in the DCFs were mainly associated to  
241 the (solid) CF (1000-10 nm), i.e. minor concentrations of the elements remained in the  
242 DF, and thus the percentage of the element concentration found in the CF to that in the  
243 DCF ( $CF/DCF$  in Table 4a) is 100% for Fe and Al, and over 80% for the rest of  
244 analyzed elements in all soils. All metal(oid)s concentrations in the DCF from A-B-C-D  
245 decreased with distance from the WP while their fractions in the DF were low and  
246 remained constant along the river creek except for the Cu which decreased in samples C  
247 and D. For example, As concentration in the DCF decreased from 9.6 mg L<sup>-1</sup> in A near

248 the WP, to  $1.3 \text{ mg L}^{-1}$  in D. However, As concentrations in the DF remained close to 0.2  
249  $\text{mg L}^{-1}$  in all samples collected along the river banks. Overall, the ratios of element  
250 concentration in DCFs to that in their corresponding bulk samples were low (2-4%) for  
251 all elements except for Al (17-31%) (Table 4a)

252

### 253 *3.2.2. DCF size distribution and associated metal(loid)s: AF4-ICP-MS and TEM*

254 The DCF size distribution and the associated As, Fe, and Al contents of downstream  
255 samples were analyzed by AF4-UV-vis-ICP-MS. Low pH and high EC of WP sample  
256 prevented its size-characterization due to the strong interaction with the AF4 channel  
257 membrane (Gomez-Gonzalez et al., 2016).

258 The size maxima of the colloidal distributions did not change with distance along the  
259 stream over the samples A to D (Table 5). Iron and As concentration maxima were  
260 associated to colloid mean sizes of  $260 \pm 30 \text{ nm}$  and  $257 \pm 36 \text{ nm}$ , respectively, and  
261 differed little to that of Al,  $263 \pm 30 \text{ nm}$  (Table 5, Figure 2a). These size ranges were  
262 further confirmed as colloid particles 200-300 nm large were frequently observed in the  
263 DCF by TEM analyses (Figure 2b). The EDX indicated the importance of Al- and Fe-  
264 bearing phases in the As mobilization (Table S5).

265

### 266 *3.2.3. Colloidal Arsenic and Fe XAS speciation*

267 The As K-edge EXAFS spectra acquired over the CF (1000-10 nm) of the samples  
268 pointed to ferrihydrite [ $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$ ] as the main As-bearing phase in downstream  
269 samples (Table 3, Figure 1), accompanied by low contributions of goethite [ $\alpha$ -  
270  $\text{FeO}(\text{OH})$ ] in A and B, beudantite [ $\text{PbFe}_3(\text{OH})_6\text{SO}_4\text{AsO}_4$ ] in C, and jarosite in D. In the  
271 WP, in addition to ferrihydrite and goethite, there was a significant contribution of  
272 scorodite ( $\approx 36\%$ ).

273 The Fe k-edge EXAFS spectra showed similar Fe-clays in the colloidal fraction of all  
274 samples. In the WP there were similar contributions of smectite [ $\text{Ca}_{0.17}(\text{Al}, \text{Fe}, \text{Mg})_2(\text{Si},$   
275  $\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ], schwertmannite [ $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4) \cdot n\text{H}_2\text{O}$ ] and plumbo-jarosite  
276 [ $\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$ ]. All A-B-C zones showed the main presence of schwertmannite in  
277 the CF and minor contributions of Fe-phyllsilicates (smectite and illite [(K, H<sub>3</sub>O)(Al,  
278 Mg, Fe)<sub>2</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>[(OH)<sub>2</sub>, H<sub>2</sub>O]]) and (plumbo)jarosite (Table 3, Figure 1).

279

## 280 4. DISCUSSION

### 281 4.1. Arsenic spreading and environmental impact

282 The massive sulfarsenide residues dumped on the soil surface near the creek are an  
283 important source of metal(oid) contamination in the mine surroundings, especially  
284 downstream. At about one kilometer downstream from the WP, As concentration is 43  
285 times higher than the regional legal threshold ( $24 \text{ mg kg}^{-1}$ , Moreno-Jimenez et al. 2009).  
286 Primary As-bearing mineral assemblages, mainly pyrite-like minerals, are transformed  
287 to authigenic minerals such as goethite and scorodite, the main products of low-  
288 temperature meteorization of the WP, and minor fractions of jarosite, plumbojarosite,  
289 and schwertmannite. Atmospheric oxidation of pyrite begins within minutes of  
290 exposure, resulting in the production of Fe-oxyhydroxides and sulfate species (Chandra  
291 and Gerson, 2010). The extent of oxidation is naturally controlled by access of mine  
292 wastes to oxygenated water, which is enhanced by specific geographical characteristics  
293 of the area such as its high topographic relief, and alternation of dry and wet climate  
294 (Majzlan et al., 2014). The microbial activity may also play a significant role in As-  
295 bearing mineral dissolution and As transformations in the soil-water system (Lloyd and  
296 Oremland, 2006).

297 This process is confirmed by EXAFS, indicating that As is only present as As(V) in  
298 both WP and downstream samples (Table 3). Fe-Mössbauer spectroscopy shows major  
299 proportions of structural Fe(III) over Fe(II) indicating the high oxidation state at the  
300 surface of the originally pyritic wastes (Table 2). Furthermore, As partitioning in the  
301 solid phase of the WP samples shows the largest proportion of As bound to poorly  
302 crystalline Fe-oxyhydroxide minerals (Fraction IV, 74%), and no As is associated to the  
303 most bioavailable or soluble fraction (Table S4). Similar to Slowey et al. (2007), no  
304 primary minerals were detected in the mobilizable CF in the WP and samples  
305 downstream.

306 The lower As total concentration downstream (Table 1), relative to that in the WP, is the  
307 result of geochemical mechanisms that constrain the As release into water. Arsenic(V)  
308 association to Fe-(hydr)oxides may be found in the WP in either large particles or  
309 strongly-bound colloidal aggregates with limited dispersibility. Thus, reduced amounts  
310 of As travel downstream from the WP relative to the large As pool in the WP. Although  
311 no reclamation has been performed in the residues and affected soils, acid release from  
312 pyrite oxidation is neutralized along the creek to circumneutral values due to  
313 endogenous calcite hosted in neighboring granite and the existence of hidden  
314 interstratified marble banks into the gneiss series. At  $\text{pH} > 6$ , ferrihydrite formation is  
315 favorable (Hayes et al., 2014) and can exert a metal trapping role (Fritzsche et al., 2011)  
316 attenuating As toxicity. The sequential extractions also indicate an increasing proportion  
317 of As coprecipitation with crystalline Fe-oxyhydroxides in soil samples with distance  
318 from the WP (Table S4) consistent with the As retention through stable inner-sphere  
319 complexes.

320 However, our results show a remarkable metal(oid) pollution of the soil-water system in  
321 the area. Thus, sorption onto mineral phases at the source does not prevent the release



322 and transport of As and other metals. One potential mechanism is the transport of  
323 colloid-size reactive particles rich in As and the subsequent downstream spreading of  
324 the element (Bauer and Blodau, 2009). Even though As concentration in the DCF  
325 represents approximately 3% of total As concentration in the samples (Table 4) this  
326 fraction might justify the contamination downstream over time taking into account that  
327 at the circumneutral pH of the running water and soil samples (Table 1), minor  
328 concentrations of As are encountered as truly dissolved. Subsequent organic acid-  
329 promoted dissolution or seasonal reductive dissolution of Fe-oxyhydroxides containing  
330 As(V) (Slowey et al., 2007) may release As in fresh water. Accordingly, both bulk and  
331 colloidal As concentrations in soils decrease with distance while As concentration in  
332 stream water tend to increase downstream.

333

#### 334 *4.2. The potential role of composite mineral vectors in As transport.*

335 Iron oxides play a role as both attenuating phases and geochemical carriers of As and  
336 metals in soil-water systems. Both mechanisms may coexist and the extent of each one  
337 depends on the concentration and transport behavior of the carrier phase, the carrier-  
338 contaminant association, and on particle settling and deposition processes in riverine  
339 systems (Hassellöv and von der Kammer, 2008). According to EXAFS, As-colloidal  
340 mobilization from the WP can be conducted by three potential carriers: ferrihydrite (or a  
341 mixture of it with schwertmannite), scorodite and goethite (Table 3). Among them,  
342 ferrihydrite is the largest contributor due to its high affinity for As(V) under oxic  
343 conditions (Dixit and Hering, 2003) and its prompt formation and stability at neutral pH  
344 values (Hayes et al., 2014). Ferrihydrite is the first metastable Fe phase to precipitate  
345 upon pyrite oxidation. Its transformation kinetics is retarded in sulfate-rich semi-arid  
346 environments. This allows this phase to persist over decades of weathering, even at

347 lower pHs than those predicted in its stability field (Hayes et al., 2014), although other  
348 phases such as schwertmannite are more stable at acid conditions. At  $\text{pH} < 4$ ,  
349 schwertmannite is an important host mineral for As released by acid mine-drainage  
350 (Acero et al., 2006), while at  $\text{pH} > 5$  sorption of As on ferrihydrite or poorly crystalline  
351 Fe-oxyhydroxide predominates (Carlson et al., 2002). The nanocrystalline structure of  
352 schwertmannite (Fernandez-Martinez et al., 2010) is corroborated by the fact that this  
353 phase is only detected by Fe-EXAFS in the CF (Table 3). Also, the high TOC (Table  
354 S1) of the samples downstream might explain its occurrence at  $\text{pH} > 5$  and the absence of  
355 As bound to schwertmannite as described by Vithana et al. (2014). Moreover, nanosized  
356 schwertmannite might have been transported as suspended material downstream as  
357 suggested by Yu et al. (1999) who also found traces of this mineral at  $\text{pH} > 6$ .  
358 Scorodite is only detected in the  $< 2$  mm and colloid fractions of the WP sample.  
359 Although this mineral is mobilizable through surface runoff (Gomez-Gonzalez et al.,  
360 2016), at neutral pH, it dissolves incongruently forming Fe-hydroxide and arsenate  
361 oxyanions (Harvey et al., 2006) and thus contributes to the accumulation of Fe-phases,  
362 which subsequently may sequester soluble As. The role of goethite as potential As-  
363 carrier seems secondary as compared to ferrihydrite. It was found in the WP colloid-size  
364 fraction (Table 3) and reduced contributions in the closest sampling points to the wastes  
365 (A and B). Ferrihydrite slowly transforms to more thermodynamically stable goethite in  
366 the presence of As (Ford, 2002). This could explain the increasing contribution of As  
367 bound to goethite in the total soil fraction with distance from the WP (Table 3),  
368 suggesting that As-bound goethite may be found in particles larger than the DCF.  
369 Nevertheless, Mössbauer spectroscopy conducted at room temperature suggests the only  
370 presence of goethite in the WP. The contribution of phases such as ferrihydrite or

371 lepidocrocite could not be discarded unless a significant number of Mössbauer spectra  
372 were acquired at low temperature.

373 Although our results show the role of ferrihydrite as the main As-sorbing mineral in the  
374 bulk samples, colloidal As concentration represents less than 3% of the total As  
375 concentration in all samples. This indicates that ferrihydrite is mainly encountered as  
376 coating or within bigger size aggregates, and in both cases with less reactivity and more  
377 stability than in its nano-sized form, which likely limits its transformation to more  
378 crystalline phases. Pure Fe-oxide minerals are positively charged under environmental  
379 pH conditions and thus, are promptly deposited on the generally negatively charged  
380 surface of stationary grains (e.g., clays) in soils and sediments (Hassellöv and von der  
381 Kammer, 2008).

382 This points out the potential role of composite Fe-oxyhydroxides and phyllosilicate  
383 mineral vectors as element carriers in riverine soil-water systems, acting as mineral  
384 assemblages as described by Grosbois et al. (2011). The proposed mechanism would be  
385 for As being attached to Fe-oxyhydroxide phases, which in turn use clays as an effective  
386 physical transport media. Moreover, this role is performed regardless of the carrier  
387 mineral particle size, although there is a slight enrichment in As bound to ferrihydrite in  
388 the colloid-size fraction as compared to that of total soil fraction (>2mm). This is  
389 supported by the fact that colloidal As mean peak size matches up with that of Fe and  
390 Al in the AF4-fractograms (Figure 2) suggesting that both elements are linked to As.

391 Comparing the element's total concentrations and those found in the DCF and CF  
392 (Table 4a), it is evident that the DCF becomes enriched in Al (20% or higher) while the  
393 rest of the analyzed elements are present in minor proportions relative to their bulk total  
394 concentrations. While the term, 'nanovector' (Hamon et al. 2005) describes the colloidal

395 transport of metal(oid)s in soil-water systems, it may be composed of more than one  
396 type of mineral phases for metal(oid) pollution in mine affected soil-water systems.

397

## 398 5. CONCLUSIONS

399 This work shows a potential mechanism of metal(loid) dispersion from mine wastes to  
400 adjacent soils and stream waters via long-distance transport of colloidal material.

401 The well-known role of Fe-oxyhydroxide phases as As scavenger may be limited when  
402 they precipitate as surface coatings of dispersible colloid-size mineral particles that can  
403 readily be transferred along water courses from point sources of contamination to  
404 adjacent non-polluted sites.

405 The study was performed on the bulk (<2 mm) soils and their dispersible colloidal  
406 fractions (<1000 nm) combining sequential chemical extractions, fractionation and  
407 spectrometry techniques, and showed that the dispersion occurs by isolated Fe-  
408 oxyhydroxide colloids or by greater size, stable aggregates of Fe-oxyhydroxide-clay  
409 mineral composite vectors. This mobilization mechanism and the physical carrier  
410 mineral phases can be identified by combining XAS (to confirm As-Fe oxide binding)  
411 and fractionation and elemental analysis (AF4-ICP-MS).

412 The unlimited As source provided by the accumulation of pyrite-rich mine residues  
413 along with the decades-long mobilization of toxic elements into stream water (and its  
414 potential transfer to subsurface water) pose important risks for human health. High  
415 contents of negatively-charged clay minerals may also contribute to cationic metal-  
416 bound colloid mobilization along streams.

417

## 418 ACKNOWLEDGEMENTS

419 The Spanish Ministry of Economy and Competitiveness supported this study  
420 (CGL2010-17434). M.A. Gomez-Gonzalez was supported by the Ph.D. Spanish FPI  
421 fellowship (BES-2011-046461, EEBB-I-15-09807). XAS measurements on BM25A  
422 beamline (ESRF) supported by 25-01-944 project. ICP analyses were performed at  
423 *Servicio General de Apoyo a Investigación-SAI, Universidad-Zaragoza*. TEM analyses  
424 were performed at *Centro Nacional de Microscopía Electrónica (Universidad-*  
425 *Complutense, Madrid)*. ESEM-EDX and DRX analyses were performed at *MNCN-*  
426 *CSIC*.

427

## 428 FIGURE CAPTIONS

429 1– Arsenic K-edge EXAFS spectra of (a) bulk samples and (b) colloidal fractions. Iron  
430 K-edge EXAFS spectra of (c) colloidal fractions. Black lines, experimental data; red  
431 lines, LCF results (Table 3 for LCF values).

432 2– (a) AF4-ICP-MS analyses of the downstream DCFs showing the distribution of  
433 aluminum (black), iron (red) and arsenic (blue) associated to the colloids. (b) TEM  
434 images of the DCF isolated from A, B, C and D (EDX analyses confirmed the presence  
435 of As associated to Fe-oxyhydroxides in all cases (Table S5)).

436

## 437 REFERENCES

438 Acero, P., Ayora, C., Torrento, C., Nieto, J.M. 2006. The behavior of trace elements  
439 during schwertmannite precipitation and subsequent transformation into goethite and  
440 jarosite. *Geochimica et Cosmochimica Acta* 70, 4130-4139

441 Baalousha, M., Stolpe, B., Lead, J.R., 2011. Flow field-flow fractionation for the  
442 analysis and characterization of natural colloids and manufactured nanoparticles in  
443 environmental systems: A critical review. *Journal of Chromatography A* 1218, 4078-  
444 4103.

- 445 Bauer, M., Blodau, C., 2009. Arsenic distribution in the dissolved, colloidal and  
446 particulate size fraction of experimental solutions rich in dissolved organic matter and  
447 ferric iron. *Geochimica et Cosmochimica Acta* 73, 529-542.
- 448 Bolea, E., Laborda, F., Castillo, J.R., 2010. Metal associations to microparticles,  
449 nanocolloids and macromolecules in compost leachates: Size characterization by  
450 asymmetrical flow field-flow fractionation coupled to ICP-MS. *Analytica Chimica Acta*  
451 661, 206-214.
- 452 Carlson, L., Bigham, J.M., Schwertmann, U., Kyek, A., Wagner, F., 2002. Scavenging  
453 of As from Acid Mine Drainage by Schwertmannite and Ferrihydrite: A Comparison  
454 with Synthetic Analogues. *Environmental Science & Technology* 36, 1712-1719.
- 455 Chandra, A.P., Gerson, A.R., 2010. The mechanisms of pyrite oxidation and leaching:  
456 A fundamental perspective. *Surface Science Reports* 65, 293-315.
- 457 Chen, N., Jiang, D.T., Cutler, J., Kotzer, T., Jia, Y.F., Demopoulos, G.P., Rowson, J.W.,  
458 2009. Structural characterization of poorly-crystalline scorodite, iron(III)-arsenate co-  
459 precipitates and uranium mill neutralized raffinate solids using X-ray absorption fine  
460 structure spectroscopy. *Geochimica et Cosmochimica Acta* 73, 3260-3276.
- 461 Courtin-Nomade, A., Waltzing, T., Evrard, C., Soubrand, M., Lenain, J.F., Ducloux, E.,  
462 Ghorbel, S., Grosbois, C., Bril, H., 2016. Arsenic and lead mobility: From tailing  
463 materials to the aqueous compartment. *Applied Geochemistry* 64, 10-21.
- 464 Dixit, S., Hering, J.G., 2003. Comparison of Arsenic(V) and Arsenic(III) Sorption onto  
465 Iron Oxide Minerals: Implications for Arsenic Mobility. *Environmental Science &*  
466 *Technology* 37, 4182-4189.
- 467 Doucet, F.J., Lead, J.R., Santschi, P.H., 2007. Colloid-Trace Element Interactions in  
468 Aquatic Systems, *Environmental Colloids and Particles*. John Wiley & Sons, Ltd, pp.  
469 95-157.

- 470 Fernandez-Martinez, A., Timon, V., Roman-Ross, G., Cuello, G.J., Daniels, J.E.,  
471 Ayora, C., 2010. The structure of schwertmannite, a nanocrystalline iron  
472 oxyhydroxysulfate. *American Mineralogist* 95, 1312-1322.
- 473 Ford, R.G., 2002. Rates of Hydrous Ferric Oxide Crystallization and the Influence on  
474 Coprecipitated Arsenate. *Environmental Science & Technology* 36, 2459-2463.
- 475 Fritzsche, A., Rennert, T., Totsche, K.U., 2011. Arsenic strongly associates with  
476 ferrihydrite colloids formed in a soil effluent. *Environmental Pollution* 159, 1398-1405.
- 477 Gomez-Gonzalez, M.A., Voegelin, A., Garcia-Guinea, J., Bolea, E., Laborda, F.,  
478 Garrido, F., 2016. Colloidal mobilization of arsenic from mining-affected soils by  
479 surface runoff. *Chemosphere* 144, 1123-1131.
- 480 Grosbois, C., Courtin-Nomade, A., Robin, E., Bril, H., Tamura, N., Schäfer, J., Blanc,  
481 G., 2011. Fate of arsenic-bearing phases during the suspended transport in a gold  
482 mining district (Isle river Basin, France). *Science of The Total Environment* 409, 4986-  
483 4999.
- 484 Hamon, R., Batley, G.E., Casey, P., 2005. Environmental nanovectors: an emerging  
485 science area. *SETAC Globe* 6, 21-22.
- 486 Harvey, M.C., Schreiber, M.E., Rimstidt, J.D., Griffith, M.M., 2006. Scorodite  
487 Dissolution Kinetics: Implications for Arsenic Release. *Environmental Science &*  
488 *Technology* 40, 6709-6714.
- 489 Hassellöv, M., von der Kammer, F., 2008. Iron Oxides as Geochemical Nanovectors for  
490 Metal Transport in Soil-River Systems. *Elements* 4, 401-406.
- 491 Hayes, S.M., Root, R.A., Perdrial, N., Maier, R.M., Chorover, J., 2014. Surficial  
492 weathering of iron sulfide mine tailings under semi-arid climate. *Geochimica et*  
493 *Cosmochimica Acta* 141, 240-257.



- 494 Kretzschmar, R., Borkovec, M., Grolimund, D., Elimelech, M., 1999. Mobile  
495 Subsurface Colloids and Their Role in Contaminant Transport, in: Donald, L.S. (Ed.),  
496 Advances in Agronomy. Academic Press, pp. 121-193.
- 497 Laborda, F., Ruiz-Beguería, S., Bolea, E., Castillo, J.R., 2011. Study of the size-based  
498 environmental availability of metals associated to natural organic matter by stable  
499 isotope exchange and quadrupole inductively coupled plasma mass spectrometry  
500 coupled to asymmetrical flow field flow fractionation. Journal of Chromatography A  
501 1218, 4199-4205.
- 502 Lloyd, J.R., Oremland, R.S., 2006. Microbial transformations of arsenic in the  
503 environment: From Soda lakes to aquifers. Elements 2, 85-90.
- 504 Maddock, A.G., 1985. Mössbauer Spectrometry in Mineral Chemistry. Chemical  
505 Bonding and Spectroscopy in Mineral Chemistry In: F.J. Berry and D.J. Vaughan, eds.  
506 Springer Netherlands, 141-208.
- 507 Majzlan, J., Drahota, P., Filippi, M., 2014. Parageneses and Crystal Chemistry of  
508 Arsenic Minerals. Reviews in Mineralogy and Geochemistry 79, 17-184.
- 509 Medrano, M.J., Boix, R., Pastor-Barriuso, R., Palau, M., Damián, J., Ramis, R., del  
510 Barrio, J.L., Navas-Acien, A., 2010. Arsenic in public water supplies and cardiovascular  
511 mortality in Spain. Environmental Research 110, 448-454.
- 512 Moreno-Jiménez, E., Peñalosa, J.M., Manzano, R., Carpena-Ruiz, R.O., Gamarra, R.,  
513 Esteban, E., 2009. Heavy metals distribution in soils surrounding an abandoned mine in  
514 NW Madrid (Spain) and their transference to wild flora. Journal of Hazardous Materials  
515 162, 854-859.
- 516 Neubauer, E., von der Kammer, F., Knorr, K.H., Peiffer, S., Reichert, M., Hofmann, T.,  
517 2013. Colloid-associated export of arsenic in stream water during stormflow events.  
518 Chemical Geology 352, 81-91.

- 519 O'Day, P.A., Vlassopoulos, D., Root, R., Rivera, N., 2004. The influence of sulfur and  
520 iron on dissolved arsenic concentrations in the shallow subsurface under changing redox  
521 conditions. *Proceedings of the National Academy of Sciences of the United States of*  
522 *America* 101, 13703-13708.
- 523 Plathe, K.L., von der Kammer, F., Hassellöv, M., Moore, J., Murayama, M., Hofmann,  
524 T., Hochella, M.F., 2010. Using FIFFF and aTEM to determine trace metalnanoparticle  
525 associations in riverbed sediment. *Environmental Chemistry* 7, 82-93.
- 526 Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis  
527 for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 12,  
528 537-541.
- 529 Serrano, S., Gomez-Gonzalez, M.A., O'Day, P.A., Laborda, F., Bolea, E., Garrido, F.,  
530 2015. Arsenic speciation in the dispersible colloidal fraction of soils from a mine-  
531 impacted creek. *Journal of Hazardous Materials* 286, 30-40.
- 532 Slowey, A.J., Johnson, S.B., Newville, M., Brown Jr, G.E., 2007. Speciation and colloid  
533 transport of arsenic from mine tailings. *Applied Geochemistry* 22, 1884-1898.
- 534 Villalobos, M., García-Payne, D.G., López-Zepeda, J.L., Cenicerros-Gómez, A.E.,  
535 Gutiérrez-Ruiz, M.E., 2010. Natural Arsenic Attenuation via Metal Arsenate  
536 Precipitation in Soils Contaminated with Metallurgical Wastes: I. Wet Chemical and  
537 Thermodynamic Evidences. *Aquatic Geochemistry* 16, 225-250.
- 538 Vithana, C.L., Sullivan, L.A., Burton, E.D., Bush, R.T., 2014. Liberation of acidity and  
539 arsenic from schwertmannite: Effect of fulvic acid. *Chemical Geology* 372, 1-11.
- 540 Voegelin, A., Weber, F.-A., Kretzschmar, R., 2007. Distribution and speciation of  
541 arsenic around roots in a contaminated riparian floodplain soil: Micro-XRF element  
542 mapping and EXAFS spectroscopy. *Geochimica et Cosmochimica Acta* 71, 5804-5820.

543 Yu, J-Y., Heo, B., Choi, I-K., Cho, J-P., Chang. H-W., 1999. Apparent solubilities of  
544 schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage.  
545 *Geochimica et Cosmochimica Acta*, 63, 3407–3416.

546

547

ACCEPTED MANUSCRIPT

Table 1 – Elemental concentrations of soil/sediment and stream waters

Soil/sediment	Al	Mn	Fe	Cu	Zn	As	Pb	As/Fe <sup>b</sup>
	<i>mg kg<sup>-1</sup></i> <sup>a</sup>							
WP	1550	364	6.9x10 <sup>4</sup>	369	365	2.2x10 <sup>4</sup>	3213	0.23
A	4120	957	3.4x10 <sup>4</sup>	1886	1525	3313	448	0.07
B	2930	838	2.3x10 <sup>4</sup>	1383	1172	2278	354	0.07
C	2440	668	2.1x10 <sup>4</sup>	360	1331	816	172	0.03
D	2140	467	1.9x10 <sup>4</sup>	281	1167	1041	182	0.04

Stream waters	pH <sup>c</sup>	EC <i>μS cm<sup>-1</sup></i>	Mn	Fe	As	Pb
			<i>μg L<sup>-1</sup></i> <sup>d</sup>			
WP	3.92	237	204±8.8	250±31	32±1.7	14±0.3
A	6.88	49.7	7.1±0.8	60±10	67±6.1	0.52±0.06
B	7.01	46.0	2.8±0.1	90±17	92±11	0.88±0.03
C	6.90	47.8	1.7±0.2	69±8.9	108±10	0.75±0.03
D	7.23	47.3	1.8±0.4	56±4.8	87±2.2	0.24±0.01

<sup>a</sup> Pseudo-total concentrations of soils were measured by ICP-OES after aqua-regia addition and microwave-assisted digestion. Standard deviations of the ICP-OES determinations for each analyzed element are: Al = ± 13.1 mg kg<sup>-1</sup>, Mn = ± 1.2 mg kg<sup>-1</sup>, Fe = ± 7.2 mg kg<sup>-1</sup>, Cu = ± 0.7 mg kg<sup>-1</sup>, Zn = ± 1.0 mg kg<sup>-1</sup>, As = ± 0.3 mg kg<sup>-1</sup>, Pb = ± 2.4 mg kg<sup>-1</sup>

<sup>b</sup> Arsenic/Iron molar ratio

<sup>c</sup> pH and electrical conductivity (EC) of stream samples were also analyzed

<sup>d</sup> Pseudo-total concentrations of stream waters were measured by ICP-MS after aqua-regia addition and microwave-assisted digestion. Standard deviations (n=3) are presented in the table

Table 2 – Relative areas of the different components identified in the Mössbauer spectra

Sample	Fe(III) doublet	Fe(II) doublet	Fe(III) hematite	Fe(III) goethite	Fe(II)/ Fe(III) <sup>a</sup>
	%				
WP	81	3		16	0.03
A	88	12			0.14
B	79	21			0.27
C	64	17	19		0.20
D	63	15	22		0.18

<sup>a</sup> Fe(II)/Fe(III) molar ratio after fitting the areas of the Mössbauer spectra

Table 3 – Linear combination fit results for As and Fe K-edge EXAFS spectra of soil/sediments and CF samples

Soil/sediment - As EXAFS <sup>a</sup>								
Sample	As-FH <sup>b</sup>	Scorodite	As-Jar <sup>c</sup>	As-Goe <sup>d</sup>	Total	R factor <sup>e</sup>	red $\chi^2$ <sup>f</sup>	
			%					
WP	56.0	26.2	16.9		99.1	0.010	0.171	
A	97.3			1.6	98.9	0.014	0.330	
B	70.5			23.1	93.6	0.021	0.487	
C	85.8			11.0	96.8	0.021	0.489	
D	70.7			22.1	92.8	0.052	1.08	
CF - As EXAFS <sup>a</sup>								
Sample	As-FH <sup>b</sup>	Scor.	As-Goe <sup>d</sup>	Beudan.	As-Jar <sup>c</sup>	Total (%)	R factor <sup>e</sup>	red $\chi^2$ <sup>f</sup>
			%					
WP	50.8	35.9	15.1			101.8	0.017	0.438
A	97.1		6.3			103.4	0.017	0.456
B	92.3		7.8			100.1	0.022	0.552
C	90.1			13.4		103.5	0.091	2.53
D	96.3				4.2	100.5	0.041	1.02
CF -Fe EXAFS <sup>g</sup>								
Sample	Smectite	Schwert.	Pb-Jaros.	Illite	Jarosite	Total (%)	R factor <sup>e</sup>	red $\chi^2$ <sup>f</sup>
			%					
WP	36.2	34.2	33.9			104.3	0.008	0.100
A		57.0		26.4	16.3	110.0	0.020	0.194
B	15.6	62.9	16.0			94.5	0.006	0.058
C		58.0		26.9	20.9	105.8	0.008	0.090

<sup>a</sup> Linear combination fit (LCF) was applied over the k-range: 2-10.5 Å<sup>-1</sup> on the As-EXAFS spectra

<sup>b</sup> Arsenic(V) sorbed to ferrihydrite

<sup>c</sup> Arsenic(V) sorbed to jarosite

<sup>d</sup> Arsenic(V) sorbed to goethite

<sup>e</sup> Normalized sum of the squared residuals of the fit [ $R = \sum(\text{data-fit})^2 / \sum \text{data}^2$ ]

<sup>f</sup> Goodness-of-fit was assessed by the  $\chi^2$  statistic [= (F factor) / (no. of points – no. of variables)]

<sup>g</sup> Linear combination fit (LCF) was applied over the k-range: 2-7 Å<sup>-1</sup> on the Fe-EXAFS spectra

Table 4 – (a) Pseudo-total element concentrations of DCF and DF. (b) Colloidal mass of each DCF and their corresponding As and Fe concentrations per mass of colloid.

a	Sample	As	Al	Fe	Cu	Zn	Pb
		$mg L^{-1}^a$					
WP	DCF	0.23±0.05	0.73±0.06	1.13±0.22	0.22±0.01	0.39±0.04	0.04±0.01
	DF	0.03±0.01	0.64±0.08	0.74±0.29	0.23±0.02	0.39±0.04	0.01±0.01
	CF <sup>b</sup>	0.20	0.09	0.39	- <sup>c</sup>	- <sup>c</sup>	0.03
	CF/DCF <sup>d</sup>	87%	12%	34%	0%	0%	75%
	DCF/bulk <sup>e</sup>	0.01%	0.5%	0.02%	0.6%	1%	0.01%
A	DCF	9.58±0.16	84±0.19	81±0.54	3.85±0.12	3.68±0.11	1.59±0.38
	DF	0.21±0.03	0.05±0.04	0.03±0.03	0.21±0.04	0.12±0.02	0.01±0.01
	CF	9.37	~ 84	~ 81	3.64	3.56	1.58
	CF/DCF	98%	100%	100%	95%	97%	99%
	DCF/bulk	3%	20%	2%	2%	2%	4%
B	DCF	7.54±0.19	68±0.21	55±0.60	4.80±0.17	4.12±0.24	1.44±0.35
	DF	0.20±0.06	0.08±0.07	0.03±0.03	0.23±0.05	0.18±0.01	0.01±0.01
	CF	7.34	~ 68	~ 55	4.57	3.94	1.43
	CF/DCF	97%	100%	100%	95%	96%	99%
	DCF/bulk	3%	23%	2%	3%	4%	4%
C	DCF	2.31±0.18	76±0.27	47±0.46	0.87±0.08	4.40±0.19	0.60±0.37
	DF	0.22±0.07	0.05±0.02	0.03±0.03	0.06±0.01	0.35±0.03	0.01±0.01
	CF	2.09	~ 76	~ 47	0.81	4.05	0.59
	CF/DCF	90%	100%	100%	93%	92%	98%
	DCF/bulk	3%	31%	2%	2%	3%	3%
D	DCF	1.29±0.21	37±0.15	24±0.31	0.46±0.16	1.92±0.07	0.32±0.21
	DF	0.23±0.07	0.06±0.05	0.03±0.03	0.04±0.01	0.18±0.02	0.01±0.01
	CF	1.06	~ 37	~ 24	0.42	1.74	0.31
	CF/DCF	82%	100%	100%	91%	91%	97%
	DCF/bulk	1%	17%	1%	2%	2%	2%

b	Sample	Colloids	As	Fe	As / Fe <sup>h</sup>
		$mg kg^{-1}^f$	$mg kg coloid^{-1}^g$		
	WP	1395 ± 313	1434	2796	0.15
	A	9206 ± 367	10178	87987	0.09
	B	7744 ± 639	9478	71021	0.10
	C	7989 ± 496	2616	58830	0.04
	D	7869 ± 488	1347	30498	0.04

<sup>a</sup> Pseudo-total concentrations ± standard deviations (n = 3) of the ICP-OES determinations after aqua-regia addition and microwave-assisted digestion (Soil:Ultrapure water relationship = 4g/40 mL)

<sup>b</sup> The concentration of the colloidal fraction (CF, 1000-10 nm) is calculated as the difference between the dispersible colloidal fraction (DCF, < 1000 nm) and the dissolved fraction (DF, < 10 nm)

<sup>c</sup> Most or all of the metal(loid) is present only in the DF

<sup>d</sup> Relative contribution of the element concentration in the colloidal fraction (CF) to that in the dispersible colloidal fraction (DCF)

<sup>e</sup> Relative contribution of the element concentration in the dispersible colloidal fraction (DCF) to that in the bulk concentration, after transforming the DCF concentration to  $mg kg^{-1}$

<sup>f</sup> Colloidal mass calculated following the procedure described by Plathe *et al.* (2010), ± standard deviations (n = 3)

<sup>g</sup> Arsenic and iron concentrations in the colloidal fraction (CF, Table 9b) per kilogram of colloid

<sup>h</sup> Arsenic and iron molar ratio in the colloidal fraction

Table 5 – Maximum of colloidal sizes and recoveries of the DCF determined by AF4 <sup>a</sup>

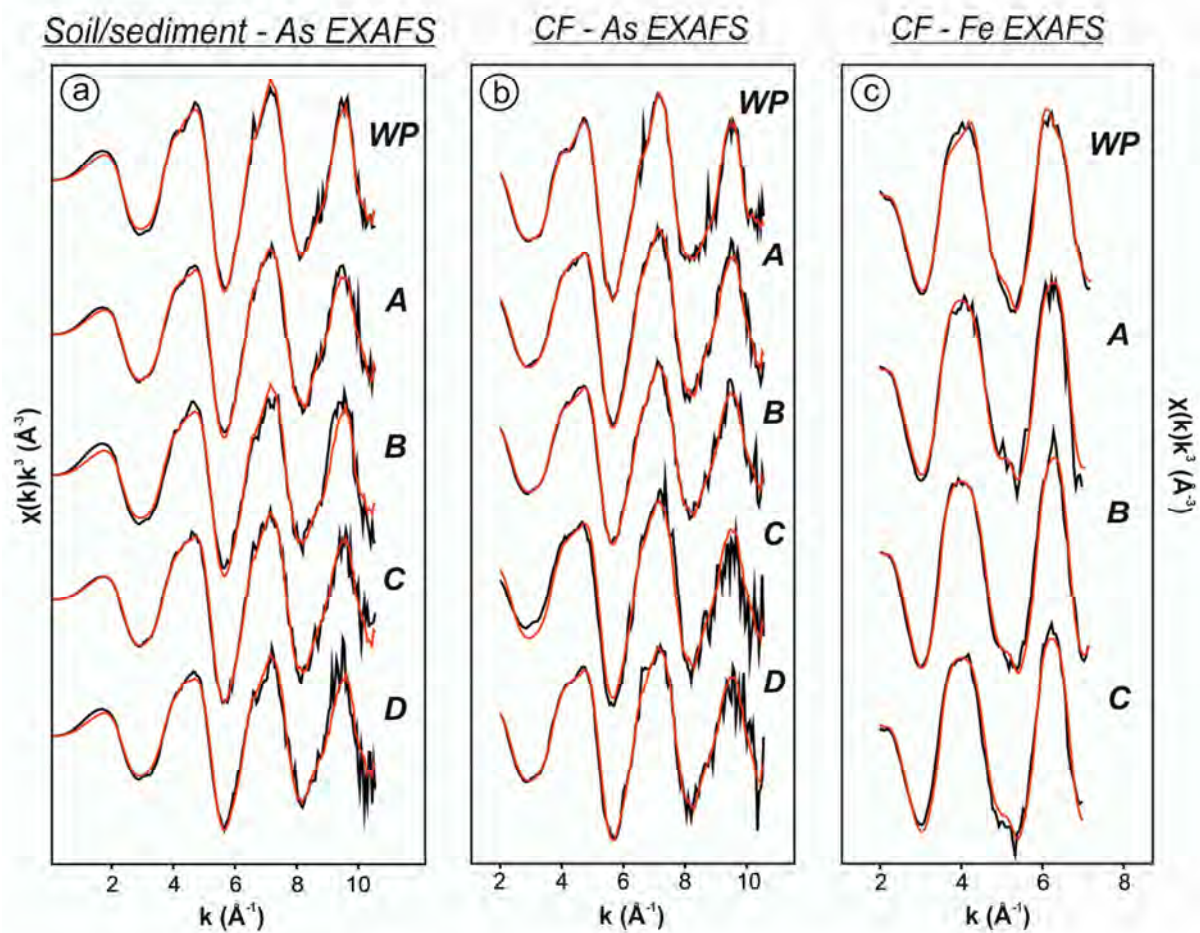
Sample	AF4-ICP-MS					
	<i>Al</i>		<i>As</i>		<i>Fe</i>	
	<i>nm</i> <sup>b</sup>	% <sup>c</sup>	<i>nm</i> <sup>b</sup>	% <sup>c</sup>	<i>nm</i> <sup>b</sup>	% <sup>c</sup>
<i>A</i>	264	71.9	257	67.8	254	68.2
<i>B</i>	306	48.7	307	53.8	305	40.4
<i>C</i>	234	56.3	221	55.5	238	43.6
<i>D</i>	251	45.7	245	52.0	246	41.3

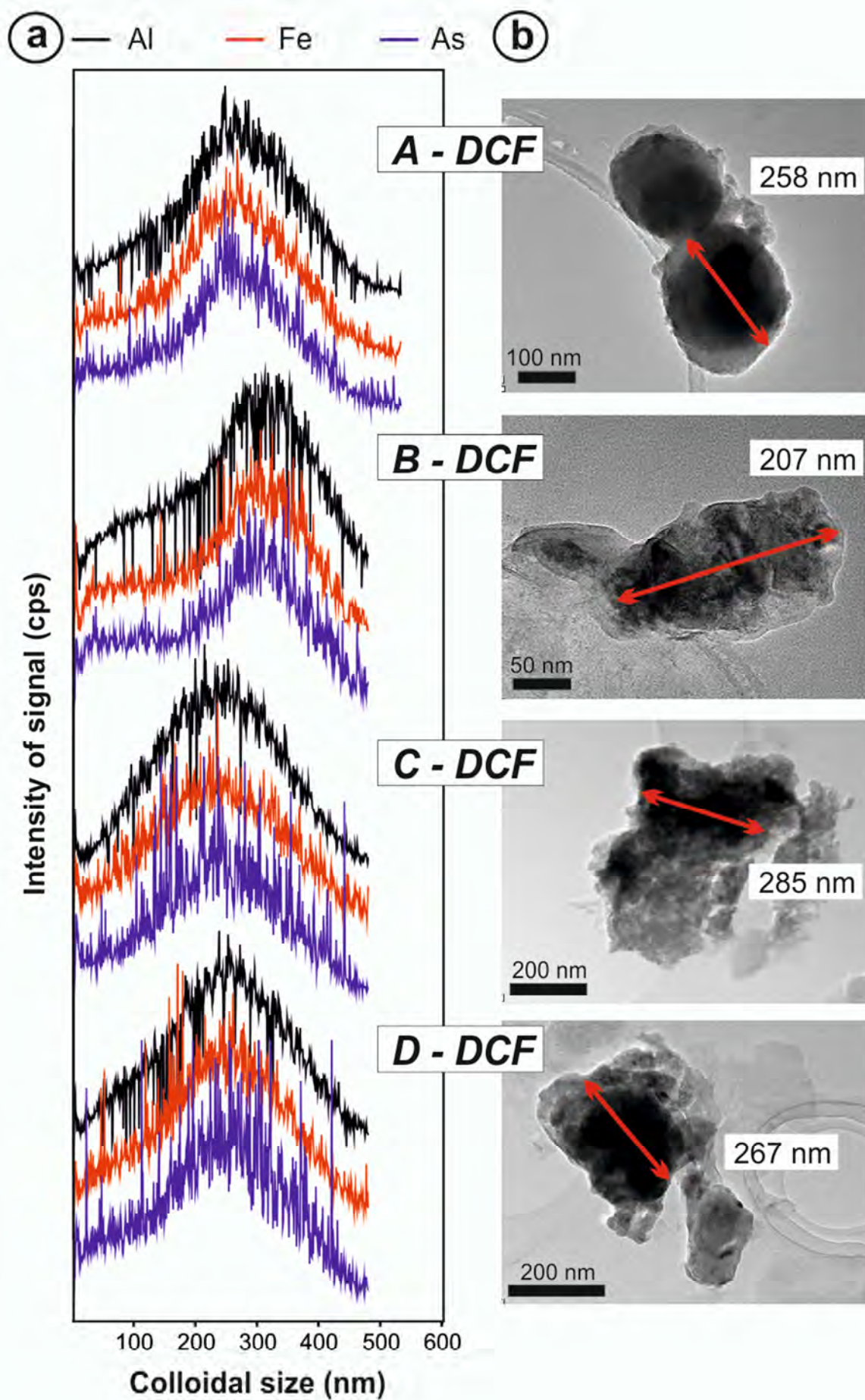
<sup>a</sup>The data shown are the average values of three replicates

<sup>b</sup>Maximum of size of the distribution found by AF4

<sup>c</sup>Recoveries (in percentage) obtained for the DCF analyzed







Iron oxide - clay composite vectors on long-distance transport of arsenic  
and toxic metals in mining-affected areas

Miguel Angel Gomez-Gonzalez<sup>a</sup>, Mario Villalobos<sup>b</sup>, Jose Francisco Marco<sup>c</sup>, Javier Garcia-Guinea<sup>a</sup>, Eduardo Bolea<sup>d</sup>, Francisco Laborda<sup>d</sup>, Fernando Garrido<sup>a</sup>

<sup>a</sup> Museo Nacional de Ciencias Naturales (MNCN, CSIC). C/ Jose Gutierrez Abascal 2, 28006, Madrid, Spain.

<sup>b</sup> Instituto de Geología. Universidad Nacional Autónoma de México (UNAM), Coyoacán, D.F. 04510, Mexico.

<sup>c</sup> Instituto de Química Física-Rocasolano (CSIC), C/ Serrano 119, 28006, Madrid, Spain.

<sup>d</sup> Instituto Universitario de Ciencias Ambientales (IUCA), Universidad de Zaragoza. C/ Pedro Cerbuna 12, 50009, Zaragoza, Spain.

## HIGHLIGHTS

- Long-distance dispersion of arsenic through mobile colloids is demonstrated
- Ferrihydrite found as thin coatings on clay minerals acts as arsenic sorbing phase
- This association carries other metals in concentrations above regulatory levels
- This association limits the role of iron oxides to attenuate arsenic pollution