Revised manuscript submitted to Chemosphere
2 September 2015

Colloidal mobilization of arsenic from mining-affected soils by surface runoff

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Keywords: Arsenic; runoff; colloids; AF4-ICP-MS; XAS; Rainfall simulation

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ABSTRACT

Scorodite-rich wastes left as a legacy of mining and smelting operations pose a threat to environmental health. Colloids formed by the weathering of processing wastes may control the release of arsenic (As) into surface waters. At a former mine site in Madrid (Spain), we investigated the mobilization of colloidal As by surface runoff from weathered processing wastes and from sediments in the bed of a draining creek and a downstream sedimentation-pond. Colloids mobilized by surfacerunoff during simulated rain events were characterized for their composition, structure and mode of As uptake using asymmetricflow field-flow fractionation coupled to inductively plasma mass spectrometry (AF4-ICP-MS) and X-ray absorption spectroscopy (XAS) at the As and Fe K-edges. Colloidal scorodite mobilized in surface runoff from the waste pile is acting as a mobile As carrier. In surface runoff from the river bed and the sedimentation pond, ferrihydrite was identified as the dominantAs-bearingcolloidal phase. The results from this study suggest that mobilization of As-bearing colloids by surface runoff may play an important role in the dispersion of Asfrom metallurgical wastes deposited above ground and needs to be considered in risk assessment.

1. INTRODUCTION

Mining and smelting operations have changed the global distributionand occurrenceof metal(oid)s at the Earth's surface(Rauch, 2012), and the release of metals and metalloidsfrom mining and processing wastes into aquatic and terrestrial environments may threaten environmental and human health.Human activities have led to substantial As contamination in the environment(Morin and Calas, 2006), as often occurs in association with economically relevant metal ores. Accordingly, the roasting and

50 smelting of metal ores has led to widespread environmentalcontamination via
51 atmospheric emissions and deposition of waste materials(Vaughan, 2006). In Spain,
52 there are many As-affected legacysites affected from former miningactivities. Often,
53 As-bearing processing wastes had beendumped aboveground and remain exposed to
54 rainfall and weathering, posing a risk for adjacent water bodies(Garcia-Sanchez and
55 Alvarez-Ayuso, 2003).
56 The weathering of processing sulfide-containing wastes leads to the formation of acid
57 mine drainage (AMD). The oxidation of Fe(II) and precipitation of Fe(III) in neutralized
58 AMD may lead to the formation of mobile colloidal carriers for As (Cheng et al.,
59 2009).Due to their physicochemical properties, colloids may persist in aqueous
60 suspensions over extended periods of time andact as carriers for poorly soluble metals
61 and metalloids in surface and surbsurface environments(Kretzschmar and Sticher,
62 1997). The affinity of As to colloidalFe(III) and the importance of such colloidal
63 particles as As-mobilizing carriers in the environment has been documented(Fritzsche et
64 al., 2011). For instance, Grosbois et al.(2011)identified different As-carriers during the
65 transport of solid particulate matter in varying abundances according to the hydrological
66 cycle of a river draining a former gold mine district in France.Furthermore, colloids and
67 colloid-associated contaminants, mobilized by rainfall within ephemeral overland
68 courses, can be transported rapidly through the vadose zone with minimal interaction
69 with the soil matrix (Ranville et al., 2005). This can be attributed to the presence of
70 preferential flow paths,which in turn may play a role inthe solid-phaseAs distribution
71 and Asretention mechanism in soils,especially in locations affected by large amounts of
72 metals released with AMD(Helmhart et al., 2012). Overall, the importance of surface
73 runoff as compared to infiltrationfor As dispersion may vary with rainfall intensity and
74 duration,vegetation cover, soil topography, as well as soil physical properties and flow

conditions through soils and riverbeds. Irrespective of the mode of colloid transport, the nature and stability of As-bearing colloids in tailings and mining wastes that control the extent of As release needs to be assessed.

The combined use of spectroscopic, spectrometric and fractionation techniques offers the means to gain information on the size-dependent elemental composition of colloids, the nature of the colloidal carrier phase, and the speciation of associated contaminants. Rainfall simulation experiments on the other hand, allow to control rainfall parameters (intensity and duration) and to exclude the inherent variability associated with natural rain that increases the complexity of stormwater quality research(Bian et al., 2011).Simulated rainfall have been used to assess heavy metal contamination in urban areas(Wicke et al., 2012),but only few studies have been performed on contaminated soils under natural conditions(Fernandez-Galvez et al., 2008). To date, however,thecolloid-facilitated release of Aswith surface runoff in mining-affected areas has not been assessed.

Asymmetric flow field-flow fractionation (AF4) is a separation techniquefor the characterization of colloids from natural samples(Laborda et al., 2011).When coupled to an inductively coupled plasma mass spectrometer (ICP-MS), the size-dependentelemental composition of the colloidal phasescan be determined. For instance, Neubauer et al.(2013) characterized the colloid distribution in soil runoff as generated by storm events using AF4-ICP-MS. The authorsshowed that a colloidal fraction ranging from 0.2 to 0.45 μm was mobilized but they did not assess the speciation of the colloidal As. Direct insight into the speciation of colloidal As and Fe can be gained using X-ray absorption spectroscopy (XAS),widely used to study the speciation of As and Fe in natural samples(O'Day et al., 2004; Voegelin et al., 2007),includingdispersible soil colloids(Regelink et al., 2014; Serrano et al., 2015).

In previous studies, we examined the dispersion and solid phase partitioning of As in soils and sediments affected by weathering and erosion of metallurgical processing wastes at a former mining and smelting site in Madrid province (Gomez-Gonzalez et al., 2014).In the same area, the molecular-scale speciation of As associated to colloids detached from soil extractshas previously been studied (Serrano et al., 2015).In this continuing work, we aimed at determining the extent and mode of colloidal As mobilization with surface runoff during simulated rain events. AF4-ICP-MS was used to determine the colloid size distribution and As partitioning between the dissolved and colloidal phase, and Fe and As K-edge XAS to determine the colloidal carrier phase and colloidal As speciation.

2. MATERIALS AND METHODS

2.1. Site description

The experiment was conducted in a sub-catchment of the Guadalix River (Madrid, Spain) at the foot of the 'Sistema Central' mountain range(40º45'34.33" N - 3º41'07.13" O, 929 meters altitude). In the area,metal sulfides and wolframite ores in association with quartz veins were mined for tungsten extraction during the Second World War. Theabandoned smelting factory along with mining wastes deposited above ground still remain at this site (Helmhart et al., 2012).The massive pile of processing wastes (approximately 6x6 m, 1 meter-thick, 19 g As kg^{-1}), is subjected to weathering and erosion (Gomez-Gonzalez et al., 2014).The site is representative for many other legacy sites in Madrid province and other regions of Spain.

The average annual rainfallin the area reaches 705 mm and the average temperature, 13.3ºC(Spanish Agency of Meteorology, AEMET). About 188-201 mm of the annual rain precipitate in winter, 197-213 mm in spring, 85-93 mm in summer and 200-233 in

125 autumn. Rainfall simulation tests were performed at: A) the arsenic-bearing waste pile
126 (WP); B) the river bed (RB) of a small stream (~ 1 m wide) that seasonally collects
127 surface runoff from WP; and C) the sediment that accumulatesdownstream in an
128 artificial sedimentation pond (SP) (Figure S1).During intense rainfall, a major part of
129 runoff waters isusually retained in the sedimentation pond remainingstagnant over
130 several days until evaporation and infiltration lead to the drying out of the pond.
131 Physical, chemical, and mineralogical properties of the topmost layer of soils and
132 sediments at the experimental locations are inTable 1.
133
134 *2.2. Rainfall simulation experiments*
135 Simulation experiments were performed using the portable rainfall simulator designed
136 byCalvo et al.(1988) and modified byCerda et al.(1997). Single rainfall events of
137 distilled water were applied at28 mm h^{-1} during 60 minutes in each experimental
138 location.The basic components of the simulator and the experimental conditions are
139 described in the Supplementary Material(FiguresS2 and S3).
140
141 *2.3. Isolation of thecolloid-suspensions in runoff*
142 Three fractions of the runoff suspensions from the rainfall simulations were analyzed:
143 (i) the colloid-containing suspension (CS, ≤ 1000 nm) obtained after centrifugation of
144 the runoff suspension for the removal of particulate material, (ii) the solid colloids
145 (1000-10 nm) isolated from the colloid-containing suspension by ultrafiltration using
146 10-nm membranes, and (iii) the dissolved fraction (DF) that passed 10-nm ultrafiltration
147 membranes. The colloid-suspension (CS, ≤ 1000 nm) thus includes both the solid
148 colloids (1000-10 nm) and the dissolved fraction (≤ 10 nm). Runoff samples were
149 subjected to the protocol described in the supplementary material (Figure S4).

150

151 *2.4. Size characterizationand elemental quantification by AF4–ICP-MS*

152 The particle sizedistribution and elemental compositionof the colloid suspensions

153 weredetermined by AF4 (AF2000 model, *Postnova Analytics*)coupled to ICP-MS, a

154 technique that has previously been shown to allowthedetermination of the size

155 distribution of natural colloids generated in contaminated soils and the quantification of

156 thecolloidaly mobilized metal(loid)s (Neubauer et al., 2013).An advantage of the AF4

157 technique is the mild separation conditions in absence of stationary phase, which

158 preserves the original colloid size distribution. The AF4-ICP-MS specifications as well

159 as recovery calculations are presented in theSupplementary Material(TablesS2 and S3).

160

161 *2.5. As and FeK-edge X-ray absorption spectroscopy (XAS) analyses*

162 Arsenic and Fe XAS measurements were done on thecolloids (1000-10 nm)

163 isolatedfrom the colloid suspension obtained from thewaste-pileand the sedimentation-

164 pondafter 20 and 50 minutes of simulated rainfall. Arsenic and Fe K-edge EXAFS

165 spectra were recorded at the bending magnet BM25A beamline at the ESRF-European

166 Synchrotron Radiation Facility (Grenoble, France). Additional As EXAFS spectra from

167 the SP colloids were recorded at beamline 22 of the ALBA Synchrotron Facility

168 (Barcelona, Spain). Methods and reference materials are described in the Supplementary

169 Material(Table S4).

170

171 3. RESULTS

172 *3.1. Characterization of colloid-suspensions*

173 The volumes, pH and electrical conductivity of runoff suspensions collected during the

174 simulated 60-minutes rain events with 28 mm of rainfall are listed in Table 2. Given the

175 collected volumes and the total amount of distilled water applied per rain event, only
176 6% (WP) to 19% (RB) of the applied rainfall contributed to surface runoff, whereas the
177 major fraction (94-81%) infiltrated into the subsurface. The acidity and electrical
178 conductivity (EC) of the colloid-suspensions remained almost constant with time. The
179 colloid concentration in the suspensions is summarized in Table 3and Figure
180 S5(Supplementary Material). In the waste-pile and river-bed, with clay contents of 47%
181 and 26% (Table 1), respectively, the colloid concentration in the suspensions remained
182 almost constantwith time over the rainfall simulation, while in the sedimentation-pond,
183 with the lowestclay content (12%), the colloid concentration in the colloid-
184 suspensiondecreased markedly during the initial 20 minutes of rainfall, and varied
185 around a mean value of 0.26 mg L^{-1}over the rest of the irrigation period(Figure S5).
186 The fractions of total As in runoff in colloidal form (97%, 0.8% 22% for waste-pile,
187 river-bed and sedimentation-pond, respectively) indicated near exclusive As
188 mobilization in colloidal form from the waste-pile, an important colloidal As
189 mobilization from the sedimentation-pond and only dissolved As mobilization from the
190 river-bed (Table 3).The fraction of dissolved Fe was negligible in all cases, indicating
191 near-exclusive association of Fe with suspended colloids.
192 The molar As/Fe ratio in colloids inmobilized form the waste-pile zone was near unity,
193 while this parameter was 0.36-0.58 and 0.05 in colloids from river-bed and
194 sediementation-pond, respectively. This disparity pointed to differences inthe As mode
195 of association to colloids that warrant examination by XAS.
196 Both As and Fe concentrations in the colloid-suspension expressed per mass of colloids
197 decreasedat the end of the experiments (50 minutes), although the colloid
198 concentrationitself remained constant. Notably, theAs concentration in the colloidal
199 phase was about 1.9 (river-bed) to 2.9 (waste-pile and sedimentation-pond) times higher

than in the corresponding bulk materials (Tables 1 and 3), indicating that As was enriched in the colloid-size fraction of the waste and sediment materials. Conversely, the Feconcentration in colloids mobilized from the waste-pile wassimilar to the Fe concentration in the waste material, whereas the Fe concentration in colloids mobilized from the river-bed and the sedimentation-pond decreased 5-10 times. This could be partially explained by the formation of Fe-(hydr)oxide coatings (Gomez-Gonzalez et al., 2014) on the surface of aluminum-silicate particles (Table 1) larger than the size of colloids (< 1000 nm) in both the river-bed and the sedimentation-pond.

3.2. Size characterization of the colloidsfrom the sedimentation-pond

The colloid suspensions from the waste-pile and the river-bed could not be measured by AF4. In the waste-pile this was due to the high electrical conductivity of its runoff suspensions (Table 2) which led to irreversible colloids absorption onto the AF4 channel membrane. The colloid concentrations in the runoff suspensions from the river-bed were too low to be determined by AF4 (Table 3, Figure S6). Conversely, the particle size distribution and associated As, Fe and Al concentrations in the colloid-suspensions(20, 35 and 50 minutes)of the sedimentation-pond zone were obtained by AF4-ICP-MS (Figures 1and S7). Size distribution maxima were 147 nm, 160 nm and 195 nm for the colloid-suspensions obtained at 20, 35 and 50 minutes of rainfall,respectively. The maxima corresponding to the secondary shoulder visible at 20 and 35 minutes and to the defined secondary peak at 50 minutes of rainfall varied little (~460 nm) as estimated by fitting the fractograms to a double-peak lorentzian function (Figure 1a).

Concentration maxima were estimatedby fitting a lognormal function (Figure 1b; maxima, white circle; confidence interval (colour line) at 95% probability). Arsenic and

225 Fe concentration maxima appeared at 143, 115 and 136 nm for the colloid-suspension
226 obtained at 20, 35 and 50 minutes of irrigation time, indicating a similar behavior of
227 these elements in the colloidal mobilization. The Al concentration maxima appeared at
228 156, 121 and 166 nm for the same irrigation times.
229
230 *3.3. Speciation of colloidal As and Fe by K-edge XAS*
231 The As and Fe K-egde XANES spectra of colloids isolated from runoff from the waste-
232 pile and sedimentation-pond (Figure S8, Supplementary Material), indicatedAs(V) and
233 Fe(III) as thedominant oxidation states.The As and Fe K-edge EXAFS spectra of
234 colloids from the waste-pile runoff and XANES spectra of colloids from the
235 sedimentation-pond together with the reconstructedlinear combination fitting (LCF)
236 spectra are shown in Figure 2and the LCF results are listed in Table 4. In the case of
237 colloids from the sedimentation-pond, only the XANES spectra were evaluateddue to
238 the low quality of the corresponding EXAFS spectra. Arsenic K-edge EXAFS spectra
239 from the waste-pile runoff indicated a major contribution (91–94%) fromscoroditeand
240 minor contribution of As(V) sorbed to ferrihydrite (6–9%) at both irrigation times. Iron
241 K-edge EXAFS spectra also showed a major contribution from scorodite (91–96%) and
242 minor amountsof nontronite (9%) and hematite (4%). Results from shell-by-shell fit
243 analysis of As and Fe K-edge EXAFS spectra of colloids from the waste-pile were in
244 line with a dominant fraction of As and Fe in scorodite (Table S5, details on shell-fit
245 procedure in Supplementary Material).
246 The LCF analysis of the As and Fe K-edge XANES spectra of colloids from the
247 sedimentation-pond on the other hand, revealed a dominant fraction of As(V) sorbed to
248 ferrihydrite and Fe(III) in smectite (50%), nontronite (21–27%) and schwertmannite

249 (23–29%) (Table 4, Figure 2)suggesting that Fe was mainly contained in clay minerals,
250 and to a lesser extent poorly crystalline Fe(III)-(hydr)oxides.
251
252 4. DISCUSSION
253 *4.1. Colloidal scorodite as potential nanovector for As dispersion with surface runoff*
254 Although scorodite may be thermodynamically unstable when exposed to water
255 containing low Fe and As concentrations, the dissolution of synthetic scorodite over the
256 pH range 5-9 has been shown to be slow(Bluteau and Demopoulos, 2007),andPaktunc
257 and Bruggeman(2010)reported that As solubility in equilibrium with scorodite is lowest
258 at pH 3-4.Our results show that colloidal scorodite mobilized with surface runoffis
259 acting as a mobileAs carrier. Molecular-scale colloidal As speciation confirms the
260 presence of scorodite in the colloids isolated from the waste-pile colloid-suspensions
261 (Tables 4 and S5, Figure 2). These results are in agreement with the molar As/Fe ratio
262 in the colloid-suspension (Table 3) andthe XRD analyses (Table 1).The colloidal
263 stability and mobility of scorodite is expected to depend on its surface charge, but
264 respective data is scarce. According toRobins(1987), scorodite formed at pH < 1.8
265 exhibit a negative surface charge, whereas the formation of a surface Fe(III)-
266 (hydr)oxide may lead to a positive surface charge. Other surface transformation on the
267 colloidal scorodite may also take place affecting the stability of weathered scorodite
268 colloids.
269 From the waste-pile material, As was mainly mobilized in colloidal form, with colloidal
270 As concentrations between 3512 and 4488 µg L^{-1}. Based on the average As
271 concentration in the colloid-suspensions from the waste-pile(Table 3) and the volume of
272 surface runoff, about 6.7 mg of colloidal As were released with the surface runoff from
273 the irrigated area (0.24 m^2) during the 60-minutes rainfall simulation, corresponding to

~28mg colloidal As per m^2waste-pile surface. Considering that the dumped processing wastes cover about 36 m^2, roughly 1 g of colloidal As could be released by surface runoff during a natural rainfall event with a duration and intensity similar to the simulation (60 minutes, 28 mm of rainfall). During the simulated rainfall event, 6% of the water volume applied to the waste pile surface was collected as surface runoff (Table 2),suggesting that most water infiltrated into the waste material.Colloidal scorodite could also contribute to vertical transport of As into deeper soil horizons. Indeed, a recent study at the same site (Gomez-Gonzalez et al., 2014)indicated the presence of scorodite at greater depths, although the fraction of scorodite decreased with depth at the expense of As(V) sorbedto Fe(III)-(hydr)oxides.

Rainfall intensity and duration affect the runoff/infiltration ratio and this should be considered site-specific. In the studied area, rainfall events with > 10 mm occur on average on 18.5 days per year, and storm events with > 30 mm of precipitation on 2 days per year(Guíaresumida del climaenEspaña (1981-2010), www.aemet.es). This indicates that the potential for continuing As dispersion via colloidal As release and surface runoff is substantial unless remediation actions are taken.

4.2. Potential migration of colloidal As into the downstream soils

Arsenic-bearing colloids in runoff suspensions from the river-bed and the sedimentation-pond greatly differ from those identified in the waste-pile zone. Two processes are depicted from our results: First, virtually no colloidal scorodite mobilized fromthe waste-pile appears at the river-bed. At this second experimental zone, colloidal As concentrations are negligible comparedto dissolved ones (Table 3). Along the river-bed, a large fraction of As released after scorodite dissolution might be leached through the river-bed itself, and through preferential flow paths in the subsoil, as suggested by

299 Helmhart et al.(2012). Second, in the sedimentation-pond, where a major part of runoff
300 waters isretained and may remain stagnant over several days before drying out, colloidal
301 As is mostly As(V) associated with ferrihydrite or other Fe(III)-(hydr)oxides.
302 The increasing pH in the river-bed and sedimendation-pond, i.e., with increasing
303 distance from the waste pile may favor scorodite dissolution and As(V) resorption to
304 (amorphous) Fe(III)-(hydr)oxide colloids(Serrano et al., 2015).Ferrihydrite has a high
305 capacity for As(V) uptake(Fritzsche et al., 2011), and their association has been
306 extensively reported(Johnson and Hallberg, 2005). The present study indicates that a
307 fraction of As-bearing Fe(III)-(hydr)oxide colloids contained in the sedimentation-pond
308 as spectroscopically described in the dispersible colloidal fraction by Serrano et al.
309 (2015) are potentially mobilizable and may behave as colloidalAs carriers within runoff
310 generated by strong rain events.
311 The differences in colloid size-distributions derived from AF4-UV-vis (Figure 1a) and
312 AF4-ICP-MS fractograms (Figure 1b) as well as the slight discrepancy in temporal
313 trends of Fe and Al (Figures 1b and S7) may be due to Al-containing clay minerals in
314 the colloidal fraction of the sedimentation-pond runoff (Table 4), whoselaminar
315 structure affects the hydrodynamic diameter of the particles measured by AF4.
316 The use of distilled water as rainfall instead of artificial rainwater with background
317 electrolyte concentrations may introduce some disparity with natural rain events.
318 However,Vazquez et al. (2003)reported ionic rainfall compositions in NW Spain with a
319 range of electrical conductivities similar to the ones obtained in our river-bed and
320 sedimentation-pond runoff suspensions. According to that, we would not expect drastic
321 differences in the use of distilled water rather than a slight enhance of colloids release.
322
323 5. CONCLUSIONS

The results from this study suggest that colloidal scorodite may be released from mining wastes and act as an As carrier in surface runoff. Similarly, As(V) immobilize by sorption to Fe(III)-(hydr)oxidesin the sediments from the sedimentation-pond may be susceptible to mobilization in colloidal form.

Deposited mine wastes from legacy mining activities in Spain, should therefore be isolated to reduce weathering and colloid transport with surface runoff which may result in the dispersion of As in both colloidal and dissolved As form.This should be taken into account when As-rich metallurgical wastes are deposited above ground, because both scorodite and ferryhidrite should not be considered as effective trapping systems of As(V). More research is needed, however, to better quantify the importance of As mobilization with surface and subsurface runoff in colloidal and dissolved form in order to effectivelyprevent As release to the environment. Also, the application of any capping system aiming to prevent the wastes from erosion could limit the colloids and contaminants migration in the environment.

Rainfall simulation experiments and advanced separation techniques such as AF4-ICP-MS are suitable analytical procedures to characterize suspended colloids in runoff and study their potential for colloid-facilitated contaminant release and transport.XAS provides complementary molecular-level insight into the speciation of inorganic contaminants in the colloidal phase.

ACKNOWLEDGEMENTS

The Spanish Ministry of Economy and Competitiveness (research project CGL2010-17434) supported this study. M.A. Gomez-Gonzalez was supported by the Ph.D. Spanish FPI fellowship (BES-2011-046461) and by graduate students (EEBB-I-14-08063) programs. XAS measurements on BM25A beamline (ESRF) were supported by

the project EV-41; XAS measurements on BL22–CLAESS beamline (ALBA-CELLS) were supported by the project 2012100332. ICP-OES and ICP-MS analyseswereperformed at *Servicio de análisis químico (Servicio General de Apoyo a la Investigación-SAI), Universidad de Zaragoza*.

FIGURE CAPTIONS

1– (a) AF4-UV-vis fractograms of colloid-suspension from the sedimentation-pond at 20 (black), 35 (red), and 50 minutes (blue). (b) Concentration maxima (white circle)fractogramsand confidence interval (colour line) at 95% probability.Dotted line represents the average size maxima of all elements and times (131 nm of size).

2– Arsenic (a) and iron (b) K-edge EXAFS spectra of waste-pile (WP) colloids.Arsenic (c) and iron (d) XANES spectra of sedimentation-pond (SP) colloids.Black lines,experimental data; red lines, LCF results(Table 4 for LCF values).

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Table

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Table 1 – Physical and chemical properties of bulk samples

Characteristics	Samples		
	WP	***RB***	***SP***
pH [a]	3.3	4.3	6.1
E.C. (µS cm^{-1}) [b]	2320	93.7	110
ECEC (eq kg^{-1}) [c]	0.79	0.11	0.05
TOC (%) [d]	0.03	0.24	0.20
Soil texture (%)[e]			
Sand	53	30	70
Silt	-	44	18
Clay	47	26	12
Element concentration (mg kg^{-1})[f]			
Al	1100	422	257
Fe	25230	45530	16980
Cu	1390	99	52
Zn	151	82	73
As	14390	620	94
Pb	465	29	22
Mineralogical composition[g]			
Major phases	Scorodite Gypsum	Illite Kaolinite Quartz	Illite Microcline Kaolinite Albite
Minor phases	Quartz Hematite	Muscovite Albite	Quartz Montmorillonite

[a]*Potassium chloride (KCl, 3 mol L^{-1}) was used as electrolyte solution for pH measurements*
[b]*E.C. = Electrical conductivity*
[c]*ECEC = Effective Cation exchange capacity as the sum of Ca, Mg, Na, K and Al (Shuman 1990)*
[d]*TOC = Total organic carbon determined by wet digestion (Walkley and Black 1934)*
[e]*Texture was determine by the pipette method after removing soil organic matter (Gee and Bauder 1982)*
[f]*Pseudo-total concentration measured by ICP-OES after aqua regia + microwave digestion (Chen and Ma 2001)*
[g]*Determined by qualitative XRD analysis. Major phases are those with more than 15 % contribution to the total composition*

Table 2 – Physical characteristics of the collected runoff suspensions[a]

Sampling location	Runoff time	***Runoff volume***[b]	***pH***	Electrical Conductivity
	min	*mm*		*µS cm^{-1}*
WP	*0-10*	0.27	3.90	1567
	10-20	0.23	4.08	1532
	20-30	0.27	4.16	1580
	30-40	0.24	4.04	1640
	40-50	0.30	4.14	1585
	50-60	0.32	4.20	1548
	Total surface runoff[c]	1.63 (6%)		
RB	*0-5*	0.45	4.54	198
	5-10	0.45	4.60	164
	10-15	0.47	4.63	143
	15-20	0.45	4.64	133
	20-25	0.44	4.60	147
	25-30	0.43	4.52	163
	30-35	0.37	4.57	169
	35-40	0.40	4.63	160

	40-45	0.46	4.56	159
	45-50	0.44	4.54	156
	50-55	0.48	4.68	136
	55-60	0.49	4.54	157
	Total surface runoff [c]	5.33 (19 %)		
SP	*0-5*	0.28	6.24	53
	5-10	0.31	6.26	52
	10-15	0.30	6.44	44
	15-20	0.37	6.33	43
	20-25	0.39	6.41	40
	25-30	0.42	6.18	41
	30-35	0.44	5.96	46
	35-40	0.46	5.90	38
	40-45	0.48	5.94	37
	45-50	0.45	6.25	33
	50-55	0.44	6.34	30
	55-60	0.48	6.43	23
	Total surface runoff [c]	4.81 (17 %)		

[a] *Distilled water was used in the rainfall simulation tests*
[b] *Volume of runoff collected during the rainfall simulation test at waste-pile (WP), river-bed (RB) and sedimentation-pond (SP)*
[c] *Defined as the sum of all volumes collected during the experiment. The percentage of water collected respect to the total water pumped during the experiment (28 mm) is presented in parenthesis*

Table 3 –As and Fe concentrationsof colloid (≤ 1000 nm) suspensions (CS) and dissolved fractions(DF)≤ 10 nm (± standard deviation, *n=3* [a])

Sample	Time	Fraction	As	Fe	Colloid concent.[d]	Molar As/Fe ratio	As concent.	Fe concent.
			µg L^{-1} [b,c]		mgL^{-1}		mg kg $colloid^{-1}$ [e]	
WP	20 min	*CS*	4500±5	3230±303				
		DF	128±7	< QL	109	1.04	$41 \cdot 10^3$	$30 \cdot 10^3$
		Colloids	4372 [f]	3230				
WP	40 min	*CS*	4600±23	3480±215				
		DF	112±2	< QL	95	0.98	$48 \cdot 10^3$	$36 \cdot 10^3$
		Colloids	4488	3480				
WP	50 min	*CS*	3590±18	2660±382				
		DF	78±2	< QL	102	1.01	$35 \cdot 10^3$	$26 \cdot 10^3$
		Colloids	3512	2660				
RB	20 min	*CS*	281±6	588±303				
		DF	298±4	< QL	200	0.36	1410	2940
		Colloids	-	588				
RB	35 min	*CS*	262±6	587±185				
		DF	260±6	<QL	207	0.33	1270	2840
		Colloids	2	587				
RB	50 min	*CS*	146±7	186±206				
		DF	148±8	< QL	154	0.58	950	1210
		Colloids	-	186				
SP	20 min	*CS*	131±5	1870±253				
		DF	100±4	< QL	399	0.05	330	4690
		Colloids	31	1870				
SP	35 min	*CS*	128±6	1990±290				
		DF	106±5	< QL	437	0.05	290	4550
		Colloids	22	1990				
SP	50 min	*CS*	96±6	1060±348				
		DF	72±6	< QL	427	0.05	200	2200
		Colloids	24	1060				

[a] *Standard deviation was calculated by triplicate determination of the same aliquot*

[b] *Elementalconcentration was expressed on µg of metal per liter of colloid suspension (CS)*
[c] *Quantification limits (QL) for ICP-MS measurement of As was 0.1 µg L^{-1} and 73 µg L^{-1} forICP-OES measurements of Fe*
[d] *Mass of colloids calculated according to Plathe et al. 2010*
[e] *Milligrams of As and Fe per kilogram of colloids (1000-10 nm)*
[f] *As and Fe concentrations of colloids (1000-10 nm) were defined as the difference between the concentration of the CS and the DF*

Table 4 – Linear combination fit results for As and FeK-edge EXAFS or XANES spectra

As EXAFS / XANES [a]

Sample	Scorodite[b]		As sorbed to Ferrihydrite[b]		R Factor[e]	red χ^{2}[f]
	%[c]	*ΔeV*[d]	*%*	*ΔeV*		
WP 20 min [g]	94.2	-	5.7	-	0.0249	0.8562
WP 50 min [g]	91.3	-	8.7	-	0.0199	0.6527
SP 20 min [h]			99.7	- 0.3	0.0116	0.0062
SP 50 min [h]			99.6	- 0.4	0.0125	0.0068

Fe EXAFS / XANES [a]

Sample	Scorodite[b]		Nontronite[b]		Hematite[b]		Smectite[b]		Schwert-mannite[b]		R factor	red χ^{2}
	%	*ΔeV*	*%*	*ΔeV*	*%*	*ΔeV*	*%*	*ΔeV*	*%*	*ΔeV*		
WP 20 min [i]	91.1	-	8.6	-							0.0517	0.665
WP 50 min [i]	95.7	-			4.2	-					0.0505	0.619
SP 20 min [j]			27.1	0.1			50.3	- 0.1	23.3	0.2	0.0003	0.0001
SP 50 min [j]			20.9	0.3			50.4	- 0.1	29.3	- 0.1	0.0003	0.0001

[a] *EXAFS spectra of waste-pile(WP) colloids and XANES spectra of sedimentation-pond (SP) colloids were analyzed by LCF analyses*
[b] *The scorodite reference spectrum was obtained from Savage et al. (2005). The As(V) sorbed to ferrihydrite spectrum was obtained from Root et al. (2009). The nontronite (NAu-1) spectrum was obtained from Gorski et al. (2013). The hematite and smectite spectra were obtained from O'Day et al. (2004). The schwertmannite spectrum was measured by S. Hayes in the BM 4-1(SSRL, Stanford, USA, unpublished) (Table S4, Supplementary Material)*
[c] *Fittings were not constrained to sum 100 %*
[d] *Fittingvariations of XANES LCF given by the software Athena (Ravel and Newville 2005)*
[e] *Normalized sum of the squared residuals of the fit [$R = \sum(data-fit)^2/\sum data^2$)]*
[f] *Goodness-of-fit was assessed by the χ^2 statistic [= (F factor) / (no. of points – no. of variables)]*
[g] *LCF EXAFS range: 2 – 11 Å, spectra measured at ESRF (Grenoble, France)*
[h] *LCF XANES range: 11855 – 11935 eV, spectra measured at ALBA (Barcelona, Spain)*
[i] *LCF EXAFS range: 2 – 9 Å, spectra measured at ESRF (Grenoble, France)*
[j] *LCF XANES range: 7105 – 7185 eV, spectra measured at ESRF (Grenoble, France)*

Figure
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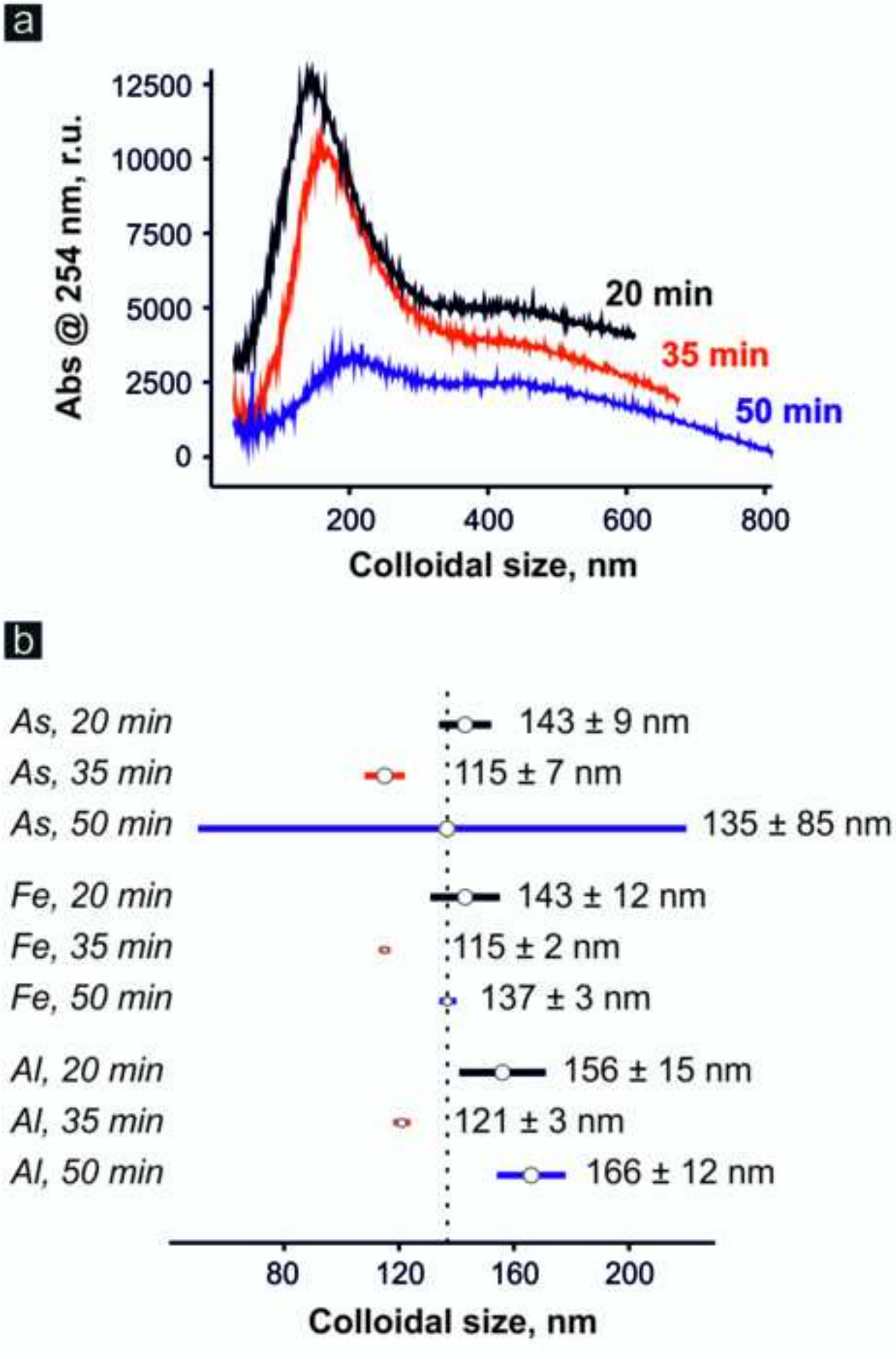

Figure 2

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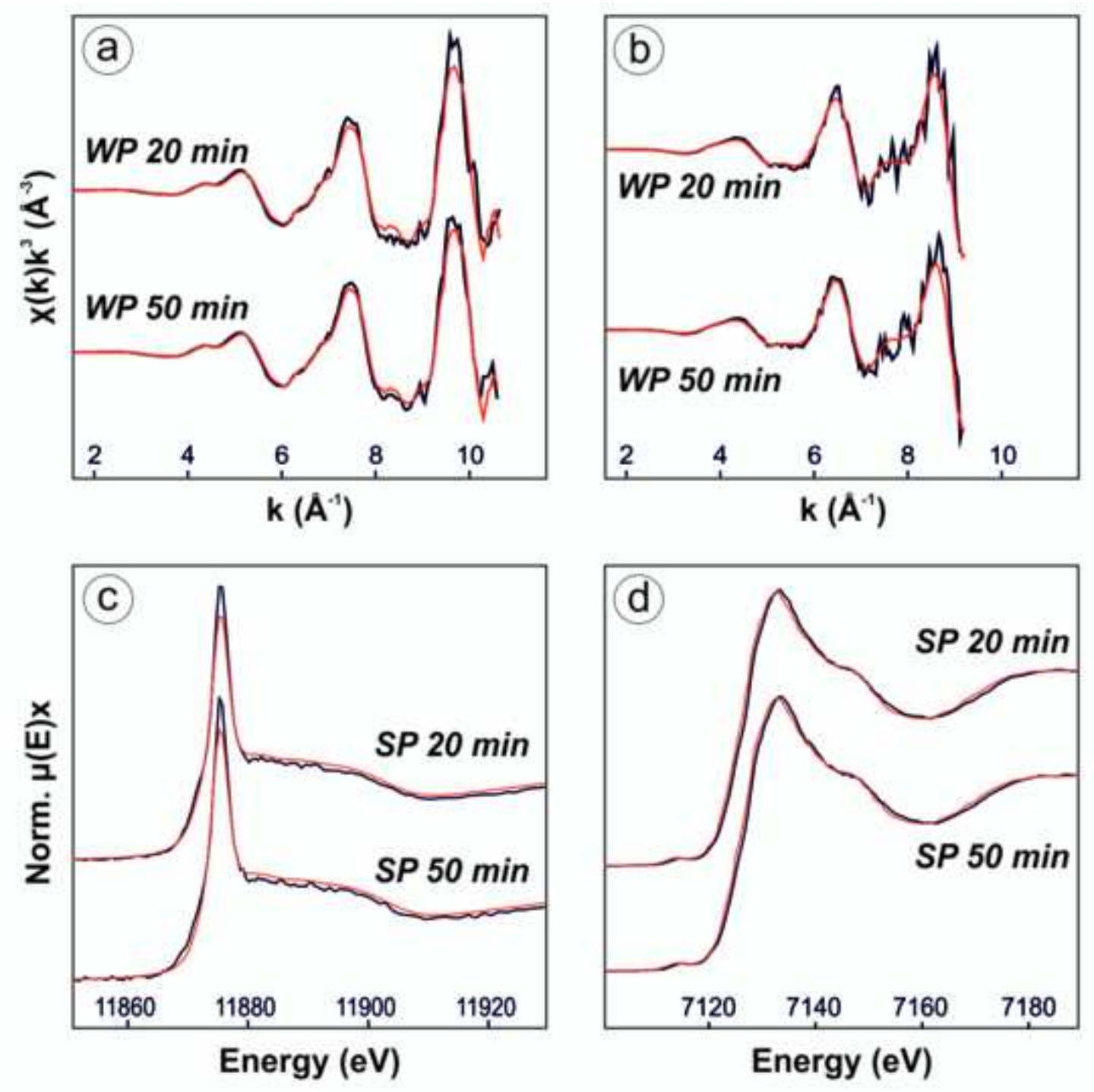

Supplementary Material

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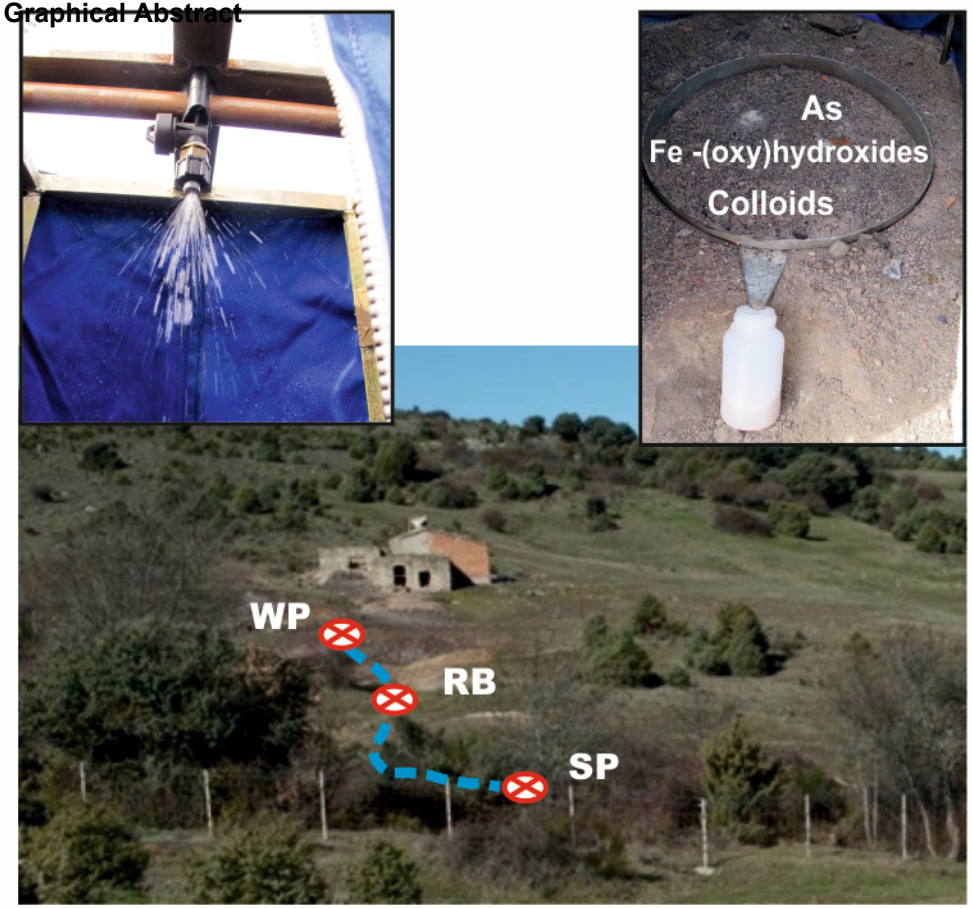
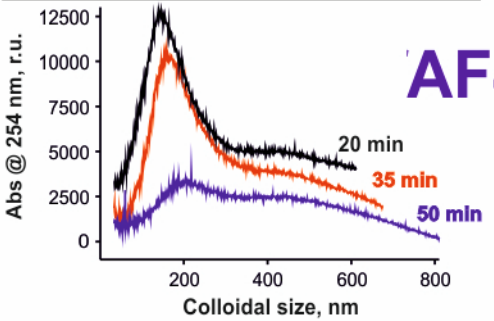
Graphical Abstract

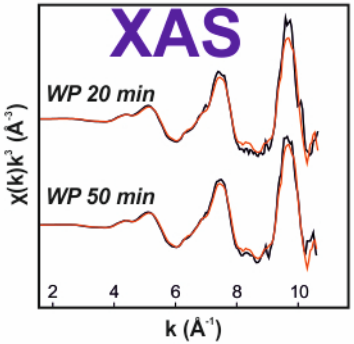


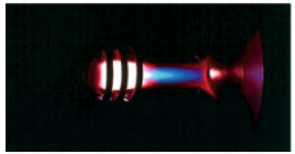
[Colloid suspension]$^{<1000nm}$



[Colloids]$^{1000-10nm}$

[Dissolved]$^{<10nm}$





ICP-MS