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J. Masbou, Jérôme Viers, Jose Antonio Grande, R. Freydier, Cyril Zouiten, Patrick Seyler, O.S. S Pokrovsky, Philippe Behra, Brigitte Dubreuil, M.L. de La Torre

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# 1 Strong temporal and spatial variation of dissolved Cu isotope 2 composition in acid mine drainage under contrasted hydrological 3 conditions 4

5 Masbou<sup>1,2</sup> J., Viers<sup>1\*</sup> J., Grande<sup>3</sup> J-A., Freydier<sup>4</sup> R., Zouiten<sup>1</sup> C., Seyler<sup>4</sup> P., Pokrovsky<sup>1,5</sup> O.,  
6 Behra<sup>6</sup> P., Dubreuil<sup>6</sup> B., de la Torre<sup>3</sup> M-L.

7  
8 1 : Géosciences Environnement Toulouse (GET), Université de Toulouse, CNRS, IRD 14  
9 avenue Edouard Belin, 31400 Toulouse, France

10 2 : Laboratoire d'Hydrologie et de Géo chimie de Strasbourg (LHyGeS), Université de  
11 Strasbourg/ENGEEES, CNRS, 1 rue Blessig, 67084, Strasbourg Cedex, France

12 3 : Centro de Investigación para la Ingeniería en Minería Sostenible, Escuela Técnica  
13 Superior de Ingeniería, Universidad de Huelva, Ctra. Palos de la Frontera, s/n, 21819 Palos de  
14 la Frontera, Huelva, Spain

15 4 : Laboratoire HydroSciences UMR 5569, CNRS, IRD, Université de Montpellier, 163 Rue  
16 Auguste Broussonnet, CC 57, 34090, Montpellier, France

17 5 : BIO-GEO-CLIM Laboratory, Tomsk State University, 36 Lenina Prs, Tomsk, Russia

18 6 : Laboratoire de Chimie Agro-industrielle, LCA, Université de Toulouse, INRA, Toulouse,  
19 France

20  
21 \* Corresponding author: Jérôme Viers, Ph.D.

22

23

## 24 **Abstract**

25 Copper export and mobility in acid mine drainage are difficult to understand with  
26 conventional approaches. Within this context, Cu isotopes could be a powerful tool and here  
27 we have examined the relative abundance of dissolved ( $< 0.22 \mu\text{m}$ ) Cu isotopes ( $\delta^{65}\text{Cu}$ ) in the  
28 Meca River which is an outlet of the Tharsis mine, one of the largest abandoned mines of the  
29 Iberian Pyrite Belt, Spain. We followed the chemical and isotopic composition of the  
30 upstream and downstream points of the catchment during a 24-h diel cycle. Additional  $\delta^{65}\text{Cu}$   
31 values were obtained from the tributary stream, suspended matter ( $> 0.22 \mu\text{m}$ ) and bed  
32 sediments samples. Our goals were to 1) assess Cu sources variability at the upstream point  
33 under contrasted hydrological conditions and 2) investigate the conservative vs. non  
34 conservative Cu behavior along a stream. Average  $\delta^{65}\text{Cu}$  values varied from -0.47 to -0.08 ‰  
35 ( $n=9$ ) upstream and from -0.63 to -0.31‰ downstream ( $n=7$ ) demonstrating that Cu isotopes  
36 are heterogeneous over the diel cycle and along the Meca River. During dry conditions, at the  
37 upstream point of the Meca River the Cu isotopic composition was heavier which is in  
38 agreement with the preferential release of heavy isotopes during the oxidative dissolution of

39 primary sulfides. The more negative values obtained during high water flow are explained by  
40 the contribution of soil and waste deposit weathering. Finally, a comparison of upstream vs.  
41 downstream Cu isotope composition is consistent with a conservative behavior of Cu, and  
42 isotope mass balance calculations estimate that 87 % of dissolved Cu detected downstream  
43 originate from the Tharsis mine outlet. These interpretations were supported by  
44 thermodynamic modelling and sediment characterisation data (X-ray diffraction, Raman  
45 Spectroscopy). Overall, based on contrasted hydrological conditions (dry vs flooded), and  
46 taking the advantage of isotope insensitivity to dilution, the present work demonstrates the  
47 efficiency of using the Cu isotopes approach for tracing sources and processes in the AMD  
48 regions.

49  
50 **Keywords:** copper; isotopes, Acid Mine Drainage (AMD); river; flood

51

## 52 **1. Introduction**

53 The Iberian Pyrite Belt (South-west Spain), which is among the largest metallogenic  
54 provinces in the world, presents serious problems of Acid Mine Drainage (AMD) (Almodovar  
55 et al., 1997; Leblanc et al., 2000 ; Grande et al., 2010, 2013; Olias et al., 2019) due to the  
56 intense mining activity that occurred during different periods of history including the present  
57 time. In particular, during the most active period, from the mid-XIX<sup>th</sup> to the XX<sup>th</sup> centuries,  
58 large amounts of abandoned waste have been left over the whole region (Pérez Ostalé, 2014).  
59 Induced AMD phenomenon leads to surface waters with low pH, and a high metal and  
60 sulphate load that strongly affect both inland and marine ecosystems since the two largest  
61 AMD affected watersheds of the region, the Odiel and Tinto Rivers, deliver their waters to the  
62 estuary of Huelva (Achterberg et al., 2003; Sainz et al., 2004; Nieto et al., 2007; Grande et al.,  
63 2018). Due to scarcity of water in this region of the South-West of Europe, the AMD can  
64 strongly impact the aquatic ecosystems and surface and groundwater quality (see

65 www.fao.org). Despite the numerous studies dealing with the AMD processes origins and  
66 consequences on waters, soils and biota (e.g., Elbaz-Poulichet et al., 2001) the metal  
67 distribution, reactivity and transport mechanisms in the rivers still remain poorly known.

68 In addition to dissolved and particulate metals concentrations monitoring in surface waters,  
69 the stable isotopes of metals (Cu, Fe, Zn...) are now routinely used to trace the source of  
70 metals in the environment and to reveal the biotic and abiotic mechanisms controlling  
71 elements transfer within a watershed (see Teng et al. (2017) for a review). As most of the  
72 mines in the Iberian Pyrite Belt were mined for copper (Saez et al., 1999), we looked at the  
73 potential contribution of copper isotopes to better understand this metal behaviour in such  
74 areas. A number of works addressed Cu isotopes in the AMD context (Mathur et al., 2005;  
75 Balistrieri et al., 2008; Borrok et al., 2008; Fernandez and Borrok, 2009; Kimball et al., 2009;  
76 Mathur et al., 2009; Pérez Rodríguez et al., 2013; Mathur et al., 2014; Song et al., 2016;  
77 Dótor-Almazán et al., 2017; Viers et al., 2018; Roebbert et al., 2018). Carried out during  
78 steady hydrological conditions, these studies showed that sulfide mineral dissolution in  
79 oxygenic conditions essentially controls the Cu isotopes distribution in surface and ground  
80 waters. Extensive natural observations and experimental works evidenced strong enrichment  
81 in heavy Cu isotopes of aqueous solution interacting with primary sulfide minerals. Moreover,  
82 in contrast to relatively narrow range of isotopic signature ( $\delta^{65}\text{Cu}$ ) in these primary minerals,  
83 the secondary mineral products exhibit a  $\delta^{65}\text{Cu}$  variability as high as from -17 to +10 ‰, see  
84 (Mathur et al., 2009). The speciation of Cu in sulfide mine environments is extremely  
85 complex because Cu is present in numerous secondary minerals whose proportions strongly  
86 depend on the hydrological regime (wetting and drying) (Valente et al., 2013). Moreover, the  
87 formation of these minerals in mine-impacted surface waters is controlled by key parameters  
88 such as pH, temperature, redox conditions, saturation state and biological activity (Sanchez-  
89 Espana et al., 2005, 2011; Sarmiento et al., 2009a,b). High sensitivity to fractionation of

90 copper isotopes in supergene environments makes copper isotopes a good potential tracer for  
91 metal transfer within the continuum mine – river – lake encountered in the Iberian Pyrite Belt.

92 To better understand the environmental factors controlling Cu concentration and isotopes  
93 fractionation in AMD aquatic settings, our initial objective was to study the evolution of  
94 chemical and isotopic fractionation during a diel cycle (24h) in an AMD impacted river.  
95 Indeed, several parameters and processes that are often interrelated ( $T^\circ$ , dissolved  $O_2$ , water  
96 discharge, pH...) may influence the concentration of the chemical species during a diel cycle  
97 in the water (Nimick et al., 2011). To address this issue within the AMD context, we used a  
98 representative scenario of strongly contaminated Meca River (Huelva, SW Spain) of the  
99 Iberian Pyrite Belt. This river drains the abandoned copper mine of Tharsis - one of the  
100 largest in the area - and delivers its waters to the Sancho Lake. Taking the advantage of an  
101 extremely strong rainy event that occurred during the sampling period, we primarily focused  
102 on studying the response of a mining system to variable hydrological stage. Further, in order  
103 to quantify the spatial variability of Cu isotope composition in the AMD-affected Meca River,  
104 we performed measurements in two points, one at the outlet of the mining district and one 20  
105 km downstream, three hours each during 24 hours. We expected that by examining the  
106 variation of Cu isotopic composition in time and space, we can better understand the transfer  
107 and origin of Cu and other metals within the mining area and reveal the mechanisms of Cu  
108 isotopes fractionation in these environmentally important riverine systems.

109

## 110 **2. Site description**

### 111 *2.1. Geology of the Iberian Pyrite Belt*

112 The study area belongs to the Iberian Pyrite Belt (IPB), located in the south-west of the  
113 Iberian Peninsula. This IPB is approximately 240 km long and 50 km wide and is one of the

114 largest stocks of massive sulfides of volcanogenic origin in the world. It includes more than  
115 90 mines (Saez et al., 1999). Pyrite ( $\text{FeS}_2$ ) is the main ore mineral but one finds a procession  
116 of other metallic sulfides such as sphalerite ( $\text{ZnS}$ ), galena ( $\text{PbS}$ ), chalcopyrite ( $\text{CuFeS}_2$ ),  
117 arsenopyrite ( $\text{FeAsS}$ ) and there is a large variety of other metal sulfides containing minor  
118 quantities of Cd, Sn, Ag, Au, Co, Hg. Today, the majority of these mines are abandoned even  
119 though some remain in operation. Details about the geology of this area can be found in  
120 Tornos et al. (2008) and Conde et al. (2009).

121

## 122 2.2. *Hydroclimatic conditions*

123 The study area, located in the Huelva province, has a Mediterranean climate, which can be  
124 classified as semi-arid. Annual precipitation is about 630 mm/year, being mostly concentrated  
125 in the wet season from October to May, and the average annual temperature is 17.1 °C  
126 (<http://www.aemet.es>).

127 Our study took place in the watershed of the Meca River, a tributary of the Odiel River.  
128 The Odiel River joins the Tinto River at the city of Huelva. The average water discharge of  
129 the Odiel River is around  $10 \text{ m}^3 \cdot \text{s}^{-1}$  at Gibraleon, a town close to the river mouth (see  
130 ConfederacionHidrografica del Guadiana; <https://www.chguadiana.es>). The Odiel watershed  
131 with a surface of  $2300 \text{ km}^2$  and a length of 140 km accounts for about 80% of the continental  
132 water reaching the estuary of Huelva (Santisteban, 2015). The whole river network is  
133 impacted by acid mine drainage (Grande et al., 2018). This is especially correct for the Meca  
134 River due to the presence of the Tharsis mine, in the upstream part of its catchment. Although  
135 it is now abandoned, Tharsis is one of the largest mining districts with almost 100 Mt of  
136 estimated resources (Conde et al., 2009). Further details of the Tharsis mine can be found in  
137 Perez Ostale (2014) and Valente et al. (2013).

138 The weather was particularly rainy during the field sampling (11 to 12-May-2016). It  
139 rained 58 mm the preceding three days (8 to 10-May-2016) to our sampling (Alosno station)  
140 and 24 mm on the 11-May-2016. Unfortunately, we do not have the whole dataset for rain  
141 water because the weather station was destroyed during this storm event; As the Meca River  
142 water discharge is not monitored continuously, we performed a measurement of the water  
143 discharge using the “bucket method” when it was possible. Using previous work done by  
144 Galvan et al. (2009) within the Meca River catchment, sulphate concentrations could be used  
145 in the first order to account for the relative variation in water discharge. Indeed, these authors  
146 proposed the following relation between sulphate concentration ( $SO_4$ ) and water discharge  
147 ( $Q$ ) : ( $[SO_4] = 362.1 * Q^{-0.30}$ ). No relation was proposed by these authors between Cu  
148 concentration and  $Q$  due to the lack of reproducibility.

149

### 150 **3. Materials and methods**

#### 151 *3.1. Sampling protocol*

152 Sampling strategy aimed to study the geochemical processes along the Meca River during  
153 a complete diel cycle (24 h). Geographical gradient was investigated by collecting water  
154 samples simultaneously by two different teams in two sampling sites (Fig. 1): *i*) the Tharsis  
155 Mine outlet located upstream of the watershed called ‘upstream’ and *ii*) a point located 20 km  
156 downstream (called ‘downstream’). Sampling was achieved in a similar timeframe of 24h for  
157 the two sites, between 11-May-2016 4:00 p.m. and 12-May-2016 5:00 p.m. with a time step  
158 of 3 hours. In addition, one sample of the main Meca tributary (between the two points) was  
159 also collected (Tributary stream, Fig. 1). In addition to water samples, a bedload sediment  
160 sample from the Meca River was collected at the upstream point.

161 At each sampling point, the values of pH, dissolved O<sub>2</sub>, temperature, and specific  
162 conductivity were measured *in-situ* using a portable multi-parameter instrument (WTW®,  
163 340i). Protocols for the measurement of these parameters and the sampling method are  
164 reported in Viers et al. (2018). Among the collected samples, the 0.22 µm membrane of four  
165 selected samples were conserved to recover suspended sediments and perform chemical  
166 analyses. In addition to 0.22 µm filtration, an ultrafiltration at 1,000 Da were carried out on  
167 four selected samples collected upstream (11-May-2016 4:00 p.m., 11-May-2016 10:00 p.m.,  
168 12-May-2016 4:00 a.m., 12-May-2016 10:00 a.m.) using a 50 mL Amicon® ultrafiltration  
169 cell. Details of ultrafiltration procedure, analyses of possible artifacts and yields are given  
170 elsewhere (Viers et al., 1997; Dupré et al., 1999; Vasyukova et al., 2010).

171

### 172 *3.2. Mineralogical characterization*

173 Two suspended sediments collected at the upstream point (ME-A 11-May-2016 10 p.m.  
174 and ME-A 12-May-2016 4 p.m. samples) were characterised by SEM-EDX (form, chemical  
175 composition) at the Centre de MicroCaractérisationRaimondCastaing (Toulouse) and by X-  
176 Ray Diffraction at the GET laboratory (Toulouse). All the details about the methods are  
177 reported in Blondet et al. (2019) and Blotevogel et al. (2018).

178 The Raman spectra of the ME-A 11-May-2016 10 p.m. sample was obtained at room  
179 temperature by the confocal microscope Raman spectrometer (Horiba Scientific Labram HR  
180 evolution spectrometer) equipped with charge coupled device (CCD) as detector at the LCA  
181 laboratory of the Ensiacet (INPT). We used the 532 nm laser as excitation source and a dry  
182 objective MPLN x100 (NA: 0.90 µm). Measurement conditions were: laser power of 2.5 mW  
183 during 1 second and 2 accumulations; pinhole: 100 µm; spectral range: 100 to 2400 cm<sup>-1</sup>  
184 scanned with a high-resolution grating with 1800 gr/mm; Raman spectra: recorded directly



185 from powder. Raman spectral libraries from Bio-Rad and KnowItAll® ID Expert™  
186 spectroscopy software were used for the identification.

187

### 188 *3.3. Elemental content determination (major and Trace Elements (TE))*

189 Major and trace element concentrations were measured using ICP-MS (iCAP Q, Thermo  
190 Scientific- Kinetic Energy Discrimination mode using He) at the AETE-ISO platform (OSU  
191 OREME/Université de Montpellier). Concentrations were determined with external  
192 calibration using (Be, Sc, Ge, Rh, Ir) as internal standards to correct potential sensitivity  
193 drifts. The quality of the analysis was checked by analyzing international certified reference  
194 waters (CNRC SLRS-6). The accuracy was better than 5% relative to the certified values and  
195 the analytical error (relative standard deviation) was better than 5% for concentrations ten  
196 times higher than the detection limits. Anions concentrations were determined by ionic  
197 chromatography at the GET laboratory.

198 In addition to total measurements, Fe speciation ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) was determined by  
199 spectrophotometry and on-site using ferrozine method (Viollier et al., 2000). These  
200 measurements were performed on the dissolved fraction ( $<0.22 \mu\text{m}$ ) immediately after  
201 sampling for the upstream samples.

202 Before analysis, sediments were digested at the GET laboratory. For each sample, 100 mg  
203 of sediment were precisely weighed in Teflon vessels. 1 mL of  $\text{H}_2\text{O}_2$  and 0.5 mL of bidistilled  
204  $\text{HNO}_3$  were added to the samples and left at room temperature for 24 hours. Then, 1 mL of  
205  $\text{HNO}_3$  is added and the solutions were warmed at  $80^\circ\text{C}$  for 24 h. The solution is then  
206 evaporated on a plate at  $80^\circ\text{C}$ . 1.2 ml of HF and 1.2 ml of bidistilled  $\text{HNO}_3$  are then added for  
207 a new warming step at  $80^\circ\text{C}$ . After evaporation, 20 drops of bidistilled HCL and 10 drops of  
208 bidistilled  $\text{HNO}_3$  are added. The acid solution was warmed at  $115^\circ\text{C}$  for 24 h and finally

209 evaporated at 80°C. After complete evaporation, the remaining solid residue for each sample  
210 was dissolved in 10 mL of a 10% HNO<sub>3</sub> solution. Acid blanks and certified reference material  
211 samples (LKSD-03, lake sediment samples) were also used to ensure the quality of the  
212 measures and their traceability.

213

#### 214 *3.4. Cu isotopes determination*

215 Water sample aliquots containing approximately 1000 ng of Cu were purified using anion  
216 exchange chromatography on AG-MP1 resin (BIORAD) following an adapted protocol from  
217 Borrok et al. (2008). The protocol was repeated twice in order to ensure a complete separation  
218 of Cu from the matrix. The total procedure blank was negligible in comparison with the  
219 amount of Cu in the samples (<1%). Column yields and remaining elements such as (Na, Mg,  
220 Ca, Ti, Cr) that can interfere with Cu and Zn isotopes (Petit et al., 2008) were checked for  
221 each samples using Q-ICP-MS iCAP Q (Thermo Scientific). The yield was 100 ± 5% and no  
222 interfering elements were found in the solutions. Cu isotopic analyses were performed on a  
223 multiple-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) Neptune  
224 Plus (Thermo Scientific®), using SIS (Stable introduction System) nebulization chamber and  
225 PFA self-aspiration nebulizer (50 µl.min<sup>-1</sup>, Elemental Scientific®) at Plateforme AETE-ISO  
226 (OSU OREME-Université de Montpellier, France). Each sample was analyzed three times  
227 and was bracketed with the SRM NIST 976 copper solution. Cu isotopes (<sup>63</sup>Cu, <sup>65</sup>Cu), Zn  
228 isotopes (<sup>64</sup>Zn, <sup>66</sup>Zn, <sup>67</sup>Zn, <sup>68</sup>Zn), and Ni isotope (<sup>62</sup>Ni) were monitored simultaneously.  
229 Measurements of <sup>62</sup>Ni signal allowed correcting the possible isobaric interference of <sup>64</sup>Ni on  
230 <sup>64</sup>Zn. A Zn solution JMC 3e0749-L from Lyon was added to the samples in order to correct  
231 instrumental mass bias using the <sup>66</sup>Zn/<sup>64</sup>Zn ratio (exponential law) and the method of sample-  
232 standard bracketing was used to determine the δ<sup>65</sup>Cu (Marechal et al., 1999). The 2σ variation  
233 obtained on the 3 independent δ<sup>65</sup>Cu measurements was 0.01-0.06 ‰.

234  $\delta^{65}\text{Cu}$  (in units of ‰) is the Cu isotopic deviation relative to a standard, the SRM NIST-  
235 976:

$$236 \quad \delta^{65}\text{Cu} = \left( \left( \frac{\left( \frac{{}^{65}\text{Cu}}{{}^{63}\text{Cu}} \right)_{\text{sample}}}{\left( \frac{{}^{65}\text{Cu}}{{}^{63}\text{Cu}} \right)_{\text{NIST976}}} \right) - 1 \right) \times 1000$$

237

### 238 2.3. Thermodynamic calculations

239 Thermodynamic analysis including calculations of the speciation and the saturation  
240 indexes have been performed for the Meca River (upstream and downstream points) with  
241 respect to the common minerals of mining environments and specifically those described for  
242 the Tharsis mine by previous studies (Sanchez-Espana et al., 2005; Valente et al., 2013).  
243 Following these studies, we considered that goethite, ferrihydrite, jarosite, gibbsite,  
244 schwertmannite, (hydro)basaluminite, and gypsum may precipitate from aqueous solution.  
245 Modelling calculations were done using Visual MINTEQ ver. 3.0. In the case of the minerals  
246 schwertmannite and hydrobasaluminite the solubility product constants ( $\log K_{\text{sp}}$ ) were taken  
247 from Sanchez-Espana et al. (2011) and the calculations were done manually using the element  
248 activities given by Visual Minteq 3.0. It is visible that their value for schwertmannite ( $\log K_{\text{sp}}$   
249 =  $18.8 \pm 3.5$ ; pH range = 2.6 – 5.2) is very similar to that proposed by Bigham et al. (1996)  
250 ( $\log K_{\text{sp}} = 18.0 \pm 2.5$ ; pH range = 2.8 – 3.2). The results of speciation and saturation indexes  
251 are reported in the supplementary information (Table S1 A and B).

252

## 253 3. Results

254 *3.1. Variation of the water conductivity and pH in the Meca River*

255 In the upstream point, conductivity varies from 2.8 to 11.4 mS/cm and pH varies between  
256 2.43 and 2.82 (Table 1). At the downstream point, conductivity is much lower (from 0.31 to  
257 0.54 mS/cm) and pH is higher with values ranging between 3.61 and 5.68. The Meca tributary  
258 exhibits intermediate values with a pH of 3.85 and a conductivity of 0.51 mS/cm.

259 Element concentrations in the river water are reported in Table 1. At the upstream point,  
260 the anionic load is dominated by  $\text{SO}_4^{2-}$  (> 99%) and the cationic load is dominated by Fe (>  
261 50%),  $\text{Mg}^{2+}$  (> 20%),  $\text{Al}^{3+}$  (> 15%),  $\text{Zn}^{2+}$  and  $\text{Ca}^{2+}$  (> 4%) and  $\text{Cu}^{2+}$  (~1%). At the  
262 downstream point, the anionic load is dominated by  $\text{SO}_4^{2-}$  (> 60%) and  $\text{Cl}^-$  (> 30%) while the  
263 cationic load is dominated by  $\text{Mg}^{2+}$  (> 35%),  $\text{Na}^+$  (> 30%),  $\text{Ca}^{2+}$  (> 20%), and Fe (> 6%).  
264 Copper accounts for less than 0.5% of the cationic load at the downstream point. In the Meca  
265 tributary, the anionic load is dominated by  $\text{SO}_4^{2-}$  (70%), followed by  $\text{Cl}^-$  and  $\text{NO}_3^-$  (15%). The  
266 cationic load is dominated by  $\text{Mg}^{2+}$  (40%),  $\text{Ca}^{2+}$  (30%) and  $\text{Na}^+$  (20%). Elemental  
267 concentrations are generally much lower in the downstream sampling point (e.g., 80 times for  
268 Cu) because of dilution process. However, we note that Cl,  $\text{NO}_3$  and K concentrations are  
269 higher in the downstream sampling point while Na concentration is rather similar in the two  
270 sampling points.

271

272 *3.2. Copper concentration and isotope composition of Meca River*

273 Upstream, dissolved Cu concentrations range from ~17 mg/L to ~120 mg/L and  
274 insignificant differences have been detected between concentrations in the < 0.22  $\mu\text{m}$  fraction  
275 and in the < 1,000 Da fraction (see Table 1), revealing the absence of Cu in the colloidal  
276 phase (1 kDa - 0.22  $\mu\text{m}$ ). Copper concentrations obtained during this campaign are in good  
277 agreement with those measured previously in the Odiel watershed and its sub-watersheds

278 (e.g., Sanchez Espana et al., 2005; Sarmiento et al., 2009a,b; Grande et al., 2010; Moreno  
279 Gonzalez et al., 2020). Dissolved Cu concentrations decrease to 0.29 - 1.65 mg/L in the  
280 downstream point. In both sampling points, dissolved Cu is highly correlated with SO<sub>4</sub>  
281 (R<sup>2</sup>=0.99 between Cu and SO<sub>4</sub>), Fe concentrations (Fig. 2 and 3) and other elements. To  
282 illustrate the link between these elements, we reported the relationship obtained between Cu  
283 and Ni concentrations for both upstream and downstream points (Figure SI-1). In order to  
284 explore multiple correlations between parameters (time, concentrations...), a Partial Least  
285 Square Analysis method was necessary since we have more variables than individuals (Wold,  
286 1985; Abdi, 2010) (see Fig. SI-2). The inertia graph reveals that only one single factor is  
287 interpretable (Fig. SI-2A). The two sites are clearly distinguished by their chemical  
288 composition and by the evolution of concentrations through time (see Fig. SI-2C). In the  
289 upstream point Cu and other element concentrations vary simultaneously as a function of time  
290 (and water discharge variation) while concentrations are much more stable at the downstream  
291 point.

292 Copper isotope compositions range from -0.47 to -0.08 ‰ (n = 9) and -0.63 to -0.31 (n = 7)  
293 ‰ at upstream and downstream point, respectively (Table 1). These values are coherent but  
294 more variable than those previously obtained in a similar context (-0.75 ± 0.13 ‰ in the Odiel  
295 River, Borrok et al., 2008). Cu isotope composition of the Meca River suspended matter  
296 collected on 12-May-2016 at 4:00 p.m. ( $\delta^{65}\text{Cu}_{\text{suspended-matter}} = -0.41 \pm 0.03 \text{ ‰}$ ) is the same as  
297 that of filtered water ( $\delta^{65}\text{Cu}_{\text{Dissolved}} = -0.42 \pm 0.01 \text{ ‰}$ , Table 2). On the contrary, the top layers  
298 of bed sediments of the Meca River revealed more negative  $\delta^{65}\text{Cu}_{\text{sediment}}$  of  $-1.92 \pm 0.04 \text{ ‰}$ .

299 Copper dissolved concentration and  $\delta^{65}\text{Cu}$  values showed significant variation over a 24-h  
300 period (Fig. 4). The upstream  $\delta^{65}\text{Cu}$  values fluctuate between  $-0.47 \pm 0.01 \text{ ‰}$  (2 $\sigma$ ) and  $-0.08 \pm$   
301  $0.02 \text{ ‰}$  (2 $\sigma$ ). During high rainfall periods (high discharge regime), lower Cu concentrations  
302 ( $\approx 17 \text{ mg/L}$ ) and  $\delta^{65}\text{Cu}$  values ( $\approx -0.4 \text{ ‰}$ ) associated with higher pH (> 2.80) are observed.

303 During low water discharge period, we observe higher Cu concentrations (up to 120 mg/L),  
304 lower pH (pH < 2.5) and higher  $\delta^{65}\text{Cu}$  values (close to 0 ‰). In the downstream point, where  
305 Cu concentrations are much lower, from 0.29 to 1.65 mg/L, the  $\delta^{65}\text{Cu}$  is between -0.31 and -  
306 0.63‰. Thus we observe similar tendency as in the upstream point with concomitant lower  
307  $\delta^{65}\text{Cu}$  and Cu content.

308

### 309 *3.3. The suspended sediment of the Meca River: mineralogical characterization and chemical* 310 *analysis*

311 Two suspended matter samples from the Meca River upstream point (ME-A 11-May-2016  
312 10:00 p.m.; ME-A 12-May-2016 4:00 p.m.) were studied using SEM-EDS and X-ray  
313 diffraction while Raman spectroscopy has been performed on the ME-A 11-May-2016 10:00  
314 p.m. sample.

315 The SEM observations of both samples revealed homogeneous composition of suspended  
316 material. We note the predominance of a muscovite type mineral (see Fig. SI-3 supplementary  
317 information) in both samples and the presence of quartz, Fe oxides, rutile ( $\text{TiO}_2$ ) and grains  
318 containing S + Fe + As + Pb or S + Fe + Pb or S + Fe associations. Based on results of the X-  
319 ray diffraction (see Fig. SI-4), the mineral containing S + Fe + Pb + As appears to be a  
320 beudantite type mineral, the mineral containing S + Fe is a copiapite type mineral and the  
321 mineral containing S + Fe + Pb is a (plumbo)jarosite type mineral. Pyrite, Ti oxides, and Fe  
322 oxides grains have been also observed in the ME-A 11-May-2016 10:00 p.m. sample. The  
323 EDS system of the SEM did not allow detecting Cu in the investigated minerals. Raman  
324 spectroscopy revealed the presence of Fe oxydes, Tioxydes, jarosite, plumbojarosite and  
325 wavellite (hydrated aluminous phosphate) confirming the X-ray diffraction data (Fig. SI-5).

326 Collected sediments were mainly composed of Fe, Al, K and Pb (between 1 and 10%)  
327 and contained Mg, Ti, As, Na, Zn, Sb and Cu as minor elements with concentrations between

328 0.1 and 1%. Due to our analytical protocol, Si and S were not analysed in the solids. All the  
329 concentrations have been normalised to the upper crust composition (Taylor and McLennan,  
330 1995) (see supplementary materials Fig. SI-6). Compare to the upper crust reference, the  
331 suspended and bed load sediments are enriched in several elements in the order Sb >Pb>>>  
332 Cu, Sn, Zn, Cd >> Co, Fe, Cr, V. Compare to the bed load sediment, the suspended sediments  
333 present a significant enrichment in Cd >> Sn, Sb, Zn, Pb, > Co.

334

## 335 **4. Discussion**

### 336 *4.1. Discharge-related variations of Cu concentration and isotopic composition at upstream* 337 *sampling point of the Meca River*

338

339 During the rain-free period and steady-state conditions, the low water discharge (< 0.5 m<sup>3</sup>/s,  
340 field measurement using the “bucket” method) is associated with low pH and high copper  
341 (>100 mg/L) and other metals and sulphate concentrations in the dissolved phase (i.e., <0.22  
342 µm) of the Meca River. An opposite tendency is observed during high rain and runoff. This  
343 behavior is consistent with the streamflow - sulphate concentration relationship defined by  
344 Galvan et al. (2009) (see chapter 2.2) and the fact that we observe in the present study a close  
345 relationship between Cu and sulphate concentrations (see Fig. 2). The upstream δ<sup>65</sup>Cu values  
346 fluctuate significantly between -0.47 ‰ during high rainfall and -0.08 ‰ during low rainfall  
347 (see Fig. 4). For the low water discharge period, we assume that the Meca River is mainly fed  
348 by emptying lakes and galleries (groundwater) from the Tharsis mining district since the  
349 upstream point is the integrative water collection point of the whole mining district (Perez-  
350 Ostale, 2014). The close to zero values obtained during low water period therefore represent

351 the isotopic composition of water in direct contact with the sulfide-rich parent materials and  
352 their host rocks.

353 The lower Cu concentrations (and other metals) obtained during the high water discharge  
354 cannot be explained by a single dilution process by meteoric waters since Cu isotopic  
355 composition drastically changed with time (Fig. 4). This implies that (an)other(s) source(s)  
356 and/or process(s) contribute(s) to the flux of metals in the Meca River. We hypothesized that  
357 the large amount of abandoned wastes ~~presents~~ within the Tharsis mining district of the Meca  
358 River watershed could be a significant contributor during flood events. Indeed, Perez-Ostale  
359 (2014) reported that more than 80 ha of wastes are present within the Tharsis mining district  
360 without any remediation measures and thus represent a major source of elements (metals and  
361 metalloids) during flood event. In the Lagunazo mine area (Iberian Pyrite Belt), negative  
362  $\delta^{65}\text{Cu}$  value ( $-0.70 \pm 0.04 \text{ ‰}$ ) has been reported for waters percolating through pyrite-rich  
363 wastes (Viers et al., 2018). The Lagunazo mine, mined for copper, is constituted by a massive  
364 sulfide deposit located North-West of the Tharsis deposit. If we consider this negative  
365 signature as a first approximation of the average isotopic composition of waters percolating  
366 through the abandoned wastes of the Tharsis mine plant, the leaching of waste during periods  
367 of intense precipitation can induce a lower isotopic composition in the Meca River since this  
368 river is the outlet of this mining area. In the event of rainfall and after prolonged dry period,  
369 rain water quickly dissolves highly soluble sulphates or other secondary minerals that have  
370 been deposited during the dry period within the wastes and in the major bed of the river  
371 (Sanchez-Espana et al., 2005; Valente et al., 2013). The mineralogical study revealed the  
372 presence of secondary minerals with characteristics of mine wastes (copiapite or jarosite type  
373 minerals) but also the predominance of a muscovite type minerals suggesting also the  
374 contribution of surrounding soils (see section 4.3).



375 We performed a mass-balance modelling to check if the isotopic composition of the Meca  
376 River at the upstream point could be explained by a mixing of waters originating from these  
377 two supposed main sources, lakes/galleries and leaching of abandoned wastes (Fig. 5). In this  
378 modelling, the isotopic compositions of waters percolating through the wastes varied from -  
379 0.45 to -1.95‰ with a Cu concentration set at 10 mg/L while the concentration and isotopic  
380 composition of Cu in galleries and lakes were set at 150 mg/L and -0.05 ( $\delta^{65}\text{Cu}$ , in ‰),  
381 respectively. The isotopic signature used to characterise the "waste" pool was chosen to  
382 encompass the value obtained by Viers et al. (2018) ( $-0.70 \pm 0.04$  ‰) for waters percolating  
383 through pyrite-rich wastes. Additional theoretical curve with  $\delta^{65}\text{Cu}$  of -1.95‰ was required to  
384 encompass the upstream points at intermediate concentrations of dissolved Cu (Fig. 5). It can  
385 be seen that, while open mine lakes are the major source of riverine Cu during dry periods,  
386 their role becomes minor during flood.

387 Another process that could interfere in the resulting isotopic composition of the Meca  
388 River at the upstream point is precipitation of secondary minerals within the main stem.  
389 Indeed, the upstream waters are slightly oversaturated with respect to jarosite  
390 ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), goethite ( $\text{FeOOH}$ ), and a cupric ferrite type mineral ( $\text{CuFe}_2\text{O}_4$ ) (see Fig.  
391 6). It has been previously shown that goethite, jarosite and schwertmannite could precipitate  
392 at the pH of 2 to 3 in the river water (Sanchez Espana et al., 2005). As the suspended matter  
393 and bed load sediment were enriched in lighter isotopes ( $\delta^{65}\text{Cu}_{\text{suspended-matter}} = -0.41 \pm 0.03$  ‰;  
394  $\delta^{65}\text{Cu}_{\text{sediment}} = -1.92 \pm 0.04$  ‰), the minerals precipitation can exert strong effect on the  
395 isotopic composition of the river water. For example, precipitation of isotopically-light solid  
396 phases will enrich the river water in heavier isotopes via mass balance effect. Copper  
397 exhibited heavier isotopic composition during low flow period but the effect cannot be  
398 quantitatively assessed. However, the absence of copper in the form of small colloids (see  
399 section 4.2) would suggest a source change rather than a process within the water column to

400 explain the variation in isotopic composition. Indeed, the precipitation of secondary minerals  
401 should take place via precursors and in particular the presence of colloidal particles.

402 Overall, based on diel cycle under contrasting hydrological regime in the upstream point,  
403 Cu isotopes allowed us to detect two distinct sources of Cu in the river, which are: *i*) lake  
404 water under dry conditions, and *ii*) a mix of lake and soil/waste deposit runoff sources under  
405 flood conditions. A multi-parametric statistical treatment suggests that the data structure is  
406 governed by one single factor that could be related to the water discharge. With the exception  
407 of Na and K, all elements exhibit a temporal pattern which is similar to that of Cu.

408  
409 *4.2 Variations of Cu concentration and isotopic composition at the downstream sampling*  
410 *point of the Meca River*

411  
412 Located 20 km down from the upstream sampling point, the downstream point exhibits  
413 much lower dissolved Cu concentrations ( ~0.28 mg/L to ~1.6 mg/L). With  $\delta^{65}\text{Cu}$  values  
414 ranging from  $-0.63 \pm 0.03\text{‰}$  ( $2\sigma$ ) to  $-0.29 \pm 0.02\text{‰}$  ( $2\sigma$ ), downstream sampling point exhibits  
415 both narrower and negative values compared to upstream during the same sampling period  
416 (Fig. 4A and 4B).

417 Because of the lack of hydrological data for both Meca River and tributaries it was impossible  
418 for us to physically constrain the mixing processes. Consequently, we will discuss  
419 qualitatively the processes that may affect the isotopic composition between the upstream and  
420 the downstream points.

421 A dilution of mine waters by tributaries and lateral input through soils of the watershed are  
422 primarily responsible for Cu isotope evolution over the Meca River watercourse. The lighter  
423 isotopic composition of the downstream point could result from direct contribution of the  
424 Meca tributaries through a dilution process. We sampled only one of these tributaries which

425 exhibited low Cu concentration (0.3 mg/L) and light isotopic composition ( $\delta^{65}\text{Cu}_{\text{tributary}} = -$   
426  $2.72 \pm 0.03 \text{ ‰}$ ). As this Meca tributary is draining non mining plant zone, we suggest our  
427 sampling to be representative of the soil catchment contribution between the mine district and  
428 the downstream sampling point. A small fraction of this Cu could be natural Cu originating  
429 from the chemical weathering of the parental rocks that have an average value of 55 mg/kg  
430 (Chopin and Alloway, 2007). A more significant fraction of Cu present in the surrounding  
431 soils may originate from the mine after deposition of atmospheric particles on these soils.  
432 Indeed, smelting activity was conducted on the Tharsis site for many years (Valente et al.,  
433 2013) and Chopin and Alloway (2007) have revealed that in the case of Tharsis, the soils  
434 appear to be contaminated significantly in the vicinity of the mine (2 to 3 km around). As  
435 copper presents a strong affinity for organic matter, organic (O) soil horizons are generally  
436 enriched in copper with respect to deepest soil horizons (Bigalke et al., 2011), what was  
437 observed by Chopin and Alloway (2007). Based on a mass balance calculation,

$$438 \quad (\delta^{65}\text{Cu} \times [\text{Cu}])_{\text{downstream}} = (\delta^{65}\text{Cu} \times [\text{Cu}])_{\text{tribute\_stream}} + (\delta^{65}\text{Cu} \times [\text{Cu}])_{\text{upstream}}$$

439 where [Cu] stands for Cu concentration, we estimated that 87 % of the downstream Cu comes  
440 from the upstream point, and only 13% from the tributary streams.

441 In this case, it seems that only inputs of tributaries with exogenous Cu would be able to  
442 affect  $\delta^{65}\text{Cu}$  downstream values.

443 Furthermore, during the water flow between the mine/upstream and downstream point,  
444 various in-stream processes could control Cu concentration and isotopic composition in the  
445 fluid. These are: i) precipitations of secondary Cu-bearing minerals; ii) Cu sorption onto  
446 major mineral phases of river bed sediments; iii) Cu uptake by aquatic microorganisms. These  
447 processes are likely to be mostly pronounced in the downstream point, given that highly  
448 acidic upstream waters (pH = 2.4 to 2.8) are not favourable for adsorption and biota

449 development. At the downstream point, speciation calculations show that the fluid is largely  
450 oversaturated with respect to schwertmannite ( $\text{Fe}_8\text{O}_8(\text{SO}_4)_x(\text{OH})_y, n\text{H}_2\text{O}$ ), a cuprite type  
451 mineral ( $\text{CuFe}_2\text{O}_4$ ) and at a lesser extent jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), goethite ( $\text{FeOOH}$ ) and  
452 ferrihydrite ( $\text{Fe}_2\text{O}_3, 0.5\text{H}_2\text{O}$ ) (see Fig. 6). Within the AMD context, it is known that the  
453 heavier Cu isotopic composition of the solution with respect to that of bulk chalcopyrite could  
454 be due to the precipitation of an isotopically light Cu-rich solid phase (Kimball et al., 2009).  
455 More recent work suggested that the progressive enrichment of Cu heavier isotope along the  
456 Cobica River, draining the Lagunazo copper mine, could be due to the precipitation of some  
457 secondary minerals enriched in light isotopes (Viers et al., 2018). The values obtained for  
458 suspended and bed sediments of the Meca River ( $\delta^{65}\text{Cu}_{\text{susp-sed}} = -0.41 \pm 0.03 \text{‰}$  and  
459  $\delta^{65}\text{Cu}_{\text{sediment}} = -1.92 \pm 0.04 \text{‰}$ ) seem to support this assumption since the secondary products  
460 are enriched in light isotopes. However, given that the isotopic composition at the  
461 downstream point ( $-0.29$  to  $-0.63\text{‰}$ ) is globally lower than that at the upstream point ( $-0.08$   
462 to  $-0.47\text{‰}$ ), we suggest that secondary mineral precipitation cannot be sole process controlling  
463 Cu isotope fractionation, and other mechanisms should be considered.

464 The higher pH measured at the downstream point (3.61 to 5.68) compared to the upstream  
465 point (2.41 to 2.82) implies a possibility of metals sorption onto the surface of suspended  
466 sediments in the course of the water flow, as it is known for other mine water-affected  
467 environments (Lee et al., 2002; Smith, 1999). We identified the presence of Fe oxides and  
468 other (hydr)oxide minerals in the suspended matter of the Meca River (see section 4.3) that  
469 can offer substantial surfaces for Cu sorption. Balistrieri et al. (2008) and Pokrovsky et al.  
470 (2008) have shown that Cu sorption onto common mineral and organic surfaces favors the  
471 heavy isotope leaving isotopically light Cu in the aqueous solution. The effect of the sorption  
472 process could not be quantified but is consistent with a lower isotopic composition in the  
473 downstream point.

474 Finally, third mechanism affecting Cu isotope composition in the river water is Cu  
475 interaction with aquatic microorganisms. During our sampling period, the temperature was  
476 low (13.6 – 17.1°C, upstream) and we did not detect any algal bloom that could have affected  
477 the dissolved Cu. Moreover, the uptake of Cu by bacteria, periphytic biofilm or algae favors  
478 the light Cu isotope into the biomass (Navarette et al. 2011; Coutaud et al., 2018). This  
479 process would enrich the river water in heavy isotope, which is not consistent with our  
480 observations.

481

## 482 ***5. Conclusions***

483 This study presented both Cu concentration and isotopic composition of the Meca River  
484 draining one of the largest abandoned mine of the Iberian Pyrite Belt during a flood event.  
485 Based on observations over the diel cycle under changing water regime conditions, Cu  
486 isotopes are useful to understand the hydrochemical functioning of a complex mining zone. In  
487 response to a change in the hydrological conditions, the system appears to react quickly since  
488 Cu isotopic composition changes following the amount of precipitation/water discharge in the  
489 mining area. In the case of the Tharsis mine, copper isotopes allowed us to detect two distinct  
490 metal sources in the headwater catchment under constrained hydrological regime. A major  
491 contribution was provided by lake/gallery source under dry conditions, whereas during the  
492 flood, a mix of lake/gallery and soil/waste deposit contributed to lateral surface runoff. These  
493 findings could be useful for mine remediation measures and monitoring practices. Twenty km  
494 downstream the mine, the Cu isotopic composition is essentially controlled by a dilution and  
495 mixing process of headwater catchment by lateral surface runoff within soils brought by  
496 tributaries. It is not strongly modified by in-stream environmental processes such as

497 precipitation of Cu secondary bearing minerals, sorption on mineral surfaces or uptake by  
498 aquatic organisms.

499

500

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514

515

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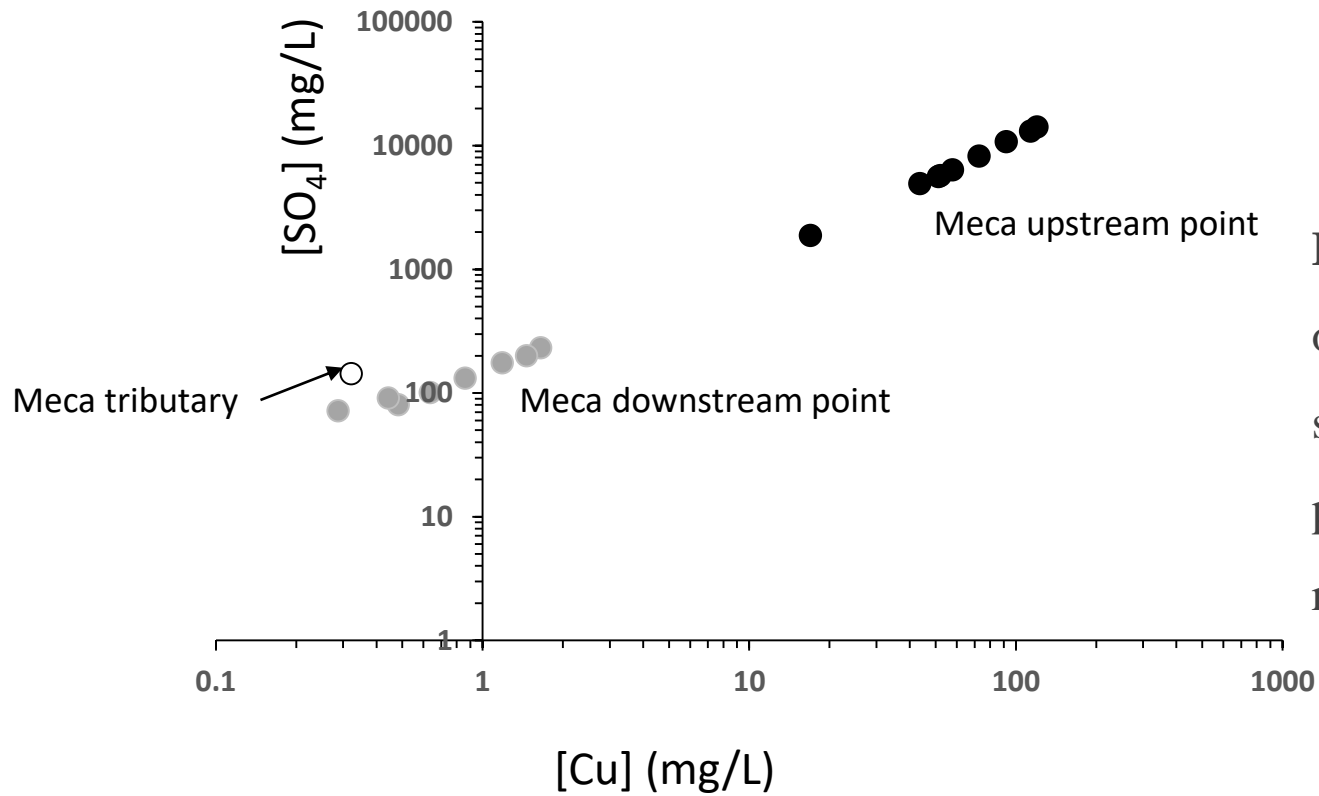
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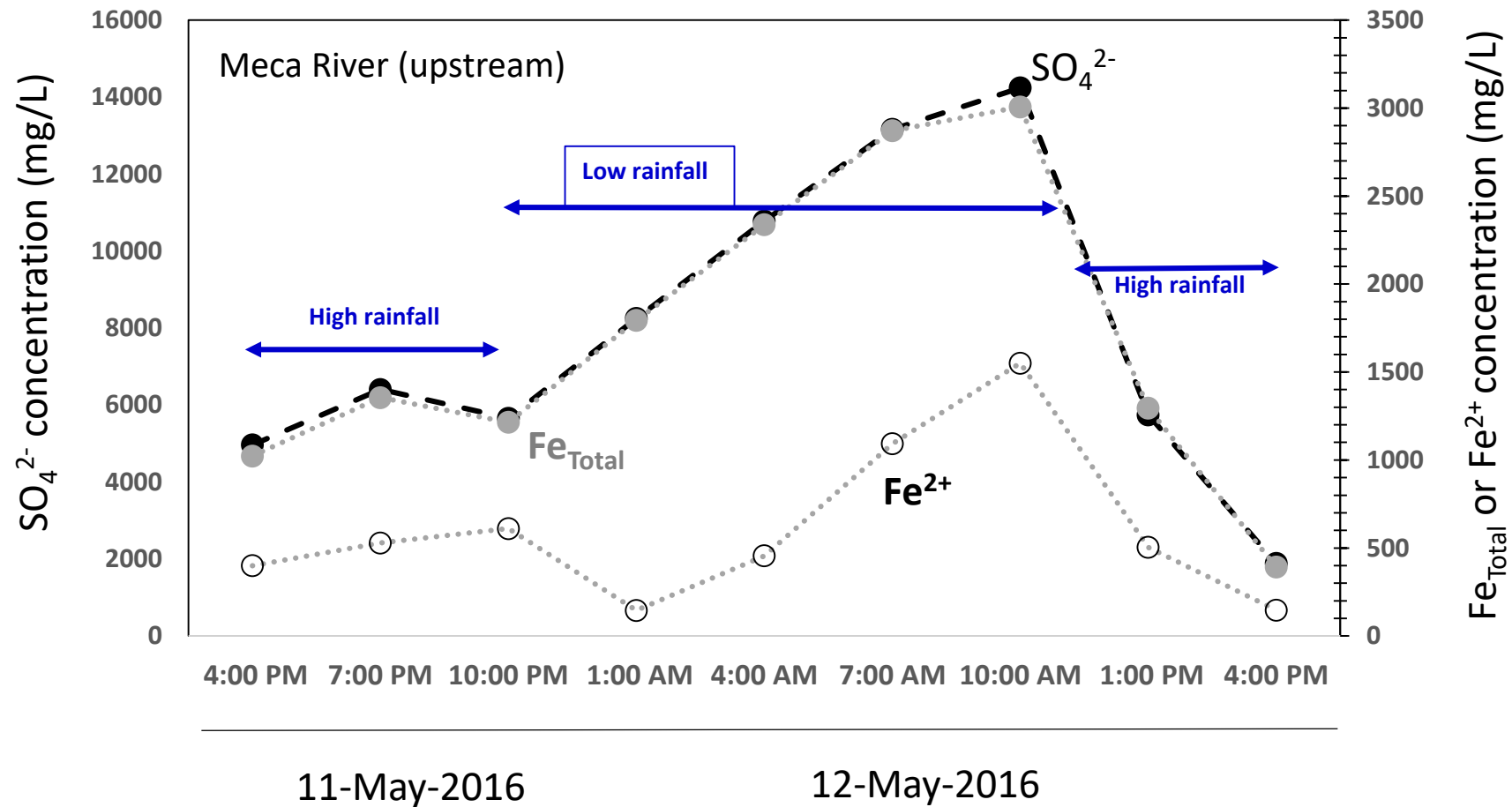
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**Fig. 1:** Upstream, tributary stream and downstream sampling locations within the Meca River. The Meca River is a tributary of the Odiel River (Huelva, Spain).



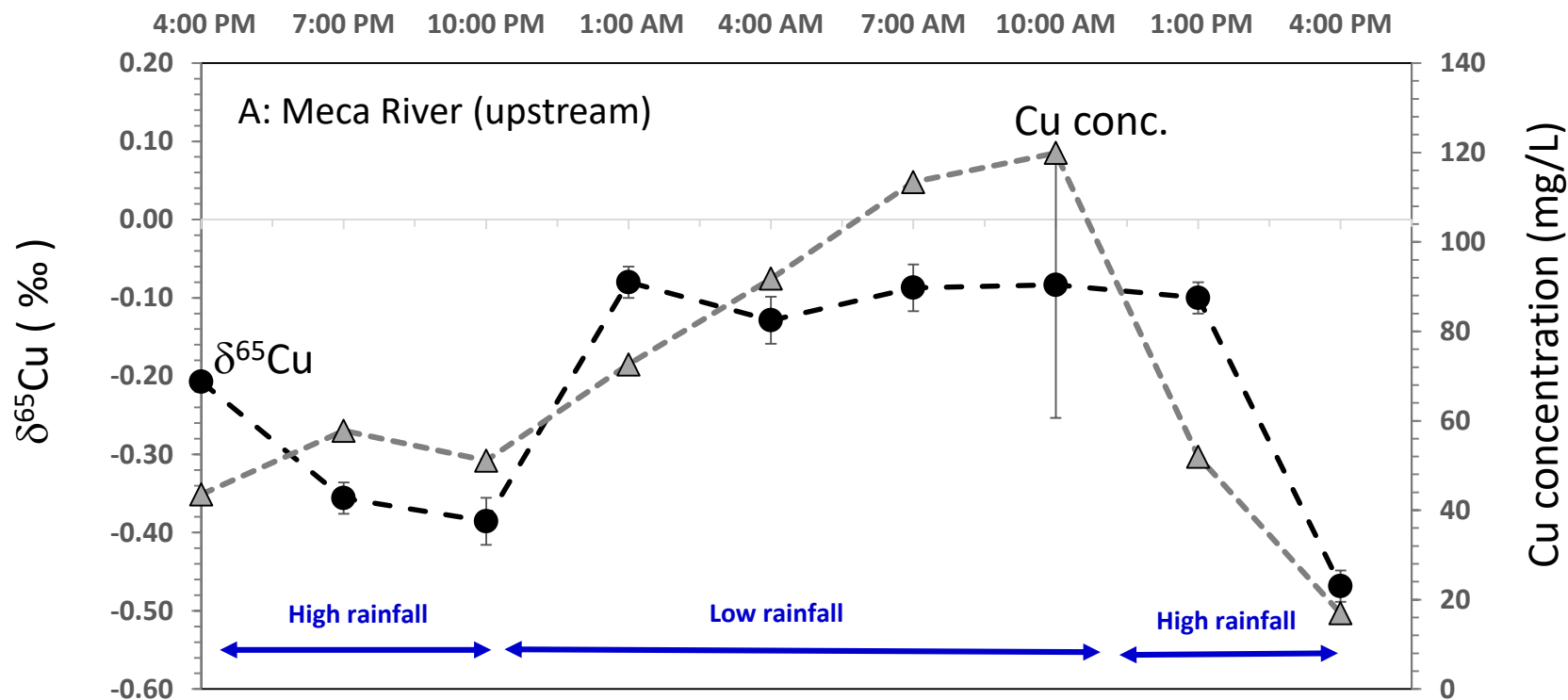
**Figure 2:** Dissolved Cu concentration as a function of  $\text{SO}_4^{2-}$  concentrations for upstream (black symbols) and downstream (gray symbols) sampling points of the Meca River. The Meca tributary is also reported.



**Figure 3:** Dissolved SO<sub>4</sub><sup>2-</sup> concentrations as a function of dissolved iron (Total and Fe<sup>2+</sup>) concentrations for upstream sampling points of the Meca River.

11-May-2016

12-May-2016



**Figure 4:** Diel variation in  $\delta^{65}\text{Cu}$  (left axis, black circle) and dissolved Cu concentrations (right axis, gray triangle) for A) upstream and B) downstream. Error bars represent  $2\sigma$  uncertainties calculated from replicate analyses.

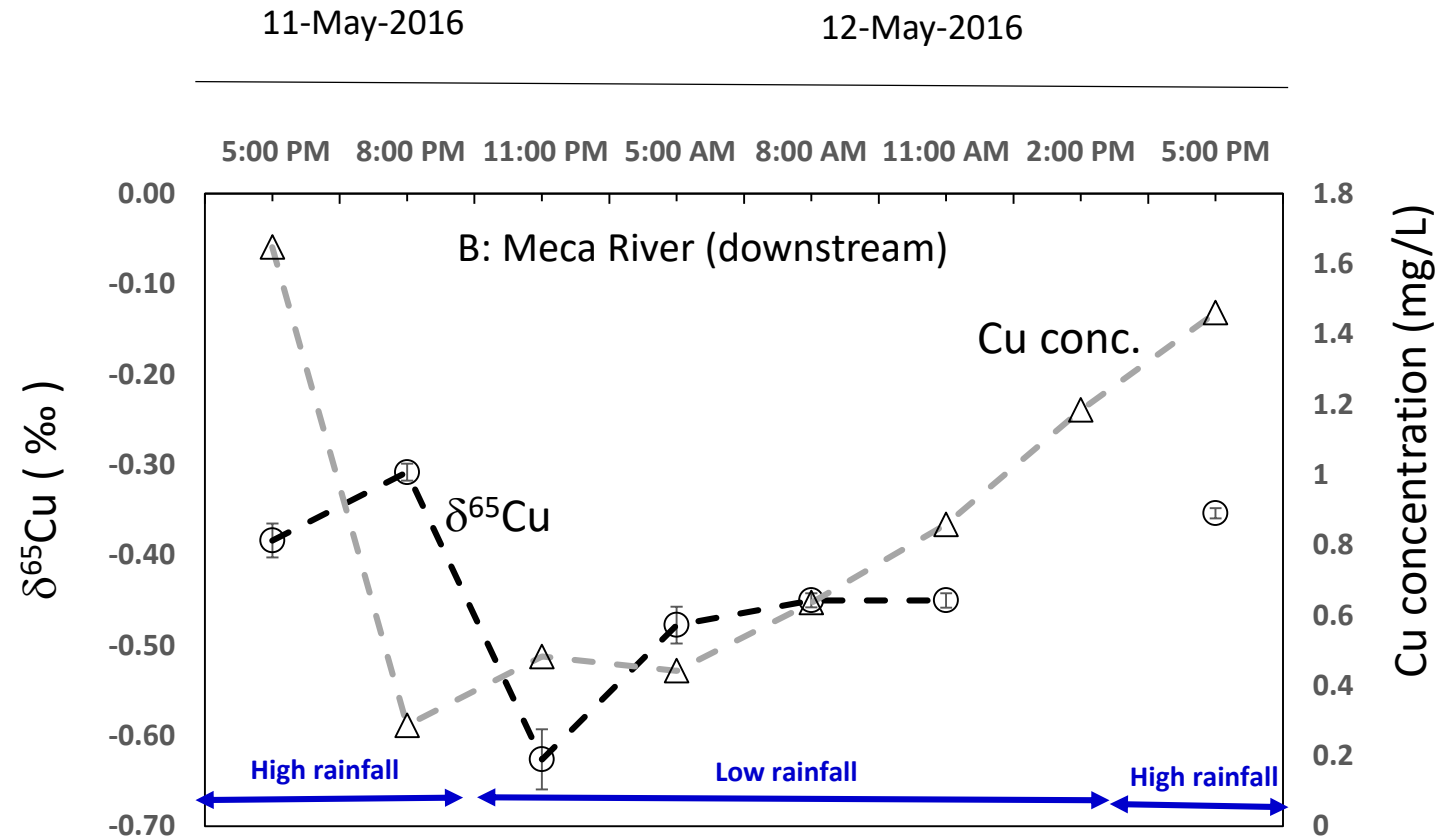
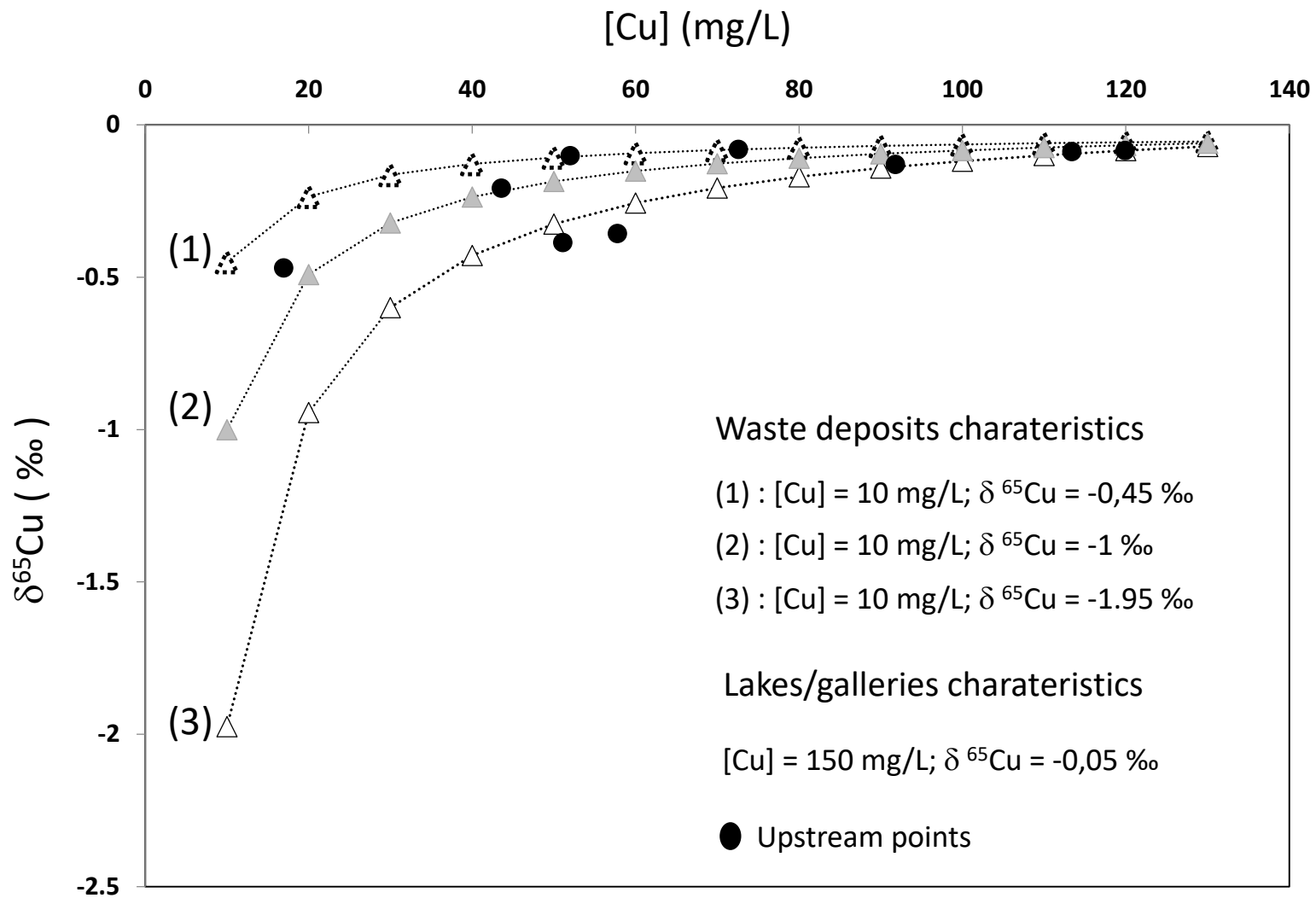
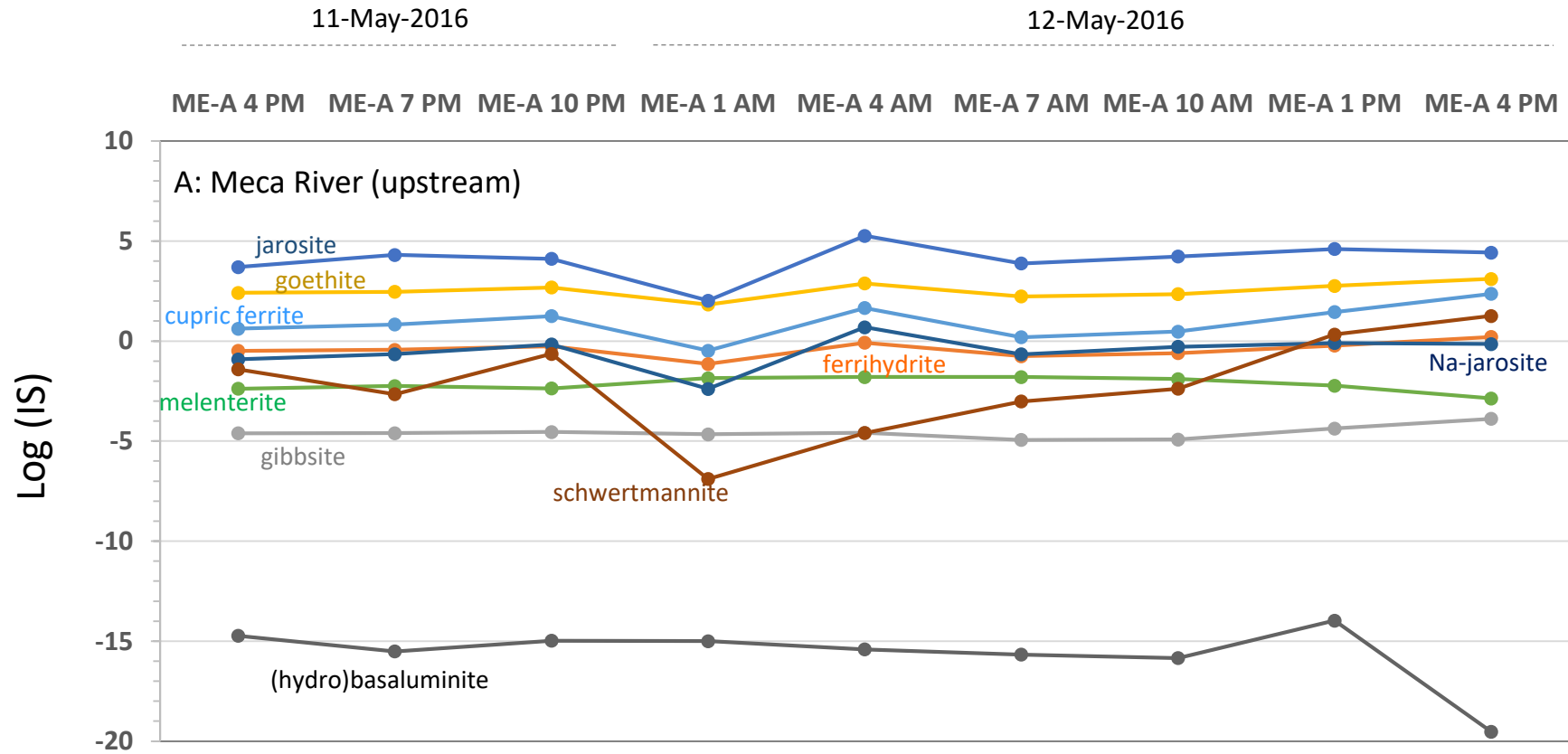


Figure 4 (to be continued)

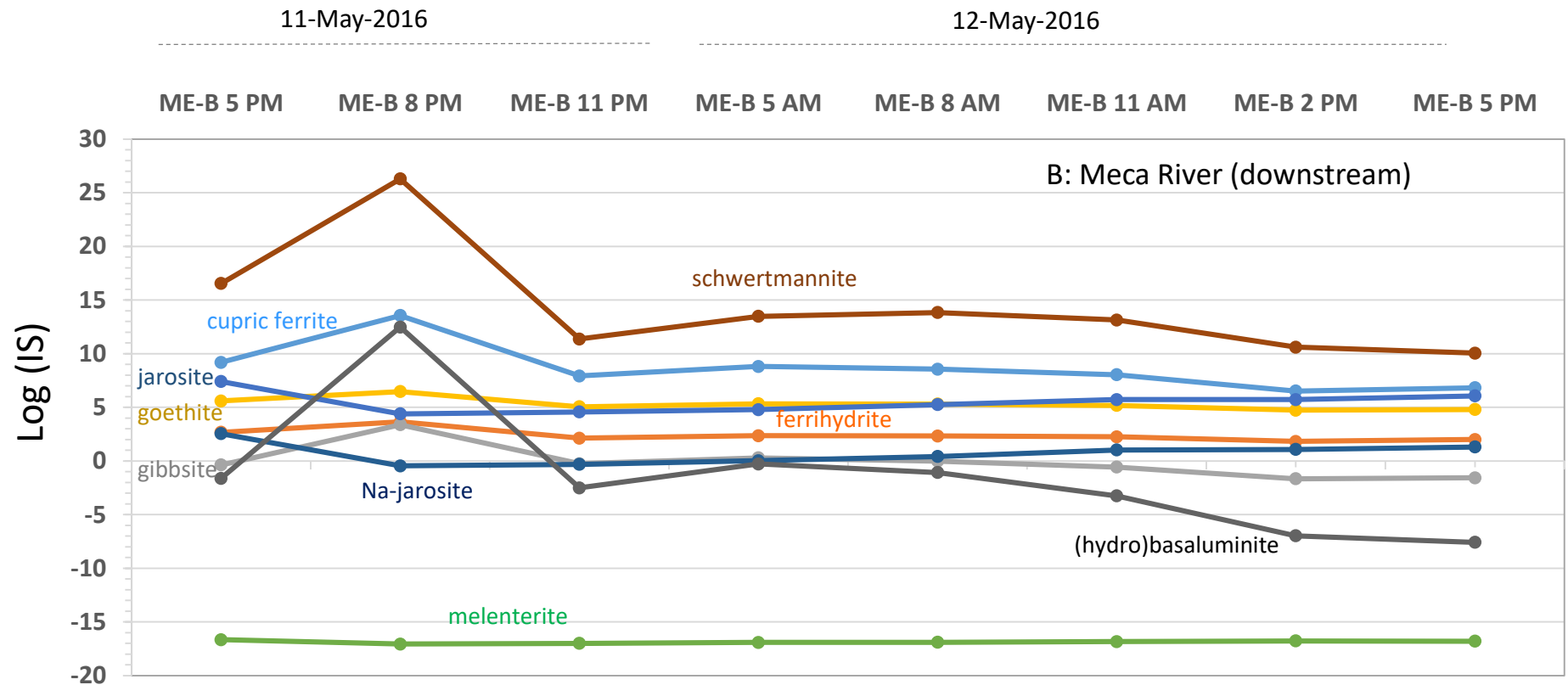


**Figure 5:** Theoretical mixing diagram between 1) water percolating through the wastes deposits and 2) water originating from the mine lakes and galleries. The black points are the values measured for the upstream sampling point.



**Figure 6:** Saturation indexes calculated using Visual MINTEQ ver. 3.0. at both upstream and downstream sampling points of the Meca River.





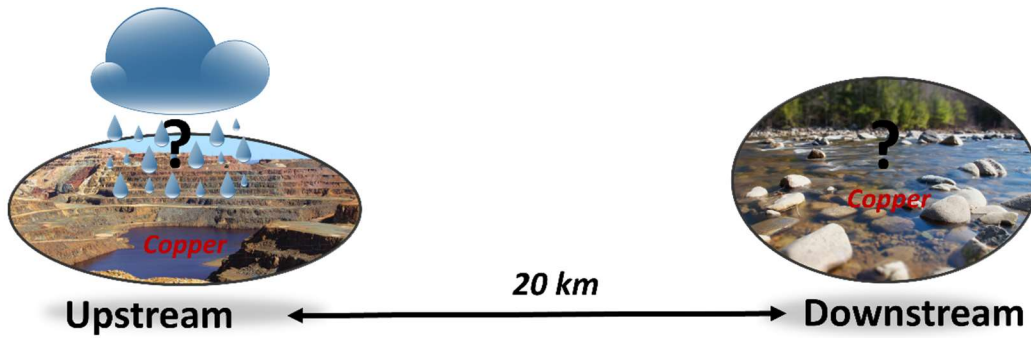
**Figure 6: (to be continued)**

Sampling date	11-May-2016	11-May-2016	11-May-2016	11-May-2016	11-May-2016	12-May-2016	12-May-2016	12-May-2016	12-May-2016	12-May-2016	12-May-2016	12-May-2016	12-May-2016	11-May-2016	11-May-2016	11-May-2016	11-May-2016	12-May-2016	12-May-2016	12-May-2016	12-May-2016	
	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-A	ME-B	ME-B	ME-B	ME-B	ME-B	ME-B	ME-B	ME-B
Sampling name	4:00 PM	4:00 PM	7:00 PM	10:00 PM	10:00 PM	1:00 AM	4:00 AM	4:00 AM	7:00 AM	10:00 AM	10:00 AM	1:00 PM	4:00 PM	ME-A	5:00 PM	8:00 PM	11:00 PM	5:00 AM	8:00 AM	11:00 AM	2:00 PM	5:00 PM
Filtration size	<0,22 µm	<1000 da	<0,22 µm	<0,22 µm	<1000 da	<0,22 µm	<0,22 µm	<1000 Da	<0,22 µm	<0,22 µm	<1000 Da	<0,22 µm	<0,22 µm	<0,22 µm	<0,22 µm	<0,22 µm	<0,22 µm	<0,22 µm	<0,22 µm	<0,22 µm	<0,22 µm	<0,22 µm
Temperature (°C)	16,6	-	17,1	15,4	-	14,3	14,3	-	13,8	15,0	-	13,6	17,0	15,7	16,6	19,7	16,2	14,4	14,4	15,6	16,7	21,0
pH	2,60	-	2,52	2,57	-	2,56	2,50	-	2,43	2,41	-	2,64	2,82	3,85	4,12	5,68	4,27	4,52	4,34	4,09	3,69	3,61
Conductivity	5,48	-	6,44	6,12	-	8,02	9,76	-	11,39	11,6	-	6,22	2,81	0,51	0,43	0,31	0,31	0,31	0,38	0,39	0,54	0,50
O <sub>2</sub>	6,46	-	6,30	6,61	-	6,64	6,45	-	6,54	6,48	-	8,4	7,65	6,94	-	-	-	-	-	-	-	-
DOC	7,348	-	16,43	7,384	-	13,58	12,7	-	5,676	5,468	-	10,22	9,917	35,93	-	-	-	-	-	-	-	-
Cl	10,67	-	11,61	11,12	-	11,98	12,85	-	13,80	14,07	-	8,85	8,28	21,84	25,03	29,11	26,29	30,19	26,89	26,76	27,69	17,32
NO <sub>3</sub>	1,07	-	0,95	1,09	-	1,19	1,08	-	1,01	0,84	-	0,80	1,25	34,74	1,93	1,88	2,12	2,26	1,65	1,74	1,89	3,09
SO <sub>4</sub>	4964	-	6407	5657	-	8251	10784	-	13163	14241	-	5746	1886	144	233	72	81	91	101	132	177	201
δ <sup>65</sup> Cu (‰)	-0,21 (± 0,00)	-	-0,36 (± 0,02)	-0,39 (± 0,02)	-	-0,08 (± 0,03)	-0,13 (± 0,16)	-	-0,09 (± 0,02)	-0,08 (± 0,17)	-	-0,10 (± 0,02)	-0,47 (± 0,02)	-2,72 (± 0,03)	-0,38 (± 0,02)	-0,31 (± 0,01)	-0,63 (± 0,03)	-0,48 (± 0,02)	-0,45 (± 0,01)	-0,45 (± 0,01)	-	-0,35 (± 0,01)
Cu	43,55	44,60	57,76	51,07	49,79	72,58	91,79	92,84	113,38	119,88	116,80	51,97	16,92	0,32	1,65	0,29	0,48	0,44	0,64	0,86	1,18	1,46
Na (mg/L)	12,24	8,06	18,61	8,63	8,61	8,72	10,90	9,41	10,34	10,02	9,22	7,41	6,80	17,11	14,18	16,22	14,28	15,43	15,06	14,97	15,42	10,85
Mg (mg/L)	267	256	334	282	283	419	530	549	672	723	693	313	91	16	17	10	9	10	11	12	14	14
Al (mg/L)	298	283	358	317	319	468	602	628	775	826	799	360	101	3	12	1	3	2	4	6	8	10
Si (mg/L)	16,04		20,12	18,12		22,56	25,06		27,63	29,33		14,33	8,54	5,29	4,95	4,12	4,03	4,31	4,77	-	5,19	5,51
K (mg/L)	1,22	1,11	2,71	0,54	1,31	0,67	0,97	1,02	0,92	0,88	1,11	1,27	1,11	3,38	2,05	2,38	2,20	1,87	1,73	1,72	1,66	1,84
Ca (mg/L)	54,10	47,81	100,17	54,25	51,10	70,70	85,65	86,89	106,17	112,66	108,95	50,72	19,05	21,92	10,49	9,81	8,56	8,96	8,90	9,34	10,04	9,48
Mn (mg/L)	34,01	33,16	42,28	36,49	35,05	51,94	65,61	65,34	80,08	84,27	82,53	37,43	11,93	1,67	1,56	0,73	0,72	0,62	0,80	1,01	1,27	1,53
Fe (total)	1023	1029	1355	1214	1157	1793	2337	2338	2872	3007	2924	1295	392	1	21	2	4	4	6	9	14	19
Fe <sup>2+</sup>	623	n.m.	826	604	n.m.	1648	1881	n.m.	1779	1456	n.m.	791	245	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Fe <sup>3+</sup>	400	n.m.	528	610	n.m.	145	456	n.m.	1093	1551	n.m.	504	147	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Co	3,07	3,14	3,99	3,43	3,35	4,97	6,31	6,36	7,82	8,17	7,99	3,58	1,09	0,05	0,12	0,03	0,04	0,04	0,05	0,07	0,09	0,11
Ni	1,06	1,10	1,39	1,16	1,15	1,71	2,16	2,19	2,70	2,88	2,81	1,23	0,39	0,02	0,05	0,02	0,02	0,02	0,02	0,03	0,04	0,04
Zn	122,7	122,7	158,1	138,2	132,7	202,7	265,7	268,9	333,8	354,0	344,4	153,2	43,9	0,5	4,8	1,0	1,3	1,3	1,8	2,5	3,5	4,3
V	220	225	290	270	255	388	512	519	629	649	629	272	87	0,33	0,10	0,06	0,05	0,07	0,05	0,04	0,04	0,05
Cr	184	181	247	217	207	314	411	408	505	538	531	229	66	1,36	5,54	0,39	0,80	0,98	1,33	2,34	3,70	5,05
Cd	264	254	328	280	272	422	543	551	682	734	719	315	88	0,66	10,77	2,63	3,20	2,97	4,21	5,65	7,75	9,49

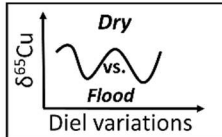
**Table 1:** Physical parameters (*measured in situ*), elemental concentrations and Cu isotopic composition for the upstream and downstream sampling points of the Meca River and for the Meca tributary. All concentrations and isotopic were measured in the dissolved fraction (i.e., <0.22 µm). n.m. indicates not measured.

Sampling date	11-May-2015	11-May-2015	12-May-2016	12-May-2016	12-May-2016
Sampling name	MES ME-A 4:00 PM	MES ME-A 10:00 PM	MES ME-A 4:00 AM	MES ME-A 4:00 PM	bed sediment ME-A
unit:	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$
$\delta^{65}\text{Cu}$ (‰)	-0,41 ( $\pm$ 0.03)	-	-	-	-1,92 ( $\pm$ 0.04)
<b>Na</b>	2507	2082	822	3575	10461
<b>Mg</b>	3434	4788	4071	3364	5144
<b>Al</b>	79220	68049	30526	102033	69998
<b>K</b>	18927	16826	4708	25216	19269
<b>Ti</b>	3037	3834	1160	3391	5024
<b>V</b>	115	102	46,7	146	126
<b>Cr</b>	86,1	82,7	43,0	96,5	85,6
<b>Mn</b>	278	439	478	214	275
<b>Fe</b>	112293	132229	66202	101090	129246
<b>Co</b>	38,2	55,2	50,4	20,7	15,6
<b>Ni</b>	27,3	25,8	22,5	28,7	34,9
<b>Cu</b>	669	909	788	479	392
<b>Zn</b>	1126	1554	1928	447	349
<b>As</b>	2831	2689	1653	1984	1009
<b>Se</b>	89	80	75	36	47
<b>Rb</b>	111	103	40	164	73
<b>Sr</b>	78,7	86,3	32,6	96,5	50,1
<b>Y</b>	12,5	15,9	6,8	15,5	19,3
<b>Mo</b>	7,68	8,73	4,15	4,73	3,96
<b>Cd</b>	2,23	3,45	4,00	0,80	0,36
<b>Sn</b>	235	91	185	46	54
<b>Sb</b>	1100	983	776	379	220
<b>Cs</b>	6,72	5,08	2,46	9,03	3,14
<b>Ba</b>	457	473	166	547	288
<b>La</b>	29,6	42,5	12,5	41,7	16,4
<b>Ce</b>	61,2	75,6	24,3	79,7	33,9
<b>Pr</b>	6,94	8,42	2,99	8,86	4,37
<b>Nd</b>	25,3	31,1	10,7	32,8	16,5
<b>Sm</b>	4,79	5,46	2,06	6,12	3,59
<b>Eu</b>	1,13	1,12	0,44	1,13	0,63
<b>Tb</b>	0,47	0,55	0,25	0,55	0,56
<b>Gd</b>	5,61	3,97	2,69	4,25	4,35
<b>Dy</b>	2,51	3,03	1,31	3,02	3,71
<b>Ho</b>	0,50	0,60	0,26	0,60	0,89
<b>ER</b>	1,63	1,97	0,85	1,97	2,71
<b>Tm</b>	0,25	0,31	0,14	0,31	0,43
<b>Yb</b>	1,92	2,25	0,90	2,22	3,03
<b>Lu</b>	0,31	0,36	0,13	0,36	0,45
<b>Pb</b>	7530	9466	4258	4320	1773
<b>Th</b>	10,0	14,9	3,9	16,0	12,1
<b>U</b>	3,45	3,95	1,75	3,13	4,15

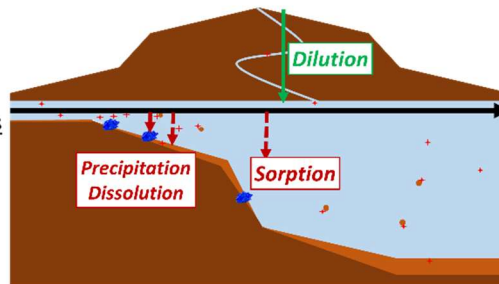
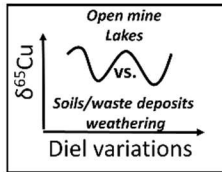
Table 2: Elemental concentrations and Cu isotopic composition for the suspended and bed sediments from the Meca River.



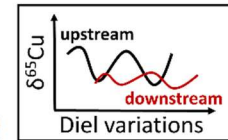
**Copper isotopes vs. hydrology**



**Copper isotopes vs. sources**



**Copper isotopes response to upstream signal**



- Detection of delayed upstream input
- Lower sensitivity
- Influence of tributary streams

Conservative processes

Non-conservative processes