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▶ To cite this version:

Hussein Jaafar Kanbar, Malak Ka
ouk. Mineral and chemical changes of sediments after Cu sorption and then desorption induced by synthetic root exudate. Chemosphere, 2019, 236, pp.124393.
 10.1016/j.chemosphere.2019.124393. hal-03914179

HAL Id: hal-03914179 https://hal.science/hal-03914179

Submitted on 28 Dec 2022

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1	Mineral and chemical changes of sediments after Cu sorption and then desorption
2	induced by synthetic root exudate
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11 Graphical Abstract



12

13 Abstract

Understanding the fate of anthropogenically introduced copper in sediments is important to comprehend the biogeochemical processes; consequently, beneficial utilization of Cu-rich materials can be proposed (e.g. soil amendment). Therefore, we address the behavior of copper and other metals at the liquid-solid interface of different grain sizes in lake sediments. Initially, the sediment fractions were characterized for mineralogy (XRD), chemical structure (FTIR), 19 physicochemical parameters (mainly pH, cation exchange capacity, and electric conductivity), 20 organic content, and chemical composition (AAS). Then, solutions of varying Cu 21 concentrations were added to the fractions; the Cu concentrations of the sorption experiment 22 were chosen according to the exchangeable cations of each fraction. A desorption experiment 23 by synthetic root exudate was followed. The physicochemical parameters, functional groups, 24 and mineralogy were noted before and after the two experiments. The sorption and desorption 25 of Cu, Ca, Mg, K, and Na were also studied. The sediment fractions had similar mineralogy 26 and chemical structure, yet the physicochemical composition and metal contents were different. 27 The Cu sorption experiment showed that surface Ca and embedded Mg were the main cations 28 that were exchanged with Cu, as shown by linear and logarithmic trends, respectively. The 29 copper-sediment interaction mainly occurred at the organic interface. Finally, synthetic root 30 exudate was able to restore part of the initial chemical structure of the sediments, indicating 31 exchangeable Cu sorption on the organic part of the sediments. The various grain sizes had an 32 insignificant influence on the behavior of metal sorption and desorption.

33

Keywords: sediment, grain size, copper, sorption, desorption, synthetic root exudate

34 **1. Introduction**

35 Copper is mainly introduced into the environment by Cu mining and smelting, waste 36 incineration bottom ash, vehicular combustion, production of Cu containing nanomaterials, and 37 the application of fertilizers and pesticides (e.g. Azzi et al., 2017; Lee et al., 2008; Seniunaite 38 and Vasarevicius, 2017). Sediments often act as the ultimate sink for metals in the environment 39 (Ammar et al., 2015; Grabowski et al., 2011). Therefore, it is important to understand Cu-40 sediment interaction. Complex processes are involved in metal-sediment interactions, such as 41 exchange, desorption, sorption, complexation, and precipitation. It is well known that the 42 metal-sediment interaction depends on the chemical state of the metal (i.e. speciation) and the 43 physical and chemical parameters of the matrix (whether liquid or solid), such as pH, redox 44 potential, mineral composition, cation exchange capacity (CEC), ionic strength, particle size, and organic matter (OM) (e.g. Carrillo-González et al., 2006; Du Laing et al., 2009). In aquatic 45 46 sediments, sedimentation depends on river hydrodynamics, particle size, and composition. Fine 47 particles are generally enriched with metals since they have higher sorption capacity (Acosta 48 et al., 2011; Du Laing et al., 2007). Moreover, Cu is reported to sorb onto clays, carbonates, 49 Mn and Fe oxides, organic matter, and organo-mineral complexes, especially under alkaline 50 pH (e.g. Fariña et al., 2018; Yuan et al., 2013).

Even though Cu exposure can have toxic effects on plants, it is an essential micronutrient. Copper is involved in metabolic processes for normal plant growth (Yamasaki et al., 2008 and articles cited therein). Therefore, controlled amendment of Cu-rich materials in agriculture can improve plant growth (e.g. Ju et al., 2019; Kobaissi et al., 2014). Importantly, plants can manage nutrient availability and limit toxicity by secreting exudates to the rhizosphere. Root exudates help plants to cope with metal stress by stabilizing metals in the rhizosphere or by changing the pH of the matrix (e.g. Badri and Vivanco, 2009).

58 Therefore, we studied Cu sorption onto different grain sizes of sediments and Cu 59 desorption induced by synthetic root exudate (SRE). The sorption and desorption of Cu were 60 followed by monitoring other metals that are involved in those processes. Additionally, the 61 change in the physicochemical parameters, mineralogy, and chemical composition of the 62 sediment fractions were investigated before and after the experiments. Coupling the Cusediment findings to the geochemical properties of the fractions give indications on the fate of 63 64 Cu in Cu rich media. More importantly, the findings can be used for selective Cu release and 65 beneficial uptake by biota.

66

2. Materials and Methods

2.1. Sampling site, sediment collection, and treatment

68 A mass of submerged sediments was collected from the east side of the Qaraaoun 69 reservoir (33°33'14.8"N, 35°42'02.0"E), which is part of the upper Litani River basin and is 70 located in the Beqaa valley of Lebanon. More information about the sampling site is found 71 elsewhere (Ammar et al., 2015; Kanbar et al., 2014). The sediments were wet sieved using the 72 adjacent river water into sizes of $0 - 64 \mu m$, $64 - 250 \mu m$, $250 - 500 \mu m$, and $500 - 2000 \mu m$ 73 (S1, S2, S3, and S4, respectively). Wet sieving was done in order to maintain *in situ* sizes (i.e. 74 aggregates and organo-mineral complexes were not broken). To limit chemical or 75 mineralogical modifications of the samples, they were immediately frozen and later freeze-76 dried. Homogeneous aliquots of the dry samples were then ground for analyses.

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2.2. Sedimentary materials: mineralogical, and physicochemical and chemical parameters

79 The mineralogical composition (by X-ray diffraction, XRD), functional groups (by 80 Fourier transform infrared, FTIR), cation exchange capacity, pH, electric conductivity (EC), 81 salinity, total dissolved solids (TDS), zeta potential, organic matter, and metal contents were 82 determined for each sediment fraction. The fractions showed similar mineralogy and functional 83 groups (Figure 1). Moreover, the coarsest fraction had the highest organic matter and metal 84 contents, emphasizing the influence of organo-mineral complexes in metal enrichment 85 (detailed information about the methodology and results is included in Supplementary material 86 SM 1).



Figure 1: The XRD patterns (a) and the FTIR spectra (b) of the sediment fractions.

a) K: Kaolinite, Phyl: phyllosilicates, Q: quartz, C: calcite, and F: feldspar. The interplanar distances (in Å) and the minerals are assigned to the peaks. b) The functional groups and the wavenumbers (in cm⁻¹) are assigned to the peaks.

S1: $0 - 64 \mu m$, S2: $64 - 250 \mu m$, S3: $250 - 500 \mu m$, and S4: $500 - 2000 \mu m$.

87 2.3.

Copper sorption onto different sediment sizes and consequent changes

88 Sorption experiments were conducted to study the Cu-sediment binding mechanisms, the 89 consequent cation release or exchange, and the change in physicochemical, mineralogical, and 90 chemical parameters. 50 ml solutions of known Cu concentrations were added to 500 mg of 91 the sediment fractions and mixed for 24 hours under ambient room temperature. The Cu 92 concentrations used in the sorption experiment are equivalent to the CEC values of each 93 fraction. Therefore, the solutions used for each fraction contain different Cu concentrations 94 (SM 2). The Cu concentrations are considered as treatments and are termed C1, C2, C3, C4,

95 and C5 for the concentrations of Cu equivalent to 0.5CEC, 1CEC, 2.5CEC, 5CEC, and 10CEC, 96 respectively. Each sample was run as four replicates (n=4). Additionally, duplicate negative 97 controls (sediments mixed with ultrapure water, n=8) and positive controls (Cu solutions 98 without sediments, n=20) were prepared and run along with the samples. Electric conductivity 99 and pH values were recorded for the initial solutions (pHi and ECi) and after 24 hours (pHf and 100 EC_f); the final measurements were taken after the solutions were filtered over a 0.45 µm filter. 101 The filtered solutions were also used to quantify Cu, Ca, and Mg by AAS and K and Na by 102 flame photometry. The equilibrium uptake (qe) of Cu was calculated according to the following 103 equation:

110
$$qe_{(mg/g)} = \frac{(C_i - C_f)_{(mg/L)} \times V_{(L)}}{m_{(g)}}$$

where qe is the equilibrium uptake of Cu (in mg/g), C_i and C_f are the initial and final concentrations of Cu in the solutions (in mg/L), respectively, V is the volume of the sorption solutions (in L), and m is the mass of the sediments (in g). After the sorption experiment, the surface charge (zeta potential, as duplicates), functional groups (FTIR), and mineralogy (XRD) were determined for one sample out of each quadruplicate. The remaining triplicates were used for the Cu desorption experiment.

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2.4. Copper desorption induced by synthetic root exudate and consequent changes

The fate of the sorbed Cu from the sorption experiment was followed after mixing with SRE. The SRE components and their concentrations depend on several factors, such as soil type, soil physicochemical conditions (e.g. pH, redox potential, and temperature), nutrient deficiency, metal toxicity, microbiome, plant species, and plant stage of development (e.g. Badri and Vivanco, 2009; Grayston et al., 1997). The SRE components and concentrations used in this study are mainly based on Huang et al. (2017). The concentrations of the compounds are included in SM 3. However, 1 ml of the prepared SRE and 49 ml ultrapure water were added to each sample from the previous experiment (i.e. a triplicate for
each treatment). The mixtures were rotated for 24 hours. Similar to the sorption experiment,
the pH and EC values were recorded, the desorbed metals were quantified, and the functional
groups and mineralogy were determined.

123

3. Results and Discussion

124 **3.1.** Cu sorption onto sediment fractions

125 *3.1.1. Change in physicochemical parameters*

The final EC values (i.e. EC_f) were higher than the initial ones in most cases, such as S1C1-C2 and S2C1-C4 (Figure 2a); this is explained by the cation exchange or release induced by Cu or by the dissolution of sedimentary phases. However, some EC_f values were lower than EC_i, such as S1C3-C5 and S2C5. Even though the high Cu concentrations of the solutions cause the exchange or release of cations, some of those cations might have precipitated, as suggested by EC_f < EC_i. Nonetheless, the variation in EC showed a clear and increasing trend with increasing Cu concentrations .

133 The pH_i values were different for the solutions used in the sorption experiment. Moreover, the 134 variation between pH_i and pH_f (i.e. ΔpH ; $\Delta pH = pH_f - pH_i$) was generally prominent for the 135 lower concentrations in the cases of S1, S2, and S4 (mainly C1 in Figure 2b). The pH_i and pH_f 136 values are included in SM 4. Sediments naturally buffer the pH, nonetheless, high Cu 137 concentrations overwhelmed the buffering capacity to some extent, which lead to a drop in the 138 final pH (Δ pH generally decreases from C1 to C5). Furthermore, S4 showed the least variation 139 in ΔpH for all the treatments (C1-C5), possibly linked to the low buffering capacity due to the 140 relatively low Ca contents and carbonates (SM 1).



Figure 2: The variation of a) EC (μ S/cm) and b) ΔpH (pH_f-pH_i) for the different grain sizes treated with solutions having different Cu concentrations. Whiskers indicate standard deviations of the technical quadruplicates.

S1: $0 - 64 \mu m$, S2: $64 - 250 \mu m$, S3: $250 - 500 \mu m$, and S4: $500 - 2000 \mu m$. For the values of C1 – C5, please refer to SM 2.

141 *3.1.2.* Behavior of Cu and other cations

The sediment fractions nearly sorbed 100mg/g of Cu (Figure 3a), which is equivalent to 143 10-fold the CEC; high Cu sorption values (~ 1000 mg/g) are reported in soils and sediments 144 (e.g. Arias et al., 2006; Liu et al., 2015; Ratasuk et al., 2003). Unexpectedly, Cu sorption was 145 identical in all the fractions and 97 to 100% of the added Cu was sorbed after 24 hours (SM 5). 146 The equilibrium uptake of Cu for mainly C5 treatments might be overestimated due to 147 precipitation (see SM 6 for the margin of error). Regression showed a linear fit between Ca 148 release and added Cu concentrations (R^2 >0.98 for all fractions; Figure 3b). This direct and

- 149 linear relationship suggests that the major exchange between Ca and Cu occurred on the surface.
- 150 It is worth noting that S4 had the highest Ca release in comparison to the other fractions.

151 As for Mg release, regression analysis showed a logarithmic fit with the initially added Cu 152 concentrations (Figure 3c), indicating that surface-bound Mg was majorly released when the 153 initial Cu concentrations were low (e.g. C1-2). The decline in Mg release rate with higher Cu 154 concentrations indicates the release of embedded Mg, i.e. Mg absorbed or located in the 155 structure of macropores (Jain and Sharma, 2002). Moreover, Mg release was different for the 156 sediment fractions. It is worth noting that S4 had the highest Ca and Mg release, followed by 157 S3, S2, and finally S1. This trend was also seen for EC (Figure 2a), CEC, and LoI (SM 1). 158 Furthermore, having the highest CEC and Fe and Mn contents (SM 1), S4 is relatively rich in 159 interlayered clay minerals, organic matter, and organo-mineral complexes, which also support 160 the high Ca and Mg release in that fraction (e.g. Jain and Sharma, 2002; K. Li et al., 2018; Q. 161 Li et al., 2018). This further supports that organo-mineral complexes are the key sites for the 162 Cu-cation exchange. According to the trends of Ca and Mg release, Cu mainly competes with 163 Ca and to a lower extent with Mg. Control samples were also run. Due to the absence of a 164 competing cation (i.e. Cu) in the control samples, the release of Ca and Mg were lower than 165 the treated samples. The values for Ca and Mg release in the control samples were 6.8 and 0.7, 166 5.9 and 0.7, 5.8 and 1.1, and 5.1 and 1.2 mg/L for S1, S2, S3, and S4, respectively (the data are 167 not included in the graphs for clarity reasons). Na and K release did not follow a trend with 168 grain size nor with treatment (SM 7).



Figure 3: a) The equilibrium uptake (qe) of Cu (mg/g) for the different fractions and treatments; the blue region indicates possible precipitation (SM 6). b) Ca and c) Mg release (in mg/L) for the different fractions and treatments. Whiskers indicate standard deviations of the quadruplicates.

S1: $0 - 64 \mu m$, S2: $64 - 250 \mu m$, S3: $250 - 500 \mu m$, and S4: $500 - 2000 \mu m$.

169 *3.1.3. Mineralogical and chemical changes*

In addition to the minerals previously identified in the initial samples (Figure 1a), the XRD patterns showed the protrusion of posnjakite in the C3, C4, and C5 treatments. The intensity of the posnjakite peaks (at 6.98, 3.47, 2.70, and 2.41 Å) increased from C3 to C5 (the example of S3 is given in Figure 4a). The precipitation of this mineral might explain the decline of EC in some samples after Cu sorption (e.g. S1C3-C5 in Figure 2a). Indeed, the experimental 175 conditions in the sorption experiment, i.e. mixing, temperature, and increase in pH (Δ pH>0), 176 are adequate to produce posnjakite (Zaffino et al., 2015; Zittlau et al., 2013).

177 Even though the XRD patterns identified posnjakite in samples that underwent C3 - C5178 treatments, the FTIR spectra showed this mineral in all the treatments (Figure 4b). Even though 179 it is not possible to indicate what percentage of Cu sorbed onto the sediments and what percentage precipitated, it is well known that Cu sorption starts rather instantly (e.g. Al-180 181 Qunaibit et al., 2005; Liu et al., 2015; Veli and Alyüz, 2007), while posnjakite forms within 20 182 minutes (Zittlau et al., 2013). Therefore, Cu sorption is favored. Posnjakite was identified by FTIR based on O-H stretching at 3549, 3405, and 3244 cm⁻¹, $v_3 SO_4^{2-}$ at 1116 and 1069 cm⁻¹, 183 Cu-OH bending at 792 cm⁻¹, $v_4 SO_4^{2-}$ at 605 cm⁻¹, $v_2 SO_4^{2-}$ and Cu-O stretching at 435 cm⁻¹, 184 and by small peaks at 733, 3950 - 3750, and 1700 - 1200 cm⁻¹ (Zaffino et al., 2015). 185 Interestingly, the C-O peak at 1025 cm⁻¹ decreased after Cu sorption, mainly in S1, S3, and S4 186 187 (Figure 4b), which could indicate the binding of Cu to organic matter by forming a covalent Cu-C bond (e.g. Golubeva et al., 2013). Indeed, Hossain et al. (2012) reported that the carboxyl 188 189 group can chelate Cu. This might also explain the change in the O-H carboxylic groups in the $3500 - 3200 \text{ cm}^{-1}$ region. 190

The CH₂ and CH₃ deformation vibrations at 1470 and 1350 cm⁻¹ and the C=O (carboxyl) 191 stretching or O-H deformation at 1725 cm⁻¹ are attributed to Cu sorption (Chen et al., 2015; 192 193 Gallé et al., 2004); Cu is highly correlated with the carboxyl and alkyl carbon groups of organic 194 matter (Q. Li et al., 2018). Additionally, Cu can form ternary complexes (Alcacio et al., 2001). The protrusion of the 1725 cm⁻¹ peak and the fluctuation in the 1700 - 1200 cm⁻¹ region after 195 Cu sorption was detected for all the samples except S4C1. The aliphatic or aromatic group at 196 1795 cm⁻¹ and the bands at 2370 - 2280 cm⁻¹ disappeared after Cu sorption (except for S3), 197 198 suggesting the disruption of these functional groups by the formation of Cu-bonds. Interestingly, in the S3 samples, the peak at 1640 cm⁻¹ split into two peaks, a unique 199

deformation was detected at 1725 cm⁻¹, and the peaks at 3549, 3405, and 3244 cm⁻¹ (belonging to posnjakite) were relatively more prominent. Finally, the change in surface charge (zeta potential) after Cu sorption is included in SM 8.



Figure 4: a) XRD patterns showing the protrusion of posnjakite peaks (denoted by P) in the C3 – C5 treatments (example of S3 is given here). b) FTIR spectra after the sorption experiment (example of C1 is given here). The peaks assigned to changes due to Cu sorption are indicated in bold. For the identification of the other peaks, please refer to Figure 1b. S1: $0 - 64 \mu m$, S2: $64 - 250 \mu m$, S3: $250 - 500 \mu m$, and S4: $500 - 2000 \mu m$.

203

3.2. Cu desorption induced by synthetic root exudate

204 *3.2.1. Physicochemical changes*

205 The treatments indicated hereafter denote the different concentrations of Cu that were 206 applied for the Cu sorption experiment; the same SRE solution was used for all the treatments. 207 The pH_f values ranged between 5.7 and 7.5 (Figure 5a). The highest pH change was seen for 208 S4, which also showed the lowest buffering capacity in the sorption experiment. The similar pHf values for S4C1 and S4C5 indicate that the different Cu concentrations (treatments) in the 209 210 sorption experiment had similar effects. S2 showed relatively low pH_f values and had a low 211 buffering capacity in the sorption experiment (as seen by a relatively small ΔpH in Figure 2b). 212 As for EC, there was no common trend for the different grain sizes nor for the previously 213 underwent treatments (Figure 5b). The highest ECf values were recorded for S4, which could 214 be related to the dissolution of carbonates that buffered the pH of the SRE solution from 3.7 to 215 nearly 7.4 (Figure 5a). As for the other fractions, EC fluctuated between 210 and 300 µS/cm.



Figure 5: a) pH and b) EC variation after the exposure to SRE. $pH_i = 3.37$ and $EC_i = 196 \,\mu$ S/cm (dotted horizontal line). Whiskers indicate standard deviations of the triplicates.

S1: 0 – 64 μm, S2: 64 – 250 μm, S3: 250 – 500 μm, and S4: 500 – 2000 μm.

216

3.2.2. Metal behavior after the exposure to synthetic root exudate

217 As much as 5 mg/g of Cu was released after the addition of SRE (Figure 6a). In terms of 218 percentage (i.e. released Cu out of the sorbed Cu from the Cu sorption experiment), the values 219 were relatively low, notably for samples treated with high Cu concentrations (Figure 6b). As the case of Cu sorption, Cu release was similar for the different fractions after mixing with 220 221 SRE. The remaining Cu is thought to have formed stable complexes, such as inner monodentate 222 or bidentate sphere complexes to C, N, P, and O functional groups of organic matter (e.g. Moon 223 and Peacock, 2012; Sheals et al., 2001; Strawn and Baker, 2009). In the Cu sorption experiment, 224 the treatments with higher Cu concentrations released higher Ca and Mg concentrations (Figure 225 3b and c); this indicates that the remaining cations that can be further released by SRE are 226 minimal for those treatments, as generally seen in the C5 treatments (Figure 6c and d). 227 Magnesium release showed a logarithmic decreasing trend for the different sediment fractions. 228 The highest Mg release was recorded for S4, followed by S3, S2, and finally S1. However, 229 S4C5 showed a relatively higher Mg release. Again, this sample had relatively higher ECf and 230 pH_f values (Figure 5), which suggest that Mg was released among other cations to buffer the 231 pH. Indeed, S4C5 showed a relatively high Ca release (Figure 6c), which further supports the 232 aforesaid notion. Calcium release followed a similar behavior to Mg. However, S4 showed a 233 peculiar behavior, while the other fractions (S1 - S3) were quite similar (Figure 6c). It is worth 234 noting that the logarithmic trend was clear for all the grain sizes concerning Ca and Mg release, except for Ca release in S4 (as indicated by the R^2 values in Figure 6c and d). The average Ca 235 236 and Mg concentrations released from the control samples (that were treated with 0 mg/L Cu 237 solutions) showed the highest values in comparison to those that were treated with Cu. The 238 values for Ca and Mg release were 56 and 5.0, 57 and 6.1, 54 and 6.9, and 57 and 7.0 mg/L for



S1, S2, S3, and S4, respectively (the data are not included in the graphs for clarity reasons). As
for the monovalent cations (Na and K), they did not show a clear trend (SM 7).

Figure 6: a) The contents of released Cu (mg/g) after the exposure to SRE for the different grain sizes and b) the percentage of Cu released out of the sorbed Cu from the sorption experiment. The concentrations of c) Ca and d) Mg released after the exposure to SRE for the different grain sizes. Whiskers indicate standard deviations of the triplicates. e) FTIR

spectra of the sediment fractions after the exposure to SRE (the example of C1 treatment is given here). The peaks assigned to changes due to Cu sorption are indicated in bold. S1: $0 - 64 \mu m$, S2: $64 - 250 \mu m$, S3: $250 - 500 \mu m$, and S4: $500 - 2000 \mu m$

241 *3.2.3. The ability of SRE to restore the mineral and chemical status of the sediments*

The deformed peak at 1725 cm⁻¹, the small peaks in the 1700 - 1200 cm⁻¹ region, and 242 the peak at 1560 cm⁻¹ that protruded after Cu sorption disappeared or significantly decreased 243 after mixing with SRE (Figure 6e); the peaks at 3549, 3405, and 3244 cm⁻¹ (partially belonging 244 245 to posnjakite) in S3 almost disappeared after mixing with SRE as well. This strongly suggests 246 that those peaks represent exchangeable binding sites for Cu. Moreover, the peaks at 1795 cm⁻ ¹ (aliphatic or aromatic), the nitrile group at 2370 - 2280 cm⁻¹, and the C-O peak at 1025 cm⁻¹ 247 248 (mainly seen in S1 and S3) disappeared or significantly decreased after Cu sorption (Figure 249 4b); those peaks reemerged after mixing with SRE (Figure 6e), suggesting that those functional 250 groups are responsible for the exchangeable binding of Cu, such as the formation of Cu-C 251 bonds (e.g. Golubeva et al., 2013; Q. Li et al., 2018). Consequently, this indicates that SRE 252 was able to partially restore the chemical and mineral state of the sediments. The detectable 253 and possibly exchangeable Cu bindings sites belong to organic matter, as reported by other 254 studies (e.g. Eggleton and Thomas, 2004; Kanbar et al., 2018; Q. Li et al., 2018; Matar et al., 255 2015; Shi et al., 2018). Furthermore, the carbonyl moiety is considered as one of the critical sites for Cu mobility (Moon and Peacock, 2012). 256

In this study, we focused on the behavior of Cu at the solid-liquid interface in a relatively simple system (Cu dissolved in ultrapure water and an SRE solution); which is a first step towards understanding Cu-sediment interaction in complex ones. Therefore, the results might not be applicable in the case of lake systems. The next step would be to make the experimental conditions resemble lake waters and see the behavior of other metals (e.g. As, Cd, Zn, and Fe) as well. Finally, a summarizing schema representing the main sorption and desorption processes of Ca, Mg, and Cu onto and from the organic and mineral parts of the sediments ispresented (Figure 7).



Figure 7: Schematic representation of the main sorption processes of Cu followed by the release of Ca and Mg, and the desorption of Cu, Ca, and Mg after the exposure to synthetic root exudate (SRE). The schema roughly represents the sites where the metals are most likely to be associated (mineral and organic parts); the number of the cations (shapes) is also roughly representative of the data (according to the text). Schema not drawn to scale.

265 **4.** Conclusion

Lake sediments were collected from the Qaraaoun reservoir and divided into four fractions $(0 - 64 \,\mu\text{m}, 64 - 250 \,\mu\text{m}, 250 - 500 \,\mu\text{m}, \text{and } 500 - 2000 \,\mu\text{m})$. The bulk mineralogy and the functional groups were comparable, while the physicochemical parameters and the organic matter and chemical contents were different. The sorption and desorption of copper 270 were peculiar in the coarsest fraction due to the abundance of organo-mineral complexes. The 271 Cu sorption experiment evidenced that Ca and Mg are the main cations that are exchanged; Ca 272 is mainly released from the surface while Mg is released from the inner structure of the 273 sediment particles and aggregates. Furthermore, Cu sorption mainly occurred on the organic 274 fraction. Interestingly, synthetic root exudate was able to desorb some of the Cu that was bound 275 to exchangeable sites of organic matter. The sorption and desorption of Cu did not vary for the 276 different fractions. However, a variation in the exchanged Ca and Mg concentrations was seen, 277 where the coarsest particles had the highest Ca and Mg release after Cu sorption and after SRE 278 treatment. Finally, and based on the geochemical composition of the matrix, the understanding 279 of Cu-sediment interaction opens the way for safe re-use of Cu-rich media in the environment 280 (e.g. soil amendments).

281

5. Declaration of Interest

282

283

6. Acknowledgment

None.

284 This research was financed by the research grant programs of the Lebanese University 285 (The funding source had no involvement in the study design, writing of the report, and decision 286 to submit the article for publication). We would like to thank the research assistants of the 287 Research and Analysis Platform for Environmental Sciences (PRASE), namely Ms. Sarah 288 Haddad (zeta potential), Ms. Sahar Rihane and Ms. Malak Tofeily (FTIR), Ms. Manal Houhou-289 Hadada and Mr. Ali Berro (AAS), and Ms. Layal Hajjar (assistance in laboratory work). We 290 also thank Mr. Nassar Nassar who helped during the sampling campaign, Ms. Delennda Akoum 291 and Ms. Zaynab Nemr for participating in part of the Cu desorption experiment, and two 292 anonymous reviewers for their critical review and constructive comments that improved the 293 quality of this paper.

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426	8.	Supplementary	Materials

427	Mineral and chemical changes of sediments after Cu sorption and then desorption
428	induced by synthetic root exudate
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438	

440 SM 1: Sedimentary materials: mineralogical, physicochemical, and chemical parameters

441 Methodology

442 <u>Mineralogical composition</u>

The major and well crystalline minerals were detected by qualitative X-ray diffraction (XRD) using a D8 Bruker X-ray diffractometer (Cu K_{α} source of wavelength 1.5418 Å). The diffractograms were collected in the 2 θ range between 3° and 64°, and with a step size of 0.034° and a 3 sec collecting time. The functional groups were detected by Fourier transform infrared (FTIR-6300 from JASCO). The spectra were collected from 4000 to 400 cm⁻¹.

448

Physicochemical characterization

449 Each sediment fraction was analyzed for physicochemical parameters, namely cation 450 exchange capacity (CEC), pH, electric conductivity (EC), salinity, total dissolved solids (TDS), 451 and zeta potential. All the samples were run as duplicates except CEC, which was run as 452 triplicates. The CEC was determined by replacing the exchangeable cations of each fraction by 453 copper (Thien and Graveel, 2003). As for pH measurements, a 1:5 volumetric ratio of 454 sediment:KCl (1M) was stirred for an hour, let to settle, and the pH was measured using a 455 combined soil pH electrode (MA920B/1 from Milwaukee). The EC, salinity, and TDS were 456 measured by creating a 1:5 volumetric ratio of sediment: distilled water, according to AFNOR 457 (NF ISO 11265, 1994); after vigorously stirring for one hour and resting for 30 minutes, the 458 EC, TDS, and salinity values were measured using a LaMotte pH/TDS/Salt portable meter 459 (Tracer PockeTester). The organic matter content was estimated by loss on ignition (LoI) after 460 calcinating the fractions at 550°C for four hours (Heiri et al., 2001). The surface charge or zeta 461 potential (ζ-potential in mV) of each sediment fraction was determined by Zeta Meter 4.0 (Zeta-462 Meter, Inc, USA).

463

Metal content

The chemical composition of the sediment fractions was determined after digestion with aqua regia (each sample was run as triplicates). Briefly, 1 g of finely ground sediment fraction was digested with a 1:3 (v:v) solution of HNO₃:HCl (more information is found in Kanbar et al., (2014)). The metals (Cu, Pb, Cr, Mn, Fe, Zn, Mg, Cd, and Ca) were quantified by atomic absorption spectroscopy (AAS Rayleigh WFX-210) equipped with a WF-10A autosampler and flame and graphite furnace modes; the concentrations of Na and K were determined by flame photometry (AFP100 flame photometer, from Biotech Engineering Management Co. Ltd.). 471 Manually prepared standards were used for calibration and QA/QC procedures were 472 implemented based on external standards. Reproducibility and accuracy of the measurements 473 were validated by external calibrations that were run between every ~ 10 samples. The values 474 were taken unless the error exceeded 5-10%. The quantification and detection limits (LOQ and 475 LOD, respectively) were calculated according to the ICH Harmonised Tripartite Guideline 476 (ICH Harmonized Tripartite Guideline, 2005). The LOD was calculated as 3.3 times the 477 standard deviation (σ) of the response of reference materials over the slope (s) of the calibration 478 curve (over 25 measurements). The LOQ was calculated as 10 times the standard deviation (σ) 479 of the response of reference materials over the slope (s) of the calibration curve (over 25 480 measurements).

481 **Results**

482

Mineralogical composition (XRD and FTIR)

483 The mineralogical composition of the sediment fractions was quite similar, except for the 484 detection of feldspar in S1 (see figure below). The well crystalline minerals in the sediment 485 fractions are calcite (carbonate mineral), quartz (primary silicate mineral), and phyllosilicates 486 (secondary weathered silicate minerals) such as kaolinite. The presence of calcite in the 487 sediments is anticipated due to the carbonaceous geological formation, high Ca contents, and 488 alkaline pH (see figure below) (Abdel-Rahman and Nader, 2002; Ammar et al., 2015; Kanbar 489 et al., 2014). Phyllosilicates, as indicated by the diffraction lines at 7.14, 4.47, and 2.57 Å were 490 also detected in S4. Even though phyllosilicates are fine materials (clays), their presence in the 491 coarsest fraction (S4) indicates that these coarse particles certainly contain aggregates, such as 492 organo-mineral complexes.

493 Similar to XRD, the FTIR results showed comparable findings among the different fractions (see figure below). The bands at 520 and 465 cm⁻¹ might indicate salt (Parikh et al., 494 2014). The presence of the 620 cm⁻¹ band could indicate Fe-O vibrations of Fe oxyhydroxides; 495 496 indeed, that peak was prominent in S4, which also had the highest Fe content. The samples also 497 showed aromatic C-H (915, 875, 785, and 710 cm⁻¹), C-O groups of carboxylic acid (1115 and 498 1025 cm⁻¹), aliphatic or aromatic compounds $(1800 - 1400 \text{ cm}^{-1})$, nitrile C=N groups 499 (2370 – 2280 cm⁻¹), alkyl functional groups (-CH3, -CH2, and CH between 2960 and 2855 cm⁻¹ 500 ¹), C=C groups of aromatic alkenes (1640 cm⁻¹), and O-H groups of carboxylic acid (3435, 501 3351, and 3300, and 2515 cm⁻¹), indicating organic matter (Bishop et al., 2013; Levard et al., 502 2012; Margenot et al., 2015; Parikh et al., 2014; Schuttlefield et al., 2007). Moreover, the bands

between 930 - 730 cm⁻¹ and 1425 cm⁻¹ could also indicate calcite (Legodi et al., 2001), which 503 was predominantly detected by XRD; bands at 1115 and 1025 cm⁻¹ can also indicate Si-O-Si 504 quartz bond and Si-O stretching of silicates/clays, and the 2515 cm⁻¹ peak could refer to thiol 505 (S-H) (Bishop et al., 2013; Parikh et al., 2014). Moreover, the peak at 1640 cm⁻¹ might indicate 506 507 the bending mode of water molecules, C=O from amides, and carboxylates (Parikh et al., 2014). In addition, kaolinite was slightly detected by XRD (7.14Å), which is supported by the 508 vibration bands between 3800 and 3500 cm⁻¹ and belong to the O-H stretching motion of 509 510 interlayer hydroxyl groups of kaolinite (Schuttlefield et al., 2007).

511

Initial physicochemical parameters

512 The different sediment fractions showed alkaline pH (7.5 - 8), with higher alkalinity for 513 finer particles. These alkaline pH values reflect the calcareous nature of the geological 514 formation of the Litani watershed (Abdel-Rahman and Nader, 2002). The CEC and LoI values 515 ranged between 22 and 31 meq/100g and between 6.0% and 8.7%, respectively (part a of the 516 figure below). Those findings are similar to other studies conducted in the vicinity of the 517 Qaraaoun reservoir (Ammar et al., 2016, 2015; Kanbar et al., 2014; Wazne and Korfali, 2016). 518 In general, elevated CEC in sediments is due to organic matter and certain clay minerals 519 (e.g. Manceau et al., 2002). Interestingly, the coarsest fraction S4 $(500 - 2000 \,\mu\text{m})$ had the 520 highest organic content and CEC. This suggests that the elevated CEC values are due to organic 521 matter, rather than fine mineral particles (i.e. clays). Another possibility would be the presence 522 of organo-mineral complexes that explain high CEC and OM in the coarse fraction. The EC, 523 TDS, and salinity values were also different among the fractions.

524

Metal contents in the different sediment fractions

525 The coarsest fraction of the sediments was enriched with Cu, Pb, Cr, Mn, Fe, and Zn 526 (part b of the figure below), which is contradictory to the general case (e.g. Du Laing et al., 527 2007; Prasad et al., 2006; Quenea et al., 2009). In another study in the Qaraaoun reservoir, the 528 metal contents of the sediments did not correlate to particle size (Kanbar et al., 2014). Then 529 again, metals are usually associated to sediments with high OM, which is S4 in our case; the 530 higher metal and organic matter contents are explained by the predominance of organo-mineral 531 complexes in the coarsest fraction. Copper has high affinity to organic matter and Fe 532 oxyhydroxides in riverine and lacustrine systems (e.g. Eggleton and Thomas, 2004; Korfali et 533 al., 2006; Matar et al., 2015; Shi et al., 2018). Potassium and Na showed comparable values 534 between the different fractions, and Ca and Cd were mostly enriched in S1, followed by S2,

535 S3, and S4 (Figure 1b). The elevated Ca contents are expected due to natural weathering in the 536 watershed. Indeed, the basin is mostly made from carbonaceous materials (Abdel-Rahman and 537 Nader, 2002). It should be noted that the grain sizes in this study represent the actual sizes of 538 the aggregates (i.e. *in situ* sizes); in other words, the aggregates and complexes were not broken 539 during size separation (wet sieving) to maintain the representativeness of the actual lake 540 sediment sizes.



a) CEC (meq/100g), pH, and LoI (%), b) EC (μ S/cm), TDS (mg/L), and salinity (mg/L), and c) metal contents (Cu, Pb, Cr, Mn, Zn, and Cd in mg/kg, Fe, Mg, and Ca in %, and K and Na in mg/g) of the different sediment fractions. Whiskers, whenever present, indicate standard deviations of the technical replicates.

S1: $0 - 64 \mu m$, S2: $64 - 250 \mu m$, S3: $250 - 500 \mu m$, and S4: $500 - 2000 \mu m$.

SM 2: The concentrations of Cu (in mg/L and mM) used in the Cu sorption experiment for each fraction and for all the treatments. The Cu concentrations are based on the CEC values. For example, a solution with 0.5CEC equivalent contains a Cu concentration that can fill half of the exchangeable sites for the certain sediment fraction. The average CEC values are included with their standard deviations (n=3).

Fraction	CEC	Treatment	Equivalent to	Cu (mg/L)	Cu (mM)
	(meq/100g)	-			
		C1	0.5CEC	36.2	0.57
S 1		C2	1CEC	72.4	1.14
0 64 um	22.8±0.3	C3	2.5CEC	181.1	2.85
$0 - 04 \mu m$		C4	5CEC	362.1	5.70
		C5	10CEC	724.3	11.40
		C1	0.5CEC	39.0	0.61
52		C2	1CEC	77.9	1.23
52 64 250 um	24.4±0.8	C3	2.5CEC	194.8	3.07
$64 - 250 \mu m$		C4	5CEC	389.6	6.13
		C5	10CEC	779.1	12.26
		C1	0.5CEC	39.8	0.63
52	25.0±1.4	C2	1CEC	79.5	1.25
55 250 500 um		C3	2.5CEC	198.8	3.13
230 – 300 μm		C4	5CEC	397.6	6.26
		C5	10CEC	795.3	12.51
	31.2±0.9 m	C1	0.5CEC	49.5	0.78
S /		C2	1CEC	99.1	1.56
500 2000 um		C3	2.5CEC	247.7	3.90
500 – 2000 μm		C4	5CEC	495.4	7.80
		C5	10CEC	990.8	15.59

Component	Compound	Concentration (mM)
	Glucose	25
Sugars	D-Fructose	25
	Sucrose	25
	Citric acid	12.5
Small organia agida	Malic acid	12.5
Sman organic acids	Succinic acid	12.5
	Oxalic acid	12.5
Amino acida	Leucine	6.25
Annino actus	Proline	6.25

SM 3: The composition of the synthetic root exudate and the concentrations of the components used in the desorption experiment





Whiskers indicate standard deviations of the triplicates.

S1: 0 – 64 $\mu m,$ S2: 64 – 250 $\mu m,$ S3: 250 – 500 $\mu m,$ and S4: 500 – 2000 μm

546



548 SM 5: The percentage of Cu sorbed onto the different sediment fractions after 24 hours.

550 Whiskers indicate standard deviations of the triplicates.

551 S1: $0 - 64 \mu m$, S2: $64 - 250 \mu m$, S3: $250 - 500 \mu m$, and S4: $500 - 2000 \mu m$

553 SM 6: The concentrations (mg/L) and equivalent contents (mg/g) of Cu in the positive 554 controls.



556 Some of the final Cu concentrations (after 24 hours shaking) were below the initial 557 concentrations in the positive control samples. This indicates that either Cu precipitated or 558 sorbed onto the walls of the tubes during the sorption experiment. Since the final Cu 559 concentrations that shifted below the expected values (y=x in the figure) concerned Cu values 560 above ~ 350 mg/L (i.e. for C4 and C5), the decline in Cu concentration is expected to be due to precipitation (as clearly evidenced in Figure 4a). According to the values given by the 561 562 positive controls, the qe might be overestimated up to 30% for C5. More specifically, only 563 688 mg/L of Cu is thought to be sorbed in the case of S4C5, while the rest (300 mg/L) probably precipitated. Therefore, the Cu equilibrium uptake for the treatments with high Cu 564 565 concentrations might have a margin of error (as indicated by the blue region in Figure 3a).

567 SM 7: The release of Na and K for different grain sizes and different treatments after Cu
568 sorption (a and b) and after the exposure to SRE (c and d).



569

- 570 Whiskers indicate standard deviations of the triplicates.
- 571 S1: $0 64 \mu m$, S2: $64 250 \mu m$, S3: $250 500 \mu m$, and S4: $500 2000 \mu m$

573 SM 8: Surface charge of the sedimentary materials after Cu sorption.

574 The negative surface charges of particles, including clays, become less negative upon the 575 sorption of cations (Cu in our case). As expected, the surface charge leaned towards zero as the 576 Cu concentrations in the solutions increased (see figure below). The preference of Cu binding 577 onto surface layers is seen by the critical drop in the surface charges between C0 and C1. Upon 578 further increase in Cu concentrations, the drop in the surface charge was only minor, indicating 579 that Cu binding occurred on sites other than the surface (e.g. exchanged with embedded Mg, 580 as explained in section 3.1.2 in the main text). Interestingly, the surface charge of only S4 581 reached zero when treated with maximum concentration of Cu (i.e. C5), indicating that no more 582 Cu could sorb onto the surface. This, however, does not mean that Cu cannot further bind to 583 sites other than the surface. This clearly shows that Cu-cation exchange (mainly Ca and Mg) 584 did not solely happen on the surface. Moreover, another notion that should not be overlooked 585 is that the decrease in surface charge reduces the repulsion between particles. Consequently, 586 aggregation occurs, which could also be responsible for further reduction of the zeta potential.



The surface charge of the sediment fractions after Cu sorption for the different treatments. C0: control. S1: $0 - 64 \mu m$, S2: $64 - 250 \mu m$, S3: $250 - 500 \mu m$, and S4: $500 - 2000 \mu m$.

- 588 SM 9: XRD patterns of S3 after the application of synthetic root exudate
- 589 At the XRD level, there were no detectable changes in the diffractograms between the samples
- 590 after Cu sorption and those after the addition of SRE.



P: posnjakite, Phyl: phyllosilicates, Q: quartz, and C: calcite. The interplanar distances (in Å) and the minerals are assigned to the peaks.

591

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