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1	Experimental redox transformations of uranium phosphate
2	minerals and mononuclear species in a contaminated wetland
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GRAPHICAL ABSTRACT



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53 ABSTRACT

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Reducing conditions and high organic carbon content make wetlands favorable to uranium 55 (U) sequestration. However, such environments are subjected to water-table fluctuations that 56 could impact the redox behavior of U and its mobility. Our previous study on U speciation in 57 58 a highly contaminated wetland has suggested a major role of water-table redox fluctuations in the redistribution of U from U(IV)-phosphate minerals to organic U(VI) and U(IV) 59 mononuclear species. Here, we investigate the mechanisms of these putative processes by 60 61 mimicking drying or flooding periods via laboratory incubations of wetland samples. LCF-XANES and EXAFS analyses show the total oxidation/reduction of U(IV)/U(VI)-62 63 mononuclear species after 20 days of oxic/anoxic incubation, whereas U-phosphate minerals appear to be partly oxidized/reduced. SEM-EDXS combined with µ-XRF and µ-XANES 64 65 analyses suggest that autunite Ca(UO₂)₂(PO₄)₂•11H₂O is reduced into lermontovite 66 U(PO₄)(OH)•H₂O, whereas oxidized ningyoite CaU(PO₄)₂•2H₂O is locally dissolved. The release of U from this latter process is observed to be limited by U(VI) adsorption to the 67 surrounding soil matrix and further re-reduction into mononuclear U(IV) upon anoxic 68 69 cycling. Analysis of incubation waters show, however, that dissolved organic carbon enhances U solubilization even under anoxic conditions. This study brings important 70 71 information that help to assess the long-term stability of U in seasonally saturated organicrich contaminated environments. 72

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75 Keywords: wetland, uranium, redox transformations, soil incubation, X-ray absorption

76 spectroscopy

77 **1. INTRODUCTION**

78 Uranium is a toxic element [1] that naturally occurs in the continental crust at an average concentration of 2.7 mg.kg⁻¹ [2]. It locally concentrates in economic deposits via 79 reductive precipitation and/or hydrothermal processes [3] and has been mined for decades in 80 81 several countries worldwide. Uranium mining operations and legacies have been shown to be responsible for local increases of U contaminations in surrounding surface environments. For 82 instance, U concentrations exceeding the geochemical background were found in aquifer 83 sediments [4], lacustrine sediments [5], soils [6] and wetlands [7-10] in the vicinity of former 84 85 U mining sites.

Organic-rich wetlands are favorable to develop reducing conditions and have been 86 recognized to accumulate uranium both via organic complexation of U(VI) and U(VI) 87 reduction to less soluble U(IV) species. These environments are thus considered as being able 88 to naturally attenuate U migration from nearby mining sites [7,10]. However, the long-term 89 fate of U in wetlands remains unclear, especially when they exhibit intermittent oxidizing 90 conditions due to water-table fluctuations [10]. Indeed, non-crystalline U species that have 91 92 been identified as major U species in wetlands, such as mononuclear U(VI) and U(IV) 93 complexes bound to organic matter [10,11-13], are known to be potentially mobile under both 94 oxic [14-17] and anoxic conditions [7,18]. In addition, U(IV)-phosphate minerals may also 95 play an important role in U retention in mining-contaminated wetlands. Indeed, such phases have been recently recognized as important U hosts in contaminated environments [10,19] 96 and as possible products of microbial U(VI) reduction [16,20-21]. However, the geochemical 97 98 reactivity of these phases when submitted to redox fluctuations is still scarcely documented 99 and remains debated. For instance, Latta et al. (2016) [22] reported that the oxidation of a

synthetic amorphous U(IV)-phosphate resulted in the formation of a low-solubility U(VI)-100 phosphate phase. In contrast, oxidation of a ningvoite-like mineral (ideal formula 101 102 $CaU(PO_4)_2 \cdot 2H_2O)$ has been shown to lead to significant U remobilization [16]. To this regard, the reactivity of U(IV)-phosphate minerals such as ningvoite needs to be further investigated. 103 104 In this context, our recent study of U speciation in a highly contaminated wetland in Brittany, 105 France [10] has suggested that low water-table level conditions can lead to oxidative 106 dissolution of U(IV)-phosphate minerals, especially ningvoite, and to subsequent sorption of 107 U(VI) to soil organic matter, while flooding conditions could favor further reduction of U(VI) 108 to U(IV) organic complexes. Based on these findings, the present study aims at elucidating the micro- and molecular-scale mechanisms underlying such U redistribution processes, by 109 110 performing incubations experiments that mimics typical redox changes induced by water-111 table fluctuations in a seasonally saturated wetland.

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113 2. MATERIALS & METHODS

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115 2. 1. Wetland soil samples

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The wetland soil samples selected for the present incubation experiments were collected in the highly contaminated wetland previously studied by Stetten et al. (2018b) [10], located near the former U-mine Ty Gallen in Brittany, France. Four types of soil layers were distinguished: a humus layer almost devoid of crystalline mineral components (O-type), organic-rich or organic-poor soil layers (A₁- and A₂-type layers respectively), and mine water deposit layers inherited from former mining operations (Figure SI-1b) [10].

For oxic incubations, three pristine reduced soil samples were selected below the water-table(Figure 1): an organo-mineral soil sample from a A₂-type layer (C2-25 cm sample) and two

samples from mine water deposit layers (C2-30 cm and C6-33 cm samples). These samples
were obtained from the C2 and C6 soil cores that were collected, vacuum-dried in a desiccator
to a vacuum limit of 0.5 mbar and preserved under anoxic conditions [10].

128 For anoxic incubations, a humus layer sample (S1 sample; Figure 2) and a mine water deposit 129 layer sample (S2 sample) were collected with a spade in the wetland in November 2015 and 130 were stored under aerobic conditions at ambient temperature (21 °C), before the incubation experiments. These two latter samples were considered as representative of wetland soil 131 132 samples exposed to a prolonged period of dryness and were thus used as starting samples for 133 anoxic incubation experiments. In addition, a pristine organic-rich soil sample from the C2 core corresponding to the A₁-type layer above the water-table level (C2-5 cm sample) was 134 also used as starting sample for anoxic incubation. 135

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137 2. 2. Incubation experiments

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139 For oxic incubation experiments, ~300 mg of dry soil was supplemented with ~1 ml of O₂-140 free milli-Q water and were put in 50 ml tinted glass vials. The glass vials were then left open 141 to air on a lab bench during 20 days in order to simulate a period of dryness. As these pristine soil samples exhibit similar uranium speciation [10], they were used as triplicates for this 142 experiment (C2-25cm oxic; C2-30cm oxic; C6-33cm oxic). Anoxic incubation experiments 143 were conducted in an anaerobic glove box ($O_2 < 20$ ppm vol. in N_2) at IMPMC in sealed glass 144 145 vials, in order to simulate a flooding period. Anoxic incubation of the S1 and S2 samples (S1 anox bio 1ml t20; S2 anox bio 1ml t20) were carried out with ~1 g of air-stored 146 147 sample in 1ml of O₂-free milli-Q water in 50 ml tinted glass vials sealed with a butyl rubber 148 stopper for 20 days. Similar conditions were applied for the C2-5cm sample (C2-5

149 cm_anox_bio_1ml_t20) with ~300 mg of vacuum dry solid sample. No duplicates were150 carried out for these anoxic incubations.

151 Additional anoxic incubations of the S1 and S2 samples were carried out in duplicate, with a 152 lower solid:liquid ratio (1:10)during 14 days (S1 anox bio 10ml t14 A; 153 S1 anox bio 10ml t14 B; S2 anox bio 10ml t14 A; S2 anox bio 10ml t14 B; A and B 154 corresponding to duplicates). Abiotic control incubations were conducted similarly but with samples previously autoclaved at 120°C for 20 min (S1 anox abio 10ml t14; 155 156 S2 anox abio 10ml t14). For these 1:10 incubations, ~1 g of wet soil sample was supplemented by 10 ml of an anoxic 9 mg.L⁻¹ NaCl solution, put in 50 ml tinted glass vials, 157 sealed by a butyl rubber stopper and tumbled for 14 days. For these latter experiments, NaCl 158 159 was used as background electrolyte in order to avoid osmotic stress of the microbial biomass. 160 At the end of these experiments, the incubation solutions were collected by centrifugation, 161 filtered through 0.2 µm and an aliquot was acidified to pH~1 using 67 % HNO₃ for further 162 dissolved U analysis.

At the end of all incubation experiments solid samples were vacuum dried in a desiccatorplaced in a glove box and stored under anaerobic conditions for further analyses.

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- 166 **2.3.** Chemical Analyses procedures
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The initial solid soil samples of the C2 and C6 cores were previously analyzed for majors and traces elements [10]. For S1 and S2 initial solid samples, U content was measured by gamma spectrometry using a Ge HP type N - GEN27 detector at IRSN laboratory. For this purpose, solid samples were dried at 105 °C until a constant mass was obtained. They were 2mm sieved and ~40 g of the fraction inferior to 2mm was conditioned under vacuum in aluminized bag. Each sample was measured for 24 hours. Dissolved uranium in the 1:10 incubation experiments were measured on acidified aliquots using an ICP-MS (X7 série 1
ThermoFisher[®]). Dissolved Organic Carbon (DOC) and Dissolved Inorganic Carbon (DIC)
were measured following the method described in Stetten et al. (2018b) [10].

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178 2. 4. X-ray Absorption Spectroscopy

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X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine 180 181 Structure (EXAFS) spectra at the Uranium L_{III}-edge were collected on the 11-2 wiggler 182 beamline at the Stanford Synchrotron Radiation Lightsource (SSRL) and on the CRG-FAME bending-magnet beamline at the European Synchrotron Radiation Facility (ESRF). The S1, 183 184 S2 and anoxic incubation samples were analyzed on the 11-2 beamline at liquid N_2 185 temperature in fluorescence mode detection using a Si(220) double crystal monochromator 186 and a 100-element solid state Ge array fluorescence detector. The oxic incubation samples 187 were analyzed on the FAME beamline at liquid He temperature using a Si(220) double crystal 188 monochromator and a 30 elements Ge fluorescence detector (ESRF) [23]. The incident beam 189 energy was calibrated using a Y-foil in double transmission setup, with first inflection point 190 set to E=17038 eV. XAS spectra collected at BL 11-2 were deadtime corrected and average 191 using SIXPACK [24], and those collected at FAME-CRG beamline were averaged using 192 ATHENA [25]. Energy calibration, normalization and background subtraction were 193 performed with ATHENA.

In order to quantitatively determine the fractions of U(VI) and U(IV), U-L_{III} edge XANES spectra were least-squares fit by linear combinations (LCF) of pure U(IV) and U(VI) model compounds XANES spectra, using a home-built code [10,19,26]. The chosen model compounds were a U(IV) humus sample and a synthetic U(VI)-humic acid model compound [10]. Uranium L_{III}-edge EXAFS spectra of the incubated samples were least-squares fit by linear combinations (LCF) of model compounds EXAFS spectra using a home-built code [10,19,26]. The model compounds chosen for this procedure were already used by Stetten et al. (2018b) [10] to fit the U L_{III}-edge EXAFS spectra of the C2 and C6 soil samples and were previously interpreted using shell-by-shell fitting of the k^3 -EXAFS spectra. This latter procedure yielded a description of the first and second neighbor shells around the U atom in these model compounds, as detailed in Stetten et al. (2018a) [5] and Stetten et al. (2018b) [10].

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207 2. 5. μ-XRF and μ-XAS data collection and analysis.

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209 Microfocused X-ray fluorescence (µ-XRF) and U L_{III}-edge micro-X-ray Absorption Near 210 Edge Structure (µ-XANES) spectroscopy analyses were conducted at the 2-3 beamline 211 (SSRL) on polished sections of epoxy resin-embedded samples. The chosen samples were the mine water deposit sample (S2) and the product of its 20-day incubation under anoxic 212 213 conditions (S2 anox bio 1ml t20). The µ-XRF maps were collected at room temperature 214 and an incident energy of 17200 eV, using a Vortex silicon drift detector, a beam spot size of $\sim 2x2 \mu m$, a step of 10 μm and a counting time of 50ms. In order to limit U(IV) oxidation, a 215 216 continuous flow of N₂ gas was applied on the surface of the samples during the 217 measurements. Points of interest were selected on the u-XRF maps for U L_{III}-edge u-XANES analyses using a Si(111) monochomator calibrated with elemental Y (K-edge at 17038 eV). 218 219 The spectra were averaged using SIXPACK [24], normalized with ATHENA and analyzed by LCF with a custom-built software based on Levenberg-Marquardt least-squares minimization 220 221 algorithm, using U(VI)-humic acid and U(IV)-humus model compound spectra as fitting 222 components [5,10].

224 2. 6. SEM-EDXS data collection and analysis

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Scanning electron microscopy analyses were performed at IMPMC, using a Zeiss ultra 55 equipped with a Field Emission Gun. Backscattered images and EDX Spectra were collected at 15 keV with a working distance of 7.5 mm. The beam intensity was calibrated using the Cu K-alpha emission from a TEM copper grid. Semi-quantification of the EDXS spectra was performed using the Bruker[®] Esprit program and the Phi(rho,*z*) method using mineral standard spectra. The atomic content in U, Ca and P obtained with this method were then plotted in ternary diagrams using TERNPLOT [27].

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3. RESULTS AND DISCUSSION

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- **3.1. Effect of oxic incubations**
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In the pristine wetland soil samples (C2-25 cm, C2-30 cm and C6-33 cm samples), ~40-58% U(IV) is present as mononuclear U(IV) species that were fitted with a U(IV)-humus component (Figure 1, Table SI-2). In this model compound, the U-P at 3.1 Å and U-C at 3.7 Å EXAFS scattering paths are interpreted as bidentate and monodentate binding of U to phosphate and carboxylate groups, respectively [10]. The remaining ~35-55 % U in the soil samples was fitted with a U(IV)-rhabdophane component, used as proxy for U(IV) phosphate minerals identified as ningyoite and lermontovite [10].

After 20 days of incubation under oxic conditions, the proportion of mononuclear U(IV)

decreased down to 0-17% and that of U(IV)-phosphate mineral decreased down to 20-38 %,

while mononuclear U(VI) increased to 51-89 %, as fitted with a U(VI)-biosorbed component

248 (Figure 1; Table SI-2). In this latter model compound, U(VI) is bound to both phosphate in

monodentate geometry (U-P path at ~3.6 Å; [10,28,29]) and carboxylate in bidentate 249 geometry (~2 U-C paths at 2.9 Å; [10]). These data are consistent with the extent of U 250 251 oxidation measured by LCF-XANES analysis of the same samples (Figure SI-3, Table SI-2). 252 These results indicate complete oxidation of mononuclear U(IV) (Figure 1), except for sample 253 C2-25 cm in which 17 % of mononuclear U(IV) persisted, which is consistent with the 254 reported higher sensitivity of mononuclear species to redox change than crystalline U(IV) species [15-18]. In addition, except in sample C2-25 cm, 30-45 % of the U(IV)-phosphate 255 256 minerals oxidized, likely into U(VI)-mononuclear species that were accounted by an increase 257 of the U(VI)-biosorbed component in the LCF. These oxidized species could correspond to 258 mononuclear U(VI) bound to organic phosphate groups of humic substances or biomass 259 [28,30], as well as to inorganic phosphate groups [28,33] for instance at the surface of the oxidized U(IV)-minerals. Finally, 55-100 % of the U(IV) mineral phases were resistant to 260 261 oxidation. The study of Newsome et al. (2015a) [16] also highlighted that U(IV)-phosphate minerals were partly resistant to oxidation. In this previous study, only ~20 % of U(IV) was 262 263 reoxidized from a biologically precipitated ningyoite-like phase after 90 days of air exposure.

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Figure 1. LCF analysis of U L_{III} EXAFS data of pristine reduced soil samples from the A₂-type and
 mine water deposit layers and same samples after incubation under oxic conditions. Experimental and
 fit curves are displayed in black and red colors respectively. Modulus and Imaginary part of the Fast
 Fourier Transforms of the experimental and fit curves are also reported. The proportions of the fitting
 components, represented by the bar-diagram, are normalized to 100 %. Non-normalized results and
 uncertainties are given in Table SI-2.





Figure 2. LCF analysis of U L_{III} EXAFS data of initial samples (S1 and S2 samples) and incubated
 samples under anoxic conditions. Experimental and fit curves are displayed in black and red colors
 respectively. Modulus and Imaginary part of the Fast Fourier Transforms of the experimental and fit
 curves are also reported. The proportions of the fitting components, represented by the histograms, are
 normalized to 100 %. Non-normalized results and uncertainties are given in Table SI-2.

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281 In order to evaluate the consequences of the oxidation of U(IV)-mineral phases on the 282 potential U redistribution in the soil matrix, the spatial distribution of U was investigated by µ-XRF mapping. The sample studied was a polished cut of the air dried S2 mine water 283 284 deposit sample that exhibited the same U speciation as C2-30cm oxic and C6-33 cm samples 285 (Figures 2 and 1; Table SI-2). Uranium was mainly found by μ -XRF as hot spots (Figure 3a) suggesting the presence of U minerals grains. LCF analysis of µ-XANES spectra collected at 286 hotspots #1 and #2 showed only U(IV) (Table SI-4). These grains could thus be interpreted as 287 288 corresponding to abundant ningyoite CaU(PO₄)₂•2H₂O (Figures 4d,4a, SI-4a), and to a lesser 289 extent lermontovite U(PO₄)(OH)•H₂O (Figures 4c; SI-4b) grains identified by SEM-EDXS in

the same S2 sample.



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Figure 3: μ -XRF mapping of U distribution and μ -XANES analyses of U redox state in a mine water deposit sample collected in the wetland (Sample S2) and the product of its incubation under anoxic conditions (S2 anox bio 1ml t20); The data were obtained by analyzing polished sections of epoxy295 resin embedded samples. The µ-XRF elemental maps are displayed in the same color intensity scale 296 and show the spreading of U around U-rich grains in the incubated sample. The color scale of the μ -297 XRF elemental maps corresponds to the background subtracted area of the U La emission line, 298 increasing from blue to red with U content; U oxidation state was determined by LCF fit of the micro-299 XANES spectra collected on selected points in the XRF maps using U(VI)-humic acid and U(IV)-300 humus model compound spectra as fitting components. Spectrum of these model compounds are 301 plotted in black lines. Experimental and calculated spectra are plotted as black and red solid lines, 302 respectively. No oxidation of U(IV) was reported during the time of the measurement as shown in Figure SI-6. Non-normalized results and uncertainties are given in Table SI-4. 303

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only U(VI) could be 305 Spot #3 exhibited attributed to crystalline autunite 306 $Ca(UO_2)_2(PO_4)_2 \cdot 11H_2O$ that was scarcely observed in this sample (Figure SI-4c). Since no 307 U(VI)-bearing mineral was detected by EXAFS analysis of this sample, autunite likely do not 308 account for more than 10 % of total U in the S2 sample. The formation of an autunite-like mineral after oxidation of an amorphous U(IV)-phosphate was reported by Latta et al. (2016) 309 310 [22]. By contrast, in the mine water deposit S2 sample, the scarce and massive autunite 311 crystals (Figure SI-4c) differs from the reticulated microcrystals observed by Latta et al. (2016) [22], and thus did not likely formed by the oxidation of ningyoite. Instead, our μ -XAS 312 dataset and the non-detectability of U(VI)-mineral by EXAFS suggest that U(IV) minerals 313 grains oxidized into mixed U(IV)/U(VI) grains, in which U(VI) may be mainly present as 314 sorbed mononuclear U(VI). Indeed, the observation of U(VI) in hot spots #4, 5 and 6 315 316 suggested that these U-rich grains contain sorbed U(VI) that could coat or replace former 317 U(IV)-phosphate phases. Finally, the µ-XRF map of the initial S2 sample (Figure 3) displayed 318 a diffuse distribution of U, which was consistent with the occurrence of U(VI) mononuclear 319 complexes determined by LCF-EXAFS (Figure 2; Table SI-2). Altogether, these results 320 confirmed that a fraction of U is distributed in the soil matrix, which might account for the 321 non-crystalline U(VI) species observed by EXAFS analysis.



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325 Figure 4. Backscattered electrons SEM images and semi-quantitative EDXS analyses of U minerals in 326 the mine water deposit (S2 sample; red crosses) and in the same sample after anoxic incubation 327 (S2 anox bio 1ml t20; purple crosses). (a) Ningyoite in the S2 sample, (b) Ningyoite with prismatic 328 morphology [34] and (c) Lermontovite with platy morphology [37] in the S2 anox bio 1ml t20 329 incubated sample. (d) Ternary diagram showing P, Ca and U compositions of the U-mineral grains 330 observed in these samples. Ideal stoichiometric composition of Autunite Ca(UO₂)₂(PO₄)₂•11H₂O 331 (orange diamond), ningyoite CaU(PO₄)₂•2H₂O (green triangle) and lermontovite U(PO₄)(OH)•H₂O (green square) minerals are also reported. 332

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335 3. 3. Effect of anoxic incubations

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337 Two types of samples were incubated under anoxic conditions: S1 and C2 5cm humus samples in which U mainly occurs as mononuclear species and S2 mine water deposit sample 338 339 in which U is partitioned between U-phosphate minerals and mononuclear species. Full reduction of U(VI) was observed for S1 and C2 5 cm, whereas partial reduction was 340 observed for S2 (Figures 2 and SI-3; Tables SI-2 and SI-3) after 20 days. The extent of U 341

reduction was systematically lower at shorter incubation times (14 days) and at lower 342 solid:liquid ratio (1:10) (Figure 2; Table SI-2). We may hypothesize that a lag phase in the 343 344 growth of the microbial biomass could have delayed the effective microbial-mediated U reduction during the first 14 days of incubation. The reduction of U(VI) to U(IV) species 345 346 could be enhanced by both enzymatic and abiotic U(VI) reduction pathways [5, 37-40]. Here, 347 the role of microorganisms in U reduction was confirmed by the absence of U reduction in the abiotic incubations conducted for 14 days at solid:liquid ratio (1:10) (Figure SI-3; Table SI-348 349 3). The higher reduction rate observed for S1 samples could be explained by the high organic 350 carbon content of these samples that would have enhanced biotic reduction processes [37], likely via direct or indirect dissimilatory reduction of U(VI) [38-40]. Even if it has been 351 352 shown that direct enzymatic U reduction pathways dominate in sediments [36, 39], we cannot 353 exclude that U is reduced by indirect microbial pathways, for example via the release of 354 abiotic reductants such as Fe(II), itself possibly produced by the bioreduction of Fe(III)-355 bearing minerals [5, 40].

356 For the S1 sample, the best EXAFS LCF was obtained with 60% of U(VI)-biosorbed model 357 compound and 40% of U(IV)-humus model compound (Figure 2; Table SI-2). This latter 358 model compound also used by Stetten et al. (2018b) [10] corresponds to the product of 359 reduction of the S1 sample after 20 days of incubation at high solid:liquid ratio 360 (S1 anox bio 1ml t20 sample), in which U was fully reduced (Figures 2 and SI-3; Tables SI-2 and SI-3). Shell-by-shell fitting of the k^3 -EXAFS spectra was performed in Stetten et al. 361 (2018b) [10] for this humus model compound and indicated the presence of bidentate U(IV)-362 363 phosphate and monodentate U(IV)-carboxylate complexes.

Altogether, these results suggest that the reduction of monodentate U(VI)-phosphate and bidentate U(VI)-carboxylate complexes lead to the formation of bidentate U(IV)-phosphate and monodentate U(IV)-carboxylate complexes, without formation of U(IV) mineral, likely due to the abundance of organic-bound phosphate and carboxylate ligands inhibiting uraninite
formation [41,42]. Additionally, the lack of free orthophosphate may also prevent U(IV)phosphate minerals precipitation in such organic-rich layers.

370 Sample S2 was chosen to investigate the effect of anoxic conditions on oxidized mine water 371 deposits that contained mainly sorbed mononuclear U(VI) species (~80 %) and recalcitrant 372 U(IV)-phosphate minerals (~20 %) (Figures 2, 3 and 4; Table SI-2). LCF-EXAFS results indicated that after 14 days of anoxic incubation (sample S2 anox bio 10ml t14 A), the 373 374 proportion of U(IV)-phosphate minerals increased up to 40% whereas sorbed mononuclear 375 U(VI) species decreased by 20 % (Figures 2; Table SI-2). After 20 days of anoxic incubation (sample S2 anox bio 1ml t20), the proportion of U(IV) phosphate did not increase above 376 377 ~40 %. In contrast, the proportion of sorbed U(VI) decreased down to 31 % while a proportion of ~30 % of U was found as U(IV)-humus (Figure 2, Table SI-2). This latter result 378 379 could be interpreted as the reduction of sorbed U(VI) to sorbed U(IV), as discussed in the 380 previous section for S1 sample.

381 The increase in the proportion of U(IV)-phosphate minerals after 14 and 20 days of anoxic 382 incubation suggests the formation of U(IV)-phosphate minerals. Such a reaction may likely 383 occur via reduction of U(VI) bound to phosphate mineral surfaces since the reduction of organically-bound U(VI) was found to lead to organically bound U(IV) as shown for S1 384 385 sample. The formation of U(IV)-phosphate such as ningvoite-like minerals from the 386 bioreduction of inorganic U(VI)-phosphate species is supported by previous laboratory assays 387 [21,43]. Indeed, these previous studies reported slow reduction kinetics of Hydrated Uranium Phosphate (HUP), with ~20-80 % of U(VI) remaining in the solid phase after 10 days 388 389 incubation of a biogenic HUP, and ~ 30 % of U(VI) after 20 days incubation of abiotic HUP. 390 To this regard, the lower reduction rate observed in S2 sample compared to the organic S1

391 sample may be due to a slower bioreduction rate of inorganic U(VI)-phosphate species 392 compared to organic ones.

393 In the incubated S2 anox bio 1ml t20 sample, µ-XANES spectra for U(IV)/U(VI) ratio showed that a minor (10-35%) proportion of U(VI) remained at hot spots (Figure 3b; Table 394 SI-4), suggesting almost complete reduction of U(VI)-bearing mineral grains. In addition, the 395 amount of U in the soil matrix appeared to be higher after than before incubation (Figures 3a 396 397 and 3b), suggesting U migration from U hot-spots to the surrounding organic-rich soil matrix 398 (Figure 3b). One may hypothesize that such migration process could have occurred at the beginning of the incubation experiment via the dissolution of U(VI) initially sorbed to 399 oxidized phosphate minerals grains (Figure 5). The presence of U(IV) in the soil matrix 400 (Figure 3b; Table SI-4) suggests that U(VI) was then further reduced to U(IV) mononuclear 401 species under the reducing conditions that developed in these anoxic incubations. 402

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405

406 Figure 5. Schematic view of the effect of successive oxic and anoxic incubations on the redistribution 407 of U from U(IV)-phosphate mineral such as ningyoite in mine water deposits layers in the studied 408 contaminated wetland.



(Figures 4d, SI-4b). Conversely, ningyoite was also found in the S2 anox bio 1ml t20 412 sample (Figure SI-5ab) but in a lower amount than in the S2 sample (Figures 4d, SI-4a). 413 414 Moreover, some ningyoite grains observed in this sample exhibited a weathered morphology 415 with acicular apexes and eroded surfaces (Figures 4b, SI-5b), whereas lermontovite grains 416 exhibited massive and non-weathered morphology (Figure 4c, SI-5c). These results suggest 417 that sorbed U(VI) previously resulting from the oxidation of ningyoite grains could have dissolved at the beginning of the anoxic incubation, whereas lermontovite-like minerals may 418 419 be more recalcitrant to oxidation and dissolution. Moreover, we hypothesize that autunite-like 420 minerals of the S2 sample could have been transformed into lermontovite-like minerals via a loss in Ca during the reduction process. Indeed, lermontovite is known to mainly occur as 421 422 secondary mineral in reducing environments and is found in intimate intergrowth with U(VI)-423 phosphates from the autunite or meta-autunite group [35]. In addition, although the crystal 424 structure of lermontovite is still unsolved, it has been reported to crystallize in the 425 orthorhombic system and could thus have a layered structure like autunite [35], which could favor transformation of autunite phase to lermontovite via the loss of Ca^{2+} in the interlayer 426 427 and reduction of U(VI) to U(IV). The scarcity of autunite in the wetland soil, while it is an abundant mineral of the oxidation zone of the Ty Gallen ore (https://www.mindat.org/min-428 433.html), and in return the abundance of lermontovite in the reduced mine water deposits 429 430 layers of the wetland could be explained by a progressive transformation of autunite into lermontovite under prolonged reducing conditions. In contrast, the progressive oxidation and 431 432 dissolution of ningyoite, after repeated redox cycles could explain the redistribution of U 433 toward the organic compartment of the wetland soil. Finally, neoformation of ningyoite under 434 reducing conditions cannot be excluded since Khijniak et al. (2005) [43] reported the 435 formation of a ningyoite-like mineral after bioreduction of a meta-autunite mineral uramphite 436 (NH₄)(UO₂)(PO₄).3H₂O at 65°C in a laboratory experiment with *Thermoterrabacterium*437 *ferrireducens*.

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439 **3.4.** Uranium mobility after a redox cycle: experiment vs field investigation

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In order to investigate the release of U during a flooding event following a dry period, we 441 have measured dissolved U concentrations in 0.2 µm filtered supernatant solutions collected 442 443 at the end of the anoxic incubation. Figure 6 shows the dissolved uranium concentrations at 444 the end of the 1:10 incubation performed under biotic and abiotic anoxic conditions. Uranium concentrations in the humus sample S1 experiments (S1 anox biotic 10ml ([U]= 1520 µg.L⁻ 445 ¹) and S1 anox abiotic 10ml ($[U] = 2156 \mu g. L^{-1}$) are far higher than U concentrations of the 446 mine water deposit layer sample S2 experiments (S2 anox biotic 10ml ([U]=160 µg.L⁻¹) and 447 S2 anox abiotic 10ml ([U]=913 µg.L⁻¹)). Such high concentrations represented however less 448 than 0.05 % of both S1 and S2 solid U concentrations (4516 mg.kg⁻¹ for S1 and 2750 mg.kg⁻¹ 449 450 for S2). These results showed that, in the conditions of our experiments, the remobilization of 451 U in the aqueous media after a complete redox cycle is limited and did not exceed 0.05 % of 452 the total U solid pool. Despite that the aqueous environments established in the experiments 453 are simplified, these results were consistent with our previously developed hypothesis of the 454 redistribution and scavenging of U in the solid phase during the incubation experiment, mostly by adsorption and subsequent reduction (Figure 3a). These results agree with a recent 455 456 study showing a release of U of 0.8% from initially reoxidized mononuclear U species under reducing conditions in carbonate-free media [18]. 457

In all anoxic incubations, dissolved organic carbon release was high, especially for organic S1
samples (Table SI-5) and was positively correlated to dissolved U concentration, which
strongly suggests solubilization of U by complexation to soluble organic ligands. Such results

are in line with the study of Grybos et al. (2009) [44], in which large quantities of dissolved 461 organic matter were reported to be solubilized under reducing conditions in a wetland soil, 462 463 likely because of the reductive dissolution of ferric iron oxides involved in the stabilization of 464 organic matter. Organic species have been shown to complex U(VI) and U(IV) in aqueous or 465 colloidal mobile species in the laboratory and the field [7,45-46]. In the study of Seder-466 Colomina et al. (2018) [18], U release under anoxic condition was mainly explained by inorganic carbon complexation except in experiments without added HCO₃, where a minor U 467 468 mobilization was explained by the release of organic carbon. In addition, in the same study, 469 geochemical modeling confirms the presence of dissolved U(VI) and U(IV) organic species as 470 major species in the aqueous media in carbonate-free experiments. In our experiments, DIC 471 was found negligible to the opposite of DOC. In addition, EXAFS results show an important 472 fraction of U bound to organic moieties (Figure 2) in the solid phase. The final dissolved U in all our incubated samples could therefore be associated with soluble or colloidal forms of 473 474 organic carbon. Then, for the S1 sample, the release of U could be due to the release of U-475 bearing organic molecules. For the S2 sample, the dissolution of U(VI)-phosphate minerals 476 could be more limited because of the lower amount of organic carbon, but still promoted by 477 complexation to soluble organic ligands. Accordingly, laboratory experiment have reported important remobilization of U after reoxydation of non crystalline U(IV) [15]. In contrast, 478 479 U(IV)-phosphate minerals were found to be more recalcitrant to oxidative remobilisation, but significant release of U was also reported [16]. Here, our results suggested that such 480 481 remobilization could be limited in organic-rich environmental samples, via U sorption onto 482 particulate matter. Indeed, uranium remobilization was found to be minor (< 1% of total solid U). However, the high concentrations of U in the soil ($< 4500 \text{ mg.kg}^{-1}$) could contribute to 483 484 significant dissolved U concentrations in pore waters under reducing condition. Moreover, the presence of U(IV)-phosphate minerals that are subject to reoxidation events and subsequent 485

dissolution appears to play an important role in the long-term release of U under redox
fluctuations, even in the absence of carbonates. In addition, mobility of U bound to particulate
and colloidal organic matter would be important to consider in order to evaluate U fluxes out
of the studied wetland.

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491

492 Figure 6. (a) Uranium concentration and redox in S1. S1 anox bio 10ml t14, 493 S1 anox abio 10ml t14 and S2, S2 anox bio 10ml t14 A and S2 anox abio 10ml t14 solid 494 samples. (b) U concentration in biotic and abiotic incubation solutions of S1 anox and S2 anox 495 incubated samples at the end of the 14 days (c) Dissolved organic carbon concentrations in biotic and 496 abiotic incubation solutions of S1 anox and S2 anox incubated samples at the end of the 14 days. 497 Corresponding data are reported in Table SI-5. Errors bars represent the standard deviation over the 498 duplicates samples for biotic incubations and the relative uncertainty of the measurement for abiotic 499 incubations.

500

501 4. CONCLUSION

In our previous study of the same wetland, we showed an important redistribution of U from U(IV)-phosphates to mononuclear U(VI)/U(IV) species, interpreted as the result of the oxidative dissolution of U-phosphate minerals and subsequent adsorption of U by organic matter occuring during redox oscillations [10]. Here, our results confirm that a drying period could enhance rapid oxidation of non crystalline species and, to a lesser extent, of U(IV)-

phosphate minerals. Even if such oxidation has been shown to lead to an important 507 508 remobilization of U, especially if it is under non-crystalline forms [15-16], our results show 509 that in organic-rich samples, the adsorption onto soil organic ligands limits U spreading from 510 mineral hotspots. In addition, the dissolution of U(IV)-phosphate minerals upon redox cycling 511 raises important issues concerning the long-term fate of U in seasonnaly saturated 512 environments. Our results further suggest that mononuclear U(VI) species resulting from such oxidative dissolution processes can be fully reduced after 20 days under reducing condition. 513 514 Thus, in organic-rich and carbonate-free environments, U mobility appears to be mainly 515 controlled by the fate of organic matter rather than by redox processes [7,47], which is 516 supported by the observed positive correlation between aqueous U and DOC content in our 517 anoxic incubation solutions. This observation raises questions concerning the long-term fate of U in highly contaminated organic-rich wetlands, since U could be slowly mobilized under 518 519 both oxic and reducing conditions. As a perspective of this work, we hope that the molecular 520 scale processes identified in this study will help to design efficient monitoring and modeling 521 approaches to manage U migration at the landscape scale in organic-rich environments.

522

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