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Uranium sorption to organic matter and long-term accumulation in a pristine alpine wetland

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1 **ABSTRACT**

2 Understanding the controls on uranium (U) mobility in the environment is key to
3 improve the management of sites contaminated by U mining activities. Previous research has
4 shown that natural or engineered wetlands are particularly able to scavenge high amounts of
5 U(VI) and U(IV) under noncrystalline forms. However, questions remain on the respective roles
6 of sorption and reduction processes in the removal of U from running waters in wetlands, as
7 well as on the long-term stability of U storage. Here, we performed a series of geochemical,
8 isotopic ($\delta^{238}\text{U}$, ($^{234}\text{U}/^{238}\text{U}$)), microscopic (SEM-EDXS, EPMA) and spectroscopic ($\mu\text{-XRF}$, $\mu\text{-XAS}$,
9 XANES and EXAFS at the U L_3 and M_4 -edges and Fe K -edge) investigations to determine the
10 modes of U accumulation and assess U mobility in a natural exceptionally U-enriched (up to
11 5000 $\mu\text{g/g}$) wetland on the shore of Lake Nègre (Mediterranean Alps, France). Uranium (VI) was
12 largely dominant in the two studied soil cores, except a few samples containing as much as
13 $\sim 50\%$ U(IV). At the particle scale, U is associated to a variety of organic constituents of the soil
14 matrix with a homogenous oxidation state. Bulk EXAFS spectroscopy at the U L_3 -edge shows that
15 U is mostly mononuclear, with dominant monodentate binding to organic moieties (C neighbors
16 at $\sim 3.45 \text{ \AA}$). An additional minor fraction of U under polymeric forms is inferred from wavelet
17 (CCWT) analysis of the EXAFS data. These observations are reinforced by 1 M bicarbonate
18 extractions that result in the dissolution of 82-96 % of total U, including putative polymeric
19 species. At the wetland scale, similar or slightly fractionated isotopic ratios ($\delta^{238}\text{U}$) between the
20 wetland-feeding creek waters and the wetland soils are observed, supporting the idea that U(VI)
21 sorption on organic matter is the primary U scavenging mechanism. Furthermore, it indicates
22 that partial U(VI) reduction to U(IV) occurs as a second step, after sorption. Analysis of U decay
23 chain disequilibria in the cores as a function of depth suggests that U accumulation in this
24 wetland has lasted for several thousand years. We propose that the wetland acts as an active
25 reactor where U has been massively accumulating for ~ 14500 years, especially as U(VI) forms
26 associated to organic matter, and is further partly exported to the lake through soil erosion.

27

28 **KEYWORDS**

29 Noncrystalline Uranium; Wetland; Uranium speciation; Uranium isotopes; U(VI) polymeric
30 species

31

32

33 1. INTRODUCTION

34 Past uranium (U) mining activities have raised worldwide environmental, health,
35 remediation and long-term management concerns (Abdelouas, 2006; Newsome et al., 2014),
36 including in France (GEP, 2010; IRSN, 2019). As part of the global strategy to improve the
37 management of U-contaminated sites, particularly to strengthen the projections on the short-
38 and long-term U behavior, it is critical to understand the factors controlling the speciation and
39 mobility of U in natural environments (e.g., Regenspurg et al., 2010; Campbell et al., 2012; Wang
40 et al., 2013; Morin et al., 2016; Mikutta et al., 2016; Gourgiotis et al., 2020). In that context, the
41 Lake Nègre catchment in the Mercantour-Argentera massif (Mediterranean Alps, South-East
42 France) appears as a natural analogue of contaminated sites since exceptionally high U
43 concentrations of natural origin were observed in the lake sediments and in the watershed
44 streams (AERMC, 2008; Lefebvre et al., 2021a, b). In this pristine environment, the processes
45 involving U species can be observed at several scales of time and space. In the long term, U
46 speciation provided important clues about climatic and mineralogical controls on the sources,
47 composition and diagenetic fate of U in the lake sediments since the last deglaciation (Lefebvre
48 et al., 2021a, b). These previous studies referred to the potential role of the wetland located right
49 upstream of Lake Nègre, along with the watershed soils, in controlling U inputs to the lake
50 through U scavenging by organic matter (OM) followed by U export to the lake through soil
51 erosion (Lefebvre et al., 2021b).

52 Uranium accumulation in wetlands has been well documented (e.g., Owen and Otton, 1995)
53 and several studies over the past decade have contributed to improve our understanding of
54 micro-scale processes responsible for U scavenging (Regenspurg et al., 2010; Wang et al., 2013,
55 2014; Li et al., 2015; Mikutta et al., 2016; Stetten et al., 2018a, 2020; Fuller et al., 2020; Le Pape
56 et al., 2020). A main underlying objective of these studies was to evaluate the potential of
57 artificial wetlands to attenuate U release from highly contaminated sites such as mine tailings
58 (e.g., Schöner et al., 2009; Fuller et al., 2020). In pristine environments, U usually originates from
59 the leaching of a U-rich igneous source rock (e.g., Regenspurg et al., 2010; Fuller et al., 2020) and
60 is subsequently trapped downstream by the soil OM. In organic-rich soils, U accumulation can
61 reach several thousand parts per million ($\mu\text{g/g}$) in both its oxidized (U(VI)) and reduced (U(IV))
62 states. The U(VI) form is usually dominating, in particular as noncrystalline (also known as
63 mononuclear) species bound to organic moieties (Regenspurg et al., 2010; Mikutta et al., 2016;
64 Fuller et al., 2020). Similar observations were made in U mining-contaminated wetlands with
65 even higher U accumulation, primarily originating from mine waste piles but also locally from
66 redistribution from U particles-rich discharge layers (Schöner et al., 2009; Wang et al., 2013,

67 2014; Mangeret et al., 2018; Stetten et al., 2018a, 2020; Gourgiotis et al., 2020; Le Pape et al.,
68 2020; Martin et al., 2020; Kaplan et al., 2020).

69 In wetland soils, high U accumulation is enhanced by elevated organic matter content, which
70 provides abundant U binding sites and boosts microbial activity. Microbial respiration in such
71 water-saturated media then potentially generates reducing conditions, favoring U(VI) reduction
72 to less soluble U(IV) species (Maher et al., 2013). Uranium partitioning in the solid phase may
73 occur through complexation of U(VI) and U(IV) to organic moieties, and, to a lesser extent,
74 sorption to mineral surfaces (Regenspurg et al., 2010; Mikutta et al., 2016; Bone et al., 2017b,
75 2020; Stetten et al., 2018a; Fuller et al., 2020) and/or through precipitation of U(IV) or U(VI)
76 mineral species, as evidenced for instance in organic-rich lenses in alluvial sediments (Noël et
77 al., 2017, 2019). Uranium mobility is then driven by the solubility of solid U species, in other
78 words by the solid-phase U speciation. In that respect, noncrystalline U species have raised
79 attention over the past decade because of their higher sensitivity to redox cycling and
80 dissolution (e.g., Cerrato et al., 2013; Seder-Colomina et al., 2018; Newsome et al., 2015 and
81 references therein). Additionally, questions remain about the long-term evolution of
82 mononuclear U species in soils subject to redox fluctuations, as is often the case for wetland
83 soils.

84 Several questions remain unsolved regarding the exact mechanisms leading to both U(IV)
85 and U(VI) fixation by wetland soil OM. Among these, the relative importance of sorption and
86 microbially-mediated reduction and the timing of both reactions need to be further investigated
87 (Mikutta et al., 2016). The observation of significant U(IV) proportions in soils may indeed be
88 attributed either to reduction of aqueous U(VI) followed by U(IV) incorporation in the solid
89 phase (Noël et al., 2017, 2019), or to the reduction of already-bound U(VI), as proposed for
90 instance by Stetten et al. (2018a, 2020) in a contaminated wetland. The reaction sequence may
91 impact the composition of U solid products and consequently U mobility. Deciphering between
92 both processes requires a selective proxy, such as the $^{238}\text{U}/^{235}\text{U}$ isotope ratio (expressed as
93 $\delta^{238}\text{U}$), which has been shown to discriminate between reduction and adsorption (Andersen et
94 al., 2017 and references therein). In this framework, the use of this proxy could be strengthened
95 by the determination of the U oxidation state and speciation, notably in a direct way *via* X-Ray
96 Absorption Spectroscopy (XAS). Such an approach may help to determine whether the formation
97 of mononuclear U(IV) solid species in wetland soils primarily results from the reduction of
98 aqueous U(VI) species and subsequent sorption of U(IV) and/or if the affinity of U(VI) for
99 organic moieties leads to efficient U(VI) sorption and further reduction into mononuclear U(IV).

100 In this perspective, better determining whether U(VI) to U(IV) reduction remains a
101 prerequisite for U scavenging in wetlands may help to better assess the capacity of various types

102 of wetlands to accumulate U as a function of hydrological conditions and geological settings.
103 Moreover, evaluating the necessity to maintain reducing conditions in the long term to
104 immobilize uranium may be useful to improve contaminated soils management strategies, and
105 to optimize natural remediation processes.

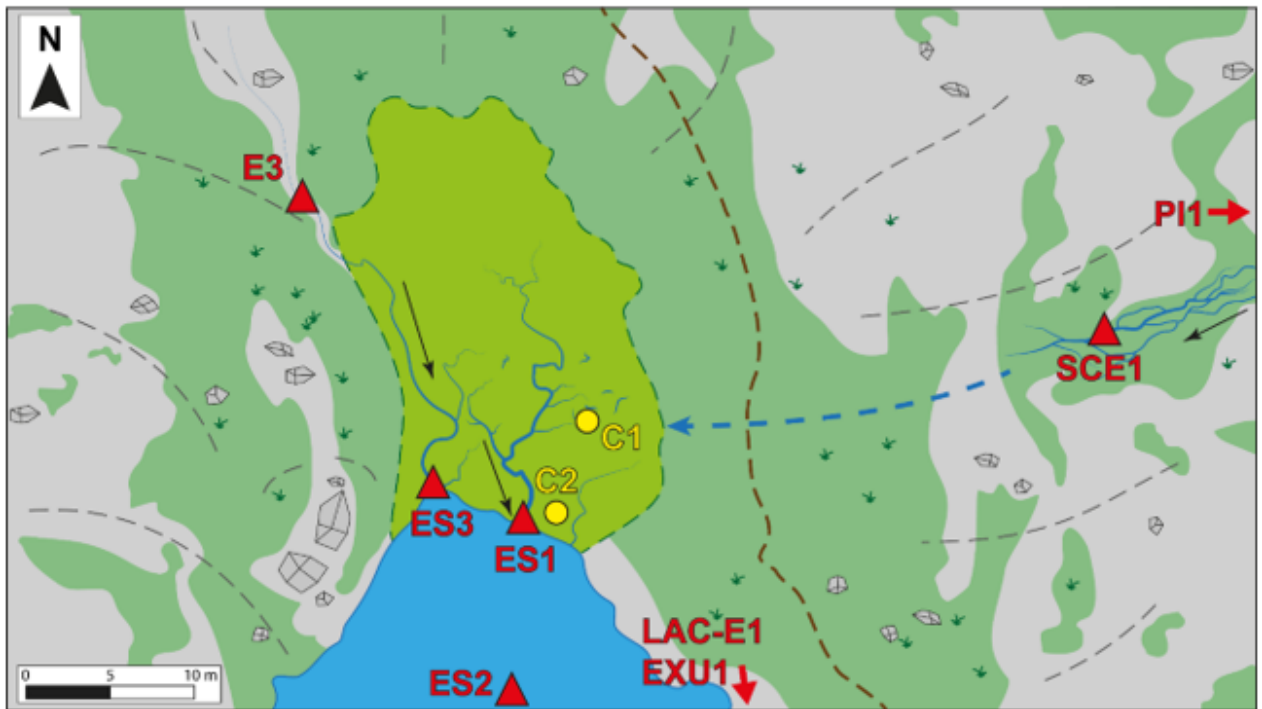
106 To that purpose, we combined a series of complementary analyses including U isotope ratios
107 ($\delta^{238}\text{U}$ and $(^{234}\text{U}/^{238}\text{U})$), gamma spectrometry, micro-and meso-scale U solid state redox and
108 speciation data (determined by $(\mu\text{-})\text{XAS}$) along with micro-X-Ray Fluorescence ($\mu\text{-XRF}$),
109 scanning electron microscopy (SEM-EDXS) and electron microprobe (EPMA) analyses on two
110 pedologically distinct cores from the Lake Nègre wetland. We show that the wetland
111 accumulated massive amounts of U (up to $> 5000 \mu\text{g/g}$) and we discuss (i) the molecular-scale
112 mechanisms responsible for such a remarkable enrichment and (ii) the U redox and sorption
113 dynamics in this waterlogged soil over a several thousand years period.

114 **2. MATERIALS AND METHODS**

115 ***2.1. Study site and sampling***

116 ***2.1.1. Soil cores sampling***

117 Lake Nègre is located at the outlet of a high-altitude catchment (alt. 2356 m) with scarce
118 alpine meadows covering a granitic bedrock, as described in Lefebvre et al. (2021a, b). The
119 wetland studied here is located on a flat area north of the lake where two creeks meander on the
120 eastern and western sides of the wetland before flowing into the lake (Figure 1). The organic-
121 rich, non-peaty waterlogged soils of the wetland (that might be compared to sediments, see
122 Discussion section 4.1.1) are covered by herbaceous plants and are variably water-saturated. In
123 September 2018, two soil cores of 30 cm (NEG18-ZH1-C1 and -C2) were sampled by push coring
124 (PVC tubes, 50 mm diameter) down to the bedrock and immediately conditioned into sealed
125 aluminized plastic bags purged with N₂ (Figure S1). Core C1 was sampled in a flooded area
126 covered with stagnant water; core C2 was collected in a dry creek bed and was partially water-
127 saturated (water level 5 cm below ground surface). Both cores are located on the eastern side of
128 the wetland, downstream of a discontinuous stream which flows partially underground and is
129 presumed to resurge in the cores sampling area (Figure 1). The cores were transported and
130 stored at ~4 °C before being opened at the laboratory in a COY anaerobic glovebox (O₂ <
131 20 ppm) and cut into 2 cm slices (except C2 between 24 and 30cm: one sample). These slices
132 were cut into two halves: one half was vacuum-dried and stored in sealed vials inside the
133 glovebox for further analyses; the second half was dried in open air at 30 °C in an oven for
134 gamma spectrometry. Chemical, isotopic and radiochemical analyses were conducted in open
135 air, whereas bicarbonate extractions (section 2.4) and micro/bulk X-ray absorption
136 spectroscopy analyses (section 2.5) were performed in anoxic atmospheres.



- | | | | |
|--------------------------------|---------------------------|----------------|--------|
| Wetland | Scree | Streams | Rocks |
| Alpine meadows | Lake | Flow direction | Shrubs |
| C1 Soil core sampling location | Slope | Trail | |
| ES1 Water sampling location | Presumed underground flow | | |

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Figure 1 – Sampling locations in the studied wetland upstream of Lake Nègre. (Top) Soil cores (yellow circles) and water (red triangles) sampling points located in a photograph taken from point SCE1); (Bottom) Sketch map of the wetland system with sampling locations. (Photograph courtesy of P. Blanchart, IRSN).

142 2.1.2. Stream waters sampling

143 In September 2019, we collected stream waters upstream of the wetland and downstream
144 where the creeks flow into the lake (Figure 1). In the eastern creek, we collected water at the
145 spring, downhill of a large scree (PI1), then downstream in the slope overlooking the wetland
146 where the stream is braided over a vegetation-covered soil (SCE1). This stream then disappears
147 and flows underground, probably feeding on a large scale the east side of the wetland where
148 cores C1 and C2 were sampled. Sampling point ES1, at the outlet of the eastern stream crossing
149 the wetland, is therefore thought to be hydrologically connected to PI1 and SCE1. The ES2
150 sampling point is located in the lake ~20 m downstream of ES1, at the south end of a flat shallow
151 platform where abundant vegetal particles settled on the lake bottom (roughly visible in
152 Figure 1). We also sampled waters up- (E3) and downstream (ES3) of the wetland in the western
153 stream, as well as on the eastern shore of the lake ~100 m from the wetland (LAC-E1) and in the
154 lake outlet stream (EXU1).

155 At three locations up- and downstream of the east side of the wetland (SCE1, ES1, ES2), the
156 waters were vacuum-filtered in the field at 0.2 μm (nitrocellulose filters – GSWP) with a
157 Sartorius filtration unit and subsequently ultrafiltered under positive pressure at 100 kDa with
158 an Amicon cell equipped with regenerated cellulose ultrafiltration disks. Additional
159 (ultra)filtration steps were done but not retained here: a 0.01 μm filtration because of a filter
160 size similar to 100 kDa, and a 1 kDa ultrafiltration which results are not reliable because of
161 potential U retention by the membrane (Guo et al., 2007). Filtration results at point ES2 were
162 already described in Lefebvre et al. (2021a). At other sites (PI1, E3, ES3, LAC-E1 and EXU1), a
163 single 0.2 μm filtration step was used. The filtration units and sample vials were washed
164 beforehand with nitric acid (HNO_3 0.1 N). Filtration blanks were realized in the field with
165 ultrapure (milliQ) water. All samples were acidified with distilled (ultrapure) HNO_3 after
166 subsampling aliquots for anions and dissolved organic carbon (DOC) measurements and stored
167 at 4 °C before analysis. The physicochemical parameters (pH, temperature T, oxidation
168 reduction potential ORP, dissolved O_2 , conductivity σ) of all sampled waters except LAC-E1 and
169 EXU1 were measured onsite at the time of sampling with field WTW 350i and 3420 multi-
170 parameter probes. The redox potential (ORP) was measured with a WTW Sentix ORP platinum-
171 Ag/AgCl electrode. During the same field trip, i.e., one year after sampling the soil cores, we
172 measured the depth profile of the same parameters at the sampling locations of cores C1 and C2
173 (see *Supplementary Material* page 8).

174 **2.2. Chemical and mineralogical analyses**

175 **2.2.1. Chemical and radiochemical analyses**

176 Unless stated otherwise, most chemical analysis protocols used in this study are
177 reported in Lefebvre et al. (2021a). Briefly, a selection of soil samples was ground, sieved
178 (~500 µm) and digested with a mix of HNO₃, HF and HClO₄. Major, minor and trace elements of
179 soils and waters were analyzed by optical and mass spectrometry with a ThermoFisher ICAP
180 7600 DUO ICP-AES and an Agilent 8800 ICP-MS/MS at the LUTECE laboratory (IRSN). Major
181 anions in the filtered waters were analyzed by ionic chromatography with a Metrohm 930
182 Compact IC Flex. Total organic and inorganic carbon (TOC, TIC) were measured with a carbon
183 analyzer (Vario TOC Elementar); TIC was found to be negligible in the acidic soils, located in a
184 carbonate-free watershed. Light elements (C, H, N, S) were also analyzed in the soil samples with
185 a ThermoScientific FlashSmart elemental analyzer; the soil TOC contents given below are
186 average values of the two measurements. Gamma spectrometry measurements of radionuclides
187 (²³⁸U (from ²³⁴Th), ²³²Th (from ²²⁸Ac), ²³⁰Th, ²²⁶Ra, ²¹⁰Pb, ¹³⁷Cs, ⁴⁰K) were performed along both
188 cores with a well-type high-purity/low-noise Ge ORTEC GWL Series detector. We also analyzed
189 reference compounds RGU-1, RGTh-1, 131SL300 and 161SL300 (from IRSN), IAEA-312 and 314
190 (from IAEA) to control the detectors efficiency and background noise. ²³⁸U and ²³²Th activities
191 (in Bq/kg) were converted to mass concentrations (in µg/g) using the specific activity values of
192 12.44 and 4.06 kBq/g respectively.

193 Because uranium is much more mobile in surface environments than thorium (Th), the
194 proportion of detrital U $F(U_{\text{detrital}})$ in the core soils can be classically estimated from U/Th
195 (²³⁸U/²³²Th) ratios, using a simple mixing model where all Th is considered detrital (Equation 1):

$$F(U_{\text{detrital}}) [\%] = \frac{(U/Th)_{\text{det}}}{(U/Th)_{\text{soil}}} \times 100 \quad (1)$$

196 Where $(U/Th)_{\text{soil}}$ is the measured soil atomic ratio and $(U/Th)_{\text{det}}$ is the detrital atomic
197 ratio corresponding to the bedrock of the studied watershed, measured at 0.26 ± 0.13 (Lefebvre
198 et al., 2021a) in agreement with the average Upper Continental Crust value (Rudnick and Gao,
199 2003). For calculating $F(U_{\text{detrital}})$ values, we used U/Th ratios measured by ICP-MS or by gamma
200 spectrometry.

201 **2.2.2. Mineralogical observations and analyses**

202 The bulk mineralogical composition of the soils was determined by powder X-Ray
203 Diffraction (XRD) using the Co K_{α} radiation over the 4-80° 2θ range with a 0.03° step. Data were

204 collected in continuous scan mode in Bragg-Brentano geometry using a Panalytical Xpert-Pro
205 diffractometer. For SEM observations, sample powders were embedded into a Mecaprex MT1
206 epoxy resin, polished and carbon coated. A Zeiss Ultra 55 microscope at IMPMC, equipped with a
207 Field Emission Gun (FEG) and a Bruker Si-drift detector for energy-dispersive X-ray
208 spectrometry (EDXS), was used in back-scattered electron mode with a 15 kV emission and at a
209 working distance of 7.5 mm. EDXS micro-analyses were performed as well as EDXS chemical
210 mapping.

211 The micro-scale chemical composition of a few samples was additionally quantified using
212 a Cameca SX-Five Electron Probe Micro Analyzer (EPMA) equipped with 5 Wavelength-
213 Dispersive Spectrometers (WDS) and an Energy Dispersive Spectrometer (EDS), at the
214 CAMPARIS platform (OSU Ecce Terra). The samples were prepared as for SEM-EDXS with an
215 additional C metallization layer. The EPMA was operated with an accelerating voltage of 15 kV
216 and a beam current of 10 nA. Ten elements (Na, Al, Mg, K, Ca, P, Fe, Si, S, U) calibrated with
217 standard minerals were analyzed on several positions of each observed structure. We targeted
218 U-bearing phases previously observed by SEM along with additional phases. Because of the high
219 organic content of the studied soil samples, the total values of EPMA analyses are well below
220 100 wt% (10 to 35 wt%). Results are thus expressed only in atomic percentages (at%).

221 **2.3. Isotopic analyses**

222 For the determination of U isotopic ratios ($^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$), digested solids and
223 waters were spiked with a double-tracer (IRMM-3636a) and U fractions were separated on an
224 UTEVA resin column (Eichrom Technologies). The measurements were performed on a Thermo
225 Finnigan Neptune MC-ICP-MS housed at the PARI platform (IPGP). A dual Scott/cyclonic spray
226 chamber with a micro-flow PFA nebulizer (ESI, USA) were used as the introduction system. All
227 isotope signals were collected simultaneously in Faraday cups equipped with $10^{11} \Omega$
228 (for ^{233}U , ^{235}U , ^{236}U , $^{238}\text{U}^+$ and ^{232}Th isotopes) and $10^{13} \Omega$ (for $^{234}\text{U}^+$ isotope and the $^{239}\text{Pu}^+$ for the
229 estimation of $^{238}\text{U}^+$ formation) feedback resistors. The instrumental settings were optimized
230 before each new analytical session and typical sensitivity for $^{238}\text{U}^+$ was $\sim 70 \text{ mV} / \text{ppb}$ of U. The
231 instrumental mass bias was corrected internally using the exponential mass fraction law
232 (Russell et al., 1978) and the corrected ratios were bracketed with the IRMM-184 certified
233 solution in order to express the $^{238}\text{U}/^{235}\text{U}$ ratios with the delta notation relative to the more
234 common standard CRM-145 (Equation 2):

$$\delta^{238}\text{U} \text{ [‰]} = \left(\frac{^{238}\text{U}/^{235}\text{U}_{\text{sample}}}{^{238}\text{U}/^{235}\text{U}_{\text{standard}}} - 1 \right) \times 1000 \quad (2)$$

235 ($^{234}\text{U}/^{238}\text{U}$) activity ratios were obtained by multiplying the $^{234}\text{U}/^{238}\text{U}$ isotope ratio with the
236 half-life ratio T_{238}/T_{234} of the isotopes. Each sample was analyzed 3-5 times, the uncertainties
237 (2SD) being calculated on all replicates. Reference materials (BCR-2, HU-1, AGV-2, RGU-1) were
238 processed and analyzed along with the samples: their isotopic composition are in good
239 agreement with published data (see Lefebvre et al., 2021a).

240 **2.4. Bicarbonate extractions**

241 In order to quantify the fraction of noncrystalline U, bicarbonate extractions were
242 performed by reacting soils samples with 1 M NaHCO_3 for 100 h in an anoxic glovebox using
243 O_2 -free water, as described in Lefebvre et al. (2021a) following a protocol adapted from Alessi et
244 al. (2012). After two rinsing steps with O_2 -free milliQ water, the solid residues were centrifuged,
245 vacuum-dried, acid-digested and then analyzed for U and Th by ICP-MS. Duplicate extractions
246 were performed on three samples with consistent results. Based on these duplicates, the
247 combined uncertainty (2SD) on bicarbonate-extracted fractions (in % of total U) was 9.0 %.

248 **2.5. X-Ray Absorption Spectroscopy (XAS)**

249 *2.5.1. Bulk U L_3 -edge XANES and EXAFS data collection and analysis*

250 Bulk soil samples were finely ground in an agate mortar, prepared as Kapton tape-covered
251 pellets and mounted on cryostat multi-sample holders that were shipped to synchrotron
252 facilities in individual air-tight containers to preserve the samples from oxidation. The
253 containers were handled in glove bag or glovebox at the synchrotron beamlines. The sample
254 holder was rapidly screwed on the cryostat rod and immediately inserted in the cryostat sample
255 chamber, and further maintained under purged He atmosphere during the measurements.

256 A first set of U L_3 -edge XAS data was collected in December 2018 at 10 K on the undulator
257 beamline P64 (Deutsches Elektronen-Synchrotron – DESY). Ten bulk wetland soil samples from
258 cores C1 (2-4, 8-10, 14-16, 20-22 and 26-28 cm) and C2 (2-4, 8-10, 14-16, 20-22 and 24-30 cm)
259 were analyzed (this study), as well as the Lake Nègre sediment bulk sample NEG18-07
260 189-194 cm (Lefebvre et al. 2021a). The beamline incident energy was selected with a Si(111)
261 double crystal monochromator, and the sample fluorescence intensity was measured using a
262 Passivated Implanted Planar Silicon total fluorescence detector. Between 5 and 40 XAS scans
263 were acquired in continuous mode (5.5 min per scan) on each sample. Because of moderate but
264 measurable photo-reduction of U under beam exposure on this high-flux beamline, only the first
265 scan was used for X-Ray Absorption Near-Edge Structure (XANES) analysis. In the same way,
266 only the first scans exhibiting less than 17% of U photo-reduction were merged for extracting
267 Extended X-ray Absorption Fine Structure (EXAFS) data. This value was chosen as a compromise

268 for obtaining reliable signal/noise ratio and maintaining beam-damage effects close to the
269 EXAFS detection limit.

270 A second set of U L_3 -edge XAS data was collected in June 2021 at 10 K on the 2-pole wiggler
271 beamline BM23 (European Synchrotron Radiation Facility – ESRF) in order to obtain higher
272 k -range data for the bulk wetland soil samples C1 18-20 cm and C1 20-22 cm (duplicate of P64
273 measurement). In addition, solid residues obtained after 1 M bicarbonate extraction of samples
274 C1 20-22 cm and C2 2-4 cm, together with the Lake Nègre sediment bulk sample
275 NEG18-07 184-189 cm already analyzed by Lefebvre et al. (2021a) were also analyzed for
276 XANES data. The energy was selected with a Si(111) double-crystal monochromator and the
277 samples were placed in a liquid He cryostat maintained at a temperature of 10 K. XAS
278 measurements were performed in transmission detection mode for the two U-rich soil samples
279 and in fluorescence detection mode with a Vortex silicon-drift energy-dispersive fluorescence
280 detector for the other samples. Between 40 and 121 scans were collected on each sample, in
281 continuous mode at a speed of 6.8 eV/s using a 50 ms sampling time (0.34 eV steps). Variable
282 energy ranges within the XANES to EXAFS region were chosen depending on the samples, which
283 resulted in 2- to 4-min long XAS scans. No beam-damage was observed for any sample under
284 these data collection conditions.

285 All bulk XAS spectra at the U L_3 -edge were merged, normalized and background-subtracted
286 using the Athena software (Ravel and Newville, 2005). The incident beam energy was calibrated
287 by setting to 17,038.0 eV the first inflection point of the yttrium (Y) K -edge transmission
288 spectrum acquired on an Y foil using a double-transmission setup. The EXAFS spectra were
289 binned to a 0.04 \AA^{-1} k -step and deglitched when necessary, and the E_0 value was set to
290 17173.4 eV, which corresponds to the inflexion point of the U(VI) L_3 -edge (e.g., Seder-Colomina
291 et al., 2015). For samples acquired at DESY, we limited the EXAFS energy range to the 17.140-
292 17.965 keV region because of the presence of Y and Zr in our natural samples, which yield X-ray
293 absorption K -edges at 17.038 and 17.998 keV, respectively.

294 U L_3 -edge data for a large set of model compounds (Tables S2 and S5) was used to help
295 determining the U redox state and molecular-level speciation in the soil samples studied. Our
296 database contains especially U(VI) and/or U(IV) humate, citrate, pyrophosphate and biosorbed
297 complexes (Seder-Colomina et al., 2015; Morin et al., 2016; Stetten et al., 2018a, 2020), U(VI)
298 sorbed/coprecipitated to/with ferrihydrite or amorphous iron phosphate (Seder-Colomina et
299 al., 2015), U(VI) sorbed to illite and chlorite (Othmane et al., 2013), as well as natural and
300 synthetic U-minerals (Morin et al., 2016; Stetten et al., 2018a; Lefebvre et al., 2021a). Our
301 reference database also includes natural sediment samples NEG18-07 184-189 cm and
302 NEG18-07 189-194 cm from Lake Nègre (Lefebvre et al., 2021a) that are naturally reduced, as

303 well as a reduced U(IV)-humus natural sample (Stetten et al., 2018a, 2020). In the present study
304 our set of model compounds was completed with a U(VI)-citrate complex prepared following a
305 similar method to that used for preparing U(IV)-citrate, as well as U(IV)- and U(IV)-
306 pyrophosphate (Morin et al., 2016). Briefly, U(VI)-citrate was prepared in a Jacomex anoxic
307 glovebox by mixing ~1.5 mL of a 260 mM citric acid O₂-free solution at pH 2 (100 mg sodium
308 citrate in 1.5 mL H₂O + a droplet of 35 wt % HCl), with 0.4 mL of a 2 mM U(VI) nitrate O₂-free
309 solution, and raising the pH of the mixture to 6.5 with an appropriate volume of 1 M NaOH O₂-
310 free solution. The mixed solution was stirred for 1 h and then evaporated under vacuum within
311 the glovebox to obtain U(VI)-citrate as a solid paste with U concentration of about 1.9 wt%.

312 Least-square linear combination fitting (LCF) of XANES spectra at the U L₃-edge was
313 performed using a Fortran 90 custom-built software based on a Levenberg-Marquardt
314 minimization algorithm, similar to the software used in previous studies from our group (e.g.,
315 Seder-Colomina et al., 2015; Morin et al., 2016; Stetten et al., 2018b; Lefebvre et al., 2021a). The
316 fit quality was estimated with a *R*-factor, $R_f = \Sigma[\mu_{\text{exp}} - \mu_{\text{fit}}]^2 / \Sigma\mu_{\text{exp}}^2$, where μ is the normalized
317 absorbance and with a reduced chi-square, $Chi^2_R = N / (N - N_p) \Sigma[\mu_{\text{exp}} - \mu_{\text{fit}}]^2 / \Sigma\mu_{\text{exp}}^2$, where N_p is the
318 number of fitting components and N is the number of independent parameters corresponding to
319 the energy range divided by the natural width of the U L₃ levels reported by Krause and Oliver
320 (1979). The uncertainty on each fitting parameter p was estimated to 99.7% confidence as
321 $3\sqrt{\text{var}(p) \cdot Chi^2_R}$, where $\text{var}(p)$ is the variance of parameter p returned by the Levenberg-
322 Marquardt routine for the lowest Chi^2_R value.

323 Prior to LCF analysis of EXAFS data, a Principal Component Analysis (PCA) of the k^3 -
324 weighted U L₃-edge EXAFS spectra dataset of our wetland samples was performed over the 2-
325 12 Å⁻¹ k -range using the SIXpack program (Webb, 2005). The PCA was followed by a Target
326 Transform (TT) analysis of our model compound spectra database in order to select the most
327 relevant components to perform LCF analysis of the wetland samples EXAFS data. Least-square
328 LCF of EXAFS spectra was then performed using a Fortran 90 custom-built software based on a
329 Levenberg-Marquardt minimization algorithm, similar to the software used in previous studies
330 (e.g., Stetten et al., 2018a, 2020). The unfiltered experimental $k^3\chi(k)$ functions were fit in k -space
331 over the 2-12 or 2-10 Å⁻¹ k -range, for the C1 and C2 cores samples, respectively, data being
332 noisier for C2. The fit quality was estimated with a *R*-factor, $R_f = \Sigma[\mu_{\text{exp}} - \mu_{\text{fit}}]^2 / \Sigma\mu_{\text{exp}}^2$, and with a
333 reduced chi-square, Chi^2_R , similar to that used for shell-by-shell fitting described hereafter.

334 Shell-by-shell fitting of the unfiltered U L₃-edge k^3 -weighted EXAFS spectra was performed
335 using a Fortran 90 custom-built least-squares fitting software based on a Levenberg-Marquardt
336 minimizing algorithm, similar to the code used in previous studies (e.g., Seder-Colomina et al.,
337 2015; Morin et al., 2016; Stetten et al., 2018b; Lefebvre et al., 2021a). In this code, the $\chi(k)$

338 function is calculated with the plane-wave formalism (Teo, 1986), implementing backscattering
339 amplitude and phase functions calculated using the curved-waves theory with the FEFF8.1 code
340 (Ankudinov et al., 1998). Single and multiple backscattering functions were calculated from the
341 crystal structures of torbernite (Locock and Burns, 2003) for U-O (axial and equatorial) and U-P
342 paths, uranyl acetate dehydrate (Howatson et al., 1975) for U-C paths, $\text{CaU}(\text{PO}_4)_2$ (Dusausoy et
343 al., 1996) for U-P paths, and coffinite (Fuchs and Gebert, 1958) for U-Si and U-U paths.

344 For both EXAFS LCF and shell-by-shell fitting, the fit quality was estimated by a reduced chi-
345 square parameter $\text{Chi}^2_R = N_{ind}/[(N_{ind}-N_p).n.\epsilon^2] \sum [k^3\chi(k)_{exp} - k^3\chi(k)_{calc}]^2$, with $N_{ind} = (2\Delta k\Delta R)/\pi$,
346 the number of independent parameters, N_p the number of free fitting parameters, n the number
347 of data points, and ϵ the root mean square of the data noise. This latter value was estimated as
348 the Fourier back-transform of the data in the 15–25 Å R -range, following a method modified
349 after Ravel and Newville (2005). The uncertainty on EXAFS fitting parameters was estimated by
350 $3.\sqrt{(\text{var}(p).\text{Chi}^2_R)}$, where $\text{var}(p)$ is the variance of parameter p returned by the Levenberg-
351 Marquardt routine for the lowest Chi^2_R value.

352 Fast Fourier Transforms (FFT) of the k^3 -weighted experimental and fit EXAFS spectra were
353 calculated after having applied a Keiser-Bessel window with a Bessel weight of 2.5. Continuous
354 Cauchy Wavelet Transforms (CCWT) of the experimental and fitted EXAFS spectra were
355 calculated using the MATLAB script by Muñoz et al. (2003, 2005). In order to decipher between
356 close fitting solutions, fit quality of the second neighbor contributions were examined in R space
357 (e.g., Wang et al., 2011) by a reduced chi-square parameter $\text{Chi}^2_{R-FFT} = N_{ind}/[(N_{ind}-N_p).n.\epsilon_r^2] \sum$
358 $[|FFT_{exp}| - |FFT_{calc}|]^2$, within the 1.5-5 Å R -range, with ϵ_r the root mean square of the data noise in
359 the 15–25 Å R -range. Comparisons of fit solutions were done according to F-tests at 95 or 90 %
360 confidence.

361 2.5.2. Micro-XRF and U L_3 -edge micro-XANES analysis

362 Micro-X-Ray Fluorescence (μ -XRF) mapping and subsequent μ -XANES analyses of soil
363 sample C1 18-20 cm were conducted at ESRF beamline BM23. Data were collected at room
364 temperature and the X-ray beam was focused with two mirrors in Kirkpatrick–Baez (KB)
365 geometry to a $\sim 3 \times 3 \mu\text{m}^2$ full width at half maximum at sample position. An optical microscope
366 focused on sample position was placed right above the beam for proper tracking of the analyzed
367 spot. The sample was embedded in epoxy resin as for SEM observations but within a N_2 -filled
368 glove bag to prevent exposure to air, covered with Kapton tape to limit oxidation during the
369 experiment and placed perpendicular to the X-Ray beam. A continuous N_2 flow was applied on
370 the sample surface to prevent oxidation by air over the course of the experiment. The Si-drift
371 fluorescence detector was placed at a 45° angle between the beam and the sample plane.

372 The incident beam energy was selected using a Si(111) double-crystal monochromator and
373 was set to 17.5 keV for μ -XRF mapping. The emission spectrum energy was calibrated using the
374 Cu K_α and K_β emission lines from Cu tape. The XRF spectra were converted to element-specific
375 fluorescence intensity maps with the PyMca software (Solé et al., 2007) through batch curve
376 fitting of emission lines of elements of interest (including U L_α and Fe K_α). We acquired $2 \times 2 \text{ mm}^2$
377 μ -XRF maps with horizontal 5 μm steps and vertical 10 μm steps, with a counting time of 0.2 s
378 per point. After μ -XRF mapping, U-rich areas of interest were analyzed for their U oxidation state
379 by μ -XANES at the U L_3 -edge. For this purpose, μ -XAS spectra (1000 points, 50 ms/point) were
380 measured from 17.050 to 17.550 keV (17.400 keV for the first spectra), for a total duration of
381 ~ 66 seconds.

382 Room-temperature beam-damage kinetics (U(VI) photo-reduction) was estimated by
383 acquiring 7 to 10 successive scans on the same spot, at four different locations (see [Figure 7](#),
384 points *a* to *d*). Each scan was LC fitted to determine the evolution of U(VI) and U(IV) proportions
385 over time ([Figures S2 and S3](#)). At all spots, the U(IV) proportion significantly increased over
386 time, ultimately exceeding U(VI) at two spots after 4 to 6 minutes. These kinetic measurements
387 showed that every second scan acquired on the same position was significantly impacted by
388 beam exposure, while the first scan (66 s acquisition time) was always affected by less than
389 10 % of relative U(VI) reduction. Proper U redox could thus be determined by LCF of μ -XANES
390 spectra obtained by merging individual first scans acquired on pristine spots of a same U-
391 bearing area through successive displacements of $> 10 \mu\text{m}$ between each scan acquisition. To do
392 so, additional μ -XRF map were acquired on selected areas where necessary, with horizontal and
393 vertical 2.5 μm steps to obtain more detailed chemical maps.

394 These μ -XANES spectra were rebinned, normalized and merged using the Athena software.
395 LC fitting was done with the same code and same U(VI) and U(IV) standards as for bulk XANES
396 spectra. Energy was calibrated once at the start of the beamtime using an Y foil in single
397 transmission mode. Monochromator instability – i.e., the deviation of the incident energy during
398 the course of the experiment – was then accounted for by refining an energy shift parameter for
399 the experimental μ -XANES spectra to properly fit with the mixture of U(VI) and U(IV) reference
400 spectra. The obtained energy shift values consistently showed a regular deviation trend over
401 time.

402 *2.5.3. Bulk U M_4 -edge XANES analysis*

403 In order to complement U redox determination by U L_3 -edge XANES and document the
404 possible occurrence of U(V) species, we performed U M_4 -edge High Energy-Resolution
405 Fluorescence Detected (HERFD)-XANES spectroscopy measurements on the MARS beamline at

406 the SOLEIL synchrotron in July 2020. Five soil samples (3 from core C1 and 2 from core C2) were
407 prepared as thin sample pellets. The measurements were performed at room temperature, in
408 similar conditions as those described in Le Pape et al. (2020). Briefly, the incident beam energy
409 was selected with a double Si(111) crystal monochromator and calibrated by setting the
410 inflection point of the absorption K-edge of potassium from a KBr pellet at 3608 eV. The U M_{β}
411 emission line was analyzed with a Si(220) crystal analyzer with a curvature radius of 1 m. The
412 measurements were done at the maximum of the M_{β} emission line at 3336.0 eV. As the
413 experiment was performed at low energy (3.7 keV), we sought to avoid attenuation of the
414 incident and fluorescence-emitted X-rays through absorption by thick Kapton tape and
415 scattering by air. To this end, the sample pellets were sealed with thin 12 μm Kapton tape, in
416 addition to another similar Kapton layer on the sample holder for double-containment, and a
417 He-filled bag was placed between the sample holder and the detector. As a development from
418 the protocol of Le Pape et al. (2020), we applied a continuous He flow inside the sample holder
419 to prevent oxidation by air over the course of the experiment.

420 Substantial photo-reduction (beam-damage) was observed on the successive spectra
421 obtained on soil samples during the experiment. To limit such effects, the HERFD-XANES spectra
422 were acquired dynamically by continuous displacements over pristine areas of the sample pellet.

423 A qualitative analysis of the U M_4 -edge HERFD-XANES spectra was done by comparing
424 experimental spectra of the wetland soils with spectra of reference compounds. We selected
425 autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12 \text{ H}_2\text{O}$) as U(VI) reference (Le Pape et al., 2020), triuranium
426 octoxide U_3O_8 from the IMPMC chemical stocks containing in theory 67 % U(V) and 33 % U(VI)
427 (Kvashnina et al., 2013) that was analyzed with the samples, and biogenic nanocrystalline
428 uraninite UO_2 as U(IV) reference (Le Pape et al., 2020). This analysis is based on strong
429 differences between the spectral features of U(VI)-uranyl compounds with three main
430 fluorescence peaks at 3727.7, 3729.6 and 3733.4 eV due to the splitting of the $5f$ orbitals, and the
431 spectral features of U(V)- and U(IV)-uranate with single peaks at distinct energies (3727.5 and
432 3726.2 eV respectively) (see [Figure 8b](#)). The HERFD-XANES spectrum of U_3O_8 contains both
433 U(V) and U(VI) contributions (two close peaks), and our biogenic UO_2 is partly oxidized (Le Pape
434 et al., 2020), although composed of predominant U(IV) with a fraction of U(V) ([Figure 8b](#)).

435 *2.5.4. Bulk Fe K-edge XANES and EXAFS analysis*

436 The redox and speciation of iron (Fe) in four soil samples (2 of each core) was analyzed by
437 XAS at the Fe K -edge on beamline 4-3 at the Stanford Synchrotron Radiation Lightsource (SSRL,
438 SLAC National Accelerator Laboratory) in January 2020. Sample aliquots were mixed with
439 cellulose and pressed as Kapton-covered pellets that were preserved from oxidation by air. The

440 measurements were performed at liquid N₂ temperature in transmission detection mode.
441 Incident energy was calibrated by setting the first inflection point of Fe metal foil at 7112 eV,
442 using a double-transmission setup.

443 XANES and EXAFS spectra at the Fe *K*-edge were analyzed by LCF using the same code as for
444 U *L*₃-edge data, using a set of model compound spectra chosen from a large database that
445 includes several types of iron phosphate, carbonate, phyllosilicate, (oxyhydr)oxide, sulfide
446 minerals in crystalline, nanocrystalline or amorphous state, as well as Fe(II) and Fe(III)-
447 polyphosphate complexes and a natural Fe(III)-humate sample. After a PCA-TT analysis detailed
448 in Supplementary Material, the best fits were obtained with a combination of a minimal set of
449 5 components that yielded good fits to the whole set of soil samples studied and accounted as
450 reasonable proxies for the diversity of occurring Fe-bearing species: synthetic Fe(II)-
451 triphosphate (Baumgartner et al., 2016) as a proxy of OM-bound Fe(II), natural Fe(III)-illite
452 (Ildefonse et al., 1998; Merrot et al., 2019) and synthetic nano-Fe(II)-talc (Zeyen et al., 2019) as
453 proxies for structural Fe(III) and Fe(II) in 2:1 clay minerals, synthetic Fe(III) 2-lines ferrihydrite
454 (Maillot et al., 2011) and natural Fe(III)-humate (Cosmidis et al., 2014). As detailed in
455 Supplementary Material, the use of the same five Fe components to fit our data both in XANES
456 and in EXAFS ranges is expected to minimize the bias related to non-unique fit solutions. The
457 LCF fit quality was estimated with a R-factor and a χ^2_R as described above for U *L*₃ data LCF.

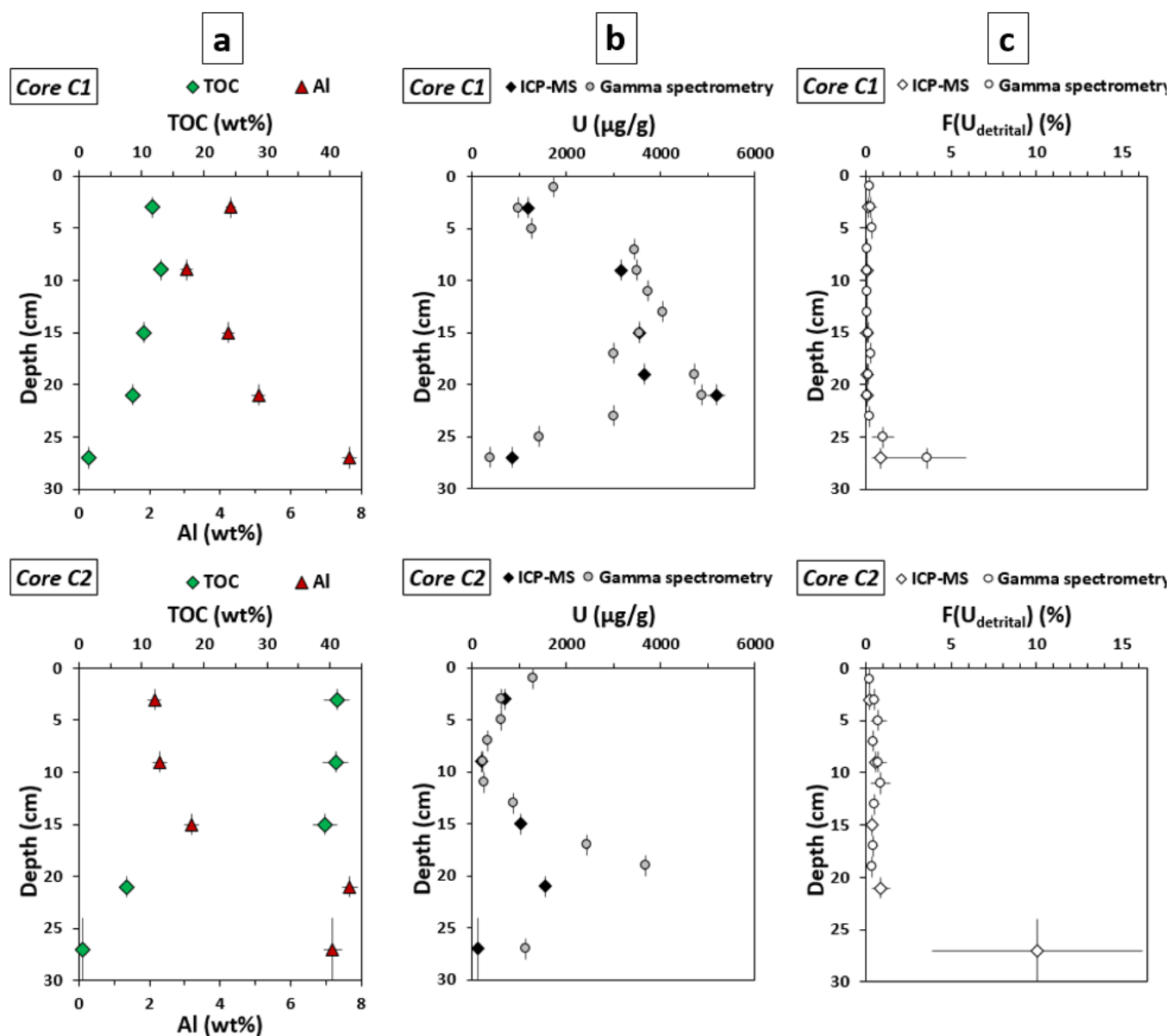
458 3. RESULTS

459 3.1. Bulk mineralogical and chemical content of the soil cores

460 3.1.1. General geochemical and mineralogical description

461 Physicochemical parameters (pH, T, ORP, O₂, σ) were measured one year after core sampling
462 at the exact location of the cores (Figure S4). At core C1 location, the stagnant water above the
463 ground was slightly acidic (pH ~6.2) and showed dissolved O₂ and redox potential gradients
464 decreasing down to 2.5 mg/L and 47 mV at the water-soil interface. At core C2 location, the
465 water filling the core-hole was acidic (pH 5.5) and suboxic especially at depth (O₂ from 4 to
466 0.15 mg/L at 16.5 cm depth) but still with a positive redox potential (50-90 mV). It should be
467 considered that O₂ could have been overestimated close to the water-air interface due to air
468 diffusion during sampling (see *Supplementary Material* page 8). Hence, the bottom O₂ and ORP
469 values in the sampling holes (Figure S4) may be more representative of the oxidation reduction
470 potential at depth in these organic-rich soils, in which oxygen is likely consumed quickly by
471 microorganisms in the pore waters. At both locations, the conductivity was low (~50 μ S/cm).

472 C1 consists of three ~10 cm layers of dark brown (top) to beige (bottom) colors, overlying
473 the granitic sand in the bottom 3 cm; C2 is homogeneously dark brown in the upper part, the
474 bottom granitic sand being met at 22 cm (Figure S1). Both cores mainly differ in their organic
475 content as attested by TOC concentration profiles (Figure 2a). They display a similar mineral
476 content composed of major granitic minerals, as shown by powder XRD patterns (Figure S5). C1
477 has a moderate and decreasing organic content from top to bottom (10-13 to 1.4 wt% TOC),
478 concomitant with an increase in the proportion of detrital granitic material (represented by Al
479 contents, Figure 2a). C2 is highly organic (~40 wt% TOC) in the upper section above the granitic
480 sand met at 22 cm (Figure 2). C1 show a relatively constant C/N atomic ratio around 12.7, except
481 at depth (26-28 cm) with a lower ratio of 9.5 (Figure S6), which may however be linked to
482 higher uncertainties due to a low N content slightly above the limit of quantification. The C/N
483 ratios are higher in core C2, increasing with depth from 17.2 to 25.6 (Figure S6).



484

485 **Figure 2 – Chemical composition of the wetland soils from cores C1 (top) and C2 (bottom).**
 486 (a) Total organic carbon (TOC, green diamonds) and Aluminum (Al, red triangles) contents;
 487 (b) Uranium content measured by ICP-MS after sample digestion (black diamonds) and by gamma
 488 spectrometry (gray circles); (c) Detrital U fraction ($F(U_{\text{detrital}})$) estimated from U/Th ratios
 489 measured by ICP-MS (diamonds) and gamma spectrometry (circles).

490 **3.1.2. Fe oxidation state and speciation**

491 Depending on the Fe speciation, the Fe oxidation state in the soil cores may give indications
 492 on the soil redox conditions. The soils contain low Fe amounts, increasing with depth from 0.5 to
 493 2.0 wt% in core C1 and from 0.3 to 1.5 wt% in C2. Results of the LCF analysis of the Fe K-edge
 494 XANES spectra, as reported in [Table S1a](#), should be considered as more reliable than EXAFS ones
 495 for redox-state determination. They indicate moderate but detectable differences in the Fe
 496 oxidation state between the C1 and C2 cores ([Table S1, Figure S7](#)). In core C1, Fe is essentially

497 present as Fe(III) ($79 \pm 8 \%$ at 2-4 cm, $88 \pm 3 \%$ at 14-16 cm), while Fe is slightly more reduced
498 in core C2 (31 ± 10 and $28 \pm 8 \%$ Fe(II) at 2-4 cm and 14-16 cm respectively).

499 A combined XANES and EXAFS LCF analysis (Figure S7a, Table S1a), guided by a PCA-TT
500 analysis for EXAFS (Figure S7b, Table S1b), allowed us to propose an evaluation of Fe speciation
501 using a minimal set of proxies for Fe-clays, Fe-oxyhydroxides and Fe-organic components.
502 Although the contribution of these Fe species is subject to uncertainties (Table S1a), it appears
503 that a significant proportion of Fe is hosted by clay minerals (represented by our Fe(III)-illite
504 and Fe(II)-talc proxies) accounting for 30 to $85 \pm 20\%$ of total Fe in all samples. XANES LCF
505 analysis also suggested a change in the nature of the additional Fe(II) and to a lesser extent
506 Fe(III) species between the C1 and C2 core, with a better match to Fe-organic proxies in the
507 C2 14-16 cm sample. These latter species could be consistently included as EXAFS fitting
508 components, but with less statistical confidence than for XANES, as detailed in the note of Table
509 S1a. Despite these analytical limitations, these results suggest that a significant fraction of Fe(II),
510 and to a lesser extent Fe(III), could be ~~is~~ bound to organic matter in the C2 core, with 45 ± 30 to
511 $68 \pm 19 \%$ of Fe accounted for by our Fe(II)-triphosphate and Fe(III)-humate proxies. Our
512 interpretation of the XAS data is consistent with the significant differences in TOC contents of
513 the two cores down to 20 cm depth (Figure 2a).

514 3.1.3. Uranium content

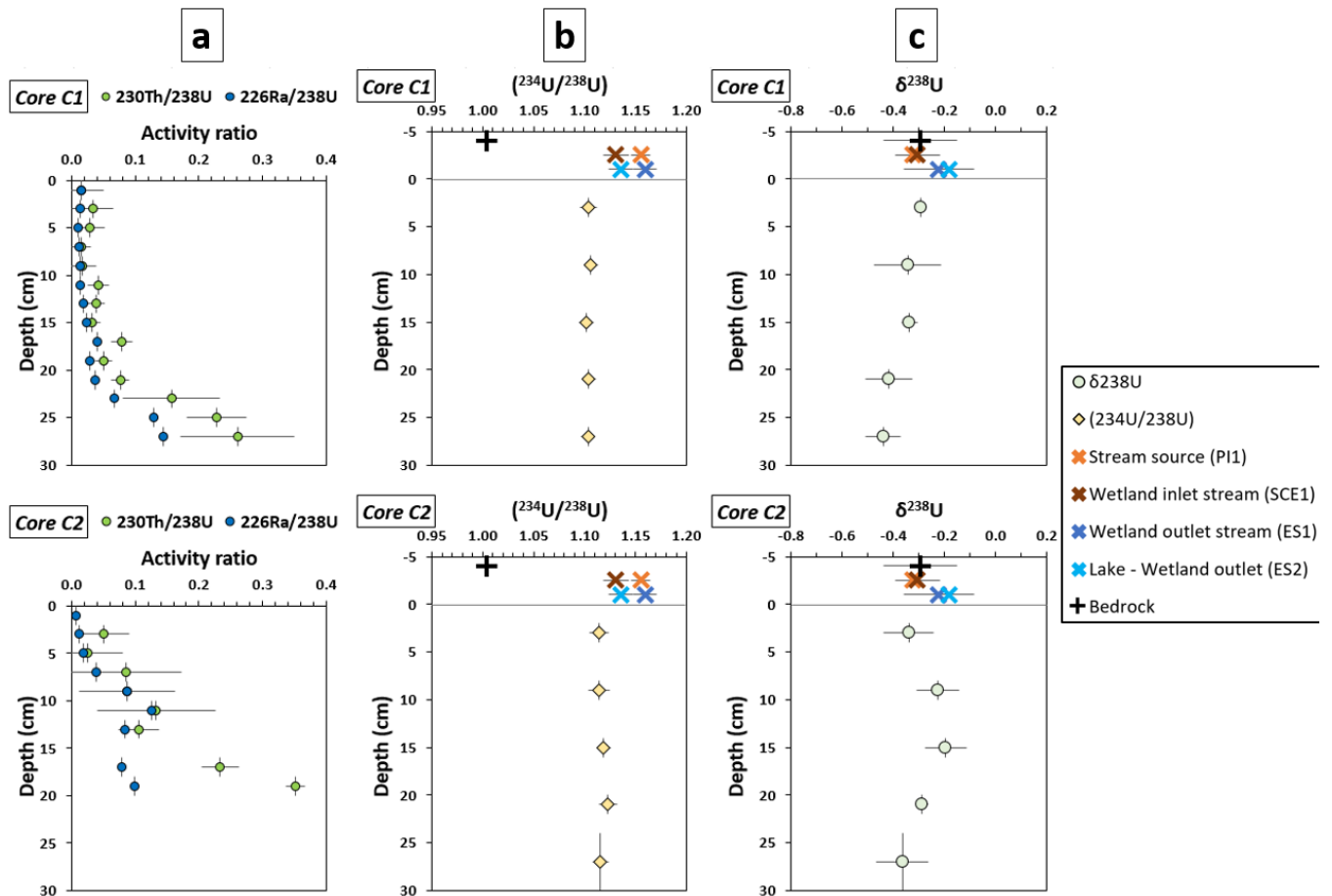
515 Major differences are observed in the uranium content of the two cores (Table 1, Figure 2).
516 Core C1 displays very high U concentrations above $3000 \mu\text{g/g}$ between 6 and 24 cm –
517 culminating at 20-22 cm with $5180 \mu\text{g/g}$, with lower U at the top and bottom. C2 shows a
518 distinct trend with U decreasing from 1280 to $200 \mu\text{g/g}$ in the upper 12 cm before reaching a
519 peak U content of $3670 \mu\text{g/g}$ at 18-20 cm, at the transition between the organic-rich, fine-
520 grained upper section and the organic-poor, coarse-grained bottom section, where U contents
521 decrease down to $110 \mu\text{g/g}$ in the fine (sieved) fraction of the bottom granitic sand. The ICP-MS
522 and gamma spectrometry measurements are overall in good agreement (Figure 2b); the little
523 discrepancies are attributed to horizontal heterogeneity of the sample slices that were cut into
524 two halves for distinct analyses (see Methods section 2.1.1).

525 As calculated from U/Th ratios, a negligible U fraction ($< 1 \%$) is incorporated into detrital
526 minerals, except in the granitic sand at the bottom of both cores, where up to 10% of U in the
527 fine-grained (sieved) fraction is detrital (Table 1, Figure 2c). This indicates that most U ($> 99 \%$
528 in general) is authigenic, i.e., was in the dissolved/colloid-sorbed form prior to its transport and
529 accumulation in the wetland soils.

530 **3.2. Radioactive disequilibria in the ^{238}U decay chain**

531 Both cores show substantial disequilibria in the ^{238}U decay chain, highlighting differences in
532 the mobility of U and its daughter radionuclides (Figure 3a). Gamma spectrometry
533 measurements allowed the detection of ^{230}Th and ^{226}Ra isotopes that are strongly depleted with
534 respect to their parent radionuclide ^{238}U (at the top of the radioactive decay chain), with
535 ($^{230}\text{Th}/^{238}\text{U}$) and ($^{226}\text{Ra}/^{238}\text{U}$) activity ratios well below 1 (mostly below 0.3). An apparent
536 regrowth over time is observed as both ratios increase with depth, with the exception of
537 ($^{226}\text{Ra}/^{238}\text{U}$) in core C2 that stabilizes around 0.1 below 10 cm depth. Considering the high
538 amount of authigenic U combined with low detrital U and total Th contents, we assume that
539 most ^{230}Th measured in the wetland soils originates from onsite regrowth from ^{238}U . In other
540 words, the fraction of ^{230}Th originating from upstream U decay followed by particle transport is
541 considered negligible. This hypothesis is reinforced by high ($^{230}\text{Th}/^{232}\text{Th}$) ratios in the soil
542 samples (see *Supplementary Dataset*), well above the detrital ratio of 0.83 (corresponding to a
543 $^{238}\text{U}/^{232}\text{Th}$ atomic ratio of 0.26). Following this reasoning, ^{226}Ra is also expected to originate
544 mostly from regrowth in the wetland soils.

545 ($^{234}\text{U}/^{238}\text{U}$) activity ratios also show a radioactive disequilibrium but in the opposite
546 direction: here, the daughter isotope (^{234}U) is enriched compared to its parent (^{238}U), with
547 activity ratios constantly around 1.10-1.11 (Table 1, Figure 3b). Such values are above the
548 secular equilibrium value of 1, that is measured in the background granite (Lefebvre et al.,
549 2021a). This ^{234}U excess indicates that U mainly originates from chemical erosion of the bedrock
550 resulting in preferential leaching of ^{234}U because of alpha recoil, which is consistent with the
551 authigenic origin of U attested by U/Th ratios, as also observed in the sediments of Lake Nègre
552 (Lefebvre et al., 2021a, b).



553

554 **Figure 3 – Activity ratios and U isotopic ratios of the wetland soils from cores C1 (top) and**
 555 **C2 (bottom), compared to the bedrock and waters from the watershed. (a) ($^{230}\text{Th}/^{238}\text{U}$) (green**
 556 **circles) and ($^{226}\text{Ra}/^{238}\text{U}$) (blue circles) activity ratios; (b) ($^{234}\text{U}/^{238}\text{U}$) activity ratios of the soils**
 557 **(orange diamonds) and (c) $\delta^{238}\text{U}$ isotopic signatures of the soils (light green diamonds), compared**
 558 **to isotopic signatures of the bedrock (black cross) and waters from the eastern stream up- and**
 559 **downstream of the wetland: at the spring (PI1, light orange cross), right upstream of the wetland**
 560 **(SCE1, dark orange cross), at the wetland outlet (ES1, dark blue cross) and 20 m downstream in the**
 561 **lake (ES2, light blue cross).**

562

563 **Table 1 – Uranium concentrations, isotopic ratios, detrital fractions and oxidation states in**
564 **bulk soil samples from cores C1 and C2. Uncertainties are given as 2 or 3 standard deviations**
565 **(σ). N.A.: not analyzed. R_f : R-factor indicating the U L_3 -edge XANES fit quality. The U oxidation state**
566 **of sample C2 24-30 cm (*italicized*) is uncertain due to low data quality. All XANES data in this table**
567 **were acquired at DESY beamline P64, except data for samples C1 18-20 and 20-22 cm acquired at**
568 **ESRF beamline BM23.**

569

Table 1 – Uranium concentrations, isotopic ratios, detrital fractions and oxidation states in bulk soil samples from cores C1 and C2. Uncertainties are given as 2 or 3 standard deviations (σ). N.A.: not analyzed. R_f : R-factor indicating the U L_3 -edge XANES fit quality. The U oxidation state of sample C2 24-30 cm (*italicized*) is uncertain due to low data quality. All XANES data in this table were acquired at DESY beamline P64, except data for samples C1 18-20 and 20-22 cm acquired at ESRF beamline BM23.

Sample	U ($\mu\text{g/g}$)	2σ	$\delta^{238}\text{U}$ (‰)	2σ	$(^{234}\text{U}/^{238}\text{U})$	2σ	$F(\text{U}_{\text{detrital}})$ (%)	2σ	% U(VI)	% U(IV)	3σ	R_f ($\cdot 10^{-4}$)
C1 2-4 cm	1185	45	-0.29	0.01	1.104	0.008	0.16	0.10	58	42	3	0.6
C1 8-10 cm	3171	120	-0.34	0.13	1.106	0.007	0.09	0.05	81	19	3	0.6
C1 14-16 cm	3552	135	-0.34	0.03	1.102	0.007	0.10	0.06	65	35	4	0.9
C1 18-20 cm	3650	142	N.A.		N.A.		0.09	0.05	89	11	9	3.9
C1 20-22 cm	5184	197	-0.42	0.09	1.104	0.007	0.09	0.06	90	10	7	2.2
C1 26-28 cm	835	32	-0.44	0.07	1.104	0.007	0.87	0.54	90	10	7	2.5
C2 2-4 cm	678	26	-0.34	0.10	1.114	0.009	0.22	0.14	46	54	4	0.9
C2 8-10 cm	197	7	-0.22	0.08	1.114	0.011	0.59	0.36	78	22	13	9.0
C2 14-16 cm	1028	39	-0.20	0.08	1.119	0.007	0.39	0.24	80	20	5	1.3
C2 20-22 cm	1550	59	-0.29	0.03	1.123	0.009	0.90	0.55	61	39	3	0.6
C2 24-30 cm	113	4	-0.36	0.10	1.116	0.008	10.0	6.2	73	27	39	77.0

570 **3.3. Uranium isotopic ratios $\delta^{238}\text{U}$ in soil cores**

571 The uranium isotopic ratios $^{238}\text{U}/^{235}\text{U}$ – expressed as $\delta^{238}\text{U}$ – measured in the soils of cores
572 C1 and C2 are homogeneous (Table 1, Figure 3c) and lie (within uncertainties) in the range of
573 $\delta^{238}\text{U}$ values measured in the watershed bedrock ($-0.29 \pm 0.14 \text{ ‰}$, $n=6$) (Lefebvre et al., 2021a).
574 In core C2, the isotope signatures seem to form a curved trend with higher $\delta^{238}\text{U}$ at mid-depth
575 than in the upper and lower parts, but this trend is not statistically significant as uncertainties
576 overlap. There is no clear relationship between $\delta^{238}\text{U}$ and U concentrations or ($^{234}\text{U}/^{238}\text{U}$)
577 activity ratios (Figure S8).

578 **3.4. Chemical and isotopic composition of the stream waters**

579 **3.4.1. Physicochemical parameters**

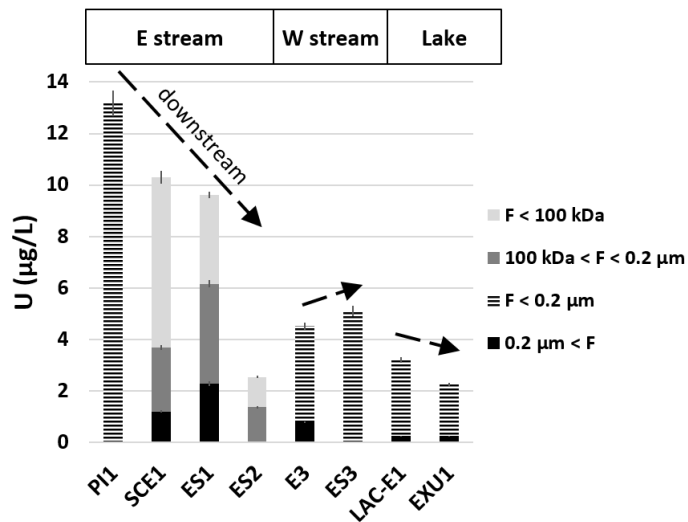
580 As reported in the *Supplementary Dataset*, the water of the eastern stream (PI1, SCE1, ES1)
581 show dissolved O_2 levels (from 7.9 to 6.7 mg/L) at or close to equilibrium with the atmosphere
582 (~ 7.5 mg/L at 13-16 °C and 2350 m elevation). The conductivity is typical of mountainous
583 streams with low values between 31.1 and 34.5 $\mu\text{S}/\text{cm}$. Redox potentials gradually increase from
584 157 to 216 mV along the stream course and are higher than that of the soil water at the location
585 of cores C1 and C2. The pH of the stream is circumneutral (pH 6.9-7.4) and increases shortly
586 after entering the lake at ES2, up to 8.2, which may be explained by photosynthetic activity in the
587 lake surface water.

588 Lower O_2 (4.6-5.6 mg/L), σ and ORP as well as slightly acidic pH values (6.1 and 6.4) were
589 measured in the western stream (E3 and ES3). At the time of sampling, this stream was
590 resurging just before crossing the wetland and thus could not have fully equilibrated with the
591 atmosphere.

592 **3.4.2. Uranium partition in particulate, colloidal and dissolved fractions**

593 In the ultra-filtered waters (SCE1, ES1, ES2), the partition of U among particles ($> 0.2 \mu\text{m}$),
594 colloids (between $0.2 \mu\text{m}$ and 100 kDa) and “dissolved species” (< 100 kDa, including small
595 colloids) was determined by measuring U concentrations (in $\mu\text{g}/\text{L}$) after the different filtration
596 steps (Figure 4). For all other samples (PI1, E3, ES3, LAC-E1 and EXU1), a single $0.2 \mu\text{m}$ filtration
597 step was applied and only the particulate U fraction was distinguished from the $< 0.2 \mu\text{m}$
598 fraction, which includes colloidal and dissolved species. In the studied stream and lake waters,
599 the particles and colloids are thought to be mainly organic (brown to green deposits on the
600 filters), which could not be assessed by DOC measurements because of very low organic carbon
601 contents (< 1 mg/L) barely above the instrumental detection limit.

602 Uranium concentrations in the creeks and in the lake are in the 2.3-13.2 $\mu\text{g/L}$ range. These
 603 concentrations are well above the average U concentration in freshwater systems ($\sim 0.3 \mu\text{g/L}$
 604 (Palmer and Edmond, 1993)) and are particularly elevated considering the absence of carbonate
 605 rocks (i.e., low dissolved inorganic carbon (DIC)) and the low dissolved Ca contents ($\sim 0.1 \text{ mM}$)
 606 of watershed waters. Such conditions should limit the formation of stable U calcium carbonate
 607 complexes (e.g., Maher et al., 2013). In all sampled waters, most of U ($> 76 \%$) is transported in
 608 the colloidal and dissolved fractions (Figure 4). As the eastern stream flows down the mountain
 609 slope to the wetland and then to the lake (PI1 to SCE1 to ES1), U concentration decreases by
 610 $\sim 24 \%$ (12.6 to $9.6 \mu\text{g/L}$) and the colloidal and particulate U fractions increase (from 0 to 24 %
 611 in particles). Twenty meters downstream from the stream outlet (ES2, in the lake), dilution in
 612 the lake causes a drastic drop of the U concentration (from 9.6 to $2.6 \mu\text{g/L}$) and no more
 613 significant U-bearing particles are detected.



614

615 **Figure 4 – Total uranium concentration in waters sampled up- and downstream of the**
 616 **wetland and its repartition among particulate ($> 0.2 \mu\text{m}$), colloidal ($100 \text{ kDa} < F < 0.2 \mu\text{m}$)**
 617 **and dissolved fractions ($< 100 \text{ kDa}$ or $< 0.2 \mu\text{m}$, see Section 2.1.2). PI1 is the spring of the**
 618 **eastern stream (E stream) feeding the wetland through SCE1, before flowing into the lake at ES1,**
 619 **diluted 20 m further at ES2. E3 is located upstream of the western stream (W stream) feeding the**
 620 **wetland, flowing into the lake at ES3. LAC-E1 was taken on the lake shore 100 m downstream from**
 621 **the wetland, EXU1 at the lake outlet. The sampling locations are illustrated in Figure 1.**

622 The western stream contains three times less U than the eastern one, and is slightly enriched
 623 in U (+ 13 %) after flowing across the wetland. The proportion of U borne by particles decreases
 624 from 18 to 1 % in the same interval. The lake water on the eastern shore (LAC-E1) and at the
 625 lake outlet has comparable U concentrations to ES2, however with significant particulate U
 626 fraction (8 and 11 % respectively).

627 *3.4.3. Uranium isotopic composition of the water samples*

628 The uranium isotopic composition ($(^{234}\text{U}/^{238}\text{U})$ and $\delta^{238}\text{U}$) could be determined in the bulk
629 (non-filtered) and 0.2 μm -filtered samples at SCE1, ES1 and ES2 (eastern stream), and in the
630 bulk water of the eastern spring (PI1). As no significant difference was observed between the
631 isotopic signatures of bulk and filtered samples, we further use the average values of both
632 samples.

633 All waters display $(^{234}\text{U}/^{238}\text{U})$ activity ratios above that of soils from cores C1 and C2
634 (Figure 3b). The spring water (PI1) has a high $(^{234}\text{U}/^{238}\text{U})$ value of 1.155 ± 0.009 , typical of U
635 originating from weathered granite with ^{234}U supply by alpha recoil (e.g., Chabaux et al., 2003;
636 Andersen et al., 2009). Further on the stream course upstream of the wetland (SCE1), the
637 $(^{234}\text{U}/^{238}\text{U})$ ratio decreases to 1.131 ± 0.013 . After flowing through the wetland (ES1), the stream
638 $(^{234}\text{U}/^{238}\text{U})$ signature increases to 1.159 ± 0.011 and is finally lower again after dilution in the
639 lake (ES2), at 1.136 ± 0.012 .

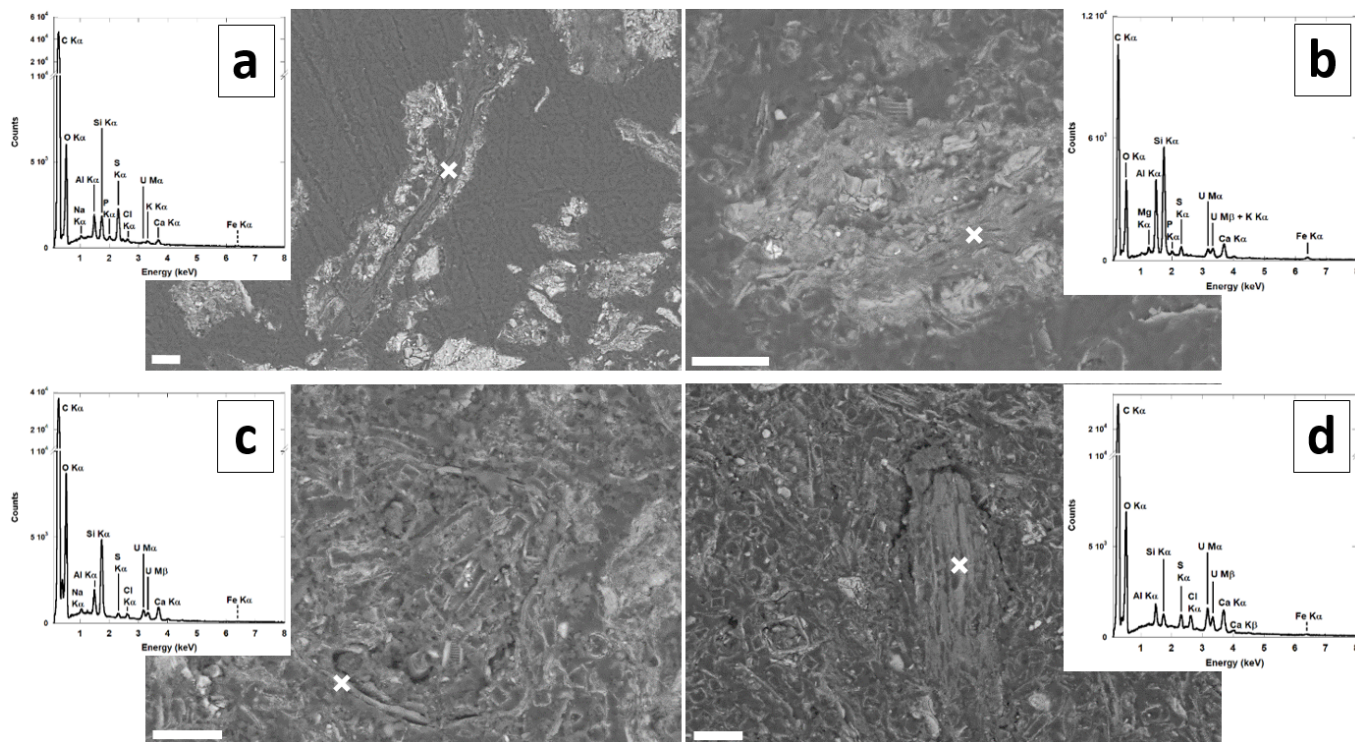
640 The $\delta^{238}\text{U}$ signatures of waters shows lower variations: both waters sampled upstream of the
641 wetland (PI1 and SCE1) have similar average $\delta^{238}\text{U}$ values of -0.32 ± 0.06 and -0.31 ± 0.09 ‰
642 respectively. After flowing through the wetland (ES1 and ES2), the stream displays a slightly
643 higher $\delta^{238}\text{U}$ of -0.23 ± 0.13 and -0.18 ± 0.10 ‰ respectively; this difference is consistently
644 observed among all measured $\delta^{238}\text{U}$ of the bulk and filtered samples (see *Supplementary*
645 *Dataset*). All waters $\delta^{238}\text{U}$ signatures are indistinguishable from that of the soils within
646 uncertainties, except for the lower half of core C1 where the soils are slightly isotopically lighter
647 than the outlet waters ES1 and ES2 (Figure 3c).

648 ***3.5. Uranium distribution, redox and speciation in the soil samples***

649 *3.5.1. Identification of U-bearing phases by SEM, EPMA and micro-XRF mapping*

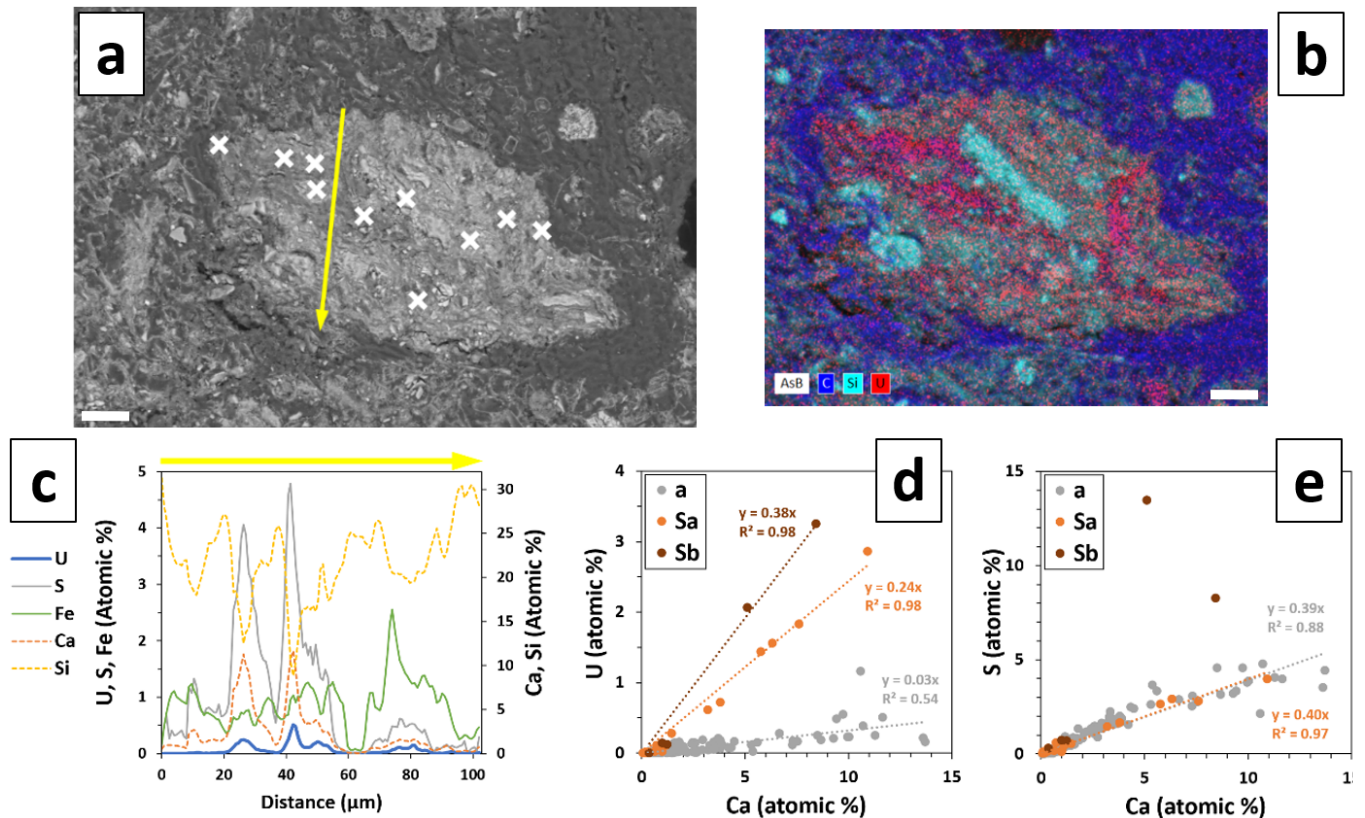
650 High U content in the soils allowed the investigation of resin-embedded samples by SEM,
651 revealing a variety of U-bearing phases detectable by EDXS. Representative examples of such
652 U-rich particles are shown in backscattered electron imaging in Figure 5. Significant U amounts
653 were detected by the means of the U M_{α} emission line, mainly in organic structures of various
654 morphologies presenting a low intensity backscattering signal, such as vegetal remains
655 (Figure 5a) or organic debris (Figure 5c,d) some with substantial U enrichment (Figure 5c,d), as
656 well as organo-mineral aggregates (Figure 5b). Very rare occurrences of detrital grains
657 containing traces of U and/or Th were found, such as zircon and monazite.

658 Additionally, thorough SEM-EDXS observation of the samples showed abundant diatom
 659 tests, especially in the C1 core, and scarce isolated sulfide grains (pyrite FeS_2 or $(\text{Zn,Fe,Cu})\text{S}_x$) in
 660 core C1 at depth (18-20 cm) indicating the local occurrence of sulfidic conditions.



661
 662 **Figure 5 – SEM images and EDX spectra of uranium-bearing phases in the wetland samples.**
 663 (a) Vegetal remain containing trace U and coated by mineral grains, in sample C2 20-22 cm;
 664 (b) organo-mineral aggregate, which organic component contains U, in sample C1 20-22 cm;
 665 (c) U-rich organic debris in sample C1 14-16 cm; (d) U-rich organic debris in sample C1 18-20 cm.
 666 Diatom tests are abundant in core C1 (b-d). White crosses indicate EDX spectra spots. All scale bars
 667 are 20 μm .

668
 669 A few U-bearing phases were further analyzed by EPMA to quantitatively measure their
 670 chemical composition: two organo-mineral aggregates (100-200 μm wide) and a mineral-coated
 671 vegetal remain (200x500 μm) (Figure 6a and Figure S9). They show a heterogeneous U
 672 distribution, with U mainly associated to organic phases. U contents can reach as much as
 673 3.25 at% in the vegetal remain displayed in Figure S9 with analyses reported in Figure 6d.
 674 Interestingly, we observe good correlations between the U, Ca and S contents (Figure 6c-e) in
 675 these organic soil constituents.

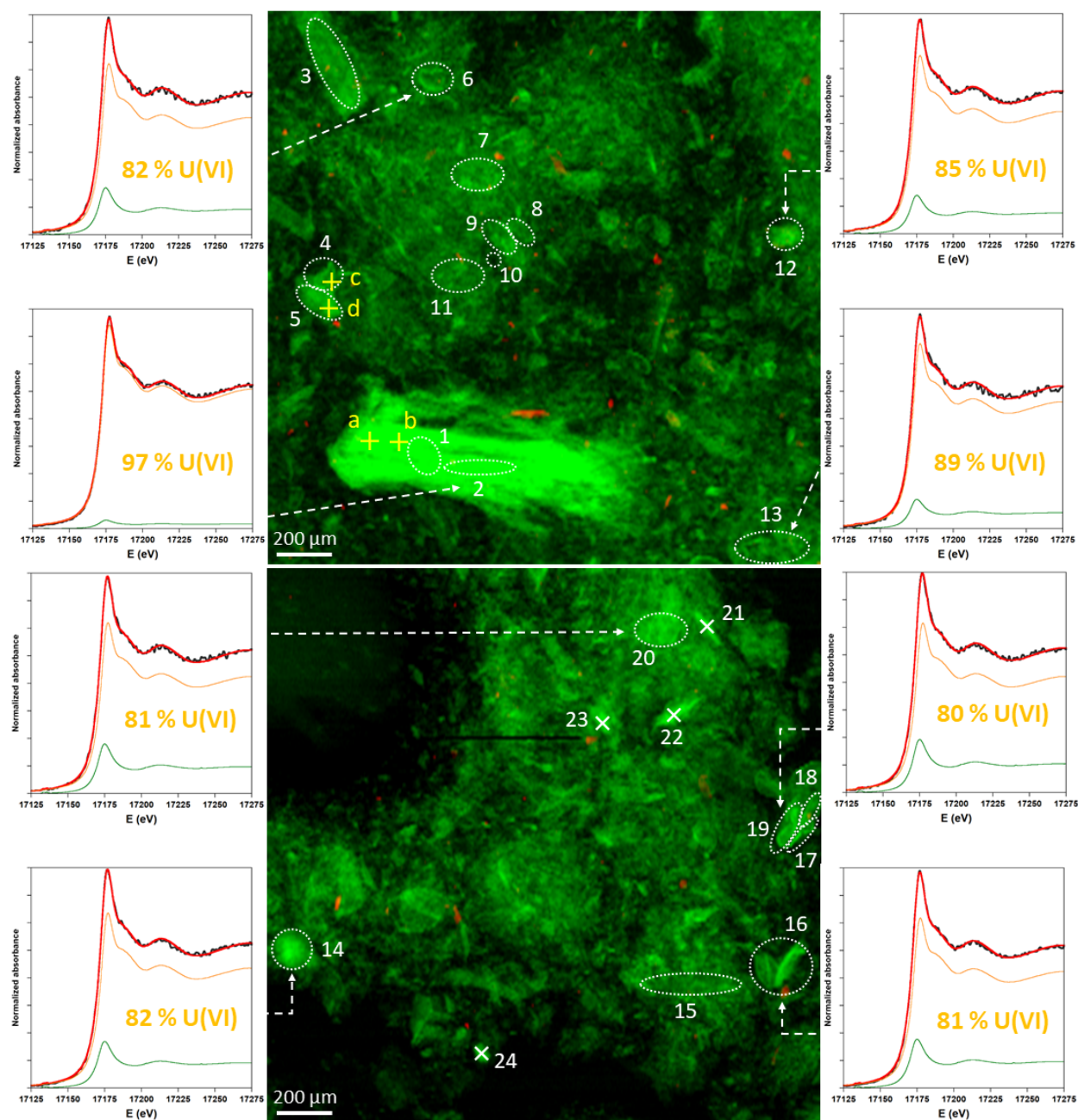


676

677 **Figure 6 – Chemical micro-analyses by SEM-EDXS and EPMA of uranium-bearing phases in**
 678 **the wetland samples.** (a) Organo-mineral aggregate analyzed with EPMA (white crosses: spots,
 679 and yellow arrow: transect of 102- μm length, with 0.8 μm steps); (b) EDX mapping of C (blue), Si
 680 (turquoise) and U (red) in the same aggregate that is embedded in a C-rich resin. All scale bars are
 681 20 μm . (c) Chemical composition (U, S, Fe – left axis, Ca, Si – right axis) along the yellow transect in
 682 (a). Covariations of U and Ca (d) and S and Ca (e) at all analyzed points on (a) including the
 683 transect, and on **Figure S9a** (Sa) and **S9b** (Sb); determination coefficients (R^2) and slopes of linear
 684 relationships are indicated.

685

686 Further investigation of soil sample C1 18-20 cm (4726 $\mu\text{g/g}$ U) was performed using
 687 synchrotron-based $\mu\text{-XRF}$ mapping in order to determine the micro-scale distribution of U with a
 688 better detection limit than SEM-EDX and EMPA, and to determine the redox state of U in areas of
 689 interest (**Figure 7**). In the $\mu\text{-XRF}$ maps, uranium appeared to be broadly distributed within the
 690 soil matrix in which U could not be detected by SEM-EDXS. In **Figure 7**, it should be noted that
 691 the U-rich elongated pattern at the bottom of the upper map is likely a vegetal debris which
 692 fluorescence is enhanced by its thickness. Numerous thinner U-rich particles are spread over the
 693 sample matrix that contains low but detectable amounts of U.



694

695 **Figure 7 – Uranium-bearing phases observed by micro-XRF mapping and analyzed by**
 696 **micro-XANES.** These 2x2 mm μ -XRF maps show a diversity of U-bearing particles of various sizes
 697 and morphologies. U L α and Fe K α fluorescence lines intensities are displayed in green and red,
 698 respectively. Areas analyzed by μ -XANES at the U L $_3$ -edge are delimited by white dashed lines and
 699 numbered from 1 to 20. Within each area, several scans collected on pristine spots were merged in
 700 order to limit beam-damage. In addition, four single spectra were acquired on U-rich spots and
 701 merged (21-24, white crosses). Examples of μ -XANES experimental spectra (black) and their
 702 corresponding LC-LS fit (red) with contributions of U(VI) (synthetic uranyl triscarbonato complex,
 703 orange) and U(IV) (reduced U-rich sediment NEG18-07 184-189 cm, green) components are shown
 704 on the sides for areas 2, 6, 12, 13, 14, 16, 19 and 20; the corresponding U(VI) proportions (% of
 705 total U) are indicated on each spectrum. U oxidation state obtained from LC-LS fits of the μ -XANES
 706 spectra (Figure S11) are reported in Table S3. Four spots lettered from a to d (yellow crosses, top)
 707 were chosen to estimate the beam-damage kinetics (Figures S2 and S3).

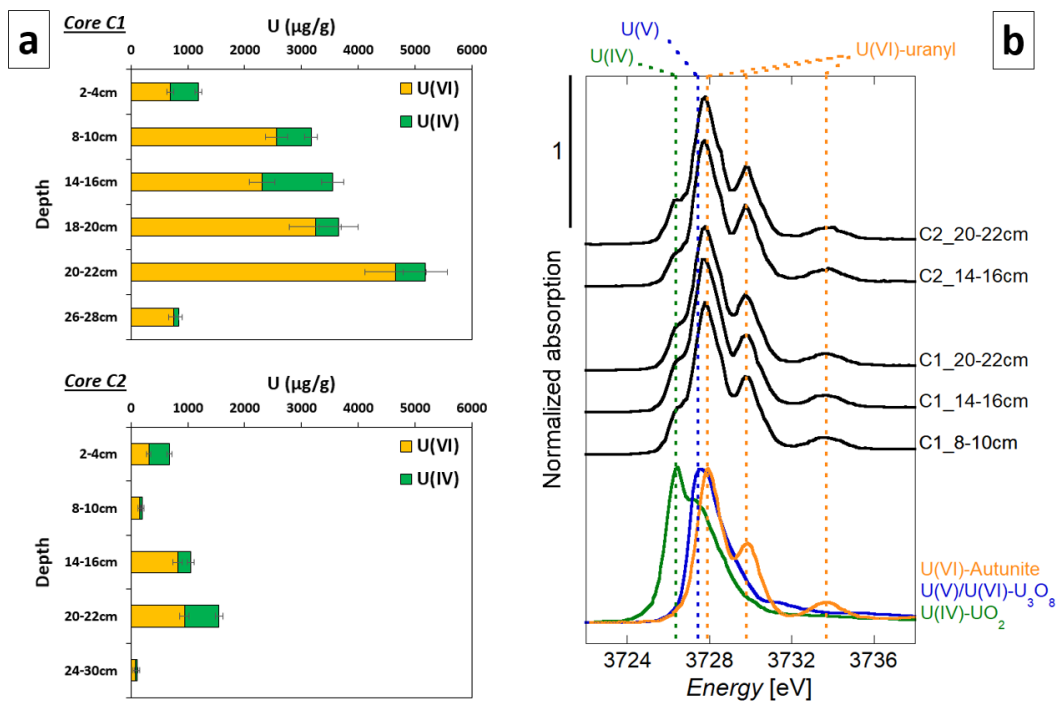
708 *3.5.2. Bulk and micro-scale U redox state determined by (μ -)XANES*

709 The uranium oxidation state was determined by Linear Combination Fit analysis of U L_3 -
710 edge XANES spectra, after having chosen a single set of U(IV) and U(VI) model compounds that
711 were relevant to nano-crystalline or non-crystalline U(IV) species encountered in soils and
712 sediments and that were among the pure oxidized U(VI) and reduced U(IV) model compounds of
713 our database (Table S2, Figure S10). According to these criteria, the best fits to the wetland soil
714 XANES data were obtained using U(VI)-humic acid and U(IV)-sediment NEG18-07 189-194 cm
715 as fitting components (Table S4, Figure S12).

716 Experimental U L_3 -edge XANES spectra of bulk soil samples from cores C1 and C2 with their
717 corresponding LC fits are displayed in Figure S12, with U(VI)-U(IV) proportions reported in
718 Tables 1 and S4. The resulting U(VI) and U(IV) concentrations profiles are represented as a
719 function of depth in Figure 8a. U(VI) is overall dominating at 58 to 90 % in most samples, with
720 the notable exception of the C2 upper sample (2-4 cm), in which U(VI) and U(IV) are found in
721 similar proportions. Overall, U(IV) proportions appear to be slightly higher in core C2 than in C1.

722 U M_4 -edge HERFD-XANES spectra collected for five of the bulk soil samples corroborate the
723 results of U L_3 -edge XANES analysis. U(VI) appears to be dominant as indicated by absorption
724 peaks at 3727.7, 3729.6 and 3733.4 eV similar to the U(VI)-autunite reference spectrum
725 (Figure 8b). Some U(IV) is also present in all samples as attested by small shoulders at 3726.2 eV
726 similar to the main absorption peak of uraninite. The lack of a shoulder at 3727.5 eV, main peak
727 of U_3O_8 , our U(V)-containing reference compound (Figure 8b), indicates that no detectable U(V)
728 is present in our soil samples within the 10-15 % uncertainty range of the method.

729 Experimental U L_3 -edge μ -XANES spectra of U-rich areas identified by μ -XRF in sample
730 C1 18-20 cm are shown with their corresponding LC fits in Figures 7 and S11, with fitting results
731 reported in Table S3. In accordance with the U redox state in the bulk sample (89 ± 9 % U(VI)),
732 U(VI) dominates at all 21 analyzed areas (Figure 7), with proportions ranging from 80 to 97 %.
733 Owing to the fit uncertainty (± 7 -25 %; Table S3), U oxidation state in the 2x2 mm μ -XRF maps in
734 Figure 7 can thus be considered homogeneous. Comparison of the XANES spectrum of the bulk
735 sample (C1 18-20 cm) with the merge of all μ -XANES spectra yielded equal redox states within
736 uncertainties, 86 ± 9 and 89 ± 9 % of U(VI) respectively (Figure S13).



737

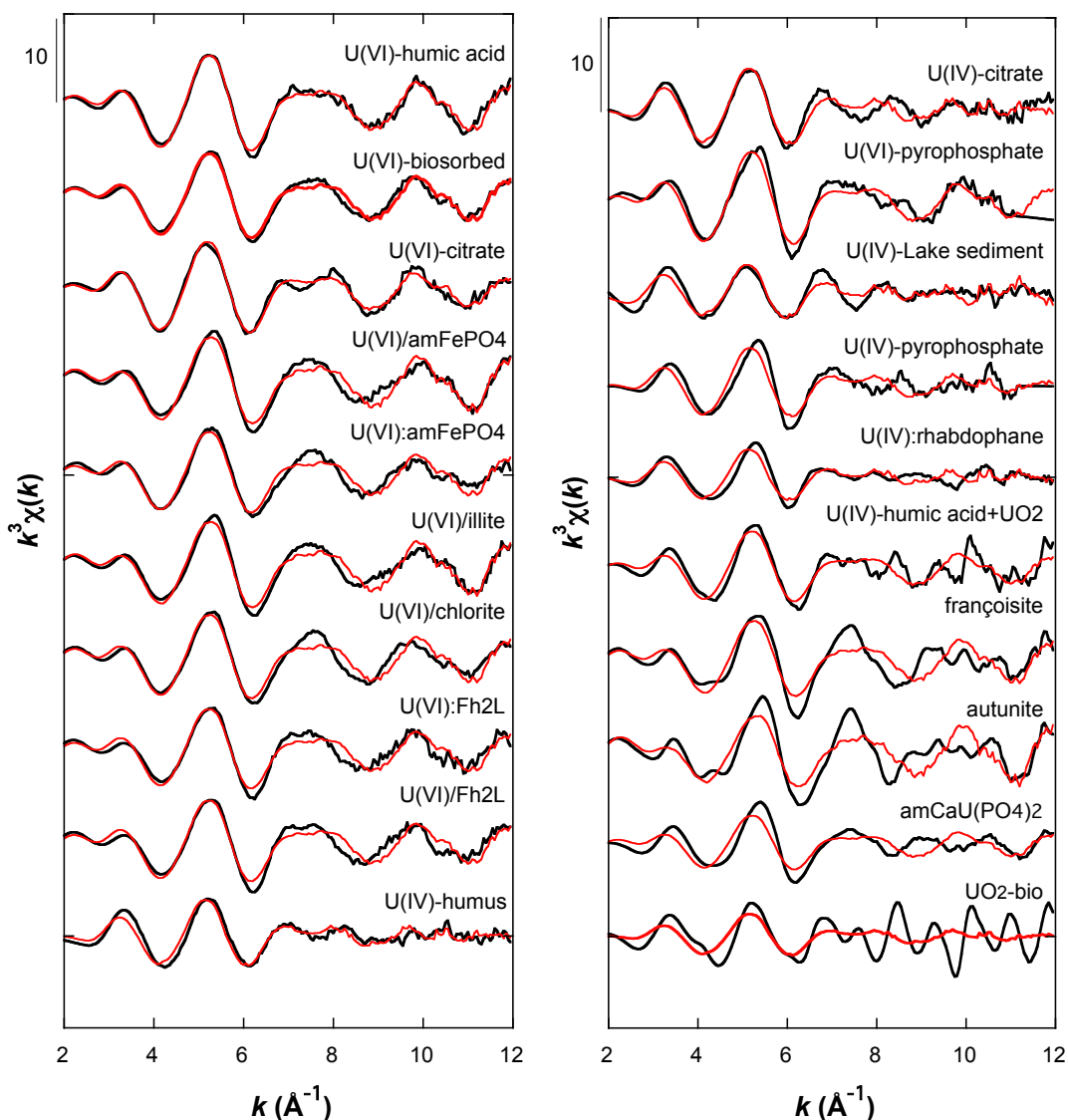
738 **Figure 8 –Oxidation state of uranium in soil cores C1 and C2 determined by U L₃-edge XANES**
 739 **and U M₄-edge HERFD-XANES spectroscopies.** (a) Depth profiles along cores C1 and C2 of the
 740 U(VI) and U(IV) contents (in µg/g) determined from LC-LS fitting of U L₃-edge XANES spectra.
 741 U(VI) concentrations are shown in orange, U(IV) in green. Error bars represent 3σ uncertainties.
 742 Fitting results are reported in **Table 1**. (b) HERFD-XANES spectra at the U M₄-edge of reference
 743 compounds and soil samples from cores C1 and C2. Autunite was used as U(VI) reference, U₃O₈
 744 contains 67 % U(V) and 33 % U(VI), and UO₂ was used as U(IV) reference (with a fraction of U(V)).
 745 Vertical dashed lines indicate the absorption features of U(IV) (green), U(V) (blue) and U(VI)
 746 (orange).

747

748 3.5.3. Bulk U speciation determined by EXAFS

749 Following the Principal Component Analysis (PCA) of EXAFS spectra of our wetland samples,
 750 a minimum IND value (Malinowski, 1977) was obtained by including only the two first principal
 751 components that explained 98.4 % of the variance, thus suggesting that no more than 2
 752 theoretical components should be necessary to explain our dataset. Samples C1 26-28 cm and
 753 C2 8-10 cm were not included in the PCA because their noisy EXAFS spectra led to
 754 overestimating the variance and would thus have introduced a bias in the PCA. Target
 755 Transform analysis was performed over our EXAFS spectra dataset of 20 model compounds.
 756 Results of this TT analysis are reported in **Figure 9** and **Table S5**, in which a R-factor, $R_f = \sum$
 757 $[k^3\chi(k) - k^3\chi(k)_{TT}]^2 / \sum [k^3\chi(k)]^2$, is used to compare the model compound spectrum to its target
 758 transform (Webb, 2005). The lowest R_f values were obtained for U noncrystalline species, such
 759 as U(IV) and U(VI) bound to organic or microbial compounds as well as clay mineral surfaces,

760 indicating that these species were the most relevant to U speciation in our wetland samples.
 761 Based on these results, combinations of two or three of these model compounds spectra were
 762 tested for LCF analysis of the EXAFS spectra of the wetland soils samples.



763

764 **Figure 9 – Target Transform analysis of our set of model compounds U L₃-edge EXAFS**
 765 **spectra, using the two first components of the PCA analysis of our wetland soil samples**
 766 **data.** See Table S5 for quantitative results and for information and references on the reported
 767 **model compounds spectra.**

768 The best LCF results were obtained by using two of the U(IV)-humus, U(VI)-biosorbed and
 769 U(VI)-citrate model compounds spectra as fitting components (Figures S14a and 14b; Table S6).
 770 Better matches to the wetland soil data could be obtained when including simultaneously the
 771 three components in the fit but with less reliable statistical results. Furthermore, fit
 772 combinations of two or three components including other model compounds, especially U(IV)-
 773 citrate, U(VI)-humic acid and U(VI)-sorbed to illite (Figure S10; Table S2), yielded satisfactory

774 results for some samples (data not shown) but could not account for the whole set of wetland
775 core samples studied and were thus not retained. Although being less accurate than XANES LCF
776 for determining the U redox state (Table S4), EXAFS LCF results (Table S6) confirmed the overall
777 higher proportion of U(IV) in the C2 core (Figure S14b) than in the C1 core (Figure S14a).
778 Consistently with the PCA-TT analysis (Table S5, Figure 9), LCF analysis confirmed that the
779 wetland soils EXAFS data could be reconstructed using solely non-crystalline U species as fitting
780 components. The matching of the U(VI) component with either the U(VI)-citrate or U(VI)-
781 biosorbed model compound spectra was mostly related to the shape of the spectrum in the
782 7-9 Å⁻¹ *k*-range and likely relied on the number and distribution of equatorial U-O distances as
783 suggested by the shell-by-shell fitting analysis presented thereafter (Table 2). The second
784 neighbor contribution to the EXAFS was weak in all samples but showed a small peak centered
785 at ~3 Å uncorrected for phase shift (Figures S14a and 14b), which we mainly attribute to C atom
786 neighbors at ~3.3-3.5 Å, as discussed in the following shell-by-shell fitting analysis.

787 Shell-by-shell fitting of the unfiltered *k*³-weighted EXAFS spectra was conducted over the
788 2-14 Å⁻¹ *k*-range for the U-rich samples C1 18-20 cm and 20-22 cm, as well as for the model
789 compounds that we used as fitting components for the LCF analysis (Table 2, Figure 10). For the
790 U(IV)-humus model compound, data were only available to *k* = 12 Å⁻¹. The choice of second
791 neighbors for the shell-by-shell fitting of soil samples data was first guided by the results of the
792 shell-by-shell fitting of the U-organic model compound that were the most relevant to the
793 system studied, according to PCA-TT-LCF analysis, as well as by μ -XRF, μ -XAS, SEM-EDXS and
794 EPMA data reported above in the text. Shell-by-shell fitting of the *k*³-weighted U *L*₃-edge EXAFS
795 data was conducted in *k*-space and yielded also a good match in *R*-space as illustrated by
796 comparing both the real part and magnitude of the FFT (Figure 10) and the Continuous Cauchy
797 Wavelet Transform (Figure 11) of the experimental and calculated EXAFS spectra. Because it
798 indicates in which *k*-region each FFT peak contributes to the EXAFS signal, CCWT analysis is
799 particularly sensitive to the type of backscattering neighbor atom and thus helps deciphering
800 between neighbors of U having close atomic numbers, such as C and P atoms (Morin et al., 2016;
801 Stetten et al., 2018b). Beyond this qualitative information, the fit quality was checked using
802 reduced chi-square calculations in both *k*- and *R*-space according to classical procedures
803 reported in the Materials and Methods section. Alternative fit solutions were carefully evaluated
804 and compared with those retained in Table 2 and Figure 10, according to statistical tests, as
805 reported in Supplementary Material (Figures S15, S16 and S17).

806 For the two soil samples, shell-by-shell fitting results for the first neighbor O shells was
807 consistent with the dominant U(VI) oxidation state of U in these samples. The coordination
808 number (*CN*) value of the two axial O atoms was scaled to the proportion of U(VI) determined by

809 XANES analysis (Table 1), and kept fixed during the fitting procedure (Table 2), together with
810 the associated multiple scattering paths. Two equatorial shells could be resolved with a total CN
811 value of ~5-6 (Table 2). The second neighbor contributions to the EXAFS included a dominant
812 contribution from C neighbors in monodentate (~3.5 Å) coordination, accompanied by P or Si
813 neighbors in bidentate (~3.1 Å) coordination and U neighbors at ~4 Å (Table 2, Figure 10). Such
814 U(VI)-P distance at 3.1 Å is in agreement with the results of quantum mechanical calculations
815 reported by Kubicki et al. (2009) for aqueous bidentate uranyl-phosphate complexes, including
816 organophosphate ones. Similar U-P bonding mode is also classically observed for U(IV) in humic
817 substances (Stetten et al., 2018a), in products of microbial U(VI) reduction (e.g., Bernier-Latmani
818 et al., 2010) and in U(IV)-phosphate crystal structures (Dusausoy et al., 1996; Rui et al., 2013;
819 Morin et al., 2016; Stetten et al., 2018a). In our fits, this U-P path could be replaced by a U-Si path
820 without changing the fit quality. Such a Si path at 3.1 Å has been for instance for proposed by
821 Regenspurg et al. (2010) for U(VI) samples in their EXAFS study of U speciation in a pristine
822 wetland. This U-P/Si path at ~3.1 Å could be also replaced by a U-C path at ~2.9 Å, with
823 acceptable fitting results in *k*- and *R*-spaces, but this fit solution did not match the CCWT as well
824 as the U-Si/P path at ~3.1 Å and could be discounted by an F-test at 95 % confidence (Figure
825 S15). Attempts to include other elements such as Ca or Fe in second neighbor shells did not
826 produce satisfying results. The detailed contributions to the EXAFS of the fitting shells retained
827 in Table 2 and Figures 10 and 11 are exemplified in Figure S15, which displays the successive
828 fitting results obtained when incrementing the number of fitting shells for the C1 20-22 cm
829 sample, which results in a statistically significant fit improvement. To this regard, even more
830 than the EXAFS and FFT curves, the CCWT analysis particularly shows that the U-C and U-P/Si
831 second shells significantly contribute over the U-O_{axial} multiple scattering paths (MS). This
832 analysis also clearly evidences the presence of a U-U path at ~4 Å in this sample. Hence, shell-by-
833 shell fitting results for the C1 18-20 cm and 20-22 cm indicate that U is mainly present as
834 mononuclear species bound to organic moieties in monodentate linkage geometry (U-C path at
835 ~3.5 Å), as also proposed by Stetten et al. (2018a) in their study of a highly U-contaminated
836 wetland. In addition, minor bidentate complexes with P (or Si) neighbors at 3.1 Å (or possibly C
837 neighbors at 2.9 Å) are present. Eventually, we also observe the minor but detectable presence
838 of condensed U phases as indicated by a U-U path at ~4 Å. This latter signal is particularly
839 observed in the C1 sample at depth 20-22 cm, as attested by the fitting results (Table 2) and the
840 CCWT analysis (Figures 11 and S15).

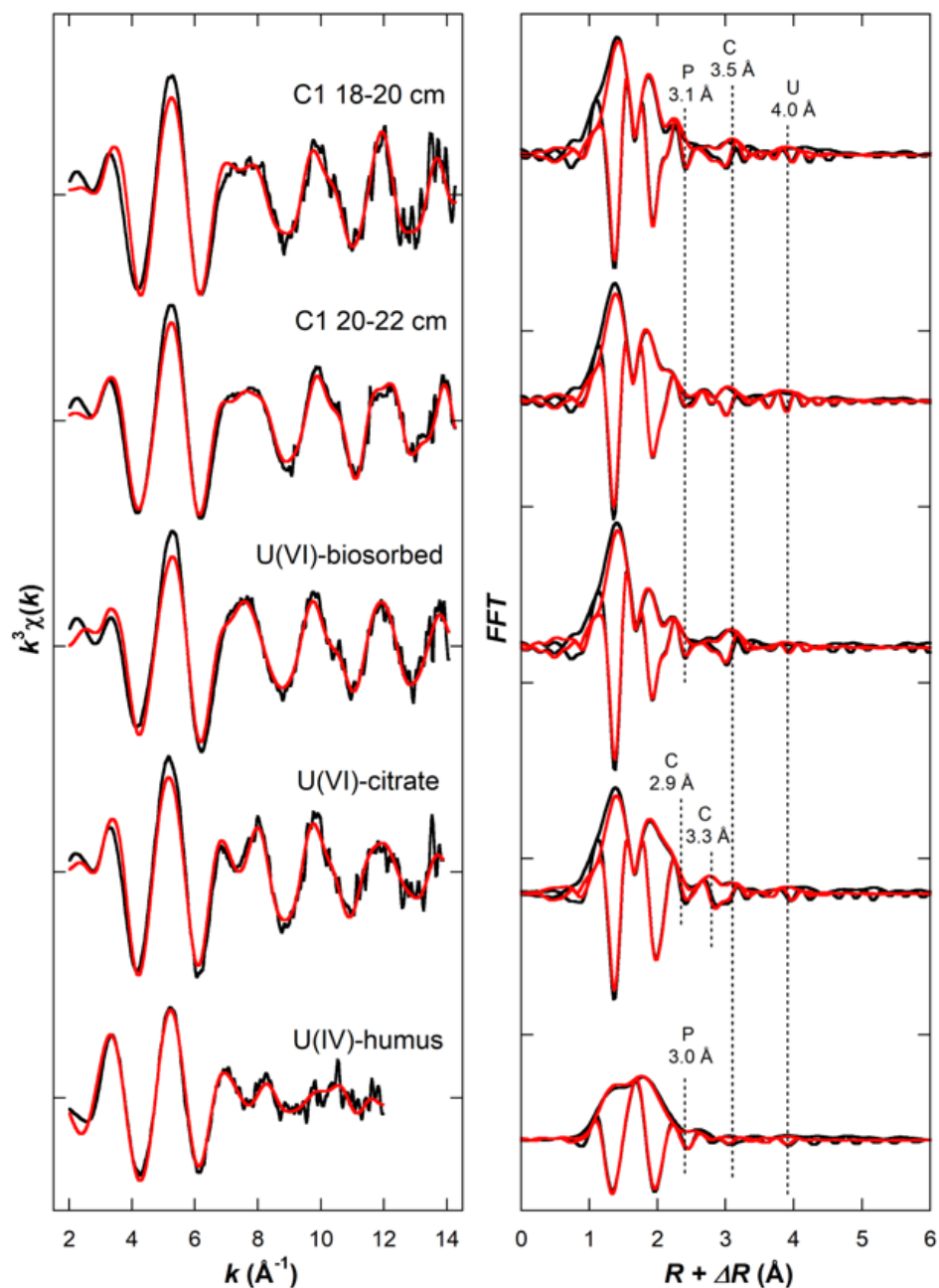
841 The shell-by-shell fitting results obtained for the U(VI)-biosorbed model compound were
842 similar to those obtained for the two soils samples, albeit with a more pronounced contribution
843 of C neighbors in monodentate (~3.5 Å) coordination and a similar contribution of U-P in
844 bidentate (~3.1 Å) coordination (Table 2, Figures 10 and 11). This fit solution differs from that

845 proposed by Seder-Colomina et al. (2015) and Stetten et al. (2018a) for the same model
846 compound EXAFS spectrum from our database. These authors reported C neighbors at 2.9 Å and
847 P neighbors at 3.6 Å, as a result of a fit in *k*-space and qualitative straightforward comparison in
848 *R*-space, in agreement with the results reported in previous EXAFS studies of U(VI) sorption to
849 bacterial cells (Merroun et al., 2005; Dunham-Cheatham et al., 2011). This latter set of C and P
850 paths was actually complemented by a MS U-O-P path at 3.7 Å in the study of Seder-Colomina et
851 al. (2015), following the fit solutions proposed by Kelly et al. (2002) and Llorens et al. (2012). A
852 comparison of these different fit solutions is presented in [Figure S16](#), including the CCWT of
853 experimental and fit EXAFS curves. Comparing both FFTs and CCWTs suggests that the fit
854 solution retained in [Table 2 and Figures 10 and 11](#), with P and C shells at 3.1 and 3.5 Å
855 respectively, is the most reliable, according to an F-test at 90% confidence ([Figure S16](#)),
856 considering that only a limited number of shells can be included in the fit and even though the
857 presence of additional C and P shells at 2.9 Å and 3.6 Å, respectively, cannot be excluded.
858 Interestingly, quantum mechanical calculations conducted by Kubicki et al. (2009) on aqueous
859 uranyl-phosphate complexes were reported by these authors to converge towards bidentate
860 uranyl-phosphate bonding with a U-P distance at ~3.1 Å even when starting from a
861 monodentate configuration. Moreover, in the same study, both monodentate U(VI)-C and
862 bidentate U(VI)-P binding modes were found in significant proportions in calculated uranyl-
863 organophosphate complexes. These findings further support our interpretation of the U *L*₃-
864 EXAFS data of the soil samples and of the biosorbed model compound ([Table 2, Figures 10, S15](#)
865 [and S16](#)). In the present EXAFS analysis, beyond the inherent uncertainties in determining the
866 exact distribution of U-C and U-P distances in such complex samples as U(VI) sorbed to bacterial
867 cell walls, shell-by-shell analysis of EXAFS data show a similarity in the results obtained for the
868 U(VI)-biosorbed model compound and for the C1 18-20 cm and 20-22 cm soil samples, which
869 may explain the dominant contribution of this model compound in the LCF analysis of these soils
870 samples ([Figure S14a, Table S6](#)).

871 The shell-by-shell fitting results obtained for the U(VI)-citrate model compound
872 (synthesized in this study) indicated 6 equatorial atoms with a narrow distance distribution, and
873 second neighbor C atoms showing a distribution of U-C distances in the 2.9-3.5 Å range ([Table 2,](#)
874 [Figure 10](#)). According to Rossberg et al. (2009), the U-C path at ~2.9 Å is only significant with a
875 *CN* > 1 since these authors detected this contribution in a C-free system. Consequently, the
876 significance of this U-C path at 2.9 Å cannot be definitively proven from the EXAFS analysis of
877 our U(VI)-citrate sample, even though such a distance corresponds to bidentate linkage of U to C
878 moieties as in the structure of crystalline U(VI)-carboxylate compounds (Howatson et al., 1975;
879 Denecke et al., 1998). This path was also proposed by Francis and Dodge (2008) for a U(VI)-
880 citrate complex albeit misinterpreted by these authors as monodentate linkage, whereas this

881 2.9 Å path was considered negligible for U(VI)-acetate by Thompson et al. (1997), based on high-
882 quality EXAFS data to k of 16 Å⁻¹. In contrast, the U-C distances at 3.3 Å and 3.5 Å with CN higher
883 than 2 appear as the main second neighbor shells. These U-C distances in the 3.3-3.5 Å range can
884 be attributed to monodentate linkage of U to C moieties, as it is common in the structure of
885 crystalline U(VI)-carboxylate compounds (Howatson et al., 1975; Denecke et al., 1998) and as it
886 has been predicted from first principles for U(VI)-carboxylate complexes (Schlosser et al., 2006).
887 The presence of such C neighbors of U at 3.3 Å was also reported for a U(VI)-humic substance
888 complex in the recent EXAFS study by Stetten et al. (2018a). The lack of observation of this
889 monodentate U-C path at 3.3-3.5 Å in previous EXAFS studies of U(VI)-carboxylates and U(VI)-
890 humic substances complexes may be related to the difficulty in distinguishing this second
891 contribution from that of U-O_{axial} MS paths in EXAFS data collected at room temperature
892 (Denecke et al., 1997, 1998; Schmeide et al., 2003), as compared to EXAFS data collected at
893 cryogenic temperatures in the study by Stetten et al. (2018a) and in this study (Figures 10, S15
894 to S17). In addition, the fit of our U(VI)-citrate compound was significantly improved when
895 including a U-U path at ~4 Å for this high U loading sample (2 wt% U) (Table 2, Figure S17). This
896 contribution is even more pronounced in the higher loading U(VI)-citrate sample by Francis and
897 Dodge (2008), in which it was interpreted as a binuclear U(VI)-citrate complex.

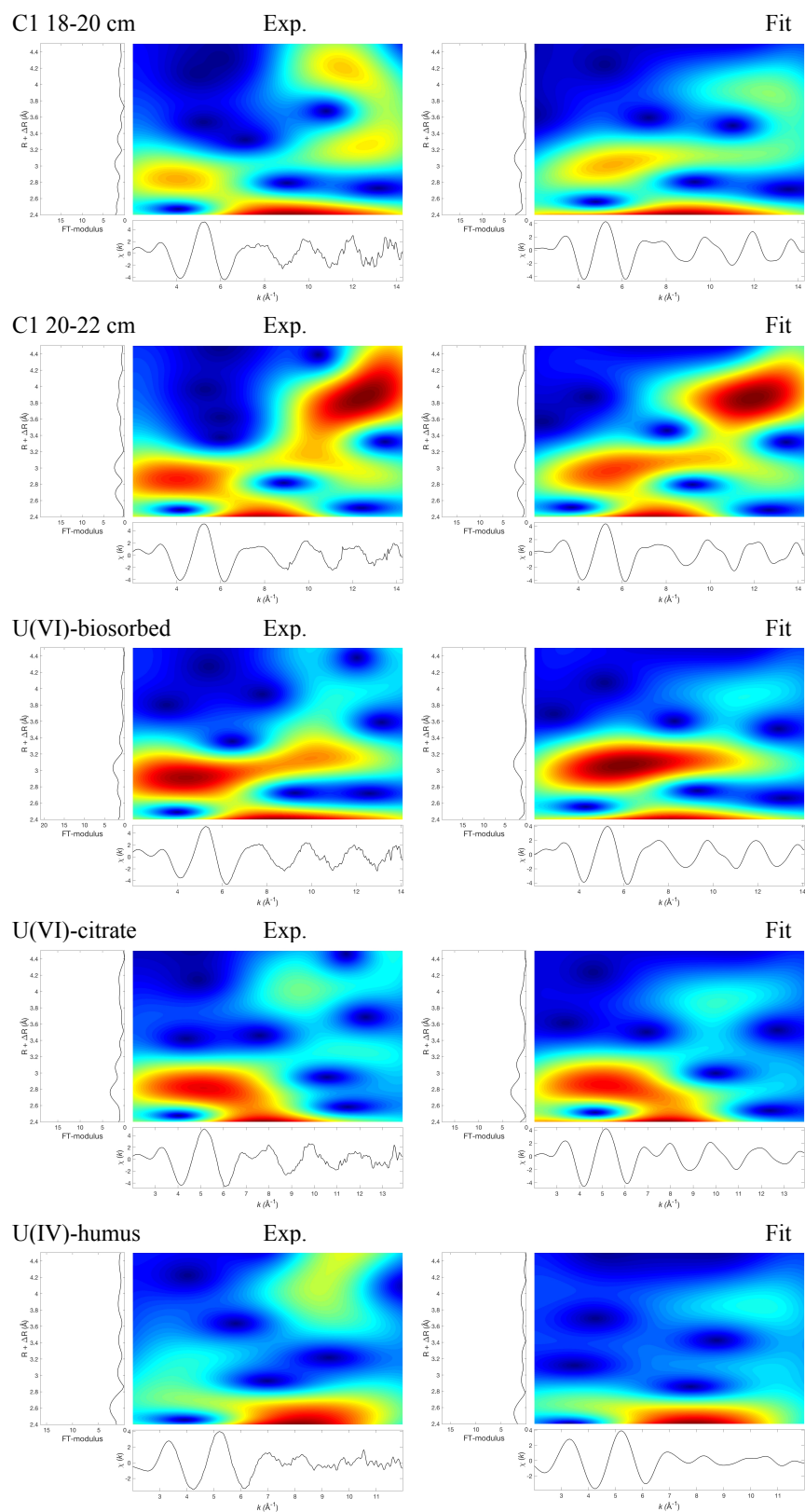
898 Shell-by-shell fitting results for the U(IV)-humus model compound sample (Table 2,
899 Figure 10) confirmed previous results reported by Stetten et al. (2018a) for the same sample,
900 with again contributions from second neighbor P/Si atoms at 3.1 Å and C atoms at 3.5 Å,
901 attributed to bidentate and monodentate binding to U(IV) in 8/9-fold coordination to oxygen.



902

903 *Figure 10 - Shell-by-shell fitting of unfiltered k^3 -weighted U L_3 -edge EXAFS data (left) and*
 904 *corresponding Fast Fourier Transforms (FFT, right) for wetland soil samples C1 18-20 cm*
 905 *and C1 20-22 cm and for the three model compounds used in our LCF analysis (U(VI)-*
 906 *biosorbed, U(VI)-citrate and U(IV)-humus). The main second-neighbor contributions to the*
 907 *EXAFS are indexed by dotted vertical lines. The experimental and fit curves are displayed in black*
 908 *and red color respectively. The corresponding fitting parameters are reported in Table 2.*

909



910

911 **Figure 11** – Continuous Cauchy Wavelet Transform of experimental (exp, left) and shell-by-
 912 shell fitted (fit, right) unfiltered k^3 -weighted $U L_3$ -edge EXAFS data for wetland samples C1
 913 18-20 cm and C1 20-22 cm and for the three model compounds used in our LCF analysis
 914 (U(VI)-bisorbed, U(VI)-citrate and U(IV)-humus). The corresponding fits are plotted in
 915 *Figure 10*. Similar z-scales were used to allow comparison.

916 **Table 2 – Results of shell-by-shell fitting of U L₃-edge EXAFS data for wetland soil samples**
 917 **C1 18-20 cm and C1 20-22 cm, and selected model compounds (U(VI)-biosorbed, U(VI)-**
 918 **citrate and U(IV)-humus).** References for model compounds data are given in [Table S5](#). The
 919 number of neighbors (CN) for the axial oxygen of uranyl ion together with associated multiple
 920 scattering paths (UO_{ax} MS including 2xUO₀’, 2xUO_{UO}’ and 2xUO_{UO}) were fixed to values expected
 921 from the U(VI)/U(IV) ratio determined from XANES LCF analysis ([Table S4, Figure S12](#)). The CN
 922 parameter values were fixed to acceptable values for second neighbor shells in order to provide
 923 physically meaning coordination geometry, in which the number of U-O bonds resulting from
 924 bidentate and monodentate complexes does not exceed the number of equatorial oxygen atoms.
 925 Fitting parameters included interatomic distance (R) of every backscattering path included, Debye-
 926 Waller parameter (σ) for each coordination shell, and overall energy difference (ΔE₀) between the
 927 user-defined and the ab-initio (Feff8) threshold energies. Parameter values indicated by (-) were
 928 linked to the parameter value placed above in the table and those followed by (*) were fixed. The fit
 929 quality was assessed by a reduced chi-square (Chi²_R); uncertainties given in brackets relate to the
 930 last digit of each parameter and were estimated to 99.7 % confidence (3 sigma) (See Materials and
 931 Methods section). The U-U path is needed to match the CCWT (see [Figure S15](#)).

Sample	path	R (Å)	CN	σ (Å)	ΔE ₀ (eV)	Chi ² _R
C1 18-20 cm	U-O	1.797(4)	1.8*	0.051(2)	3.3(11)	17.2
	U-O _{ax} MS	3.58*	5.4*	-	-	-
	U-O	2.361(4)	2.9(3)	-	-	-
	U-O	2.519(8)	2.5(4)	-	-	-
	U-P/Si	3.06(2)	0.5*	0.054(11)	-	-
	U-C	3.47(3)	2.0*	-	-	-
	U-U	4.06(2)	0.3*	0.05(2)	-	-
C1 20-22 cm	U-O	1.775(3)	1.8*	0.055(2)	0.7(9)	7.5
	U-O _{ax} MS	3.58*	5.4*	-	-	-
	U-O	2.336(6)	2.7(2)	-	-	-
	U-O	2.483(7)	2.3(3)	-	-	-
	U-P/Si	3.07(1)	0.5*	0.058(7)	-	-
	U-C	3.47(2)	2*	-	-	-
	U-U	3.975(7)	0.3*	0.025(9)	-	-
U(VI)-biosorbed	U-O	1.802(3)	2*	0.057(2)	4.3(11)	9.9
	U-O _{ax} MS	3.58*	6*	-	-	-
	U-O	2.350(7)	2.2(2)	-	-	-
	U-O	2.506(9)	1.8(4)	-	-	-
	U-P/Si	3.06(3)	0.5*	0.07(1)	-	-
	U-C	3.50(2)	3*	-	-	-
	U-U	4.01(2)	0.3*	0.06(2)	-	-
U(VI)-citrate	U-O	1.791(4)	1.8*	0.060(3)	1.9(12)	13.9
	U-O _{ax} MS	3.58*	6*	-	-	-
	U-O	2.373(7)	2.8(2)	-	-	-
	U-O	2.506(8)	2.8(3)	-	-	-
	U-C	2.95*	1*	0.06(2)	-	-
	U-C	3.32(3)	2.5*	-	-	-
	U-C	3.48(2)	2.5*	-	-	-
U-U	4.04(2)	0.5*	0.07(2)	-	-	
U(IV)-humus	U-O	1.73(2)	0.6*	0.06(1)	4.3(26)	13.3
	U-O _{ax} MS	3.58*	1.8*	-	-	-
	U-O	2.25(3)	4.1(9)	0.09(2)	-	-
	U-O	2.41(3)	5.0(12)	0.06(1)	-	-
	U-P	3.04(3)	0.5*	-	-	-
	U-C	3.48(7)	1.0*	-	-	-
	U-U	3.93(5)	0.3*	0.07(3)	-	-

973 The lower quality of the U L_3 -edge EXAFS spectra of the other soil samples from cores C1 and
974 C2 precluded a reliable shell-by-shell analysis. However, as indicated above, LC fitting of these
975 EXAFS spectra produced similar results for all soil samples (Table S6, Figure S14) including the
976 well-characterized C1 18-20 cm and 20-22 cm samples also analyzed by shell-by-shell fitting
977 (Table 2, Figures 10, 11 and S15). Consequently, the molecular environment of U in all soil
978 samples is expected to be dominated by contributions of bidentate and monodentate complexes
979 with Si/P (~ 3.1 Å) and C (~ 3.5 Å) atom neighbors, respectively. The presence of minor U-U
980 contributions is uncertain but cannot be excluded since these contributions were detected in the
981 model compounds used for LCF (Table 2, Figures 10 and 11).

982 Altogether, the results of XAS analyses indicate that U(VI) and U(IV) are mainly sorbed to
983 organic matter and potentially mineral surfaces (since Si neighbors could be present), in
984 agreement with microscopic observations that show U association with organic soil constituents
985 (Figures 5 to 7). The detection of U-U paths in some samples also suggests the minor presence of
986 polymeric or condensed U phases.

987 **3.6. Bicarbonate extraction of noncrystalline U**

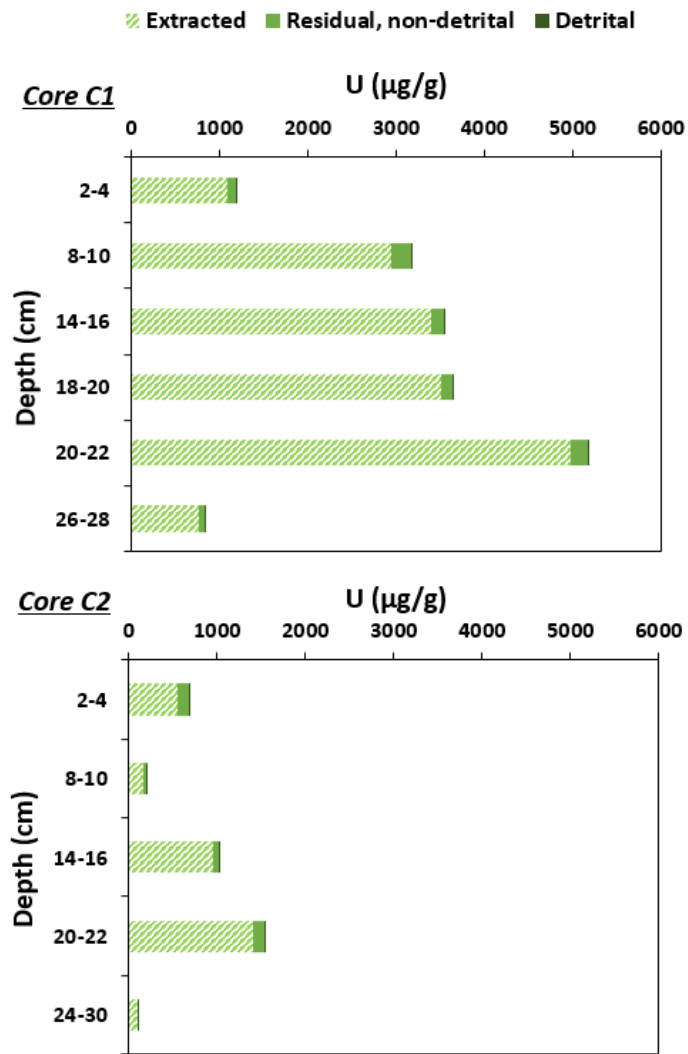
988 The 1 M bicarbonate extractions of soil samples resulted in the dissolution of most solid-
989 state U: 92 to 96 % in samples from core C1 and 82 to 93 % in samples from core C2 (Figure 12).
990 The bicarbonate-extracted U fraction is expected to be essentially composed of available
991 noncrystalline U(VI) and U(IV) (Noël et al., 2019) but may also comprise some soluble
992 crystalline U(VI) phases that may be extracted in the presence of high bicarbonate
993 concentrations such as uranyl hydroxide (Bargar et al., 2008). The high percentages of extracted
994 U are in accordance with the abundance of mononuclear U species detected by EXAFS
995 spectroscopy. Moreover, extraction of 96% of U in sample C1 20-22 cm indicates that the
996 condensed U phases detected by EXAFS (Figure 10) were almost completely extracted. This
997 result suggests that these phases are either noncrystalline, consisting of polymeric/clustered U
998 species dispersed and sorbed to the organo-mineral soil matrix, either crystalline but soluble in
999 1 M HCO_3^- .

1000 Considering the uncertainty (± 9 % of total U) of the bicarbonate extraction method as
1001 estimated from replicates (see section 2.4), the residual – non extracted – fraction is almost
1002 negligible in core C1 ($4-8 \pm 9$ % of total U), but more significant in core C2 ($7-18 \pm 9$ % of total
1003 U). The residual fraction is expected to be composed of a minor fraction of detrital U (generally
1004 < 1 % of total U as estimated from U/Th ratios (Figure 2c)) and of sparingly soluble mineral or
1005 polymeric U-bearing phases. The detrital U fraction indeed accounts for only 1-11 % of the

1006 residual U in all samples, except for sample C2 24-30 cm where a large part of residual U
1007 (88 ± 61 %) is detrital.

1008 LC fitting of the XANES spectra of two residual solids showed U oxidation states comparable
1009 to those of the initial samples (Table 1) within uncertainties, i.e. 81 ± 5 % U(VI) in the residue of
1010 C1 20-22 cm and 43 ± 9 % U(VI) in the residue of C2 2-4 cm (Table S7, Figure S18). This result
1011 shows that the residual U phases after bicarbonate extraction are not enriched in U(IV) with
1012 respect to the initial species. EXAFS spectra of the residual solids were of too low quality to
1013 allow proper shell-by-shell fitting of the data and to discuss the possible presence of crystalline
1014 U phases (*data not shown*).

1015 Interestingly, 10 to 42 % of the initial ^{232}Th content was found to be leached by the 1 M
1016 bicarbonate solution. This indicates that in organic-rich wetland soils, a significant fraction of
1017 ^{232}Th may be associated to labile phases, for example to organic colloids (e.g., Bednar et al.,
1018 2004). As a consequence, the percentage of detrital U –estimated from $^{238}\text{U}/^{232}\text{Th}$ ratios to be
1019 mostly < 1 % (Table 1, Figure 2c) – may be slightly overestimated.



1020

1021 *Figure 12 - Results of 1 M bicarbonate extractions of noncrystalline U in soil samples from*
 1022 *cores C1 (top) and C2 (bottom). Repartition in µg/g U of the bicarbonate-extracted (light green),*
 1023 *residual, non-detrital (medium green) and detrital (dark green) U fractions.*

1024 4. DISCUSSION

1025 The structure and chemistry of wetland environments such as that of Lake Nègre are largely
1026 driven by hydrological processes. First, at the wetland scale, the spatio-temporal dynamics of
1027 ground- and running surface waters exerts an important control on solutes and particles supply.
1028 Second, at the pore scale, complex reactive transport processes take place and regulate U
1029 mobility by controlling the spatio-temporal input of nutrients, oxidants and reductants, and by
1030 subsequently driving the local microbial activity. For instance, the local U supply may depend on
1031 the position relative to the spring input (e.g., Owen and Otton, 1995), and the lateral and vertical
1032 flow influence the soil redox dynamics and therefore the U mobility within the soil layers and
1033 outside of the wetland (e.g., Wang et al., 2013, 2014; Stetten et al., 2018a). For these reasons, and
1034 even in the absence of a detailed study of the wetland hydrology, the discussion below relies on
1035 some first order hypotheses on the wetland hydrology as a background rationale to interpret
1036 our dataset.

1037 ***4.1. Biogeochemical characterization of the wetland soils***

1038 *4.1.1. Environmental and redox conditions of the wetland soils*

1039 The studied wetland soils might actually be compared to alluvial sediments. They indeed
1040 developed on a flat area at the confluence of the two main creeks of the watershed that flow into
1041 Lake Nègre (Figure 1). In such a topographic setting, erosion is expected to be low and the main
1042 components of the wetland soils are thought to be (i) detrital materials (granitic primary and
1043 secondary minerals and vegetal debris) originating from upstream physical erosion and
1044 (ii) autochthonous materials, such as organic materials from plants and microorganisms that
1045 thrive in the wetland as well as secondary minerals formed by chemical weathering of the
1046 detrital granitic material. Such mineral phases have been identified in both cores by XRD and Fe
1047 K-edge XAS (Figures S5 and S7).

1048 The texture of the cores points toward an intermediate soil-sediment status, with an
1049 apparent stratigraphy (also apparent in the radionuclide regrowth profile, Figure 3) that
1050 appears to be overlapped by soil water flow in the underlying granitic sand, and crossed by the
1051 vertical penetration of plant roots. Incidentally, the latter prevents any confident radiocarbon
1052 dating. For simplicity, we will continue to refer to “soils” in the following discussion.

1053 The oxidation-reduction conditions in the soil pore water at both core locations are hardly
1054 predictable as our dissolved oxygen measurements may be overestimated close to the water-air
1055 interface. We hypothesize that the O₂ supplied by creeks or diffusing from the atmosphere is
1056 consumed by aerobic microbial activity in these organic soils. Overall, the soil redox conditions
1057 are probably controlled by seasonal variations of the water table, from fully reducing conditions

1058 when the soils are waterlogged (particularly during snowmelt) to more oxidizing conditions in
1059 dry periods (such as the time of sampling in September).

1060 These global oxidizing conditions are in line with the Fe and U oxidation states observed in
1061 bulk soil samples, that are dominated by Fe(III) (69 to 88 % of total Fe, [Table S1 and Figure S7](#))
1062 and U(VI) ([Table 1, Figure 8](#)). However, significant proportions of reduced, labile (organic-
1063 bound) Fe(II) and U(IV) species are noted, which is consistent with the fact that soil waters are
1064 overall suboxic (e.g., Maher et al., 2013).

1065 *4.1.2. Characterization of the soil organic matter*

1066 The two soil cores strongly differ in their organic matter content and composition. Core C1
1067 contains relatively low OM amounts (~10 wt% TOC) with low C/N ratios around 12.7
1068 ([Figure S6](#)), indicative of low-cellulose plants, probably driven toward lower C/N by abundant
1069 algae such as diatoms (Meyers and Teranes, 2001). The upper half of core C2 is much more
1070 organic-rich (~40 wt% TOC) because of abundant cellulose-rich plant remains characterized by
1071 high C/N (Meyers and Teranes, 2001). The measured C/N ratios in the wetland soils consistently
1072 match the range of “meadow-type environment” determined in our study of the Lake Nègre
1073 sedimentary OM (Lefebvre et al., 2021b). C/N values slightly higher than 20 – corresponding to
1074 “heathland/forest-type environments” – are recorded at depth in core C2. These ratios could
1075 indicate the past development of more cellulose-rich plants (such as shrubs) producing now-
1076 buried higher-C/N plant remains, potentially between 4.5 and 2.4 kyr before present (BP)
1077 (Lefebvre et al., 2021b).

1078 These differences between cores C1 and C2 are attributed to their contrasting depositional
1079 environments ([Figure S1](#)). Core C1 was collected under stagnant water, where algae can thrive
1080 and where relatively few vegetal remains are produced and deposited. Core C2 was taken in the
1081 bed of a seasonal stream, where algae are scarcer and vegetal remains can settle along the flow
1082 path.

1083 *4.2. Uranium supply to the wetland*

1084 As the U concentrations measured in the wetland soils (up to 5200 µg/g) are far above the U
1085 content of the bedrock (2-6 µg/g, (Lefebvre et al., 2021a)), it is evident that U was transported
1086 from upstream in the watershed and then accumulated in the wetland soils. This is further
1087 supported by high U concentrations in the creeks (~10 µg/L). We hypothesize that U initially
1088 originates from an unidentified U-rich body with higher U content than the sampled granitic
1089 bedrock, either non-sampled or located beneath the surface, and releasing U through chemical
1090 erosion and transport in fracture networks of the granite (e.g., Schumann et al., 2017). Indeed,
1091 the high ($^{234}\text{U}/^{238}\text{U}$) activity ratios of creek waters and soils, above secular equilibrium

1092 (Figure 3), unsurprisingly indicate that U originates from chemical erosion of the granitic
1093 bedrock and was further transported as dissolved/colloidal species before binding to particles
1094 and accumulating in the wetland soils. This is corroborated by the very low detrital U content in
1095 the soil cores (Table 1, Figure 2), which supports the authigenic origin of U. As the stream waters
1096 are well oxygenated, U is presumably transported as U(VI) in running waters.

1097 The apparent decrease in dissolved U concentrations along the eastern stream path
1098 (Figure 4) may be explained either by dilution from other creeks with lower U concentrations, or
1099 by U scavenging in the soils along the hydrological path (between PI1 and SCE1), including in the
1100 wetland itself (between SCE1 and ES1). The hydrological setting observed on the field at the
1101 time of sampling would support the second hypothesis, as no visible confluent creeks were
1102 found. Following this assumption, the upstream watershed soils and the wetland would most
1103 probably act as a partial U sink at the time of sampling. Along the eastern stream path, our
1104 measurements suggest that a fraction of uranium is scavenged in the soils while physical erosion
1105 leads to the transport of U-bearing particles (Figure 4). The drastic drop of U concentrations
1106 between sampling points ES1 (wetland outlet) and ES2 (20 m downstream in the lake) could be
1107 explained by dilution in the lake of the U-rich creek coupled to the deposition of large U-bearing
1108 particles on the lake platform (Figure 1). These observations are in line with our previous
1109 hypothesis stating that U was supplied to Lake Nègre sediments through soil erosion (Lefebvre
1110 et al., 2021b). One should however keep in mind that the analyzed waters only provide an
1111 instantaneous picture of the U budget at the time of sampling. A full understanding of the U cycle
1112 in the Lake Nègre watershed would require high frequency sampling throughout the entire
1113 seasonal hydrological cycle, including during high precipitation events, which was not
1114 achievable.

1115 The U concentration in the western stream (points E3, ES3) appears to slightly increase after
1116 crossing the wetland (Figure 4). This observation could be explained by seeping of the stream
1117 water through the wetland soils leading to minor U export under dissolved species, as no
1118 significant U-bearing particles were detected at the outlet (ES3).

1119 **4.3. Modes of authigenic U accumulation**

1120 *4.3.1. Sorption on organic matter likely governs U accumulation*

1121 The $\delta^{238}\text{U}$ isotopic composition of the soil samples from cores C1 and C2 was shown to be
1122 indistinguishable from the stream waters sampled up- and downstream of the wetland
1123 (Figure 3). If the sampled waters $\delta^{238}\text{U}$ were considered representative of the $\delta^{238}\text{U}$ of the U
1124 source to the wetland – which may be questionable but remains consistent regarding the
1125 similarity with the bedrock $\delta^{238}\text{U}$ –, the absence of any significant isotopic fractionation between

1126 aqueous and solid-phase U points toward U sorption to the soils as the dominant U scavenging
1127 mechanism. Uranium sorption to OM and soil minerals is indeed documented to result in a 0 to -
1128 0.4 ‰ isotopic fractionation, adsorbed U being lighter than aqueous U (Brennecke et al., 2011;
1129 Shiel et al., 2013; Dang et al., 2016; Jemison et al., 2016; Chen et al., 2020). Given the complexity
1130 of the soil matrix and considering potential U sorption on particles and colloids prior to
1131 scavenging in the wetland soils, it is not surprising to observe such low isotopic effects in the
1132 wetland. The measurement of slightly isotopically heavier U in the outlet waters compared to
1133 inlet water is in line with this sorption hypothesis. The presumed low formation of stable U(VI)-
1134 calcium carbonate complexes in the aqueous phase (because of low DIC and Ca in the creeks)
1135 may actually have favored U association with the solid phase. Conversely, higher carbonate
1136 concentrations (for example in case of a limestone bedrock) would likely have resulted in less U
1137 accumulation in the soils, although not provable here.

1138 The identification of sorption as the dominant U scavenging mechanism would be consistent
1139 with the distribution, redox and speciation of U in the soils. Uranium was shown to be dispersed
1140 on a variety of phases, especially organic particles, with variable accumulations that are
1141 attributed to heterogeneous affinities of the adsorbing substrates for U (Figures 5 to 7). Most U
1142 is present as U(VI), indicating that U reduction may not be the only required mechanism for U
1143 partitioning in the solid phase. The U speciation determined by EXAFS to be dominantly
1144 mononuclear/noncrystalline, with U bound essentially to organic C moieties in monodentate
1145 coordination, and the high extent of U extraction by 1 M bicarbonate also support U sorption as
1146 the main U fixation process. Incidentally, U binding to C-rich molecules is thought to be the main
1147 cause of beam-damage, here U(VI) photo-reduction under the synchrotron beam, which we
1148 overcame by using cryogenic temperatures (Charlet et al., 2011) and/or moving on the sample
1149 between each measurement (see Materials and Methods section). Monodentate binding of U(VI)
1150 to C moieties of humic substances is consistent with the previous results of the EXAFS study of
1151 highly U-contaminated wetland soils (Stetten et al., 2018a, 2020) and differ from bidentate
1152 binding to C reported by Mikutta et al. (2016), which might be explained by a 10-fold lower U
1153 loading in this latter study. In this context, the observation of significant U-U paths by EXAFS
1154 could be interpreted as polymers or clusters of U atoms sorbed to organic moieties.

1155 The high U contents recorded on organic particles including vegetal remains (Figures 5 to 7)
1156 – up to more than 3 at% – indicates the presence of binding sites with very high affinity for U.
1157 The type of U-binding organic moieties could not be determined, but we suspect that S and Ca
1158 play a major role, as all three elements contents are well correlated at the micro-scale (Figure 6).

1159 *4.3.2. Implications for U redox processes*

1160 One interesting finding of this study is that the U oxidation state at the micro-scale in one
1161 sample (C1 18-20 cm) was found to be homogeneous despite the variety of observed U-bearing
1162 phases (Table S3, Figure 7). This redox homogeneity could be interpreted as a direct
1163 consequence of the U speciation: the dispersion of sorbed U on OM surfaces (mononuclear or
1164 even polymeric, rather than incorporated into mineral grains) may favor a spatially
1165 homogeneous reduction rate by facilitating the electron transfers. It would thus enable all U
1166 atoms/complexes to follow the local redox conditions. To this regard, Stetten et al. (2020) have
1167 shown that U sorbed to OM in a heavily U-contaminated wetland could be fully reduced or
1168 oxidized within a few weeks during simulated flooding or drying periods, respectively.

1169 Interestingly, the residual U fractions after 1 M bicarbonate extraction have a comparable U
1170 oxidation state to that of the initial soil sample and are still dominated by U(VI) (Tables 1 and S7,
1171 Figure S18). This residual fraction, which is non-detrital (see Section 3.6), may be composed of
1172 crystalline or highly polymeric U phases that could not be found by microscopic analyses but
1173 were detected by EXAFS, with significant U-U path contributions in most samples. These
1174 insoluble U phases contain high proportions of U(VI) and are therefore not reduced U(IV)
1175 crystalline phases such as UO₂ that could be expected as products of natural U(VI) reduction
1176 (e.g., Noël et al., 2017).

1177 Although the U oxidation state is dominated by U(VI), significant proportions of U(IV) are
1178 detected. As U was supplied to the wetland by well-oxygenated streams, i.e., presumably in U(VI)
1179 forms, this means that a fraction of U(VI) was reduced to U(IV) within the wetland. A remaining
1180 question is the timing of such U(VI) reduction, before or after U(VI) sorption. $\delta^{238}\text{U}$ isotopic
1181 ratios are complementary of the redox and speciation analyses and may help in solving this
1182 issue. Direct reduction of aqueous U(VI) to U(IV) would likely have resulted in the incorporation
1183 of poorly soluble U(IV) in the solid phase following precipitation or sorption, and to an
1184 associated isotopic fractionation of ~ 1 ‰ (U(IV) being isotopically heavier than U(VI)), whether
1185 this reduction be abiotic or microbially-mediated (Basu et al., 2014, 2020; Stirling et al., 2015;
1186 Stylo et al., 2015; Dang et al., 2016; Brown et al., 2018). Conversely, the reduction of already
1187 adsorbed U(VI) should result in low fractionation factors ≤ 0.2 ‰ (Brown et al., 2018). Since we
1188 do not observe any isotope fractionation between stream waters and soils, neither between soils
1189 with different U(IV) contents, we infer that U(VI) reduction occurred after its sorption on the
1190 soil matrix. Sorption on organic matter may actually facilitate electron transfers, in conjunction
1191 with bacterial activity (Bargar et al., 2013; Bone et al., 2017b). The extent of U reduction may be
1192 driven by local redox conditions, either at the sample (centimetric) scale if the pore waters were
1193 actually anoxic, or in micro-environments where low permeability and high oxidant

1194 consumption rate favor reducing conditions. The detection of low but significant U(IV) in many
1195 U-bearing phases of sample C1 18-20 cm (Table S3, Figure 7) seems to favor the first hypothesis,
1196 but further μ -XANES investigation of other samples with higher U(IV) would be necessary to rule
1197 out or confirm the role of reducing micro-environments. Higher U(IV) proportions of ~50 % are
1198 notably measured in the upper (2-4 cm) samples of both cores C1 and C2. This observation could
1199 indicate that the soil redox conditions would be controlled by underground water flow. In
1200 particular, based on the stratigraphy of the cores and the mineral content of the observed layers,
1201 we could hypothesize that the more oxidizing conditions at depth could be linked to higher
1202 water circulation in more permeable layers, whereas lower permeability in the upper layers
1203 would result in lower oxidant penetration and thus more reducing conditions. Thus, subsurface
1204 water flow may also play a role in the vertical heterogeneity of U concentrations. In addition,
1205 higher microbial activity near the surface could also influence the soil redox conditions.

1206 Anecdotally, the absence of significant U(V) contribution in the soil samples (Figure 8) as an
1207 intermediate state between U(VI) and U(IV) may be explained by the U speciation dominated by
1208 mononuclear OM-associated species. This speciation may have prevented any stabilization of the
1209 metastable U(V) which has been observed upon U incorporation or sorption in/to Fe minerals
1210 (Ilton et al., 2005, 2012; Pidchenko et al., 2017). This finding is in line with previous
1211 observations of no to very low U(V) in both U mining-impacted wetland soils (Le Pape et al.,
1212 2020) and pristine organic-rich soils (Fuller et al., 2020).

1213 No major differences were noted in the processes of U accumulation in cores C1 and C2,
1214 despite a discrepancy in the amplitude of U accumulation (Table 1, Figure 2). We hypothetically
1215 attribute this difference to lower U supply at core C2 location than at core C1, possibly due to a
1216 different position with respect to the hydrological flow paths in the wetland network (Schumann
1217 et al., 2017). Core C1 was taken in a permanently flooded area where the water residence time is
1218 thought to be higher than at core C2, where a seasonal stream and underground water flow are
1219 the only potential U sources. Overall, our data indicate that the U accumulation mechanisms (U
1220 sorption to organic matter) are rather homogeneous at both cores locations despite their
1221 diverging mineralogical and organic compositions.

1222 **4.4. Uranium mobility in the wetland soils**

1223 *4.4.1. Mechanisms of U mobility*

1224 The heterogeneous vertical distribution of U concentrations in cores C1 and C2 suggests that
1225 the underground water flow is involved in U accumulation. As a corollary, such water circulation
1226 may also induce horizontal and vertical U mobility in the wetland soils subject to hydrological
1227 fluctuations (Wang et al., 2014; Bone et al., 2017a; Stetten et al., 2018a; Lefebvre et al., 2019;

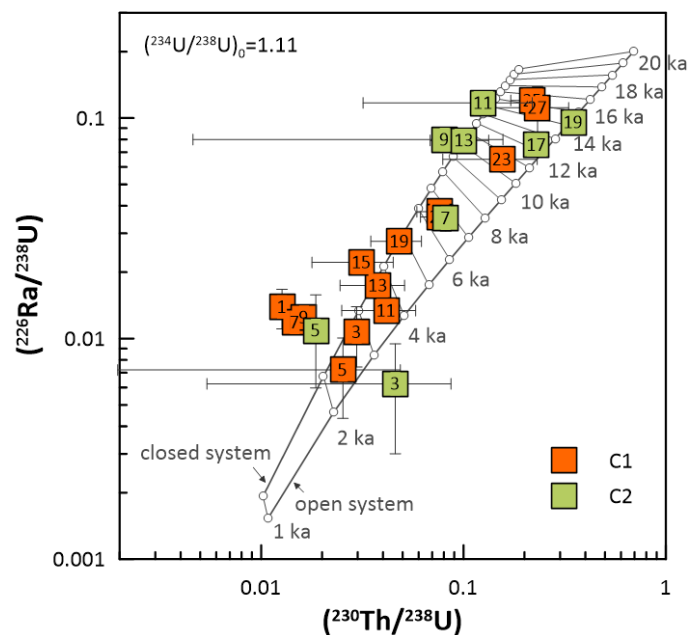
1228 Noël et al., 2019). Seasonal changes in the soil water chemical composition and redox could
1229 indeed cause U desorption and further re-sorption elsewhere, i.e., downstream and/or in an
1230 upper or lower soil layer where conditions are favorable to U fixation.

1231 Such mechanisms of U mobility in the wetland soils may provide a satisfactory explanation
1232 to the soil ($^{234}\text{U}/^{238}\text{U}$) ratios that are lower than the stream waters ratios (1.155 and 1.129)
1233 upstream from the wetland (Figure 3). The detrital U fraction at secular equilibrium being very
1234 low, such lower ratios could be explained by a loss of ^{234}U in the wetland soil, assuming that the
1235 measured ($^{234}\text{U}/^{238}\text{U}$) values in the upstream creeks are representative of the U source to the
1236 wetland soils. Even in noncrystalline U phases, the alpha-recoil effect during the production of
1237 ^{234}U from ^{238}U decay may make ^{234}U more mobile compared to its parent ^{238}U , especially through
1238 direct recoil of ^{234}Th into the pore water followed by its fast decay to ^{234}U , or by increasing the
1239 releasing ability of ^{234}U through damaging of the binding site (Chabaux et al., 2003). Following
1240 this hypothesis and assuming that the ($^{234}\text{U}/^{238}\text{U}$) ratio of U initially deposited in the wetland
1241 would be in the 1.13-1.15 range, the lower activity ratio (1.11) observed in the soils would
1242 roughly imply that a major fraction of ^{234}U produced by ^{238}U decay over the past ~10 kyr would
1243 have been leached. Such an assumption would be consistent with the estimated age of the oldest
1244 fraction of U found at depth in cores C1 and C2, as discussed in the next section. Alternatively,
1245 the low soil ($^{234}\text{U}/^{238}\text{U}$) ratios may possibly result from other sources of U to the wetland, for
1246 instance via subsurface water circulation.

1247 4.4.2. Age constraints on U accumulation

1248 The radioactive disequilibria in the ^{238}U decay chain (Figure 3a) were used to estimate age
1249 constraints on U accumulation, and roughly assess U and Ra losses caused by several thousand
1250 years of chemical erosion of the wetland. Although no precise geochronology can be established,
1251 the wetland is thought to have been developing since the end of the last deglaciation that
1252 occurred probably between 14,500 and 13,000 years BP in the Mediterranean Alps at this
1253 elevation (Brisset et al., 2015). The apparent regrowth with depth of radionuclides of the ^{238}U
1254 decay chain (^{230}Th , ^{226}Ra) (Figure 3a) can be partially interpreted based on this maximum age.
1255 The influence of radionuclide migration on ($^{226}\text{Ra}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) activity ratios in the C1
1256 and C2 cores was evaluated using a simple open system age model, detailed in the
1257 *Supplementary Material* (page 26) and based on the Bateman equations on which first-order rate
1258 constants (yr^{-1}) describing the release of radionuclides were added. We corrected the
1259 ($^{226}\text{Ra}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) from their detrital components using ($^{238}\text{U}/^{232}\text{Th}$) ratios, assuming
1260 secular equilibrium in detrital minerals; the corrected ratios show little to no difference with
1261 raw ratios in most samples. Our qualitative model is based on the assumption that authigenic U
1262 (^{238}U and ^{234}U , with an activity ratio of 1.11) was deposited without any daughter ^{230}Th and ^{226}Ra

1263 (see section 3.2). Then, the processes taken into account were losses of ^{226}Ra and ^{234}U , ^{238}U and
 1264 radioactive decay of the $^{238}\text{U} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow ^{226}\text{Ra}$ chain. ^{230}Th was considered as immobile.
 1265 The intermediate daughter radionuclides of the decay chain (^{234}Th and ^{234}Pa) were ignored
 1266 because their half-lives are too short to consider significant diffusion from the production site.
 1267 Overall, our model relies on strong assumptions and thus only provides a qualitative overview of
 1268 the age of U accumulation and of U and Ra mobility in the wetland soils.



1269
 1270 **Figure 13 – Age constraints on U accumulation in soils of cores C1 (orange) and C2 (green)**
 1271 **using radioactive disequilibria ($(^{230}\text{Th}/^{238}\text{U})$ and $(^{226}\text{Ra}/^{238}\text{U})$).** Authigenic activity ratios
 1272 (corrected from detrital components) are plotted with Concordia curves corresponding to a closed
 1273 system (upper curve) and an open system accounting for U and Ra losses (lower curve), with
 1274 corresponding ages (in ky). The numbers in squares correspond to sample depths in the cores
 1275 (in cm). See text for details on the open system model.

1276 As shown in **Figure 13**, all authigenic $(^{226}\text{Ra}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ activity ratios fall in the
 1277 range of a closed system Concordia curve, confirming that ^{226}Ra and ^{230}Th likely originate from
 1278 ^{238}U decay in the wetland soils after U accumulation. Even without accounting for U losses, the
 1279 apparent maximum age of U deposition is consistent with the expected maximum age of the
 1280 wetland at ~ 14500 y BP (Brisset et al., 2015). We then applied our open system model by
 1281 allowing U and Ra loss constants to vary, in order to fit most of the data points within a
 1282 maximum age of 14500 y (see *Supplementary Material* pages 26-27). In **Figure 13**, Ra loss results
 1283 in a downward shift of the Concordia curve, while U release affect the age on a given point: the
 1284 more U is lost, the younger the Concordia points.

1285 Our model provides an estimation of the mean age of U accumulation in the wetland soils,
 1286 which may be considered as an approximate age of soil formation, with high uncertainties due to

1287 radionuclide losses. Accordingly, the calculated soil ages span a range from 14.5 to 2-3 kyr BP
1288 and are consistent with the sample depths: deep soils generally appear to be older than upper
1289 soils (Figure 13). A few discrepancies are observed, that are attributed to differences in the soil
1290 texture and subsequent ability to accumulate and release U through hypothetical variations in
1291 groundwater circulation. For example, the soil in core C2 at 11 cm (sample 10-12 cm, containing
1292 250 µg/g U) seems older than the underlying soil sample at 13 cm (12-14 cm, 860 µg/g U). This
1293 may indicate that the soil layer at 11 cm lost a significant U amount (and no significant Ra) and
1294 thus artificially appears older than the soil below.

1295 A few upper soil samples, especially from core C1, appear to have gained Ra as they are
1296 plotted above the closed system Concordia (Figure 13). This suggests that while most soil layers
1297 released some U and Ra over the past thousand years – thus behaving as U and Ra sources –,
1298 some other layers acted as sinks and accumulated a fraction of the released radionuclides,
1299 highlighting their vertical mobility.

1300 5. CONCLUSIONS

1301 The present study combines a series of complementary geochemical and mineralogical
1302 techniques to provide a comprehensive view of the U scavenging mechanisms in two soil cores
1303 sampled in a natural mountainous wetland impacted by U supply for ~14500 y. In the Lake
1304 Nègre wetland, U likely originates from a (yet unidentified) U-rich source rock within the granite
1305 massif, the interaction of which with meteoric waters supplies dissolved U that is transported to
1306 the surface and subsequently to the wetland by running stream waters. This continuous U
1307 supply over thousands of years resulted in considerable U accumulation by organic
1308 complexation in the wetland soils, essentially in noncrystalline/mononuclear forms.

1309 Bulk and μ -XAS revealed that U is mostly present as mononuclear U(VI) sorbed to carboxyl
1310 groups of organic matter, and, to a lesser extent, as polymeric U(VI) species at least in the
1311 U-richest samples (3000 – 5000 $\mu\text{g/g}$ U). Both mononuclear and polymeric phases were
1312 extracted by 1 M bicarbonate (82-96 %). From a methodological standpoint, our extensive
1313 analyses using XAS at the U L_3 - and M_4 -edges shows that samples containing noncrystalline U
1314 species are affected by photo-reduction, which could be overcome by dynamic acquisition of
1315 short spectra on different spots. According to μ -XRF and MEB-EDX analyses, U was dispersed on
1316 a large variety of mostly organic structures, with different concentrations attributed to variable
1317 affinity of U for the binding sites. Measurement of U isotopic ratios ($\delta^{238}\text{U}$) within the inlet/outlet
1318 waters and soils supported the idea that U sorption is the primary U scavenging mechanism in
1319 the studied organic wetland soil. Qualitative analyses of isotopic disequilibria in the U decay
1320 chain suggest that a fraction of U may have been scavenged for several thousand years in the
1321 wetland, especially in the deepest layers of the studied cores. Over such a long storage period,
1322 noncrystalline U species did not significantly evolve toward more crystalline phases. The minor
1323 detection of condensed, polymeric U species may be due to high U loadings in some of the
1324 studied soil layers rather than U aging. In contrast, an evolution toward U(IV)-Si polymeric
1325 species was recently reported as a result of diagenetic evolution of mononuclear U(IV) in the
1326 anoxic Lake Nègre sediments (Lefebvre et al., 2021a). The difference here is that the observed
1327 polymeric phases consist mostly of U(VI) and may have developed under oxidizing or fluctuating
1328 suboxic conditions.

1329 The combination of mineralogical and isotopic techniques does not support significant direct
1330 reduction of aqueous U(VI) to solid U(IV) as the U scavenging process in the wetland soils. Such
1331 process, if any, is thus not responsible for the exceptional U accumulation in the Lake Nègre
1332 wetland, but rather is the sorption of U(VI) onto OM. The observed U(IV) proportions, that can
1333 reach ~50 % in the upper soil layers, are essentially due to reduction occurring after U(VI)
1334 sorption. The U oxidation state was found to be homogeneous at the micro-scale, which would

1335 suggest that the redox of mononuclear U is driven by the ambient redox conditions at the sample
1336 (centi- or millimeter) scale.

1337 From the perspective of our deep investigations at the core scale, we suggest that the
1338 wetland soils act as an active reactor where chemically eroded U supplied by the watershed
1339 creeks is scavenged through sorption to organic matter and is then exported downstream to the
1340 lake through physical erosion. These organic soils are thus both sinks and sources of U, which in-
1341 and-out U transfers probably depend on seasonal climatic events that control erosion. At the
1342 time of the creeks water sampling, our observations suggest that the wetland was globally acting
1343 as a U sink. Better estimating the current U budget of the wetland would require to spatially
1344 monitor U transfers at the annual scale, including during extreme erosion events. Depending on
1345 the relative importance of erosion intensity and of the rate of U-binding sites renewal
1346 (vegetation and OM in general), the wetland could either be in steady state, i.e., scavenge as
1347 much U as it exports, either be a global sink of U (if vegetation develops more than is eroded) or
1348 a global source (if soil erosion is faster than renewal). As a consequence, the use of artificial
1349 wetlands to attenuate the environmental dissemination of U – although likely efficient in terms
1350 of global U budget – requires stewardship in the long term, especially during high precipitation
1351 events.

1352

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1381

1382 ***Appendix A. Supplementary Material***

1383 *Supplementary text, figures and tables: field sampling, additional chemical and mineralogical*
1384 *soil data, additional XAS data, U decay model.*

1385

1386 XAS and μ -XRF data acquired at ESRF beamline BM23 will be available online from 2024 at
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