A combined DGT - DET approach for an in situ investigation of uranium resupply from large soil profiles in a wetland impacted by former mining activities

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A combined DGT - DET approach for an *in situ* investigation of Uranium resupply from large soil profiles in a wetland impacted by former mining activities

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Highlights

- A combination of 5 DET and DGT was deployed in the Rophin wetland soil layers.
- The metal resupply was assessed by calculating the R ratio ($R = [U]_{DGT}/[U]_{pore\ water}$).
- A R value of 0.87 demonstrates the resupply of U from a mine deposit layer.
- Up to 1,750 mg kg^{-1} U are retained in wetland topsoil by organic complexation.
- A change in red-ox sensitive elements occurs below the soil-water interface.

Abstract (250 words)

An *in situ* methodology combining DET and DGT probes was applied in a wetland soil, downstream of a former uranium mine (Rophin), to evaluate metal resupply by calculating the R ratio ($R = [U]_{DGT}/[U]_{pore\ water}$) from a high resolution and large (75 cm) soil profile. Our study confirms its applicability in soil layers with varying properties; only soil layers with low water content or coarse texture appear to be limiting factors. For soil profiles, DET provides new insights of the distribution of Uranium as soluble species (free ions, small inorganic complexes,…) along the pore water profile, whereas DGT highlights the presence of other "DGT labile" species. The pairing of DET and DGT, plus the calculation of the R, highlights two U behaviors in combining results from red-ox sensitive elements (Mn, Fe). First, in the organic topsoil layer, an increase in $[U]_{DET}$ and $[U]_{DGT}$ at 3-4 cm reflects the desorption of U probably trapped onto Fe- and Mn-oxohydroxides in a DGT-labile form.

However, the resupply from soil to pore water is close to a diffusion only case (R < 0.2) meaning that a portion of U is certainly tightly bound by OM in soil as non-labile species. Second, a peak in $[U]_{DGT}$ perfectly corresponding to the former mine deposit layer signifies the presence of U under DGT-labile species. Moreover, a maximum R values of 0.87 demonstrates the near complete resupply of U from a labile fraction in this layer, as opposed to other elements like Pb.

Keywords (6 words): Uranium, DGT, DET, lability, soil, mine

1. Introduction

Understanding the fate of radionuclides in the vicinity of former uranium (U) mines is of great importance given both the potential enhancement of environmental dose rates and the transfer of radionuclides into ecosystems. Uranium concentrations may locally exceed natural background levels in the vicinity of former U mining sites (Fuller et al. 2020, Chautard et al. 2020, Lottermoser and Ashley 2005, Martin et al. 2020), particularly in natural and artificial wetlands such as peats and flooded soils (Stetten et al. 2018, Wang et al. 2014, Wang et al. 2013, Schöner et al 2009). All information on the geochemical speciation and dynamics of U in soils for the purpose of regulating U transfer into other environmental compartment is therefore of major interest.

The mobility of U in soils and sediments is mainly driven by redox processes, ligand complexation, sorption (on Fe-Mn-oxohydroxides and clay) and (co)-precipitation processes (Stetten et al. 2018, Schöner et al. 2009, Sajih et al. 2014). A simple approach to summarizing the geochemical speciation of metal in soils consists of considering its presence in the soil solution (pore water) as free ions, complexes with inorganic or organic ligands, associated with colloids (inorganic or organic as well), and tightly bound and/or exchangeable species in the soil solid phase (Guan 2019, Davison 2016). Stetten et al. (2018) recently investigated the speciation of U in a wetland impacted by a seasonally flooded mine using both the XANES and EXAFS techniques. They demonstrated that U speciation is driven by the water table level, which marks the limit between oxic and anoxic environments

as well as the associated presence of U_{VI} and U_{IV} species. U_{IV} is generally expected to be a low-mobility U species, existing as precipitated UO_2, in contrast with U_{VI} species, which are typically soluble and mobile (Wang et al. 2013, Fuller et al. 2020). However, recent studies (Wang et al. 2013, Stetten et al. 2018) conducted in the pore water of mine-impacted peat demonstrated the presence of mobile U_{IV}-bearing colloids (500 kDa - 0.22 µm) composed of $Fe(OH)_2$ and organic matter (OM).

In addition to studying the geochemical properties of U, it is important to evaluate transfers to the biotope. It is well-known that the plant uptake of potentially toxic elements in soils is correlated with the exchangeable metal pool rather than with the total metal soil concentration. Therefore, increasing interest has been shown in quantifying the labile fraction by a variety of techniques that speciate U in soils and sediments (Duquene et al. 2010, Kohler et al. 2004, Leermakers et al. 2016, Gao et al. 2010, Bond et al. 2007, Zachara et al. 2007, Ahmed 2014). Such techniques however were mainly developed for laboratory experiments from dry soil samples, thus resulting in the *in situ* environmental conditions that drive U mobility being partially reproduced. Among these techniques, Diffusive Gradient in Thin film (DGT) is the only dynamic technique to be successfully applied *in situ* on soils and sediments.

DGT and DET (Diffusive Equilibrium in Thin film) (Zhang and Davison 1995, Krom 1994) have been widely used to sample trace metals in various environments (fresh and salty waters, pore water of sediments or soils) due to some key advantages: rapid equilibration time vs traditional sediment peepers (mean equilibration time < 1day for DET and 1 to 3 days for DGT, Peijnenberg et al 2014), robustness, ease of deployment, and minimal disturbance in the field. DGT and DET mainly measure free ions, small inorganic complexes and a number of organic complexes, whose dissociation rate is fast compared to the diffusion time scale in both diffusive and resin gels. However, within a typical deployment time (hours to days), DGT is unable to measure most colloids since they diffuse much more slowly than free ions in the diffusion layer (Guan 2019, Davison 2016).

The DGT-induced local depletion of metal concentration in pore water causes the release of species from the readily exchangeable fraction in the soil solid phase. The pool initially present in pore water plus the DGT-induced pool both contribute to the quantity measured by DGT. The magnitude of the flux measured by DGT is determined by: the concentration in pore water, the rate of diffusion, and the rate of resupply from both the solid phase and

complexes in pore water. These “DGT labile” species are correlated with the time available for complexes to dissociate in pore water and fractions to desorb from the solid phase. Consequently, a DGT measurement integrates all soil properties into a single key parameter, namely the DGT-labile concentration (C_{DGT}) or flux (Guan 2019). The R ratio ($R=C_{DGT}/C_{pore\ water}$) is thus a good indicator of the soil’s capability to resupply metal (labile fraction) to DGT.

While applications of a DET/DGT combination to U and other metals in sediments were initiated 14 years ago (Gao et al. 2006, Monbet et al. 2008, McKelvie and Worsfold 2008, Pradit et al. 2013, Leermakers et al. 2005), studies on soils are scarce and have mostly been performed under laboratory conditions (Hooda et al. 1999, Nowack et al. 2004, Koehler and Schulin 2004) due to both the water saturation conditions required to ensure smooth operations and the complexity of field experiments. Moreover, DGT probes were mainly used in their original 15-cm design length, which is adapted to studying the water-sediment column interface but less convenient for studying a complex soil profile. To the best of our knowledge, Leermakers *et al.* (2016) reported the first *in situ* deployment of DGT samplers in a U-contaminated soil, with use of a DGT holder yielding a high resolution profile over a 75-cm depth.

In this study, a combination of DET and DGT probes was simultaneously deployed *in situ* within a particularly interesting wetland featuring an anthropogenic anomaly (Martin et al. 2020, Roux et al. 2020). The main objective of this work is to determine the lability of U according to soil characteristics as well as the origin of the contamination. Moreover, this paper presents new data for U in pore water with a large 75-cm vertical depth relative to the characteristics of the corresponding soil profiles. Results emphasize the complementary nature of DGT and DET, in comparison to other methods for assessing U pore water composition. Soil concentrations of mine activity-related elements (U and Pb), along with fluxes of elements from the soil-water interface to DGT, was assessed by calculating the R ratio, as derived from the combined DGT and DET measurements. These results were corroborated by the measurement of red-ox sensitive elements (Mn and Fe) in order to better understand the geochemical processes involved.

2. Materials and Methods

2.1. Study site

The history, geology and hydrogeology of the Rophin tailings storage site have been described elsewhere (Martin et al. 2020, Roux et al. 2020). As a brief background, the U ore of Rophin, mainly parsonsite ($Pb_2(UO_2)(PO_4)_2$, $2H_2O$,U_{VI}), was mined from 1949 to 1955 using an ore washing plant process and associated settling ponds that continued to operate until 1957 with pitchblende (UO_2, U_{IV}) from the 'Bois-Noirs' mine. Nowadays, the storage site is covered by a vegetated soil, and forest vegetation is growing at the top of the mine waste storage heap. Soil cores extracted in the nearby wetland (200 m downstream) show high U concentrations, which appear to be associated with the presence of a whitish silt loam soil layer located at a depth of around 10-30 cm, below an organic topsoil layer. These high U concentrations have been ascribed to a discharge of U mineral particles, transported by turbid water, due to a malfunction in both the ore washing plant process and the sedimentation step. In addition to the U contamination identified in this anthropogenic layer, U is also found to be trapped in the high OM content topsoil layer. Our interest is therefore to estimate the potential lability of U in these layers. A general map of the Rophin watershed (Puy de Dôme, France) and its mapping by gamma-ray dose rate, is presented in Fig. 1.

2.2. Principles of DGT and DET use in soil

The principles of DET and DGT techniques are widely discussed in the literature (Davison 2016). While the DET probe accesses free metal, metal complex and free ligand species in soil pore water through equilibration of solutes within a diffusion layer (consisting of hydrogel plus filter membrane), the DGT probe measures the flux of solutes (through the same diffusion layer) from the soil pore water to a binding layer (Chelex® resin embedded in hydrogel).

Flux depends on: i) the concentration gradient (due to the binding layer) existing on both sides of the diffusion layer, and ii) the ability of the soil to resupply solutes when their concentrations become depleted. The solute flux can be interpreted as the time-averaged concentration at the probe surface during deployment and is calculated according to Equation 1 (derived from Fick's first law):

$$C_{DGT} = m_U \Delta_{gel} / (D_{gel} A t) \quad (1)$$

where m_U is the mass of U eluted from the Chelex® resin (µg), corrected for the elution factor (f_e), Δ_{gel} the total thickness of the diffusive gel layer and protective membrane filter (Δ_{gel} = 0.905 ± 0.0014 mm), D_{gel} the temperature-corrected diffusion coefficient of U through the diffusive gel layer (cm² s^{-1}) using the Stokes-Einstein Equation, A the exposure area (sampling window), and t the deployment time. For D_{gel}(U), a mean value derived from Gregusova and Docekal (2011) associated with a larger uncertainty accounting for discrepancies in the literature values has been chosen (D_{gel} = 4.39 ± 0.40 × 10^{-6} cm² s^{-1} at 25°C and pH = 6.4). This value is in good agreement with those reported in several studies Turner et al. 2012, Drozdzak et al. 2015, 2016). The quantitative determination by ICP-MS requires a reproducible elution of metals trapped in the Chelex® resin. The elution factor of U was experimentally determined to equal 0.84 ± 0.04 under our experimental conditions (data not shown). For the other metals (Mn, Fe and Pb), the values of elution factors and D_{gel} were drawn from Davison (Davison 2016) (Table S2).

The R ratio values ($R=C_{DGT}/C_{pore\ water}$) highlight three cases that arise with respect to the DGT-measured flux and interfacial concentration in soil. When the U flux from soil to pore water (resupply) effectively buffers the pore water concentration (R > 0.8; sustained case), DGT concentration is close to the true U pore water concentration as regards DGT labile species. However, when the U resupply is limited ($0.2 \leq R \leq 0.8$; partially sustained case) or nonexistent (R < 0.2; diffusion only case), the U concentration measured by DGT is less than the actual U pore water concentration, with both DGT-labile and inert species being present in the soil (Davison 2016 and references herein).

2.3. Preparation of DGT and DET probes in the laboratory

DGT and DET probes were purchased from DGT Research®. They consisted of plastic holders with overall dimensions of 24 × 4 × 0.5 cm with a 1.8 × 15-cm open window. DGT probes (LSPM model) were composed of a Chelex®-100 binding layer (0.4 mm) with an area of 27 cm², a polyacrylamide diffusive gel (Δg = 0.78 mm) and a polyethersulfone filter (PES) membrane (0.45 µm). DET-constrained probes were of the LCP model with 75 slits (1 × 1 × 1.8 mm) on the base plate filled with agarose diffusive gel and covered by a 0.45-µm PES filter membrane (Zhang and Davison 1995).

In order to minimize any redox disturbance during deployment in soil, the DGT and DET probes were first conditioned in a glove box under argon atmosphere. The probes were

immersed in a deoxygenated 0.01 M $NaNO_3$ solution containing 2.5 $g.L^{-1}$ Chelex® resin to remove any trace metals (Davison 2016) and allowed to rest for at least 24 h with bubbling argon gas. The DGT and DET samplers were stored at 4°C in a tight plastic bag containing a few drops of 0.01 M $NaNO_3$; they were then transported to the site in a container filled with argon gas.

After deployment, the probes were disassembled in the laboratory, and the DGT Chelex® binding phase was sliced at 1-cm intervals with a ceramic blade. The slices were inserted into pre-weighed vials and reweighed in order to obtain sample weight and, hence, the volume and surface area. DET agarose gels were also placed into pre-weighed vials and reweighed to derive gel volume. A compromise on both spatial resolution and method detection limit was struck by placing five DET slices in the same elution vial to ensure the same spatial scale as DGT (1 cm). The DGT and DET gel slices were separately soaked in 1 mL of 1 M HNO_3 for at least 24 h before analysis of the eluate by ICP-MS.

2.4. Field deployment

Field deployment took place in the wetland zone downstream of the former Rophin U mine (3°33'0.27"E and 46°0'25.23"N) in April 2018 and lasted 24 h (a complementary study was performed in November 2018). The chosen sampling area is a fully saturated zone (Fig. S1 a and b) characterized by the highest measured gamma dose rates.

A specific PVC holder was constructed to obtain continuous profiles up to 75 cm deep (equal to 5 probe lengths). This holder differs from Leermaker's study (Leermakers et al. 2016) by integrating DGT/DET probes in a back-to-back position (Fig. S3). On-site, the probes were removed from their container and quickly placed in the PVC holder, which was first manually driven into the soil to a 20-cm depth and then with a mallet up to 75 cm.

At the end of their deployment (24h), the probes were retrieved, wiped to remove any adhering soil particles, rinsed with ultrapure water and finally stored in sealed plastic bags, along with a few drops of 0.01 M $NaNO_3$ to maintain water saturation and prevent the gels from drying.

A triplicate of DGT (in the piston configuration) was used as a blank in following all steps of the protocol (including the cutting step) except for deployment. After disassembly, their diffusive and binding gels were considered as a blank for the DET and DGT probes,

respectively. Lastly, soil temperature gradients were measured every 10 cm over a 120-cm depth with a 1.5-m long temperature probe equipped with an LCD display (Agreto®).

2.5. Soil sampling and characterization

After retrieval of the DET/DGT probes, soil samples were collected at the exact same location. The sampling area was covered by approx. 2 cm of water, in assuming fully saturated soil layers in the wetland at the beginning of spring 2018 (Fig. S1). Semi-cylindrical soil cores (50 × 10 cm) were sampled with a Russian-type corer (Eijkelkamp® Soil & Water) and subdivided into soil samples according to apparent soil layers. Wet soil samples were then divided into two parts, one dried at 105°C and then sieved at 2 mm the other frozen at -18°C. In addition, pore water samples were collected using both in-field-based methods (DET, suction lysimeter) and laboratory methods (centrifugation, soil suspensions) for purposes of comparison. Details on the methods and results are available in Table S4.

Soil pH was measured according to the NF ISO 10390 method. Five grams of dry soil samples were vigorously shaken with 25 ml of UP water for 5 min (1:5 soil/water). The suspension was then left to rest at least 4 h before pH measurement (CyberScan pH 110 meter, Eutech Instruments) using an electrode dedicated to viscous media. The supernatants were then filtered at 0.45 µm, acidified and stored at 4°C until ICP-MS analysis. Water and organic matter contents were determined by loss of ignition. The procedure followed was that specified in Heiri et al. 2001, Lotter and Lemcke 2001. Between 5 and 10 g of homogenized wet samples were introduced into porcelain crucibles and first dried at 105°C overnight in a furnace (Nabertherm, Inc.), before being heated to 550°C for 4 h in order to burn the organic matter. After each temperature step, the crucibles were cooled to room temperature in a desiccator and weighed. The particle size distribution of non-organic soil samples was determined by laser granulometry (Mastersizer 3000 with a Hydro LV dispersion system, Malvern Panalytical®). Soil texture was determined according to particle size distribution and USDA definition (Fig. S5).

Prior to ICP-MS analysis, dry soil samples sieved to 200 µm were mineralized by microwave-assisted digestion using a Multiwave 3000 microwave (Anton Paar). A 7.5:1.5:1 mixture of HCl (36% vol.), HNO_3 (68% vol.) and HF (47% vol) concentrated acids was added to around 100 mg of sieved soil in a cleaned PTFE reactor. The mixture was then

heated at 600 W for 40 min. After cooling, 5 mL of a saturated solution of H_3BO_3 in HNO_3 (7.5 M) was added to neutralize the HF, and the mixture was heated a second time. The total soil sample mineralization was visually checked, and the liquid phase was transferred into tubes. Ultrapure water (10 mL two times) was added for further dilution and analysis. Additional X-ray diffraction (XRD) analyses were performed on dry soil powder using a Pananalytical Empirean diffractometer running with a Cu-Kα_1 radiation (λ=1.5406Å). XRD patterns were recorded in the 5-80° 2Θ interval with a 0.013° 2Θ step size.

2.6. Analysis

Anion (F^-, Cl^-, SO_4^{2-}, NO_3^-, Br^-, PO_4^{3-}) and cation (Na^+, K^+, Mg^{2+}, Ca^{2+}) analyses were performed on pore water samples by ion chromatography (850 Professional IC, Dionex and ICS-1000 IC, Metrohm). Physicochemical parameters such as temperature, pH and Eh were measured *in situ* using a CyberScan pH 110 meter (Eutech Instruments) coupled with dedicated probes.

Element concentrations (U, Mn, Fe and Pb) were analyzed by Single Quadrupole Inductively Coupled Plasma-Mass Spectrometry (ICP XSERIES 2, ThermoFisher Scientific). A collision chamber mode (addition of H/He gas) was used for the Fe analysis. Matrix effects were minimized by diluting the samples in 2% bi-distilled HNO_3 (v/v). DET and DGT eluates were diluted by factors of 20 and 50, respectively, or until 1,000 (for DGT eluates with high concentrations). The analytical LQ for the DGT, DET and pore water samples of each element are given in Table S2 according to field blanks for DGT and DET. Analytical uncertainties are expressed as a confidence interval (α = 0.05). In pore water samples, the [U] mean uncertainty is around 15%. For each metal (U, Mn, Fe and Pb), DET and DGT concentrations and R calculation's uncertainties were calculated according to Gauss'law of error propagation (k=2). More precisely, for Uranium, the following mean values were thus obtained: 17% (DET), 25% (DGT) and consequently, 32% for R-values

For all techniques used, quantification of trace metal concentrations (ICP-MS) and major ions (IC) were based upon calibration curves prepared from multi-element or single element standard solutions (SCP Science, Canada). Inter-laboratory standard materials (BIPEA) were used to verify the accuracy of all analytical protocols."

3. Results and Discussion

3.1. *Soil properties and chemical characteristics*

Variation in the water table level (related to a high/low flow cycle) in the DGT sampling area was measured at +2 to -23 cm (with 0 cm at the soil surface) in April 2018 and November 2018, respectively. In April 2018, the wetland was fully saturated (Fig. 1); consequently, each soil layer was considered at its maximum water holding capacity. Moreover, the O_2 profile measured over the first 3 cm decreased sharply from 100% O_2 (overlaying water) to 2% at 1.5 cm (Fig. S6), with no oxygen being present below this depth.

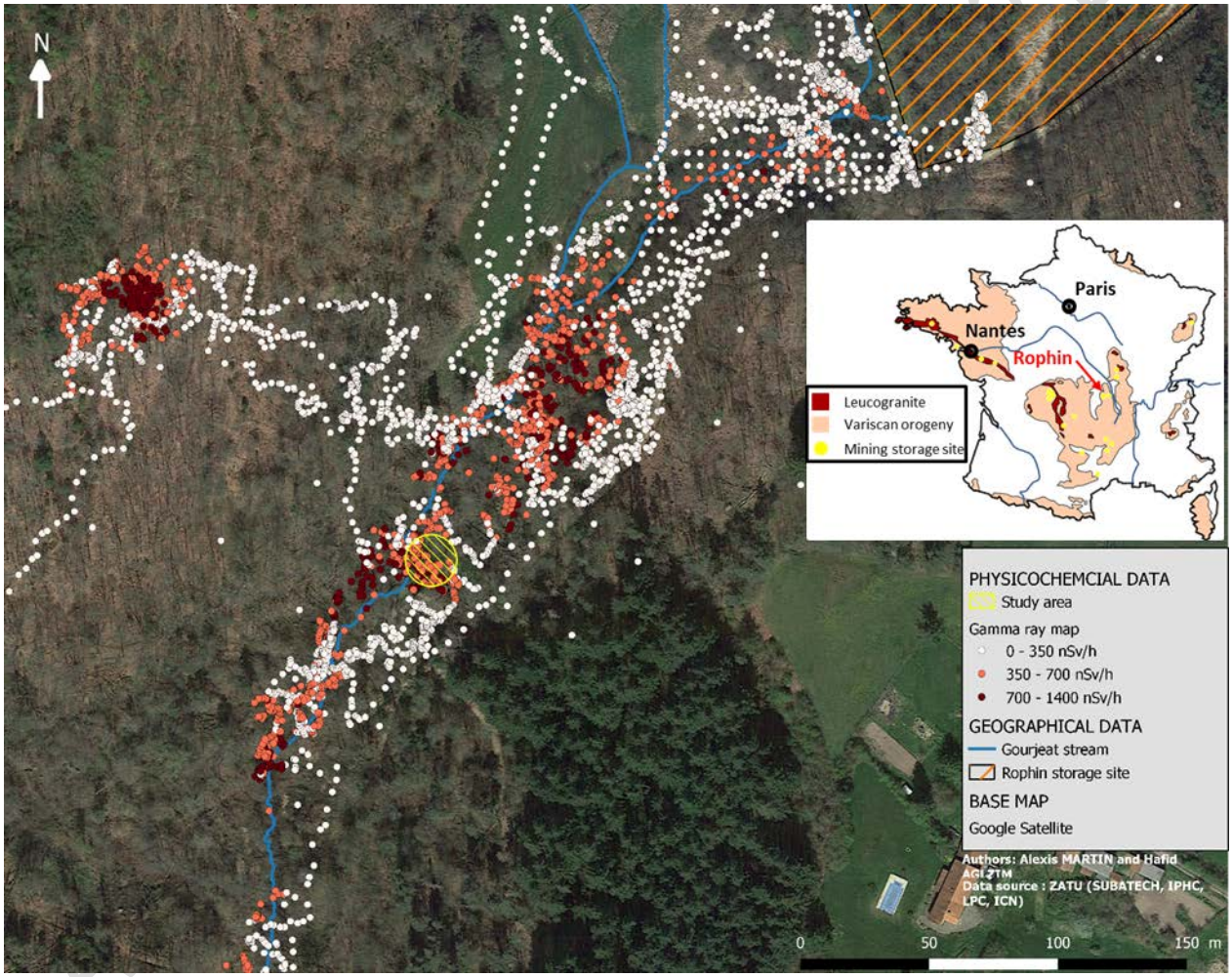

Figure 1: Location of the Rophin site in the context of mining storage in France (adapted from AREVA NC., 2009), gamma-ray dose rate mapping of the site in 2018 (colored dots) and wetland location (yellow circle).

The soil layer properties are listed in Table 1. pH values are characteristic of a wooded wetland and range from 4.06 to 4.90 (average 4.5). Six layers (L1 to L6) can be

distinguished, based on visual observations. Some are typical of wetlands, rich in organic matter (i.e. L1), while others are associated with the history of site mining operations (i.e. L3, L4). These layers were sorted into 4 main types (Baize and Girard 2008): “histosol layer” (H-type layer), “humus layer” (O-type), “organo-mineral layers” (A-type), and “technosol layer” (Z-type). Mixed layers (L2-4 and L3-4) were also observed but not sampled due to their heterogeneity and the likely complexity of any subsequent interpretation.

A rapid qualitative description of the soil profile is given below:

- The H-type layer (L1) is mainly composed of fibrous soil material and roots, which confers a black color, very low bulk density (0.17) and high water holding capacity (85%). The organic matter carbon content is the highest of the entire soil profile at 47.5% of the dry soil.
- The A-type layer consists of two different layers, Ag and A, both combining organic and mineral characteristics (L2, L5). The Ag and A layers share common characteristics, i.e. an intermediate water content (36% and 45%), a low level of organic matter (3.0% and 3.2%) and a silt loam texture. The orange color of the Ag layer suggests the occurrence of an oxidative process (precipitation of Fe-oxohydroxides).
- Z-type layers (L3, L4) are distinguished as fine (f) and sandy (s) depending on their texture, bulk density and particle size distribution (Table 1 and Fig. S5). These layers are characterized by high U concentrations (1,840 and 790 $mg.kg^{-1}$) and low organic contents (2.6% and 1.2%, respectively). Such high U concentrations, along with the abundance of finer larger particles, suggest that these layers are constituted of crushed extracted materials that had settled into the former Rophin mine ponds. According to Martin et al. (2020), these mining residues were released into the Rophin watershed, thus impacting the wetland under investigation.
- The O-type layer is the deepest horizon (below 69 cm, L6); it is characterized by a medium organic carbon content (15.5%) and a brown color highlighting a more decomposed (degraded) organic matter than that of the H-type layer. This layer exhibits a low U concentration of around 50 $mg.kg^{-1}$, which is in accordance with the local geological background. This layer is considered as the soil reference prior to the period of mining operations and discharge of residues at the Rophin site (Martin et al. 2020, Roux et al. 2020). Just above the O-layer, the presence of gravels (64 to

69 cm) should be noted, thus suggesting the existence of a former creek channeling mine discharge.

Moreover, XRD analysis shows that the soil samples are mainly composed of crystallized minerals with a small amorphous fraction. In all layers, the mineralogical assemblage is composed of quartz, alkali feldspars (microcline, orthoclase) and plagioclase (albite-anorthite) (Fig. S9). These results are consistent with the composition of Rophin stream sediments reported in Roux et al. (2020).

Table 1: Description and properties of the main soil layers

Soil layer	Depth (cm)	French type *	pH_{soil}	Water content (%)	Organic matter content (%)	Bulk density (kg/m^3)	Porosity	Soil texture class (USDA)	$[U]_{soil\ total}$ ($mg.kg^{-1}$ dry)
L1	0 - 12	H	4.67	85	47.5	0.17	0.87	-	1750 (100)
L2	12 - 18	Ag	4.90	36	3.0	1.08	0.59	Silt loam	430 (30)
L3	25 - 29	Z_f (fine)	4.45	36	2.6	1.10	0.58	Silt loam	1840 (100)
L4	42 - 49	Z_s (sandy)	4.56	40	1.2	0.92	0.65	Sandy loam	790 (50)
L5	49 - 64	A	4.06	45	3.2	0.88	0.67	Silt loam	600 (30)
L6	69 -75	Ob	4.55	54	15.5	0.57	0.58	-	50 (10)

** Baize and Girard 2008*

Such contrasted contamination levels in the soil profile raise questions about the mechanisms controlling U mobility in this contaminated wetland. However, an investigation of the main resupply mechanism that leads to the release of U from the L3 soil layer to the pore water requires additional information on the pore water composition and, more specifically, dissolved U speciation. Moreover, an investigation of U mobility with the DGT technique necessitates defining the U concentration in pore water used to calculate the R ratio.

3.2. DET and DGT results for uranium depth profiles in soil

In this study, we consider DET to be the most reliable and accurate pore water sampling method for calculating the R ratio (as suggested in Davison (2016)). DET and DGT actually feature a very similar design and deployment conditions. Therefore, the filtration of U species by membrane (< 0.45 µm) and diffusive gel is close for both techniques (free metal, metal complexes and free ligand species). Moreover, sampling with a field-based method and high spatial resolution appears to be more relevant in accurately assessing U mobility in soils. It is well known that concentrations in pore water can be strongly affected by the methodology employed (Di Bonito et al. 2018, Ullah et al. 2012, Leermakers et al. 2005).

This is especially true for redox-sensitive elements such as uranium, as we indeed observed when comparing the $[U]_{pw}$ deduced from various sampling methods along the soil profile with different spatial scales (Table S4). So, the wide range of results observed ($[U]_{pw}$ from 50 µg.L^{-1} to 60,100 µg.L^{-1} in L3) if used, does lead to bias (by a factor of 1000) R calculation. Therefore, in the framework of this study, DET results appear to be the most relevant ones for calculating R ratio. More generally, this issue raises the question about the choice of the most representative sampling method for characterizing soil's solution since this has a strong impact on R calculation and its interpretation.

The extracts obtained by centrifugation, however, allow adequate water volume for the physicochemical characterization of pore water (Table S7). In sum, pH values are acidic (from 3.9 to 6.3), except for the top layer (L1 layer) whose pH value lies close to that of the overlaying water (pH = 7.2). For ion analysis, high SO_4^{2-}, Mg^{2+} and Ca^{2+} contents were observed in pore water from non-organic soil layers and a high concentration of F^- was noted in L4. Under these working conditions, no parameter appears to exert a major influence on the diffusion coefficients used in DGT calculations (Drozdzak et al. 2015, Turner et al. 2012).

DET and DGT probes were deployed back-to-back in order to obtain profiles over a 75-cm depth (Fig. 2). However, DGT results in the 40-75 cm range are missing due to deterioration of the sampling windows (crumpling and degradation of membranes and/or gel layers). Since the DGT sampling window is in fact thicker than that of DET (1.32 mm vs. 1.14 mm), its rubbing against sandy or gravely soils produced the observed degradation. Fortunately, we have salvaged the two most interesting soil layers (with the highest U content according to Martin et al. (2020)), i.e. the surface organic soil layer (L1) and the anthropogenic zone (L3).

For DET results over the 75-cm depth, the $[U]_{DET}$ in pore water range [40-625 µg.L^{-1}] exhibits a double-peak profile. The main peak (625 µg.L^{-1}), located between 36 and 56 cm, is related to L4 and L5 (top) layers; a second much smaller peak (165 µg.L^{-1}) is located at 3-4 cm (top of the L1 layer). In between these two zones, $[U]_{DET}$ reaches a minimum (40 µg.L^{-1}) in the L2 layer (at a depth of 12-18 cm). Finally, below 64 cm, $[U]_{DET}$ decreases to low values (< 50 µg.L^{-1}).

Regarding the entire depth profile, a wide $[U]_{DET}$ range is observed. These results highlight the variation in $[U]_{pw}$ with respect to the centimeter-scale changes in soil layer properties. Note that the soil layer nature may have an impact as a coarse texture (sandy loam) may

facilitate fluxes from the soil layer to the DET probe and conversely, a fine texture (silt loam) may hinder them. Nevertheless, this outcome already reported by Hooda et al. (1999) and Docekal et al. (2003) is minimized in the studied saturated soils. Moreover, in any case, DGT results will also be affected by this hypothetical bias. Coupling DET and DGT techniques will therefore minimize impact on the R ratio calculation.

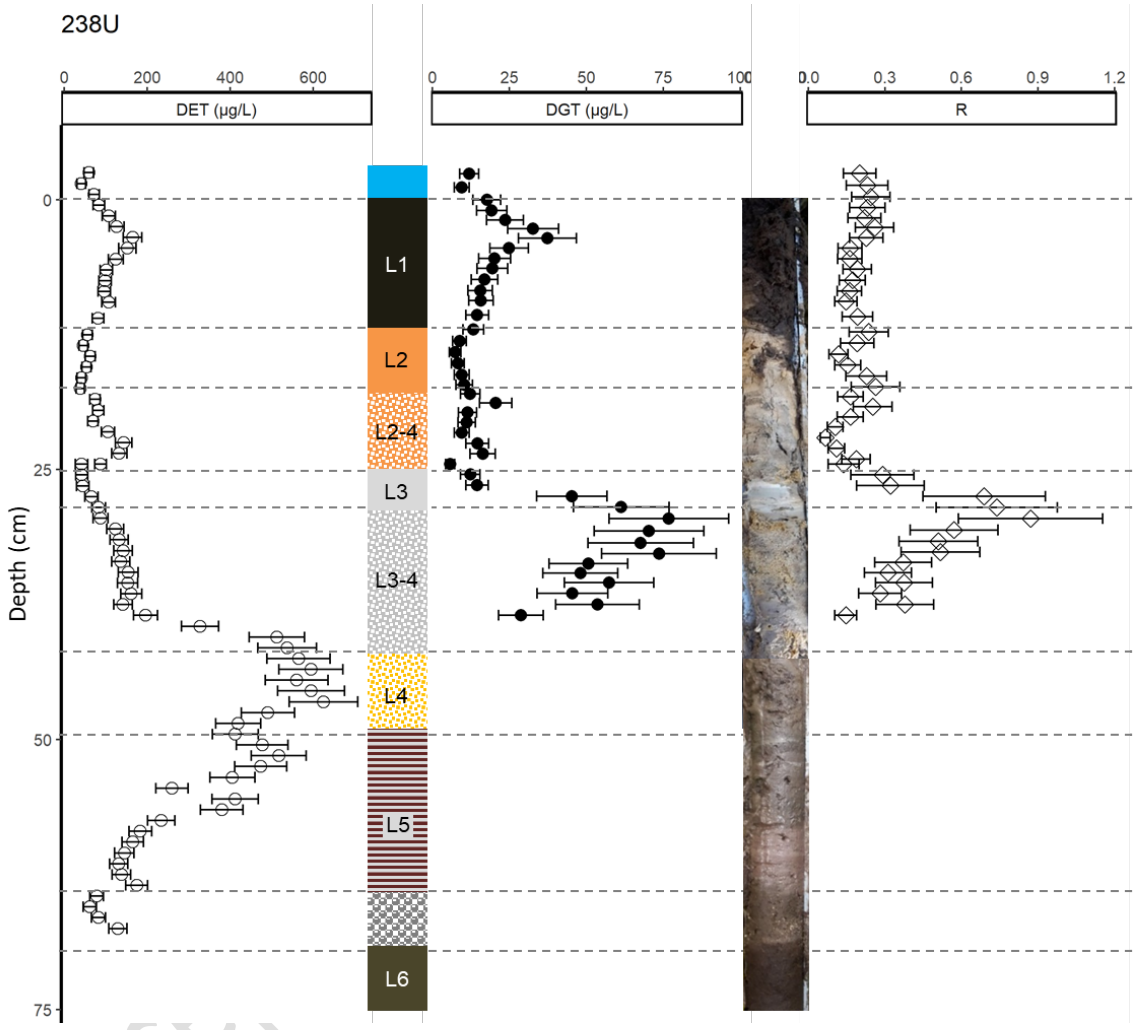

Figure 2: Uranium depth profiles obtained from the *in situ* deployment of DET and DGT, along with R ratio ($R= [U]_{DGT}/[U]_{DET}$) for a 24h deployment time (errors bars calculated by propagating all experimental uncertainties; k=2)

For the 40 cm deep DGT profile, the lowest concentration is reached at around 12-26 cm with a minimum value of 7 $\mu g.L^{-1}$; moreover, 2 peaks are exhibited. An initial peak, observed at around 3-4 cm in the top of layer L1 (37 $\mu g.L^{-1}$), mirrors the DET profile but with a lower peak value. Then, from the end of L3 up to L3-4 (27-40 cm), a second massive peak is observed with a maximum at 77 $\mu g.L^{-1}$, hence reflecting a higher flux of U to DGT. This

second peak could be explained by the existence of readily U DGT-labile species originating from the high inventory of U in the adjacent L3 layer and conveyed in pore water through the coarser texture of the mixed L3-4 layer. The ratio between DET and DGT depth profile results will differentiate the presence of tightly bound and labile U fractions in the various soil layers, i.e. the capacity of the soil to resupply U in pore water.

3.3. R ratio for mine activity-related elements U and Pb

In this soil profile, since $[U]_{DGT}$ values are as much as 15 times less than $[U]_{DET}$ values, the corresponding R ratio ranges from 0.07 to 0.87 (Fig. 2). These results indicate that U resupply from soil layers to pore water evolves from a diffusion only case to a sustained case in response to the sink imposed by the DGT probe.

Over the first 26 cm, the R ratio remains globally constant at a low value ($R_{0\text{-}26}$ = 0.19, diffusion only case). The first peak in $[U]_{DGT}$, corresponding to layer L1, is perfectly mirrored with $[U]_{DET}$, resulting in a low R value. In fact, although the total U amount and water content are high in layer L1 (17.46 $mg.kg^{-1}$ and 85%, respectively), U mobility in this layer appears to be very low. This finding is consistent with the presence of OM soil particles and its well-known properties of complexing metals, thus leading to kinetically inert compounds in which U is tightly bound (Fuller et al. 2020, Stetten et al. 2018).

The second peak in $[U]_{DGT}$ ($R_{U,27\text{-}35}$ = 0.53, partially sustained case) corresponds to the L3 and L3-4 layers, which appear to more readily transfer U to pore water than the other soil layers (DGT-labile species). As a reminder, layer L3 exhibits the highest stock of U (1,844 $mg.kg^{-1}$) and layer L3-4 is a transition zone displaying an evolution of texture from silt to sandy loam. For layer L2, with the same soil texture as L3, R remains constant at a low value ($R_{U,12\text{-}18}$ = 0.19, diffusion only case). We can therefore conclude that the use of a DGT/DET combination in silt loam soil allows detecting the exchangeable U fraction.

Given that U compounds appear to be exchangeable in layer L3, the case of Pb was also considered (Fig. 3). Lead is in fact a relevant indicator of mining activity known to be present here as a mixed U/Pb mineral (parsonsite) (Roux et al. 2020, Cuvier et al. 2016). Despite an initial increase of Pb concentration in pore water ($[Pb]_{DET}$ = 279 $\mu g.L^{-1}$) at 3.5 cm, like for U, no other variation was observed at the depths of U-impacted soil layers. The accumulation of Pb in DGT probes (after 24 h) is 7 to 50 times less than DET along the entire profile, leading to a poor resupply of Pb ($R_{U,0\text{-}40}$ = 0.05) from the soil layers close to a diffusion only

case. The difference between R_{Pb} and R_U profiles for mine-impacted layers (L3 and L3-4) suggests that Pb, present into minerals, is immobilized as a non-DGT-labile form, whereas U is present in a DGT-labile form capable of being resupplied from soil to pore water.

3.4. Soil concentration profiles for red-ox sensitive elements (Mn, Fe) and implications for U mobility

In this final section, we examined the redox-sensitive contextual elements since uranium speciation is strongly correlated with associated redox processes, e.g. the oxidation of organic matter largely affected by microbial activities (Abdelouas 2006, Duff et al. 2002, Coughlin and Hunter 2002). The DET and DGT depth profiles of Mn and Fe (Fig. 3) were then acquired in order to characterize the redox conditions and potential acceptors of electrons, as well as the metal resupply fluxes from soil to pore water.

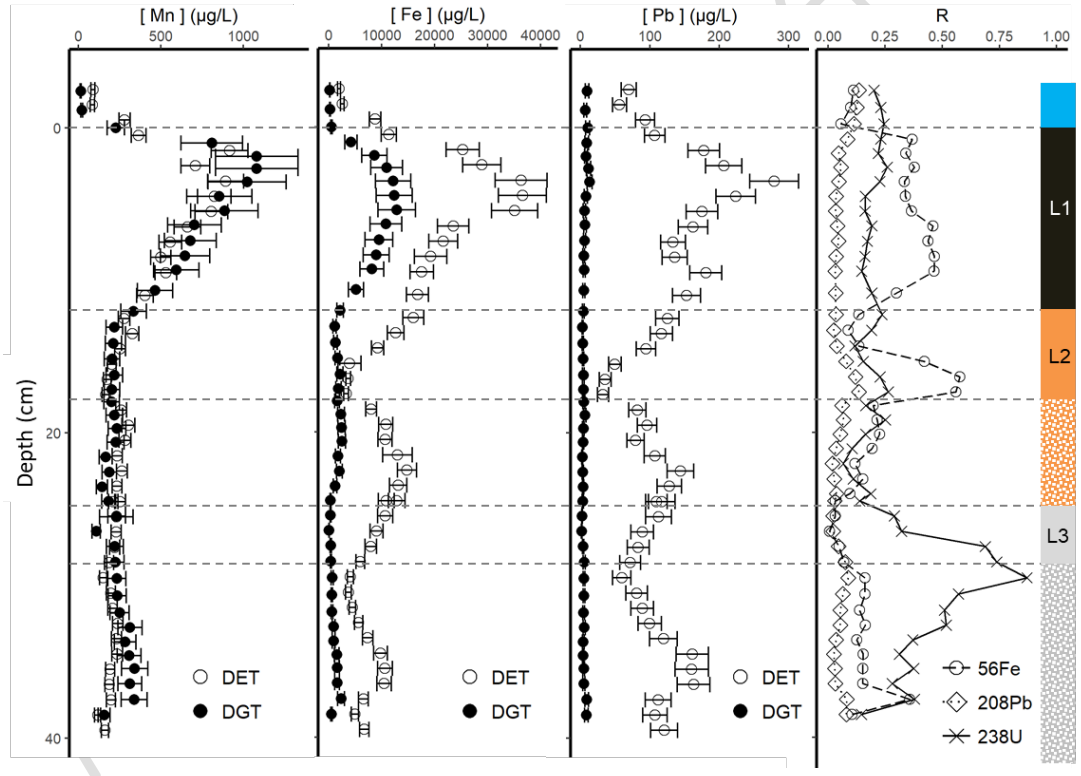

Figure 3: DET and DGT depth profiles for Mn, Fe and Pb and comparison of R values for Fe, Pb and U ; errors bars for Mn, Fe and Pb are 15%, 14% and 15% (for DET), 23%, 27% and 28% (for DGT) and 27%, 31% and 32% (for R) respectively

Both $[Mn]_{DET}$ and $[Fe]_{DET}$ profiles show successive peaks located at 1.5-4 cm and 2.5-4.5 cm, respectively. The increase of [Mn] and [Fe] in pore water is generally interpreted as a

clue for the dissolution of Mn- and Fe-oxohydroxides by microbially-mediated reduction processes given their use as terminal electron acceptors in organic matter degradation processes (Thamdrup 2000, Fuller et al. 2020) after O_2 consumption below 1.5 cm (Fig. S6).

For Mn, the superimposition of both $[Mn]_{DET}$ and $[Mn]_{DGT}$ over the full depth profiles shows that Mn species are fully DGT-labile ($R_{Mn,mean}$ = 1.1 ± 0.3), probably as Mn^{2+} species dissolved in pore water. This is a typical sustained case whereby the solid phase easily resupplies pore water depleted by DGT. The few R variations observed in the R profile may be related to a constant, $[Mn]_{soil}$ (Table S8).

In the L1 top layer, Fe exhibits a different behavior. While its initial peak mirrors DET results, the R value is typical of a partially sustained case ($R_{Fe,0-5}$ = 0.35), meaning that the iron species are not fully exchangeable. Despite a very high content of total Fe ($[Fe]_{soil,L1}$ = 27.3 $g.kg^{-1}$), the presence of a high OM content acts as a trap by complexation, leading to potentially kinetically inert compounds. In layer L2, a fluctuation of R_{Fe} between 10 and 18 cm was observed, with a successive decrease from 0.47 to 0.09 and increase to 0.48. This sharp change occurred in a soil layer containing Fe-oxohydroxides (orange coloring) and reflects the alternation of a red-ox process. At this depth, it is likely that the seasonal variation in water table level (limit between oxic and anoxic zones) induces a change in the Fe speciation from insoluble Fe(III) to soluble and mobile Fe(II) species (Thamdrup 2000).

To summarize findings on the red-ox sensitive elements, the $[Mn]_{DET}$ and $[Fe]_{DET}$ profiles reveal a reductive mobilization of these metals just below the soil-water interface, in accordance with quick oxygen consumption. The initial increase in $[U]_{DET}$ and $[U]_{DGT}$ concentrations detected around 3.5 cm (Fig. 2) could thus be explained as the desorption of U trapped onto Fe- and Mn-oxohydroxides (Abdelouas 2006, Casiot et al. 2009) in a DGT-labile form. However, the resupply from soil to pore water is close to a diffusion only case, meaning that most of the U is trapped within the topsoil layer as kinetically inert complexes with OM.

As an additional experiment, the R value of the top soil layer (Fig S10) was investigated in November 2018 at the same location (with a slightly different soil profile). The first 3 cm of soil were completely dry compared to April 2018. $[U]_{DET}$ were then below the LQ preventing any correct R value calculation. From 3 cm to 10 cm, R values corresponding to low and high flow periods matched perfectly well (R = 0.17 and 0.18 respectively). These results

show the L1 layer's capacity for complexing U whatever the season. In contrast in L2 layer, a seasonal process appears to take place as the low flow period R values (Nov.2018) increase (from 0.17 to 1) contrary to the high flow period R values (April 2018) suggesting that a red-ox process plays a major role in U lability. This result also demonstrates that U speciation in a wetland is driven by the water table level, which is in agreement with Stetten et al. (2018).

Lastly, two assumptions can be formulated in order to explain the mobility of an exchangeable U fraction in the L3 layer, identified as a residue of the former mining operations. First, some U_{VI} minerals (mined parsonsite and autunite) may remain undissolved in the L3 layer and constitute a stock of exchangeable U mobilized by the DGT sampling process as aqueous U_{VI} species (mineral dissolution). Second, a U_{IV}-exchangeable stock stemming from the reduction of these minerals may exist in the L3 layer (below the water table), and the DGT-labile fraction could be linked to the presence of mobile U_{IV}-bearing colloids (500 kDa - 0.22 µm) constituted of $Fe(OH)_2$ and OM (Stetten et al. 2018, Wang et al. 2013). Otherwise, the existence of seasonal red-ox fluctuations may also lead to a change in speciation from U_{IV}-immobilized (inert) species to U_{VI}-labile species (Stetten et al. 2018).

4. Conclusion

An *in situ* methodology is proposed in order to assess metal resupply in a wetland soil, downstream of the former "Rophin" U mine. This methodology, which combines DET and DGT probes, presents numerous advantages, namely good spatial resolution, rapid equilibration time, robustness, ease of deployment and minimal soil disturbance; nonetheless, the *in situ* deployment in soil remains poorly documented. This work has highlighted the determination of metal resupply in a wetland from large soil profiles, in combination with detailed soil properties.

Our study confirms that this approach is applicable in soil layers with varying properties; only soil layers with low water content or coarse texture appear to be limiting factors. For soil profiles, DET provides new insight of the total dissolved Uranium species distribution along the pore water profile, whereas DGT highlights the presence of other "DGT labile" species such as dissociated and available organic complexes. The pairing of DET and DGT plus calculation of the R ratio, highlight two U behaviors in combining results from red-ox

sensitive elements (Mn and Fe). First, in the organic topsoil layer, an increase in $[U]_{DET}$ and $[U]_{DGT}$ at 3-4 cm reflects the desorption of U trapped onto Fe- and Mn-oxohydroxides in a DGT-labile form. However, the resupply from soil to pore water is close to a diffusion only case ($R < 0.2$), meaning that U is tightly bound by OM in the soil. Second, a peak in $[U]_{DGT}$ perfectly corresponding to the former mine deposit layer signifies the presence of U under DGT-labile species in comparison with other soil layers. Moreover, maximum R values of 0.87 demonstrate the resupply of U from a labile fraction in this soil layer, as opposed to other elements like Pb.

In conclusion, all these information should be very helpful for interpretating data from any Uranium mining impacted wetlands similar to Rophin site.

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