¹ Supplementary information

2 A combined DGT-DET approach for an in situ investigation of Uranium resupply from

3 large soil profiles in a wetland impacted by former mining

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- **Fig. S1 (a and b):** Sampling area before and after the deployment of DGT/DET (a),
- 36 DGT/DET deployment in the wetland with the PVC holder (b)





Table S2: Limits of quantification (LQ) for ICP-MS and main parameters (diffusion coefficient,

 D_{gel} and elution factor, f_e) used in calculation for 24h deployment at 25°C.

Mn	Fe	Pb	U
0.06	0.9	0.08	0.09
5.85	6.11	8.03	4.39
0.80	0.70	0.70	0.84
	Mn 0.06 5.85 0.80	Mn Fe 0.06 0.9 5.85 6.11 0.80 0.70	Mn Fe Pb 0.06 0.9 0.08 5.85 6.11 8.03 0.80 0.70 0.70

- **Fig. S3**: Production drawings of the double side PVC holder for DGT/DET probes with exact
- 46 back to back positioning of DGT and DET probes



Comparison of U concentrations in pore water extracted with laboratory and in situ sampling methods

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54 Material and methods

55 Pore water samples were collected using in field-based methods (DET, suction lysimeter) and 56 laboratory methods (centrifugation and soil suspensions). In laboratory, centrifugation was used to 57 extract pore water from soil samples (20 to 30 g of each wet soil layer). Samples were centrifuged 58 twice during 10 min at 20 000 rpm (47600g) in order to separate pore water from soil. Supernatants 59 were filtered through 0.45 µm pore size PTFE membrane syringe filters (Millipore IC Millex C-60 H hydrophilic) and store at 4°C. For soil suspension, five grams of dry soil samples were vigorously 61 shaken with 25 ml of UP water for 5 min (1:5 soil/water). The suspension was then left to rest at 62 least 4 h and the supernatants were then filtered at 0.45 µm, acidified and stored at 4°C until ICP-63 MS analysis.

64 Pore water was *in situ* extracted using porous PTFE/Quartz suction lysimeter (D = 21 mm x L =65 95 mm, area = 33cm², Super Quartz Prenart®) with a cut-off of 2 μ m coupled to a portable vacuum 66 pump (P= - 0.5 bar). Briefly, lysimeters were rinsed with 1 M HCl and ultrapure water before use, 67 then, pushed manually with a PVC tube at an inclined position to the targeted layer in soil and 68 finally let equilibrated 24 h before sampling. The sampling rate observed on field was around 20 69 mL.h⁻¹ and 80 to 120 mL of water were collected in 250 mL HDPE bottles from different soil 70 layers. Sub-samples for trace metal and cations analysis were adjusted in situ at pH 3-4 with 71 ultrapure HNO₃ and stored at 4°C until analysis.

For those methods with different sampling process and cut-off, pore water samples were re-filtered at 0.45 μ m with the same protocol in order to look at the dissolved fraction. For interpretation, we took into account the natural spatial heterogeneity of soils (sampling in a circle of 1 m diameter

around DGT/DET probes deployment location) and that no precautions were taken to prevent
oxidation process of samples by oxygen from atmosphere. Moreover, field conditions prevented
some techniques to be used in certain sampling locations (L4, L5 and L6 for suction lysimeter and
L6 for DET).

79 *Results*

80 Table S4: Comparison of U pore water concentrations obtained from four methods (DET, suction

81 lysimeter, soil suspension and centrifugation) in the studied soil layers and Uranium

82 concentrations in soil. Errors are expressed as confidence interval ($\alpha = 0.05$) in brackets.

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Soil	Depth	[U]det	[U]suc lys	[U]soil susp	[U]centri	[U] soil total
layers	(cm)	(µg.L ⁻¹)	(µg.L ⁻¹)	(µg.L ⁻¹)	(µg.L ⁻¹)	(mg.kg ⁻¹ dry)
L1	0 - 12	102 (17)	53 (5)	210 (21)	30 (3)	1746 (96)
L2	12 - 18	47 (10)	173 (17)	417 (42)	404 (40)	430 (25)
L3	25 – 29	50 (9)	331 (33)	7540 (754)	60100 (6010)	1844 (96)
L4	42 - 49	474 (80)	-	1192 (119)	8000 (800)	791 (47)
L5	49 - 64	250 (42)	-	904 (90)	1178 (118)	600 (34)
L6	69 –75	-	-	5 (1)	11 (1)	47 (9)

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Soil lavore	[U]det	[U] suc lys	[U]soil susp	[U]centri	[U]soil total
Soll layers	(µg.L-1)	(µg.L-1)	(µg.L ⁻¹)	(µg.L-1)	(mg.kg ⁻¹ dry)
L1	102 (17)	53 (5)	210 (21)	30 (3)	1746 (96)
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By looking at the soil layer scale, we observed that the concordance of $[U]_{pw}$ by the four sampling

87 methods was completed in the first soil layer L1 ($[U]_{mean} = 99 \,\mu g.L^{-1}$, sd= 80 $\mu g.L^{-1}$, n=4). Similarly

low differences are found in L6 layer but $[U]_{pw}$ were considerably lower ($[U]_{mean} = 9.2 \ \mu g.L^{-1}$, sd= 3.3 $\mu g.L^{-1}$, n=3) than for the other soil layers. The properties of L1 and L6 soil layers, are close with the highest water and organic matter contents (respectively 85/54% and 47.5%/15.5%). Those properties suggest that U in pore water is strongly complexed by organic matter. Moreover, this specific U speciation was almost sampled similarly by all methods with a cutoff of 0.45 μ m in those layers with a high-water content.

94 On the contrary, for the intermediate soil layers (L2 to L5) between 12 and 64 cm, some differences 95 appear. A clear ranking of the methods can be defined: DET < suction lysimeter < soil suspension < centrifugation and a distinction between field and laboratory-based methods can be done. Huge 96 differences are observed for L3 layer with a maximum factor of 1150 between [U]_{DET} and [U]_{centri} 97 98 concentrations. L3 layer (whitish silt loam soil) is considered as impacted by former mining 99 activities and could contain U minerals under U_{IV} or U_{VI} form Martin et al. (2020). Therefore, 100 laboratory methods involving a shaking stage could promote the dissolution of U minerals and/or 101 favor the release of U colloidal fraction due to the presence of fine particles ($< 0.45 \mu m$) (Table 102 S4). The large difference between centrifugation and DET concentrations can be attributed to the 103 U fraction which is present as large colloidal species, which do not pass the DET gel diffusive layer 104 (Guan 2019, Davison 2016). Moreover, as no specific precaution were undertaken to prevent 105 samples from oxygen, an oxidation process may have occurred and have changed the speciation of 106 U that was less likely for field-based samples.

In conclusion, the wide range of results ($[U]_{pw}$ from 50 µg.L⁻¹ to 60,100 µg.L⁻¹) obtained is consistent with the distinction between field and laboratory-based methods and results of others studies (Di Bonito et al. 2018, Ullah et al. 2012, Leermakers et al. 2005). It raises the question of comparing different studies as this observation may have a huge impact for the calculation of R and its interpretation. The choice of the appropriate method to determine $[U]_{pw}$ appears crucial regarding the difference of concentration factors between methodologies and their direct repercussion on R values.



Fig. S5: Particle size distribution of non-organic soil layers according to USDA definition.

Fig. S6: Oxygen soil profile in the first few centimeters of the Rophin wetland acquired with

118 a Field Multimeter 8686 and an O₂ probe.





Table S7: Pore water pH, cations and anions concentrations results from the Rophin

122	wetland by centrifugation	(LQ: Lin	mit of Quantification	and ND: Not Detected).
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Soil	nЦ	[Na+]	[K+]	[Mg ²⁺]	[Ca ²⁺]
horizon	рп	(mg.L ⁻¹)	(mg.L ⁻¹)	(mg.L ⁻¹)	(mg.L ⁻¹)
L1	6.29	8.23	3.09	1.15	4.51
L2	4.52	13.40	5.20	7.07	29.10
L3	3.92	14.70	7.06	10.95	43.60
L4	3.98	13.60	5.62	1.84	12.03
L5	3.85	12.94	2.60	2.54	10.11
L6	4.58	9.12	2.68	0.98	4.33

Soil	[F ⁻]	[Cl-]	[SO4 ²⁻]	[Br ⁻]	[NO ₃ -]
horizon	(mg.L ⁻¹)	(mg.L ⁻¹)	(mg.L ⁻¹)	(mg.L-1)	(mg.L-1)
L1	< LQ	3.35	11.68	ND	< LQ
L2	< LQ	4.27	133.50	ND	ND
L3	0.25	3.05	220.00	ND	< LQ
L4	18.88	7.89	120.10	ND	1.97
L5	0.25	4.83	100.80	< LQ	< LQ
L6	< LQ	4.14	45.10	ND	1.44

127	Table S8: Soil la	vers concentrations	of Mn. Fe and Pb.	. Errors are ex	pressed as confidence
			0		

Soil	[Mn]soil total	[Fe]soil total	[Pb]soil total
layers	(mg.kg ⁻¹ dry)	(mg.kg ⁻¹ dry)	(mg.kg ⁻¹ dry)
L1	621 (36)	27267 (1510)	2117 (140)
L2	83 (14)	6085 (429)	310 (23)
L3	124 (16)	9873 (652)	1048 (65)
L4	125 (16)	8041 (508)	4613 (267)
L5	169 (17)	12236 (673)	7098 (395)
L6	133 (11)	11802 (630)	213 (17)

128 interval ($\alpha = 0.05$) in brackets.

Fig. S9: XRD diffraction patterns of the soil layers (powder). The main identified mineral



131 phases are: Albite (Alb), Anorthite (Ano), Microcline (Mic) and Quartz (Qz)





Fig. S10: Comparison of depth profiles obtained from the in situ deployment of DET and DGT with R ratio (R=C_{DGT}/C_{DET}) for U in April 2018 and November 2018 and associated depth profiles with indication of water table (+2 cm for April 2018 and -23 cm for November 2018).



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