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Article

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Groundwater uranium origin and fate control in a river valley aquifer

Andre Banning [1†], *Thomas Demmel* [1], *Thomas R. Rüde* [1]*, *Michael Wrobel* [2]

[1]Institute of Hydrogeology, RWTH Aachen University, Lochnerstraße 4-20, 52064 Aachen, Germany

[2]Bavarian Environment Agency, Hans-Högn-Straße 12, 95030 Hof/Saale, Germany

ABSTRACT

Groundwater in a Quaternary gravel aquifer partly exhibits uranium (U) concentrations exceeding the new German drinking water limitation (22 % of the samples >10 µg L^{-1}). This study assesses relevant U reservoirs and hydrogeochemical processes responsible for U transfer between them. A large dataset of solid materials (sediments and soils, 164 samples total) and groundwater (114 samples total) characteristics was created in terms of geo- and hydrochemistry, mineralogy, U microdistribution and mobilization potential. Results show that U primarily derived from lignitic inclusions in Tertiary sediments is transported to and accumulated (complexation to organic substance and UO_2 precipitation) in lowland moor peats of the river valley grown on the aquifer gravels. The alkaline character of the system predefines a hydrogeochemical framework fostering U mobility. Elevated concentrations (up to 96 µg L^{-1} U)

occur downstream of the moor areas and under Mn/NO_3-reducing groundwater conditions. Oxic and stronger reduced settings are rather little affected. Supporting previous laboratory studies, this suggests enhanced U mobility in the presence of nitrate also in the field scale. While no anthropogenic U input was detected in the study area, agricultural usage of the moor areas triggers geogenic U release via nitrate fertilization, surface peat degradation and erosion.

INTRODUCTION

In response to a successively deeper understanding and recognition of uranium (U) impact on human health, mainly as a nephrotoxic heavy metal,[1] German authorities recently established a fixed U threshold value of 10 µg L^{-1} for drinking water valid since 11/2011. This led to an enhanced necessity for water suppliers to identify geogenic and anthropogenic sources of U input especially to groundwater, and to understand hydrogeochemical processes responsible for mobilization and immobilization. The general task for researchers and practitioners is thus to unravel the trace element´s fate in potentially and actually affected environments, and to develop suitable site-specific reactions to the problem.

The Bavarian Environment Agency recently calculated an arithmetic mean U concentration of 1.32 µg L^{-1} in an evaluation of 15,182 groundwater samples from the whole southeastern German federal state. Thereby, a large geology related heterogeneity was figured out with elevated values mainly found in Upper Triassic[2] and Quaternary aquifers. The latter especially refers to fluvial gravels in the southern part of Bavaria and is assumed to be related with U output from organic matter (OM).[3] Nevertheless, distinct reservoir structures, i.e. U sources and sinks, and responsible hydrogeochemical mechanisms and conditions remain unknown. In this study, these were assessed for a postglacial gravelly aquifer used for drinking water extraction

and partly affected by elevated groundwater U concentrations in excess of the new threshold value.

The present study area (~150 km^2) is located in the valley of the river Lech, around 50 km northwest of Munich, in southern Bavaria, southeastern Germany. Quaternary carbonate-dominated gravels in the valley with a thickness of up to 10 m represent a regionally important aquifer used for drinking water supply. The contained groundwater partly exhibits U concentrations >10 µg L^{-1}. Agricultural use of the area resulted in significant nitrate contents. Due to shallow depths of water table (~0.5-2 m below ground surface), hydromorphic soils and lowland moor areas are present along the valley. The latter is surrounded and geologically underlain mainly by Miocene alluvial sandy sediments with a thickness of around 140 m in the study area. These deposits are partly covered by Pleistocene aeolian (loess) sediments.

MATERIALS AND METHODS

Sampling

Sampling of sedimentary rock, soil and groundwater was conducted in two field campaigns. Thereby, the first one represented an area-wide overview identifying relevant units and zones in terms of U occurrences, while the second one served for detailed characterization of the identified “hot spots”.

A total of 46 rock samples were obtained from outcrops and boreholes using percussion drilling. These covered both Quaternary (aquifer gravel, loess, alluvial valley deposits) and Tertiary (alluvial sands including peculiar intercalations therein: Fe-(hydr)oxide concretions,

clayey lenses, lignitic seams) sediments. Furthermore, eleven lignitic inclusions from the whole distribution area of the Miocene sands were sampled from nine sediment cores drilled in the past by rotary drilling and also percussion drilling and stored at the core warehouse of the Bavarian Environment Agency. The dm thick layers of lignitic material were drilled at a wide range of depth between 8 to 150 m below surface. Locations of these nine cores are shown in the supplementary Figure S1. Using a soil probe, soil samples were taken as mixed samples from a depth of ~0.5-0.9 m below ground level, covering all pedological units occurring in the study area whereby a focus was set on OM-rich and hydromorphic soils. Additionally, topsoil (0-0.3 m below ground level) was sampled at ten locations to characterize potential agricultural U input. Depth-oriented soils sampling was accomplished in trial pits at three lowland moor locations. Altogether, 98 soil samples were obtained for analysis. Groundwater was extracted from both the shallow Quaternary (100 samples) and the deeper Tertiary (14 samples) aquifers.

Experimental

All solid samples were homogenized, air-dried and sieved to win the <2 mm fraction which was used for further analysis. Bulk sediment geochemistry including concentrations of U and other trace elements was assessed applying Instrumental Neutron Activation Analysis (INAA, detection limit for U: 0.5 $\mu g\ g^{-1}$) or acid digestion ($HClO_4$-HNO_3-HCl-HF at 240° C) followed by ICP-OES analysis. Soil samples were digested with aqua regia, followed by trace element determination with ICP-MS. Contents of C_{org}, C_{inorg}, N and S were measured for 38 samples following dry combustion, soil pH was detected in $CaCl_2$ suspension. Physico-chemical groundwater parameters (T, eC, pH, dissolved O_2) were analyzed on-site during sampling. For selected samples, Eh was determined by addition of 200 mV to the on-site redox potential readings. TOC/DOC contents were determined in the laboratory (high temperature catalytic

oxidation), as were major and trace element concentrations applying ICP-OES, IC and ICP-MS (detection limit for U: 0.1 µg L^{-1}).

Based on the obtained data, selected solid samples were subjected to further analysis. X-ray diffraction was applied to 15 samples to study the mineralogical composition and to identify potential U host phases. Samples were finely ground in a corundum mill and measured using a Co-K_α diffractometer. Results were evaluated for mineral phase identification and quantification applying Rietveld analysis with the software BGMN 4.2.3[4] and using the database MINCRYST[5] for peak allocation (cf. Table S4).

For estimating U solid phase association and mobilization potential, an operationally defined 5-step sequential extraction procedure was performed for 16 sediment and soil samples (SEP 1: 0.4 M $MgCl_2$, 1 h at room temperature (RT), targeting the water soluble/exchangeable fraction[6] – SEP 2: 0.025 M EDTA, 1.5 h at RT, targeting the surface complexed fraction[7] – SEP 3: 0.2 M NH_4-oxalate+0.1 M ascorbic acid, 0.5 h at 96°C, targeting the reducible, e.g. Fe-(hydr)oxide-associated, fraction[8] – SEP 4: 30 % H_2O_2 3 h at 85 °C, targeting the oxidizable, e.g. sulphide-associated, fraction[9] – SEP 5: residual fraction [U_{tot}-$\Sigma U_{SEP\ 1\text{-}4}$]). After the respective extraction, centrifugation (15 min at 3000 rpm) and filtration (0.45 µm) of the supernatant solution, the remaining sediment was subjected to the subsequent step. Uranium concentrations in 0.45 µm filtered leachates were analyzed by ICP-MS.

The distribution of U and other elements on a microscale was characterized in 5 solid samples applying Laser-Ablation-ICP-MS with a spot diameter of 75 µm and the trace element standard NIST 612.

Uranium speciation in groundwater as well as mineral phase saturation states were modelled using the software code PhreeqC 2.[10] To classify dominant redox processes in groundwater samples, a USGS worksheet was used.[11] It determines prevailing redox categories based on the concentrations of redox-sensitive parameters (dissolved O_2, NO_3^-, Mn^{2+}, Fe^{2+}, SO_4^{2-} and sulphides).

RESULTS AND DISCUSSION

Collected data is presented and discussed in the following, distinguished between findings from solid materials and groundwater characterization, and finalised by some concluding remarks. A more detailed tabulation of obtained data and additional materials are accessible in the supporting information.

Sediments and soils

Geochemistry and mineralogy

Uranium concentrations in the different sediment sample groups are shown in Figure 1a. Locations of the samples are given in the supplementary Figure S2.

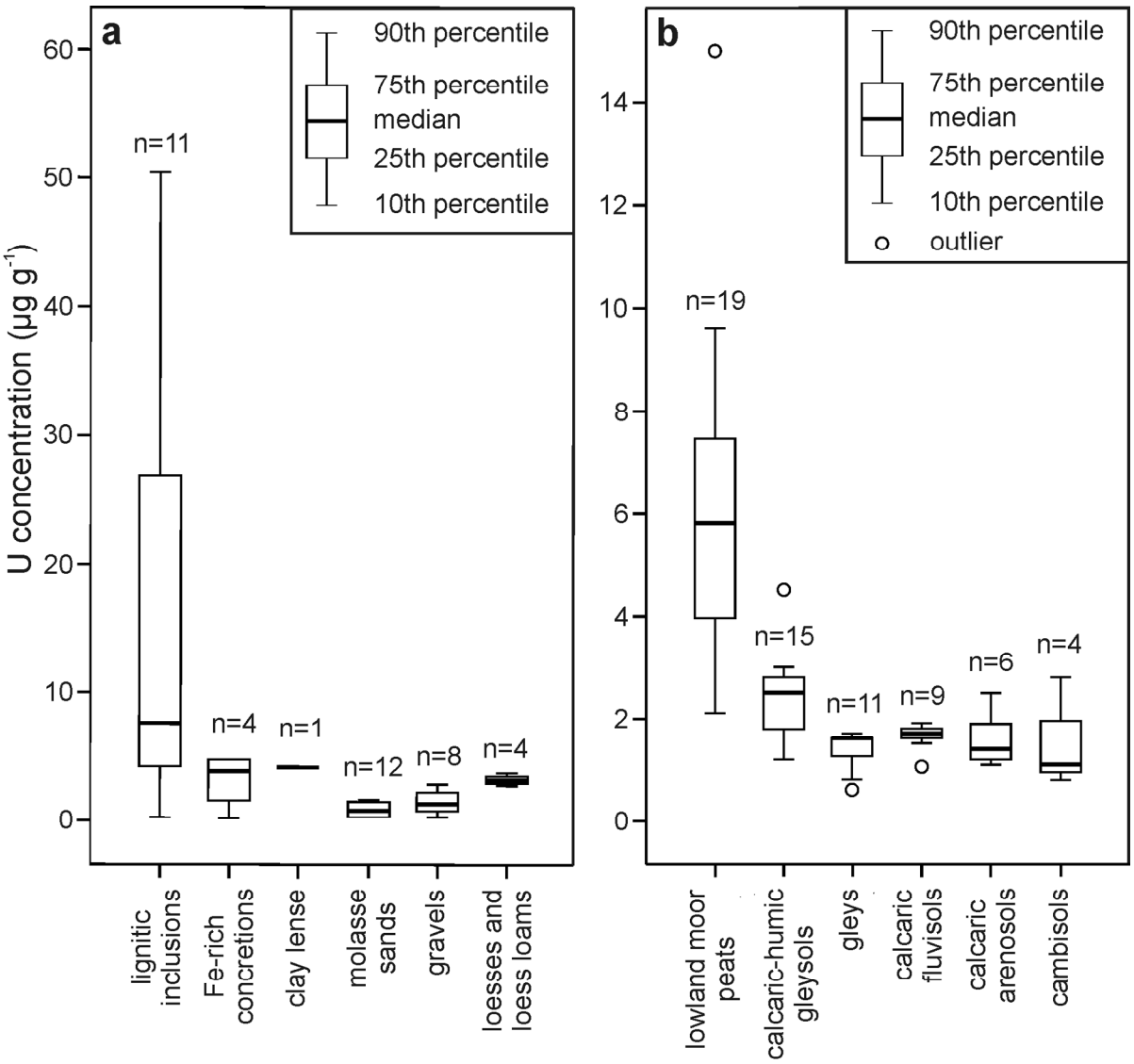

Figure 1. U distribution in different sample groups of (a) sediments and (b) soils.

Quaternary deposits exhibit relatively low and homogeneously distributed bulk U contents with higher median values in loess/loess loam sediments (3.2 µg g^{-1}) than in alluvial valley deposits (2.6 µg g^{-1}) and aquifer gravels (1.3 µg g^{-1}). Eye-catching intercalations (Fe-hydroxide concretions, clay lenses, lignitic seams) contain significantly higher U concentrations than the

ambient Tertiary pure sands (0.8 µg g^{-1}). Thereby, the lignitic inclusions show highest median values (7.6 µg g^{-1}) and variability (<0.5-50 µg g^{-1}) (Fig. 1a, Table 1). Two samples from a borehole in the direct vicinity of the study area exhibited 22.8 and 33.1 µg g^{-1} U, respectively. Iron hydroxide concretions within the Tertiary sands (median U: 3.9 µg g^{-1}) partly contain high As contents of up to 1800 µg g^{-1} which supports previous observations in similar samples.[12]

Table 1. Bulk U concentrations, water soluble/exchangeable ("SEP_1") and totally soluble ("SEP_{1-4}") U and mineralogy of sediment and soil samples (without topsoil samples). ["Q": Quaternary, "T": Tertiary, "n=" number of samples in the respective sample groups analyzed for bulk U/sequential extraction/mineralogy, "n.a."=not analysed, "Qtz"= quartz, "Dol"= dolomite, "Cal"= calcite, "Ms"= muscovite, "Fsp"= feldspars, "Cm"= clay minerals, "Ttn"= titanite, "Anh"= anhydrite, "Gt"= goethite, "Alm"= almandine]

Samples		U [µg g^{-1}]			SEP_1 [% U_{tot}]			SEP_{1-4} [% U_{tot}]			Mineralogy
		min	med	max	min	med	max	min	med	max	phases (decreasing wt.%)
Sediments	loesses and loess loams (Q, n=4/1/2)	2.7	3.2	3.7	0.3			8.2			loess: Qtz, Dol, Cal, Ms, Fsp, Cm; loess loam: Qtz, Ms, Fsp, Cm
	alluvial valley deposits (Q, n=6/0/1)	<0.5	2.6	10	n.a.			n.a.			Qtz, Dol, Ms, Cal, Cm, Fsp
	gravels (Q, n=8/0/0)	<0.5	1.3	2.8	n.a.			n.a.			n.a.
	alluvial sands (T, n=12/0/1)	<0.5	0.8	1.6	n.a.			n.a.			Qtz, Ms, Fsp
	clay lense (T, n=1/1/1)	4.2			<0.2			19			Qtz, Cm, Ms, Ttn, Fsp, Anh
	Fe-rich concretions (T, n=4/2/3)	<0.5	3.9	4.8	<0.2			6.0	6.4	6.8	Qtz, Fsp, Ms, Cm, Ttn, Gt, Alm
	lignitic inclusions (T, n=11/5/0)	<0.5	7.6	50	1.8	6.7	22	40	59	74	n.a.

Soils	cambisols (n=4/0/0)	0.8	1.1	2.8	n.a.			n.a.			n.a.
	calcaric arenosols (n=6/0/1)	1.1	1.5	2.5	n.a.			n.a.			Qtz, Dol, Cal, Ms, Fsp, Cm
	calcaric fluvisols (n=9/0/1)	1.0	1.7	1.9	n.a.			n.a.			Dol, Cal, Qtz, Ms, Fsp, Cm
	gleys (n=11/1/1)	0.6	1.6	1.7	3.6			52			Qtz, Dol, Cal, Ms, Fsp, Cm
	calcaric-humic gleysols (n=15/1/1)	1.2	2.5	4.5	2.1			100			Cal, Dol, Qtz
	lowland moor peats (n=19/5/0)	2.1	5.8	15	<0.2	0.4	1.1	18	44	59	n.a.

In terms of mineralogy (Table 1), quartz is the dominant phase in all analyzed sediment samples. Feldspars, muscovite and clay minerals are present in varying amounts. Carbonate phases (calcite, dolomite) only appear in the Quaternary sediments. For loess loam samples, decarbonatization is observed (Table 1). This carbonate loss does not seem to affect bulk U concentrations, therefore calcite is not considered a significant U carrier phase here, although the mineral can generally represent a U host.[13] In addition to silicate phases assembling the Miocene sands, reddish concretions therein contain goethite and the heavy minerals titanite and almandine (a Fe-bearing garnet). The latter reaches quantities of up to 30 wt.% – part of the eye-catching red inclusions in the Tertiary sands is therefore probably existent as garnet placers with goethite cement. While the Fe-hydroxide tends to accumulate U via surface complexation[14] or coprecipitation[15], the aforementioned garnet is able to include U in its crystal structure.[16]

Figure 1b and Table 1 show U distribution in the different soil types (mixed samples from ~0.5-0.9 m below ground surface). Values for the ten sop soil samples are discussed later. Highest median (5.8 µg g^{-1}) and single (15 µg g^{-1}) values are found in lowland moor peats, thus documenting an enrichment factor of ~4 compared to OM-poor soil types (cambisols, calcaric

arenosols, calcaric fluvisols, gleys; median U contents between 1.1 and 1.7 µg g^{-1}, no single value above 3 µg g^{-1}). The second highest median concentration (2.5 µg g^{-1}) is found in calcaric-humic gleysols – OM contents and U concentrations appear to co-vary in soils.

After having identified lowland moor as highest-U soil type, trial pits were accomplished to characterize depth-dependent distribution and behaviour of U at three relevant locations. Figure 2 illustrates soil horizonation as well as U and C_{org} concentrations development in one of these pits with a total depth of ~2 m below ground level. The location is in agricultural use.

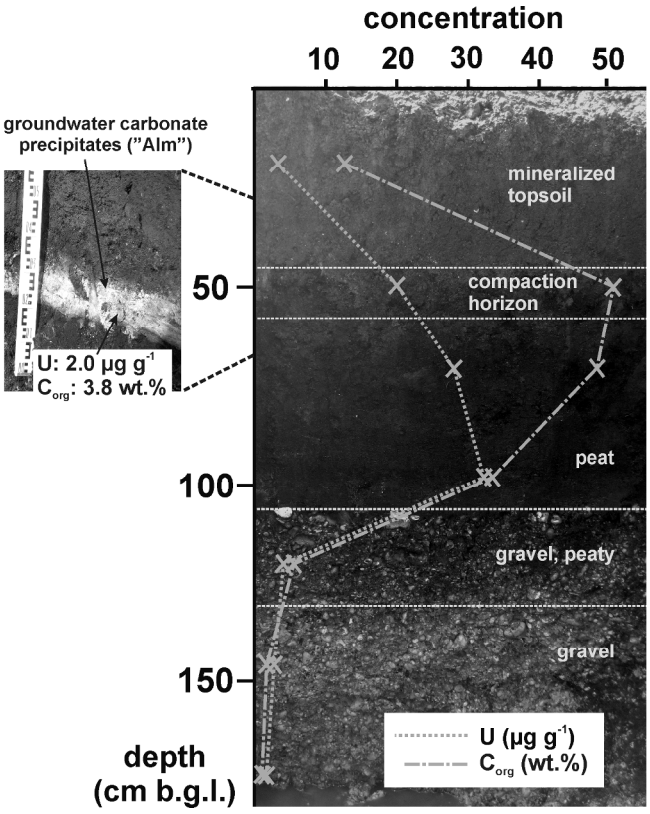

Figure 2. Soil profile and depth-dependent development of U and C_{org} concentrations in one of the lowland moor trial pits. Upper left image: example of calcite precipitates mainly found in the upper part of the peat.

The excavated representative profile can be roughly split into Quaternary aquifer gravel at the bottom and the lowland moor peat grown thereon. The latter extends to a depth of ~1.05 m b.g.l., it may be subdivided into a brownish-black lower peat horizon and a rather greyish degraded mineralized topsoil. Low concentrations of both U and C_{org} prevail in the gravels, increasing slightly in the more peaty top of the aquifer material (Fig. 2). The peat hosts significantly higher U (up to 32 µg g^{-1}) and C_{org} (up to 51 wt.%) concentrations, both of which massively decrease again in the mineralized topsoil. It is interpreted that in the course of peat degradation associated with agricultural activity, organic matter and U are released from the soil. The parallel development of both parameters documented for a large part of the profile indicates a common occurrence, i.e. U hosting by organic matter as will be discussed later on. This subparallel trend is separated at the top of the peat horizon where a well-compacted black horizon (probably derived from compaction by agricultural machinery) shows peak C_{org} contents while U values already decrease.

In the pits, occurrences of subhorizontal white carbonate intercalations were uncovered. These represent pure calcite (~99 wt.% as determined by quantitative XRD) groundwater precipitates locally referred to as “Alm” (Fig. 2). They contain little U and C_{org} but clearly indicate alkaline conditions in the lowland moor, supported by an average soil pH of 7.3 in the given profile and a pH of 7.2 measured in the groundwater sampled from the pit bottom. Moreover, horizontal orange Fe hydroxide precipitates were partly detected within the peat horizon arguing for at least temporary oxic redox conditions.

Observations in the other soil profiles support the reported findings. At locations yielding profiles without a visible mineralized topsoil (i.e. without visible signs of peat degradation; mainly under usage as grassland), U and C_{org} concentrations develop parallely throughout the

profile. Approaching the soil surface, their decrease is much less articulate as compared to agriculturally used sites (cf. Fig. 2).

The association of U and organic matter is underlined for the whole soil dataset by a U-C_{org} coefficient of determination of R^2=0.74. Uranium(VI) tends to accumulate in OM-rich soils, mostly via complexation to humic and fulvic acids.[17] This was identified as the dominant process in a lowland moor in California by Idiz et al.[18] while plant uptake and mere surface adsorption were considered to be of minor importanceFurthermore, microbiologically mediated reducing conditions in such milieus lead to U immobilization as uraninite (UO_2) or other U(IV) species associated with biomass. Bog environments can thus represent effective barriers for aqueous U transport with documented elevated concentrations, partly up to mineable levels.[19-24] This second potentially relevant U immobilization mechanism in the given environment occurs under strongly, i.e. Fe(III)-reducing, conditions.[25-29] An evaluation of this process in the study area is conducted by means of hydrogeochemical modelling as presented in the discussion on groundwater later on.

Uranium microdistribution and mobility

Laser Ablation ICP-MS (LA-ICP-MS) measurements conducted for 5 solid samples aimed at characterizing U distribution on a microscale and allowed for statements on either homogenous occurrence or existence of preferential U accumulation areas (cf. supporting information). Results supported the assumption that U in Tertiary sediments is associated with Fe concretions: point analysis in the Fe-rich sections yielded 8.0±1.9 µg g^{-1} U, compared to 1.7 µg g^{-1} in the non-mineralized area. Goethite was identified as Fe host in these intercalations (Table 1) and most likely functions as main U sorbent in the sediments. Uranium remobilization potential from these

deposits appears quite limited as evidenced by a non-detectable water soluble/exchangeable fraction (SEP 1) and a residual fraction (SEP 5) accounting for >93 % U_{tot} (Table 1).

Point measurements in two lignitic sediments obtained from different drillcores resulted in U concentrations of 49±15 µg g^{-1} and 225±67 µg g^{-1}, respectively. While this proved a certain variability within single samples as well as different sampling locations, distinctive U nests were not identified. Supported by the microscopically observed homogeneous dark brownish appearance, this argues for a rather extensive U uptake by Fe-hydroxides (40-60 % U_{tot} were dissolved in the reducible step (SEP 3), positive correlation between U and Fe from the point measurements of R^2=0.76). Water soluble/exchangeable U (SEP 1) was present in all analyzed lignites accounting for up to 5.1 µg g^{-1}. Bulk U remobilization potential (SEP 1-4) from these deposits is significantly higher as compared to the other analyzed sediments (Table 1).

Similar to the findings for lignitic inclusions, LA-ICP-MS measurements in the lowland moor peats (appearing as relatively homogenous greyish material including carbonate and silicate grains under the microscope) did not indicate the presence of primary U phases. Uranium concentrations in the two samples were 46±13 µg g^{-1} and 8.7±1.7 µg g^{-1}, respectively. In the LA-ICP-MS point analysis, positive correlations towards Fe were not detected, making U complexation by organic substances the most likely accumulation process. Total U remobilization potential (SEP 1-4) in these soils is similar to that of the lignitic inclusions described above while the water soluble/exchangeable fraction (SEP 1) yields a maximum of 0.1 µg g^{-1} only. The latter observation argues for the necessity to fully mobilize the U-hosting organic matter in order to enable significant U release to solution, i.e. groundwater. Remarkably, U content of the calcaric-humic gleysol sample was entirely dissolved during SEP which

indicates a high mobilizability and a potential U source function of this soil type despite lower bulk concentrations (Table 1).

Anthropogenic uranium input?

Phosphorus fertilizer has been recognized as a potential anthropogenic U source in agricultural areas during the past decade.[30] Partly elevated U concentrations in the raw material derive from U tendency to substitute for Ca in the mineral structure of apatite representing the dominant P carrier for fertilizer production.[31-33] Suchlike U will accumulate especially in the uppermost layers of cropping soils.[34] To evaluate a fertilizer-derived U input in the given study area, ten topsoil (0-30 cm b.g.l.) samples were taken from farmland and reference locations without agricultural usage. While the latter yielded U concentrations of 2.1±0.4 µg g^{-1}, farmland topsoils contained 1.9±0.6 µg g^{-1}. Uranium contents are therefore comparably low. Consequently, the given dataset does not suggest an anthropogenic U input to the studied soils.

Groundwater

Hydrochemistry and uranium distribution

In both the Tertiary (T) and the Quaternary (Q) aquifer, Ca-Mg-HCO_3 represents the dominant hydrochemical water type. Circumneutral to slightly alkaline pH conditions prevail in both aquifers (Q: 7.1±0.2; T: 7.4±0.1). Variable contents of Fe, Mn and dissolved O_2 in both aquifers argue for heterogenous redox conditions.

Table 2. Attributed redox category (after [11]), U and DOC concentrations and percentage of U drinking water limitation exceedance in Quaternary and Tertiary groundwater of the study area.

Aquifer	Redox category	U [µg L^{-1}]			% data > 10 µg L^{-1}	DOC [mg L^{-1}]			NO_3^- [mg L^{-1}]
		min	mean	max		min	mean	max	median
Quaternary	oxic (n=73)	0.9	7.0	19	18	<0.5	1.4	3.0	39
	Mn/NO_3 - reducing (n=18)	0.9	17	96	61	0.7	3.6	20	33
	Fe/SO_4 - reducing (n=9)	0.1	4.6	10	0	<0.5	3.9	7.4	<0.5
Tertiary	oxic (n=8)	0.4	1.8	3.7	0	<0.5	0.4	0.8	4.8
	Mn/NO_3 - reducing (n=0)	-	-	-	-	-	-	-	-
	Fe/SO_4 - reducing (n=6)	0.2	2.2	6.0	0	<0.5	0.5	0.7	<0.5

Nitrate concentrations are higher in the Quaternary groundwater than in the deeper layers. Elevated concentrations of dissolved organic carbon (DOC) and U (22 % of samples of the total dataset in excess of the new drinking water limitation) are found in the Quaternary aquifer only, whereby redox-dependent differences become obvious (Table 2). Uranium speciation is largely dominated by carbonate complexes $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ as indicated by PhreeqC equilibrium modelling.Uranium fate control: role of Eh

To unravel the mechanisms leading to the observed U distribution and accumulation in Quaternary groundwater, U behaviour towards other hydrochemical parameters was analysed. Figure 3 illustrates a scatter plot of U vs. DOC concentrations, set in relation to prevailing redox conditions.

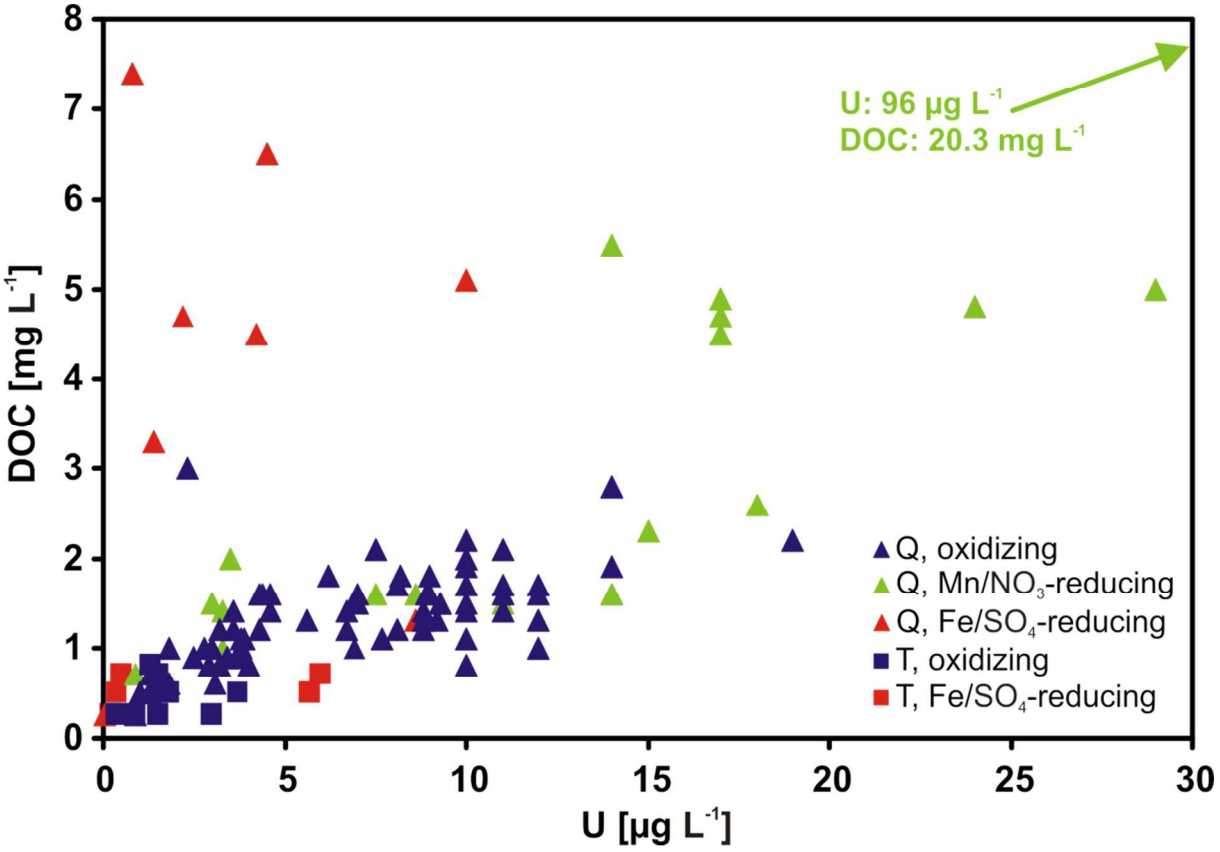

Figure 3. U vs. DOC for Quaternary (Q) and Tertiary (T) groundwater samples, distinguished by prevailing redox conditions as determined after [11].

While no trend between U and DOC is visible for Tertiary groundwater, oxidizing Quaternary samples exhibit a weak, significant ($p<1$ %) positive correlation between these parameters ($R^2=0.52$ for n=70, ignoring 3 statistical outliers). High U concentrations of up to 96 µg g^{-1} are detected especially in waters with Mn/NO_3-reducing conditions. 61 % of the samples from this cohort, which includes the groundwaters obtained from the aforementioned trial pits, exceed 10 µg g^{-1} (Table 2). Stronger (Fe/SO_4-) reducing conditions, on the other hand, coincide with lower U contents – no single value exceeds the drinking water limit (Table 2, Fig. 3). These

observations suggest a common source material for U and C_{org}, probably the lowland moor peats. Highest U groundwater concentrations within or downstream the swampy areas support this assumption. Microbiological degradation of the released humic substances leads to successively more reducing conditions in solution. As soon as Eh drops into the stability field of UO_2,[35] dissolved U is reduced and immobilized by precipitation as uraninite or other U(IV) species[36]. In summary, an ideal "redox window" appears required for allowing high U concentrations in groundwater, provided that sufficient source material (expressed by DOC) is available and redox conditions are not yet reducing enough to enable U withdrawal from solution. These findings are in accordance with earlier laboratory and field studies where U mobility was shown to be significantly enhanced in the presence of nitrate as an electron acceptor. Thereby, both abiotic and bacterial oxidation of U(IV) to U(VI), leading to U release, were observed. Furthermore, reduction and thus immobilization of U(VI) are constrained when NO_3^- is present in solution. Failure of U remediation measures by induction of reducing conditions was partly explained by this finding.[26, 37-41]

To evaluate the possibility of UO_2 precipitation in the studied environment, hydrogeochemical scenario modelling was conducted using PhreeqC. Groundwater data from the lowland moor trial pits samples representing initial conditions for U release from peat were chosen as starting points. Figure 4 shows the simulation of successively more reducing conditions aiming at a characterization of newly adapting equilibria with potential U host phases.

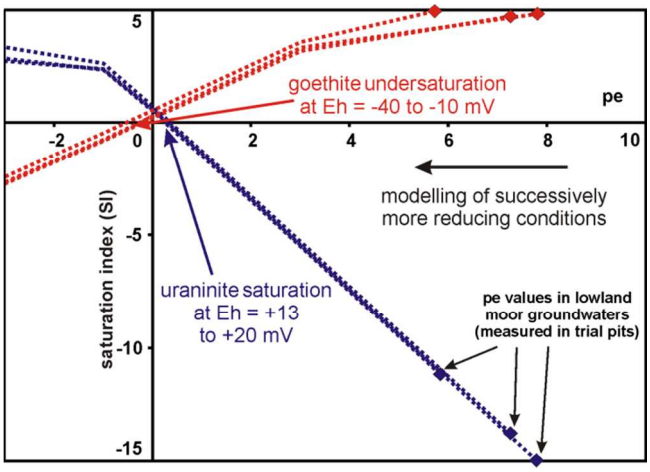

Figure 4. Modelled development of $SI_{uraninite}$ (blue lines) and $SI_{goethite}$ (red lines) during successively stronger reductive conditions (decreasing pe) for groundwater samples taken in lowland moor trial pits.

Starting from oxic conditions in the samples and associated significant undersaturation of UO_2, uraninite SI increases with decreasing pe. Saturation is reached at Eh values between +13 and +20 mV, a redox zone typical for peat bog waters.[42] Therefore, U immobilization by UO_2 precipitation is a presumable second fixation process besides complexation with organic acids in the studied environment (although, as mentioned above, UO_2 was not observed during microscopical and LA-ICP-MS analyses). Pyrite representing another potential U host phase[43] is clearly undersaturated (SI_{pyrite} around -40) over the whole modelled Eh range and therefore unlikely to contribute to U fixation in the system. Goethite saturation conditions develop oppositionally to those of uraninite: initial oversaturation inverts to undersaturation at Eh= -10 to -40 mV (Fig. 4). Thus, potentially released U in the course of Fe hydroxide reductive dissolution should be re-immobilized as UO_2. Nevertheless, caution should be exercised if applying these

findings in order to fix U in a lowland moor by inducing stronger reducing conditions via, e.g. swamp rehydration. On the one hand, Spycher et al.[44] found that UO_2 reoxidation in the presence of Fe hydroxides can occur even under SO_4-reducing conditions. On the other hand, other potentially harmful trace elements bound to sesquioxides and thus immobile under oxic conditions, e.g. As, might be remobilized. Arsenic concentrations of up to 170 µg g^{-1} were detected in the peats of the study area.

Uranium fate control: role of pH

Enhanced mobility of U under oxidizing conditions is mainly reasoned by its tendency to form stable U(VI)-carbonato-complexes governing U speciation in bicarbonate-dominated waters.[40,41,45] Uranium concentrations in the studied Quaternary groundwater do not exhibit a direct dependence from pH (R^2=0.01). Elevated values >10 µg L^{-1} appear over the whole pH range of the samples (~6.9-7.5). Nevertheless, the alkaline character of the calcaric lowland moors is likely to play a crucial role for U distribution and mobility. In lowland moor peats, Idiz et al.[18] found U concentrations elevated by a factor of ~10 compared to this study while release to groundwater was not detected – the peat functions as U sink. This was attributed to the low pH (~5) of the swamp. In laboratory experiments, the authors identified this pH as the sorption efficiency peak of UO_2^{2+} to organic matter (>90 %). With increasing pH, sorption efficiency decreases substantially reaching ~60 % in the pH range found in this study.[18] The mechanism behind this pH-dependent U release was studied by Zielinski and Meier[46] and referred to as "carbonate leaching" generally following the process

$UO_2(Hu) + 2\ CO_3^{2-} \rightarrow (Hu)^{2-} + UO_2(CO_3)_2^{2-}$ where "Hu" represents humic substances.[46]

Consequently, U bound in organic substance is released under carbonate presence forming stable carbonato complexes. Hydrogeochemical, physico-chemical and speciation analyses suggest that these conditions correspond exactly to those found in the present study area. The given process, referred to as major U release mechanism from organic matter besides peat oxidative destruction and erosion,[46] is therefore likely to further trigger U mobilization from the lowland moors and foster elevated concentrations in near-surface Quaternary groundwater.

In summary, geogenic uranium was mobilized from Tertiary lignitic sediments (primary U source), transported into a swampy river valley and accumulated in lowland moor peats (primary U sink/secondary U source). The hydrogeochemical framework determines the presence of elevated U groundwater concentrations partly exceeding drinking water limitations in the Quaternary river valley gravel aquifer whereby slightly alkaline and Mn/NO_3-reducing conditions are decisive. Against this background of naturally enhanced U mobility potential, agricultural activity further triggers the U source function of the moor via peat degradation and nitrate fertilization. Direct anthropogenic U input, however, was not identified.

The present process-oriented examination combines previous laboratory results on environmental U behaviour to explain its dynamics in a natural system and thus documents their transferability to the field scale. It was successful in characterizing the origin and fate control of elevated groundwater U concentrations in an important aquifer. Findings of this study will be used to identify U occurrences and dynamics in similar areas in southern Germany and can prove helpful in doing so for comparable environments worldwide. They have to be considered when it comes to drinking water extraction from U-affected aquifers or remediation approaches in a high U/C_{org} milieu, especially if under agricultural usage.

Supporting Information available. Study area maps and additional figures, full data tables on sediment and soil geochemistry and mineralogy, LA-ICP-MS analyses and hydrochemistry. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Author

* Corresponding author, ruede@hydro.rwth-aachen.de, phone: 0049-241-80-95743, fax: 0049-241-80-92280

Present Addresses

† Present address: Andre Banning, Hydrogeology Department, Ruhr University Bochum, Universitätsstraße 150, 44801 Bochum, Germany

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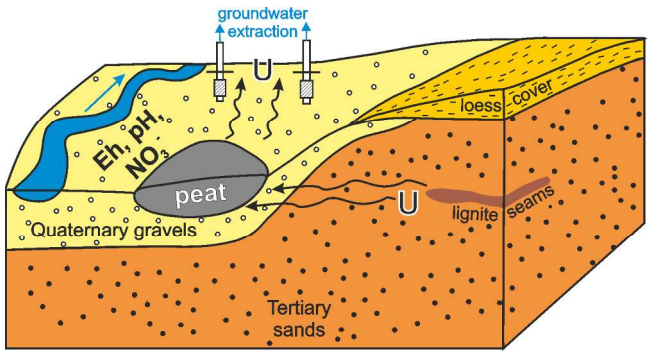
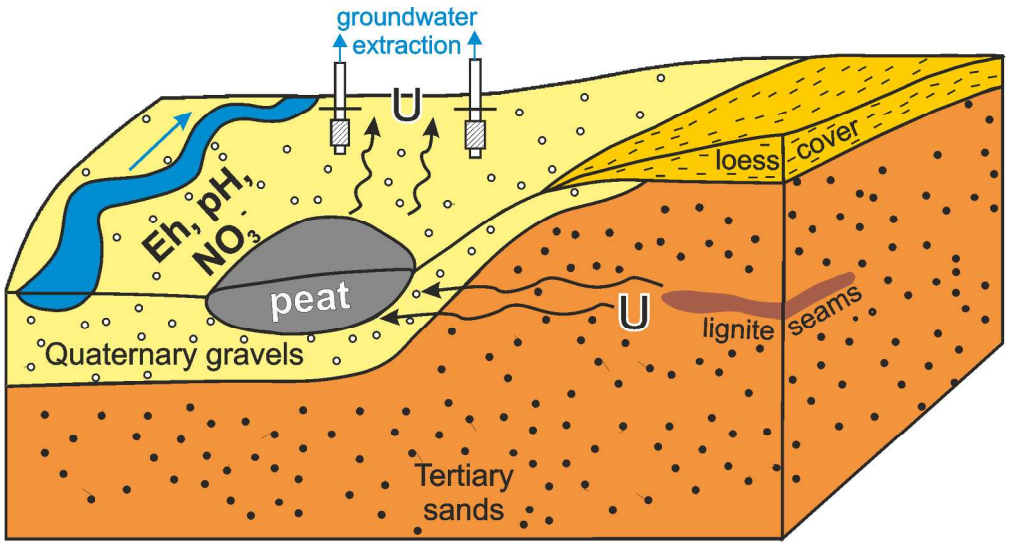
TOC/Graphical abstract





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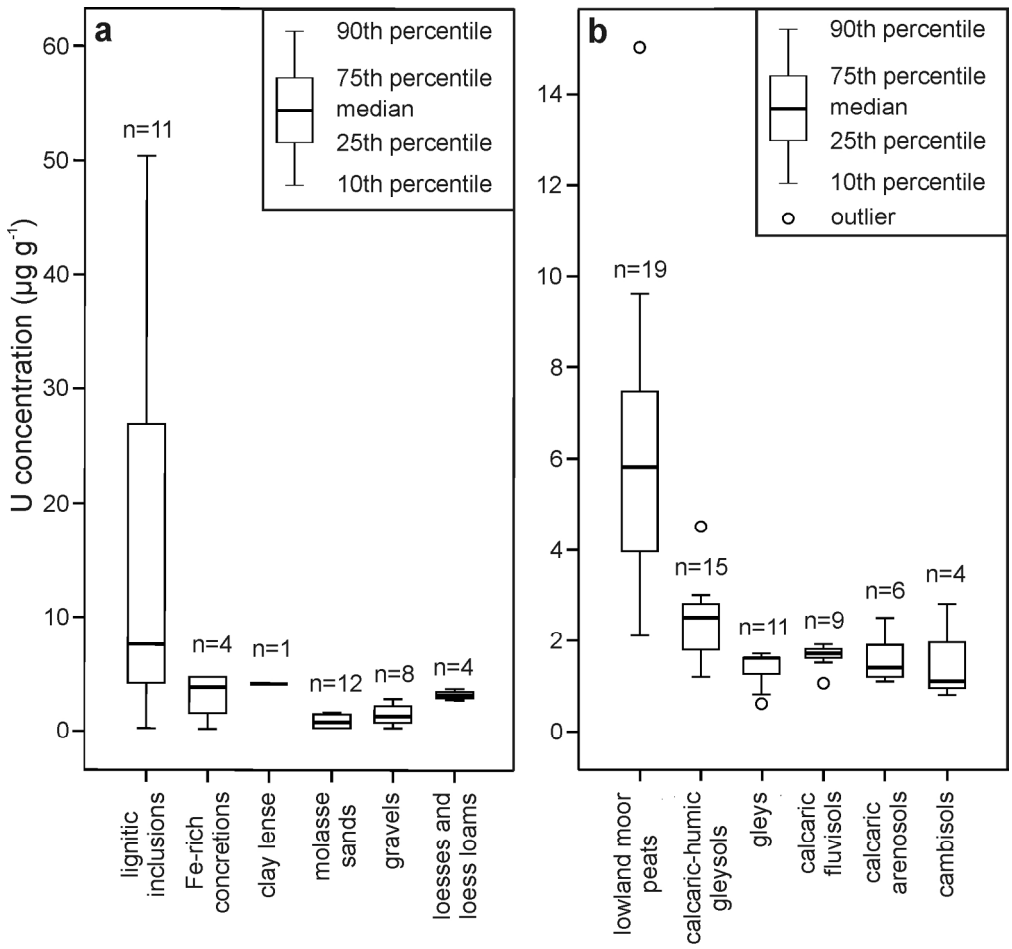

Figure 1. U distribution in different sample groups of (a) sediments and (b) soils.
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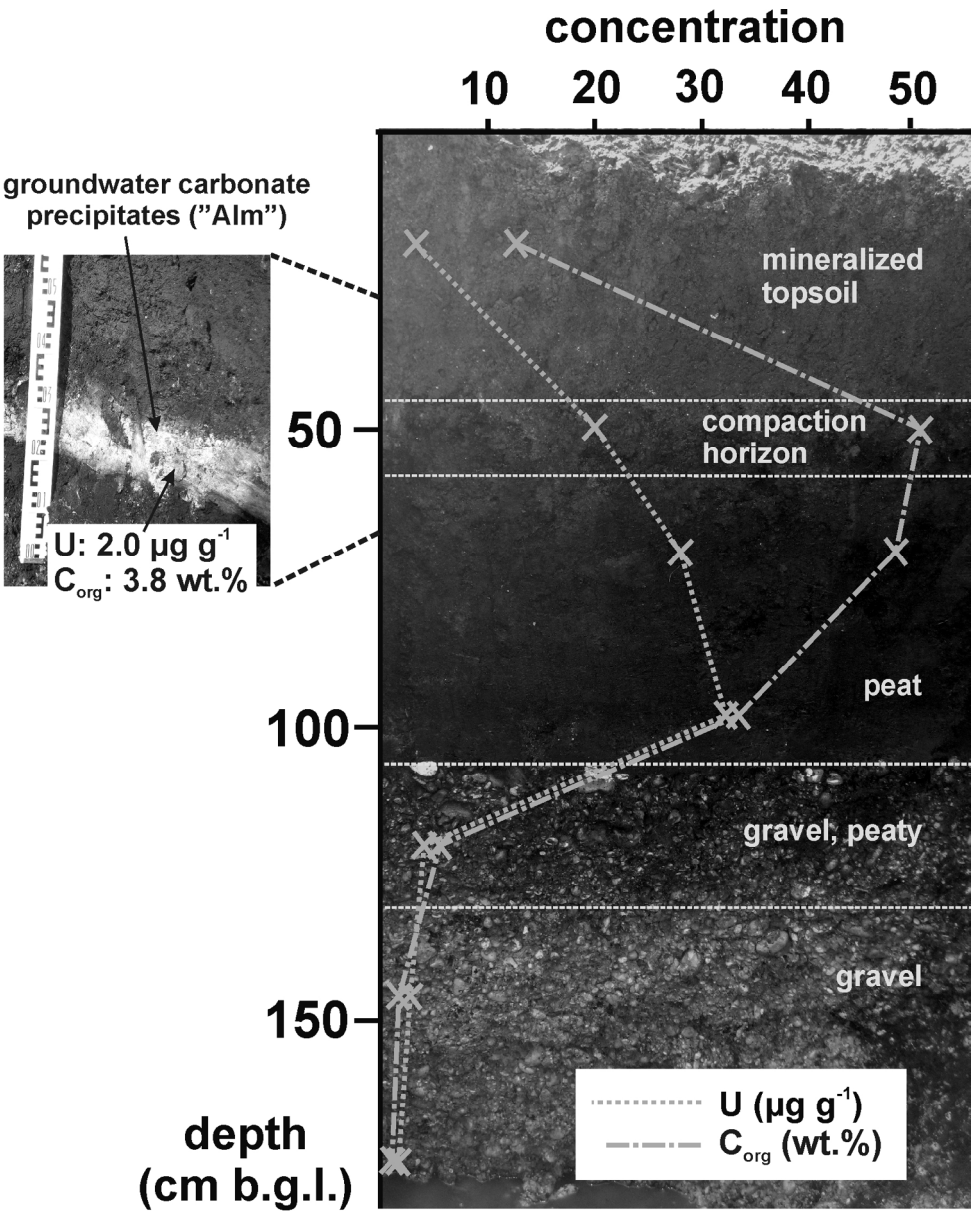

Figure 2. Soil profile and depth-dependent development of U and Corg concentrations in one of the lowland moor trial pits. Upper left image: example of calcite precipitates mainly found in the upper part of the peat.
152x189mm (300 x 300 DPI)

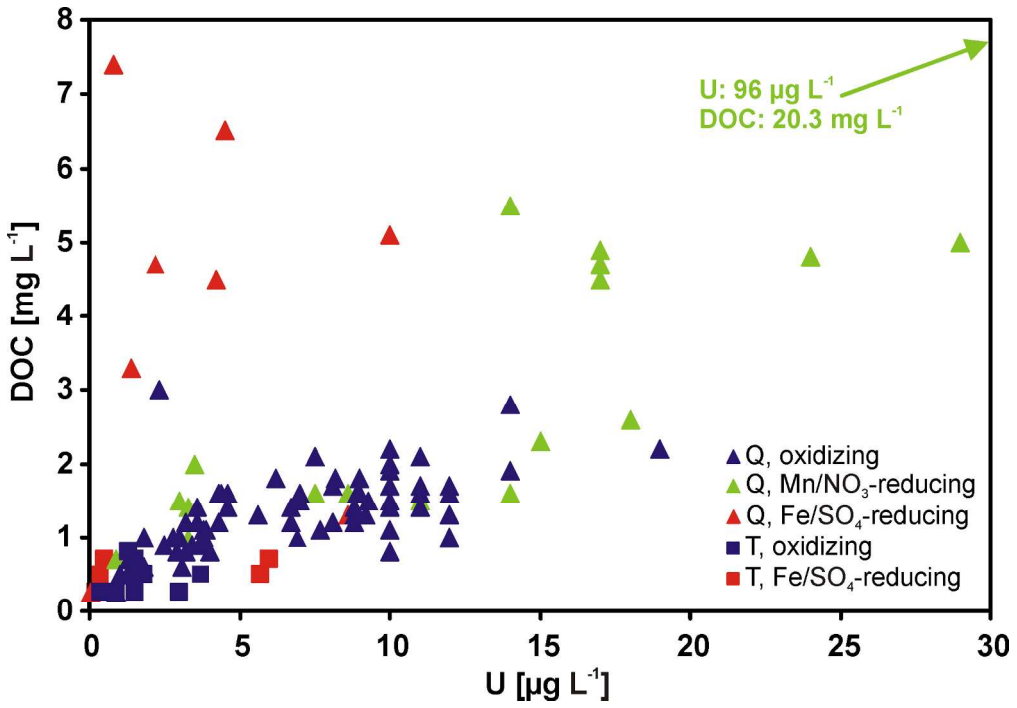

Figure 3. U vs. DOC for Quaternary (Q) and Tertiary (T) groundwater samples, distinguished by prevailing redox conditions as determined after 11.
190x131mm (300 x 300 DPI)

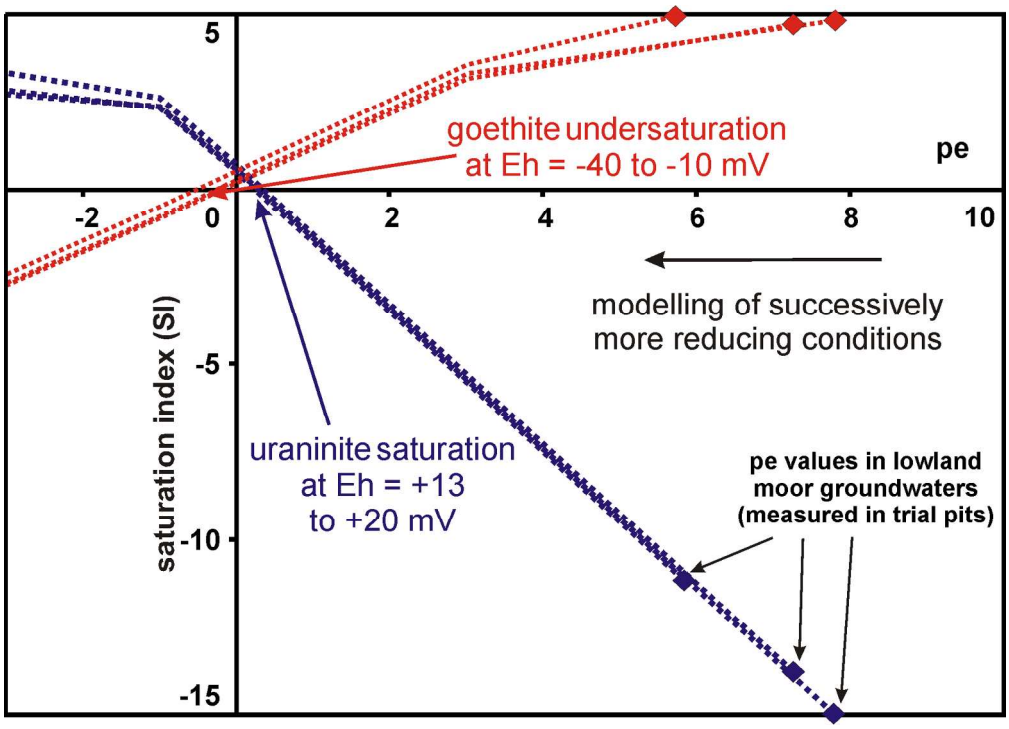

Figure 4. Modelled development of SIuraninite (blue lines) and SIgoethite (red lines) during successively stronger reductive conditions (decreasing pe) for groundwater samples taken in lowland moor trial pits.
171x123mm (300 x 300 DPI)