

Article

Peatlands as Filters for Polluted Mine Water?—A Case Study from an Uranium-Contaminated Karst System in South Africa Part II: Examples from Literature and a Conceptual Filter Model

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Abstract: As the second part of a series of four, this paper reviews a number of case studies of natural uranium attenuation in peat, as well as underlying chemical mechanisms reported in literature. Based on this review, a generic, conceptual, model for peat to act as filter for dissolved uranium (U) is developed for guiding subsequent field investigations. The model consists of a chemical and an hydraulic component which is derived largely from data reported in literature as well as from limited field observations. For the chemical model component 10 different processes, each controlled by factors relating to water chemistry, have been identified to govern the attenuation of U in peat via a net balance of immobilization and remobilization. For the hydraulic aspect of the filter model, five different principal modes of U polluted water coming in contact with peat are discussed, focusing on the associated peat-water contact time as a crucial parameter controlling chemical U attenuation. Moreover, links between the two model components are discussed and, based on the integrated conceptual model, possible effects of natural and anthropogenic events on U attenuation in peatlands are outlined. Guided by the model, various site-specific field and laboratory investigations are finally designed to verify how far the identified generic factors and processes are indeed applicable to the Gerhard Minnebron Peatland.

Keywords: uranium; peat; natural attenuation; conceptual model; immobilization; remobilization; water chemistry; hydraulic processes; Gerhard Minnebron; dolomitic karst

1. Introduction

1.1. Project Background

This paper is the second part of a four paper series. Part I outlined the regional hydrological and geohydrological settings in the study area including impacts of deep level gold mining and the large-scale dewatering of dolomitic aquifers. The latter also quantifies the amount of waterborne U transported in the fluvial system which may impact on the Gerhard Minnebron (GMB) wetland. The findings indicate that well over three tons of waterborne U is annually lost from the Wonderfonteinspruit (WFS) into underlying karst aquifers that feed the GMB peatland. Since much of the water used by the downstream community of Potchefstroom is derived from the GMB wetland this U-influx is reason for concern. Furthermore, as one of three potential outflow points in a future rewatering scenario, the GMB wetland may be subjected to massive influx of highly U-polluted water [1]. Following reports of peat being able to act as an efficient filter for U and other dissolved heavy metals (e.g., [2-8]), the aim of this paper is to develop a model to assess the ability of local peat to fulfill a filter function for U.

Currently two peat mining operations excavate peat from the GMB wetland. Results of the study are expected to inform decisions by governmental departments regarding applications to extend existing operations. Furthermore, the study also bears relevance to a current court case where one of the peat mining companies claims compensation from an upstream gold mine for polluting the peat reserve with U.

1.2. Case Studies of Natural U-Accumulation in Peat

Peat consists of partially decomposed wetland plants accumulating in waterlogged environments where the sustained influx of organic matter results in the depletion of dissolved oxygen through bacteria-aided decomposition of dead plant material. The resultant anaerobic conditions under which a complete mineralization of the plant material cannot be achieved leads in the long-term to the preservation and subsequent accumulation of organic matter as peat.

Sampling some 145 wetlands in the Rocky Mountains, Sierra Nevada, and other mountainous regions of the western United States, researchers from the U.S. Geological Survey report a maximum U-level of 10,000 ppm (mg/kg dry matter) detected in woody peat and organic rich sediments at the Flodelle Creek wetland (Washington) [2]. Similar to localized U-peaks (1,000–3,000 ppm) in other wetlands, this peak occurs near the input of naturally U-enriched groundwater. The majority of peat samples, however, contained less than 150 ppm, frequently displaying significant variations over short distances within the same wetland [2]. U-peaks of nearly 1% (10,000 ppm) were also reported by Schöner [3] for peat horizons in wetlands of the Wismut region (Germany) contaminated by seepage from adjacent tailings of former U mills. Based on 48 samples from South African peatlands, Smuts (1997) reports an average U concentration in peat of 18 mg/kg [4].

Almost half (46%) of the wetlands sampled by Owen and Otton [2] showed peat with maximum U-levels of at least 20 ppm, *i.e.*, close to ten times the natural background concentration in the continental crusts. In 15% of the investigated wetlands the highest U-concentration found in peat are comparable to those in commercially mined low-grade U-ore (>100–1,000 ppm).

Reviewing pertinent literature, Owen and Otton (1995) list a number of other examples of reported natural uranium enrichment in peat including areas where the U-content of the water did not exceed natural background levels [3,5]. Quantifying the degree of enrichment as ratio between the U-concentration in the peat and the U-level in the water phase (termed ‘Geochemical enrichment factor’, GEF) a GEF of 2×10^6 indicates that U-levels in peat could exceed groundwater concentrations by a factor of two million [5]. Lower U enrichment factors were found for natural peat deposits ranging from 500 to 10,000 [6]. Examples from the western U.S. show enrichment factors ranging from 10,000 to 20,000 for wetland sediments in California and Colorado [2]. Based on batch experiments, Szalay (1974) found a similar high value (10,000) and concluded that “peat absorbs uranium almost perfectly, even from very dilute solutions occurring in nature.” [7] quoted in [2]. This is in agreement with earlier results from Moore (1954) who found peat able to remove 98% of the dissolved U from an applied uranyl sulphate solution ([7] cited in [2]).

Apart from uranium, peat tends to accumulate other heavy metals such as mercury, lead and cadmium (including airborne) and is therefore frequently used as a geo-archive aiding the reconstruction of pollution levels in paleo-environments [9,10].

2. Conceptual Model for Peat as a Uranium Filter

The potential of peat to act as a filter for dissolved U is determined by two major components namely (i) its sorption capacity for the radioactive heavy metal (‘chemical component’) and (ii) the volume of contaminated water that comes into contact with the peat (‘hydraulic component’) per time unit.

2.1. The Chemical Filter Component

In order to characterize the chemical filter component of peat, an attempt is made to categorize the different (often competing) mechanisms responsible for the removal of dissolved U from the water phase (‘immobilization’), based on a review of relevant literature. Since the net filter function of peat not only depends on the amount of U initially removed, but also on the amount that may subsequently be released (‘remobilisation’), the mechanisms responsible for the remobilization of U are also discussed.

2.1.1. Mechanisms of U-Immobilization

Sorption onto organic material: Despite the long-term application of U-accumulation in peat and organic-rich wetland sediment for exploration purposes and, increasingly, since the early 1990s for passive water treatment in artificial wetlands, Sch öner (2006) remarks that mechanisms responsible for the removal and fixation of dissolved uranium from water are still not sufficiently understood [3].

Generally, however, it appears that sorption is the major mechanism for immobilizing dissolved U from the water phase. Partially decomposed plant fibers, as the main constituent of peat, contain cellulose and hemicellulose, humic and fulvic acids, waxes, resins, and other substances which display a range of polar functional groups such as alcohol, aldehydes, ketones, and ethers. Facilitating chemical bonding and ion exchange, such functional groups favor polyvalent cations with high atomic

weight, such as hexavalent U (U^{6+}) [11,12]. Metals are initially only loosely adsorbed to peat and may subsequently be reduced to more stable forms [13]. Since H^+ ions compete with other cations for sorption sites, the rate of metal removal from the water phase is strongly pH-dependent and appears to be at a maximum between 3.5 and 6.5 [14]. At values above 8.5, metal sorption decreases since peat starts to degrade [14]. Sorption is further strengthened by the fact that peat, as the first stage of coal formation, displays some properties of activated carbon including micro-porosity and the associated high reactive surface area as well as a high organic carbon content (a minimum of 30 weight-percent is required to be classified as peat). While confirming that a high content of organic carbon is a prerequisite for U accumulation in wetland sediments, Schöner (2006) only found correlations between the two parameters above a certain threshold content of organic carbon [3]. Winde (2003) reports somewhat lower U-levels for the same area and measured the highest U levels in black, organic-rich wetland sludge [15]. Owen and Otton [2] provide a comprehensive review that also includes older peat studies. They indicate that, apart from sorption, the complexation of the uranyl cation (UO_2^{2+}) by carboxyl groups, and the formation of insoluble uranyl humates, contributes significantly to the retention of U in peat [16,17]. Generally high pH-values, large atomic weights and high valences, favor metal retention by humic and fulvic acids, enabling the latter to strongly concentrate heavy metals from natural waters even at low concentrations [2,18]. Highly stable U-humate complexes may also form organic coatings ('biofilms') on otherwise largely inert coarser sediment components such as quartz pebbles and sand grains [19]. According to Crancon *et al.* (2010) the sorption of humic substances onto mineral surfaces creates hydrophobic mixtures that stabilize organic matter in soils. The stability of these aggregates is, in turn, dependent on soil moisture as well as the flow velocity and chemistry of the porewater [19].

Sorption onto mineral phases: Uranium (e.g., as uranyl ion UO_2^{2+}) may also adsorb directly to freshly precipitated gels of iron hydroxides (goethite: $FeO(OH)$) or iron oxide (hematite: Fe_2O_3) as well as to clay minerals displaying a negative charge of their large reactive surface area (under non-acidic conditions). Complete sorption of U onto clay and other surfaces typically occurs within a period of a few days [19]. Krepelova *et al.* (2006) found that U(VI) adsorption to clay (kaolinite) under acidic conditions increases if humic acids are present due to the formation of additional binding sites for U coming from the adsorption of humic acids to kaolinite [20]. Feng *et al.* (2005) showed in batch experiments that peat humic acid is sorbed to different clay minerals (kaolinite and montmorillonite) via cation bridging, ligand exchange and van der Waals forces. Sorption of humic acids to mineral surfaces generally increases when the pH is lowered and the ionic strength of the solution rises [21,22]. This is in contrast to the behavior of non-organic U-species which tend to increase mobility in aquatic systems when the pH is lowered and ionic strength rises. Since clay minerals are frequently found as interspersed layers in peat deposits this may contribute to U-immobilization in peat affected by acid mine drainage that lowers the pH while simultaneously increasing the ionic strength. Interestingly, sorption of humic peat acids was much stronger to kaolinite than to montmorillonite, despite the former displaying only a fraction of the reactive surface and cation exchange capacity of the latter. The presence of multivalent cations, such as Ca^{2+} and Al^{3+} , can largely enhance organic acid adsorption to clay through cation bridges [21].

The sorption of metal ions to different mineral surfaces was found to be strongly influenced by organic acids that ubiquitously occur in most natural aquatic systems [20-25]. While U bound to

inorganic species such as carbonates tends to be re-mobilized through acidification, the opposite effect occurs for U in humic complexes. In the presence of organic ligands, U sorption increases when the pH is lowered (acidification) and decreases when the pH rises [25]. That is to say, in generally acidic environments such as podzols and certain peats, the organically bound U is less mobile [19,26]. Furthermore, Ho and Miller (1985) found that the surface charge of hematite becomes negative upon adsorption of humic acid, even at low concentrations [24], potentially increasing the sorption capacity for non-organic U.

Owing to the ability to remove a wide range of contaminants, peat is frequently used as filter material for cleaning industrial waste including passive water treatment by permeable reactive barriers that remove uranium from polluted groundwater. However, the efficiency of peat to act as sorbent varies according to the composition and type of peat (degree of decomposition, fiber type and contents, ash contents, *etc.*) [7,12,14,27-33].

Precipitation of insoluble U-species: With the surplus of organic material promoting anaerobic, reducing conditions (submerged), peat may also contribute indirectly to metal fixation by triggering redox-controlled precipitation, or co-precipitation of aqueous U species [34]. The former would include the reduction of hexavalent U (U^{6+}) to its less soluble tetravalent form (U^{4+}) which could subsequently accumulate below a water table that frequently delineates the boundary between oxic and anoxic conditions [35]. However, despite thermodynamic models predicting the precipitation of tetravalent U, Schöner (2006) could not find reduced U (IV) in nature [3]. Together with the fact that the highest U levels were detected in oxidized peat horizons, this suggests that direct precipitation of reduced U species contributes little, if at all, to U accumulation in peat. While reducing conditions are often associated with the anoxic catotelm, Jacks and Norrström (2004) found that sulphate reduction increases towards the stream and preferably occurs in the surface peat, indicating the importance of degradable substance (*i.e.*, decomposing organic matter) for the sulfate reducers [36].

Co-precipitation of U along with secondary minerals: This mechanism refers to an indirect, less ion-specific form of immobilization including co-precipitation or occlusion with secondary minerals such as iron hydroxide or calcite [3]. Since precipitation of iron hydroxides as well as calcite is strongly pH-dependent, pronounced diurnal oscillations of the pH following solar-dependent photosynthesis and temperature cycles may result in distinct daily differences in the rate of U immobilization [37]. In contrast, results from a case study in South Africa showed for stream sediments strong correlations between uranium and a range of other heavy metals with the carbonate contents suggesting the existence of a non-metal-specific mechanism of U-removal (*e.g.*, co-precipitation along with calcite) [38]. Smuts (1997), for a range of different South African peatlands, found a high positive correlation between the concentration of several heavy metals and hematite (Fe_2O_3), as well as a correlation between heavy metal concentrations (including U) and the ash content of peat [39]. In situations where high phosphate inputs are present (*e.g.*, through the discharge of untreated sewage effluents into streams) the formation of insoluble uranyl phosphates could further contribute to U-removal from the water phase [2]. On surface and within the near-surface capillary fringe of peat increased evapotranspiration and associated water losses may result in dissolved U-complexes precipitating due to super-saturation in near surface porewater. In cases where all water evaporates precipitating salts such as carbonates, sulfates and, to a lesser degree, chlorides

and nitrates often contain elevated U levels which can readily be re-dissolved through subsequent re-wetting (e.g., through rainfall).

Deposition of colloidborne U: Schöner (2006) further established a clear association of U with aluminium-rich *colloids* suspended in water [3]. Displaying particle diameters from approximately 5 to 200 nm colloids constitute an intermediate phase between the truly dissolved and solid states of U (the borderline between dissolved and particulate matter is commonly defined by 0.45 μm filtration). Colloids can be of inorganic and organic origin with the former consisting of clay particles, aluminosilicates and metal oxy-hydroxides of iron (goethite, hematite) or other heavy metals including U (e.g., $\text{U}(\text{OH})_4$). Organic colloids are often less well-defined in their structure and are formed by naturally occurring, soluble organic substances (such as humin, humic and fulvic acids). These organic acids form metallo-organic complexes through binding U to their negatively charged ligands [21-23,25]. Investigating U migration through podzolic soils of battlefields in Kosovo, Crancon *et al.* (2010) estimate that a maximum of 10% of the total dissolved U (VI) species may be bound to humic colloids. Although small, this fraction was found to be responsible for the rapid and far-reaching transport of U into nearby aquatic systems [19]. Immobilization of colloidborne U may be facilitated by gravitational deposition of colloids as well as electrostatic interactions with mineral surfaces [19]. Gravitational deposition of colloids will often require prior aggregation to larger-sized particles through flocculation or coagulation. This, in turn, can be triggered by chemical processes such as changes of pH and redox conditions. In peat, such changes in porewater chemistry may be triggered by event-related hydrodynamical processes, such as the percolation of rainwater, the lateral infiltration of surface water from adjacent streams, rising groundwater levels, as well as photosynthesis- and temperature-driven diurnal and seasonal oscillations of water chemistry [37,40-42].

Dissolved U and other heavy metals, however, not only interact with colloids but also with particles of a larger diameter ('suspended solids'). In this context, iron and calcium-rich organic particles have been found to facilitate metal transport in a peat-karst system [43]. After being sorbed onto or incorporated into suspended particulate matter the physical (as opposed to chemical) mobility of U in the aquatic system is largely controlled by hydraulic processes governing, amongst others, the gravitational deposition and re-suspension (erosion) of sediments. Both processes are influenced by the diameter and density of the involved particles which are, however, not necessarily constant but may change due to aggregation, coagulation and flocculation [44,45].

Biological U uptake: A third group of indirect, peat-specific mechanisms relates to the habitat peat may provide for metal-accumulating bacteria and fungi. Apart from the latter aiding the decomposition of plant matter and the associated production of highly sorptive humic material that, in turn, enhances U absorption, bacteria and fungi themselves are able to concentrate U on or in their cell walls via metabolic biosorption [40]. Tsezos and Voleski (1981, 1982) report on a specimen of the common fungus (*Rhizopus arrhizus*) containing 18% U^{6+} (180,000 ppm) in its cell wall [46,47] cited in [2]. In addition Fe^{3+} -reducing bacteria are also able to obtain growth energy by coupling oxidation of various electron donors to the reduction of hexavalent U to its tetravalent form. Sikora and Keeney (1983) suggest that more bacteria are commonly found in mineral-rich fens (groundwater-fed) than in rain-fed bogs rendering fens generally better traps for U than bogs [48]. In addition, sulfur-reducing bacteria also contribute to geochemical U enrichment in peat by reducing sulfate to sulfide and triggering concomitant precipitation of U and other heavy metals ('bioprecipitation') [49-51]. No data have been

found on how far calcite structures of diatoms, which are also a constituent of peat, may act as bio-sorbents/sinks for U. Since algae are common in surface water of natural peatlands their metabolic absorption of U may contribute to the U contents of peatlands once the dead algae accumulate as biomass that forms part of the peat. Based on batch experiments, Dienemann *et al.* (2008) report a linear relationship between U concentration in several *Cladophora* species and U levels in surrounding water with a maximum concentration of U accumulated in algae of 360 ppm. On average, algae were able to concentrate U in their bodies from the water phase by a factor of 100 [52]. Thus, in eutrophied, algae rich peatlands with U polluted surface water the deposition of contaminated dead algae biomass may indeed significantly contribute to elevated U levels in the peat.

Bhat *et al.* (2008) suggest the use of biomass of dried red algae (*Catenella repens*) as a (passive) biosorbent to clean U contaminated waste water at large scale reporting an U-loading capacity of 303 mg/g (*i.e.*, over 3 g uranium per kg of dry algae mass) [53]. Since the dead algae essentially constitute organic matter, the observed adsorption kinetics may give some indication on the required contact time between U-contaminated water and peat for U sorption to take place. Results show that an initial electrostatic sorption of U to organic surface ligands rapidly takes place in the first 15 minutes accounting for some 80% of the total U sorption (at pH 4.5, some 60% at pH 2.5). This is followed by a slower second phase of U moving into the biomass through intracellular diffusion reaching equilibrium after 45 min. Maximum concentrations of 3,030 ppm U in the sorbent material were observed [53]. Assuming similar kinetics for true peat a relatively short contact time between U polluted stream water and peat likely to occur in nature would allow for substantial U removal from the water phase.

Phytoextraction of U: Aided by microbiological action at the rhizosphere as plant-soil interface peat-forming vegetation may also remove a certain amount of U from the water phase through biological uptake and subsequent incorporation into their biomass ('phytoextraction'). While some of the stored U will subsequently be released back into the water phase following decomposition of plant material, the proportion of U contained in only partially degraded fibers (such as roots) that contribute to the formation of peat still remains immobilized. For the plant community as a whole (with no harvesting or annual burning of reeds taking place) the seasonal vegetation cycle is likely to result in the establishment of a dynamic equilibrium between U-uptake and -release constituting a permanent (dynamic) U-reservoir. For the 12 German wetlands (Wismut region) investigated by Schöner (2006), phytoextraction was found to play only a marginal role in the overall U-accumulation in wetlands which suggests that most of the U is loosely sorbed onto biomass such as moss particles and not incorporated [3]. In contrast, Kochenov *et al.* (1965) established that plant debris contained 50% to 66% of the total U found in the peat [5]. Investigating common reeds growing in a pond of U contaminated seepage water near an uranium mill tailings deposit in the Czech Republic, Cerne *et al.* (2010) found that reeds may accumulate ^{238}U in roots and leaves by up to >300 times above the natural U level in the plant (some 2 $\mu\text{g}/\text{kg}$ dry weight). Leaves and stems of 20 analyzed plants (*Phragmites australis*) displayed an average U concentration of 691 and 192 $\mu\text{g U}/\text{kg}$ dry weight respectively [54]. With an observed reed density in South African peatlands of approximately 50 plants per m^2 and an average dry weight of 177 g/plant ($n = 3$) (own measurements) the reeds would contain approximately 2–6 mg U per m^2 . For a 1 km^2 -large wetland vegetated with reeds exhibiting the above U-levels this could translate into 2–6 kg of U per annum being removed from the wetland through harvesting the (full-

grown) reeds. Compared to a fluvial U-load of some 3.2 t U/a possibly arriving at the Gerhard Minnebron peatland [1] this would be a negligible amount.

2.1.2. Mechanisms of U-Remobilization

While peat has frequently been reported to remove dissolved U efficiently from the water phase even at low concentrations, the degree to which U is retained is not well investigated and likely to depend on a number of factors. Apart from hydraulic aspects controlling the rate of water flow through the peat, these include the physico-chemical characteristics of the peat, chemical composition of the water (e.g., the presence of other heavy metals competing for sorption sites), redox potential (Eh), temperature and pH of the water controlling the speciation and solubility of U [3]. Twardowska and Kyziol (2003) add a kinetic dimension by reporting that the contact mode between peat and dissolved metals also impacts on the efficiency of metal removal [55]. Distinguishing between static equilibrium and dynamic non-equilibrium (*i.e.*, peat in contact with stagnant or flowing water) they found in batch and column experiments, somewhat surprisingly, that through-flow conditions (*i.e.*, shorter contact time) enhanced the sorption of Cd and Zn (but not of Cu) onto peat (mainly by reducing the formation of Cl-metal-complexes that largely prevent the metals from binding to organic matter).

Schöner (2006) further distinguishes between an initial trapping of U and a long-term fixation and in three wetlands found that an average of 82% of the sediment-bound U could be remobilized by sequential extractions mainly originating from instable and moderate mobile phases [3]. In view of the conditions (Eh, pH, and temperature) applied in sequential *in vitro* leaching procedures, which have frequently little in common with natural systems, it is uncertain how far these methods are able to, reliably, mimic natural *in situ* processes governing the remobilization of U in peat.

Based on the main fixation mechanisms, a number of different processes that lead to the remobilization of U from peat can be identified. Amongst others these include the *oxidation of peat* (redox-controlled liberation), the *acidification* of porewater (pH-controlled liberation of sorbed U), the formation of *soluble inorganic and organic U complexes* (speciation-controlled liberation), changes in the *chemical composition* of peat porewater; changes in the *ionic strength* of peat porewater and the physical and biological *destruction of U-containing biomass* (e.g., by fire).

Oxidation of peat: This is likely to occur when receding water tables expose formerly submerged peat to atmospheric conditions. Kochenov *et al.* (1967) showed that sorption of U onto peat is reversible under oxidizing conditions [5] in [2]. Apart from accelerating the decay of plant fibers where sufficient oxygen for microbial activity becomes available and the subsequent release of contained U into the water, the oxidation of sulfides, such as pyrite (FeS₂), formed under reducing conditions and the subsequent formation of sulfuric acid may acidify the porewater and thus aid the liberation of sorbed U [48,56]. The use of sulfuric acid (H₂SO₄) as leaching agent in many commercial uranium mines indicates the relatively high remobilization potential of this process. With pyrite concentrations of up to 28% reported for coastal peats in north west Germany [57], the acid generation and thus metal remobilization potential of some peat deposits, is considerable. Associated peaks of sulfates released from oxidised peat into wetland streams may, in their own right, have a considerable impact on water quality [58,59]. Since oxidizing conditions generally promote the transformation of existing reduced uranium (U⁴⁺) to its much more soluble hexavalent form (U⁶⁺), this may further

remobilize U from peat. After extended exposure of dried peat to atmospheric oxygen some peat may also be affected by spontaneous combustion resulting in difficult to extinguish underground peat fires that in the process release accumulated U.

(External) Acidification: Being quite different from the above discussed acidification that follows the exposure of peat to atmospheric oxygen, this type of ‘external’ acidification of peat porewater refers to the direct influx of acidic water generated outside the peat. Sources of such water may include, amongst others, acid rain, spillages of acidic waste water and acid mine drainage (AMD) which all result in the lowering of pH in affected porewater. As the investigated peatland is located downstream of two large mining areas acid mine drainage is of particular relevance. Since lower pH-values were found to increase U remobilization from sediments and dissolution of mineral phases containing U (e.g., carbonates) the influx of AMD is likely to lower the net-attenuation of U in peat. Furthermore, at low pH, the surfaces of many mineral phases which act as potential U sorbents are positively charged resulting in the reduction of the overall sorption capacity for U.

In contrast, lower pH values were also found to increase binding strength of U-organic complexes such as humic and fulvic acids to clays and other mineral phases (goethite and hematite) somewhat counteracting the increased mobility of non-organic U species. Since organic U complexes commonly account for not more than 10% of the total U contents, with the balance of the U (*i.e.*, 90%) being associated with inorganic species, the net effect of direct acidification of peat porewater is likely to be a decrease in U-attenuation *i.e.*, a net-release of U from the AMD-affected peat.

Formation of soluble inorganic and organic complexes: A third major group of mechanisms to remobilize U, is the formation of soluble organic and inorganic complexes releasing U previously sorbed onto particles back into the aqueous phase. The latter includes uranyl complexes formed with anions such as chlorides (Cl^-) [55], phosphates (PO_4^{3-}) [3], sulfates (SO_4^{2-}) [60], as well as carbonates (CO_3^{2-}) and hydrogencarbonates (HCO_3^-) [54]. The ability of the sulfate and carbonate ions to form stable uranyl complexes is frequently used in commercially leaching uranium from milled ore and illustrates the relatively high U-mobilization potential of these ions. While most U-mines employ the faster acid leaching; for ore with tetravalent U, oxidizing agents need to be added prior to leaching. For ore of mainly carbonatic lithology the slower carbonate leaching is frequently used since the high buffer potential of carbonates renders the use of sulphuric acid uneconomical [61,62]. Francis *et al.* (1999) successfully used a carbonate-hydrogencarbonate extraction as well as citric acid to remove U from contaminated soil and found carbonates to be particularly selective for U [54]. Since all of the abovementioned ions are contained in commonly used products such as gypsum (SO_4^{2-}), lime (CO_3^{2-}), fertilizer (PO_4^{3-}) and table salt (Cl^-) they are abundant in many natural water resources. Furthermore, Krepelova *et al.* (2006) observed in batch experiments that the formation of aqueous uranyl-humate complexes reduces the sorption of U(VI) to clay minerals (kaolinite) in the near neutral pH range [20].

Changes of the ionic composition of peat porewater: Investigating the efficiency of two standard potabilization processes (*i.e.*, chlorination only and a combined process consisting of coagulation, flocculation, settling, filtration and chlorination stages) specifically designed to remove U from drinking water in a Spanish community, Baeza *et al.* (2008) found that increasing concentrations of either hydrogencarbonate (HCO_3^-), calcium (Ca^{2+}) or magnesium (Mg^{2+}) ions reduced the U-removal efficiency from 90% to 60% (at optimal pH of 6) [63]. Originating from the chemical

weathering (dissolution) of dolomite all three ions are abundant in the dolomitic water of the study area and thus of particular interest for the filter function of the investigated peat deposit. While the removal efficiency for U was significantly reduced by the three ions, it increased for Ra by 40% [63]. Since the presence of multivalent cations such as Ca^{2+} and Al^{3+} was found to increase the sorption of humic U complexes to mineral surface (through cation bridging) their reduction results in organic U complexes being released. Such reduction may, for example, be associated with the displacement of porewater by infiltrating rainwater.

Changes of the ionic strength of peat porewater: Apart from diluting the concentration of multivalent ions, the influx of rainwater can also decrease the ionic strength and thus weaken the sorption of organic U-complexes to clay and other mineral surfaces contained in the peat. Based on batch experiments, Crancon *et al.* (2010) propose that decreasing ionic strength associated with the infiltration of rainwater into sandy podzols contaminated with depleted uranium (DU) is responsible for the subsequent remobilization of U-bearing colloids and their rapid and far-reaching waterborne transport into the underlying aquifer and adjacent streams [19].

While rising ionic strength increases the adsorption of humic acids to clay minerals, it was found to have little direct effect on the sorption of U (VI) onto kaolinite [20].

In cases where ionic strength increases, e.g., through the influx of contaminated wastewater such as acid mine drainage or untreated sewage effluents, the associated increase in the concentration of major cations as well as trace metals reduces the immobilization of U through competitive adsorption to peat [14,64]. While the immobilization rate for a specific metal may be reduced, the increase in ionic strength appears to overall increase the total metal sorption capacity of peat [14].

Decomposition and physical destruction of U-containing organic matter: The extended exposure to atmospheric oxygen in some peat types may result in spontaneous combustion and subsequent burning of the organic material leaving U-enriched ash behind that could be flushed into the surface drainage.

The biological cycle of U-uptake and -release through biosorption and phytoextraction as discussed earlier, over the long-term, is likely to remain more or less constant, with possible pronounced seasonal variations. Impacting on biomass production as well as biological degradation and decomposition the influx of nutrients (N, P, S stimulating bacteriological activities, plant and algae growth, *etc.*) or toxins and contaminants (reducing biological activity) into the system, temperature changes, as well as seasonal and event-related water table fluctuations (changing redox conditions in the upper peat), may further impact the biological U-cycle.

The massive and sudden exposure of large amounts of peat to aerobic conditions associated with peat mining also falls into the category of physical destruction. How far this activity has a direct impact on the release of sorbed heavy metals into the water, is uncertain. Oxidation-related metal release may be limited since much of the extracted peat is swiftly removed from the water and stored on dry land for transportation to clients and would depend on the kinetics of U release processes.

2.1.3. Summary of the Chemical Sub-Model

The aim of the chemical model component is to determine factors and processes that control the ability of peat to retain U through filtering U containing water. This will allow determining and perhaps quantifying the impact events such as rainfall, changing water tables and the exposure of peat

to acid mine drainage may have on the retention of U. In this regard, three different aspects need to be distinguished:

- (i) the identification of *physico-chemical processes* that lead to the immobilization and remobilization of U in/from peat;
- (ii) the identification of *factors* such as water chemistry (pH, Eh, ionic strength *etc.*) and hydraulic aspects that govern the occurrence and intensity of the above processes; and
- (iii) the determination of consequences natural and anthropogenic events in peatlands may have for the attenuation of U, with special reference to the site specific conditions at the GMB peatland.

In the case of GMB peatland, U mainly originates from upstream gold mining activities. While currently the direct discharge of large volumes of U-containing (non-acidic) groundwater (pH 7–8) pumped from underground mine workings constitutes a major source of stream and groundwater pollution, future threats may include the influx of acidic water decanting from flooded mine voids. The associated change in the chemical nature of the U influx in future needs to be taken into account when assessing the filter function of the downstream peat under such a scenario.

(i) *Processes affecting U-mobility*

Case studies from peatland worldwide suggest that peat is an excellent sorbent for dissolved U and able to accumulate the radioactive heavy metal from very dilute concentrations in the water to significant concentrations in the peat. Owing to its exceptional filter capacity for heavy metals, including U, peat is, in fact, frequently used in industrial filters to clean U contaminated waste water.

Under oxidizing conditions prevalent in the upper, near-surface part of the peat column (acrotelm) U occurs as hexavalent ion U(VI) which frequently binds to oxygen to form the uranyl cation (UO_2^{2+}). Under reducing conditions, prevailing in deeper portions of the peat well below the water table, hexavalent U may be reduced to its tetravalent form U(IV) which is generally much less soluble than U(VI). The three naturally occurring isotopes of U (^{238}U , ^{234}U and ^{235}U) are regarded as behaving chemically in an identical manner.

The removal of U from the water phase is termed ‘immobilization’, a term that implies that solid U phases in peat are less mobile in the aquatic environment than dissolved U species moving along with the water phase. Under certain conditions, however, immobilized U may be released from solid phases of the peat back into the water column. This process is termed ‘remobilization’. The retention potential of peat for U will be determined by the net balance of U immobilization and remobilization. For both processes a number of different mechanisms have been identified based mainly on findings reported in literature complimented by on-site field observations. For the *immobilization of U* these mechanisms include:

The *sorption of U-species* to different solid phases (especially organic matter as a major constituent of peat which displays an exceptional high sorption capacity for multivalent cations, such as U, as well as different clays and freshly precipitated gels of iron hydroxides with their large reactive surface area). Owing to competition by H^+ ions adsorption processes, being highly pH dependent and generally reduced in acidic conditions when competition by protons for available sorption sites rises, and simultaneously sorption sites are reduced due to the surface charge of mineral phases, such as iron

hydroxide gels, turning positive. The mobilizing effect of decreasing pH values is somewhat counterbalanced by organic U-acid complexes which bind stronger to mineral phase at low pH.

The *precipitation of insoluble U-species* (largely confined to reducing conditions that allow U(IV) species to form and to U-phosphate complexes exhibiting a low solubility even under oxidizing conditions).

The *co-precipitation of U, along with precipitating mineral phases*, such as Fe-hydroxides and -oxides (goethite and hematite), as well as calcite. The rate of precipitation of these secondary minerals is highly pH-dependent and may thus show profound diurnal oscillations following photosynthesis-triggered pH changes of up to 2.5 pH units per day, as discussed by Winde *et al.* (2004) [34,37]. Furthermore, the precipitation of calcite is part of the calcium carbonate-carbon dioxide equilibrium which is controlled by the pH as well as the concentration of dissolved CO₂ that, in turn, depends on the atmospheric partial CO₂ pressure and water temperature. By implication, the latter two parameters also have some influence on the U mobility even though this is only indirect and perhaps affects only a small portion of the total U.

The *biological uptake of U through metabolic activity* of aquatic organisms commonly found in peat environments including fungi, bacteria, algae and peat forming plants (in the case of the GMB peatland these are mainly common reeds—*Phragmites australis*). Owing to the accumulation in tissue, such as cell walls of fungi, bacteria and algae, U may reach considerable concentration in living organisms. Once dead, the U contaminated biomass also contributes to the attenuation of U in peat if preserved in the peat. Dead biomass such as algae were also found to be effective bio-sorbents for U and are used for industrial waste water purification. The U uptake by plants is frequently referred to as ‘phytoextraction’ and used as a means of rehabilitating contaminated wetland soils.

The *gravitational deposition of U-bearing particles* including the macroscopic suspended solids (suspended sediment, clay particles, calcite and other mineral precipitates) as well as colloids formed by inorganic material (e.g., aluminosilicates, iron hydroxides, *etc.*). Owing to their very small diameter, colloids are usually highly mobile even within substrates of low permeability. However, under certain conditions U bearing colloids tend to form larger aggregates through flocculation and coagulation that allow for their gravitational deposition together with larger-sized suspended solids.

Regarding the *re-mobilization* of U from peat, five major processes have been identified:

De-sorption: Mainly triggered by changing pH values and/or other chemical parameters loosely sorbed U may be released from organic matter as well as other sorbents through desorption *i.e.*, reversing the initial adsorption. While decreasing pH values favor U desorption from organic matter and mineral phases, increasing pH values tend to decrease binding strength of U-organic complexes to clay and other minerals.

The *dissolution of U-bearing precipitates* such as calcite and iron oxides and hydroxides under acidic conditions may also liberate U from solid phase in the peat. In the case of evaporative salt crusts on the peat surface and the capillary fringe, rewetting through rainfall or rising groundwater tables will readily dissolve these crusts and release the incorporated U into the water.

The *remobilization of particle- and colloid-bound U*: Macroscopic U bearing particles gravitationally deposited at low flow conditions may be washed back into the stream during flood events. Where piping occurs peat particles may also be eroded subterraneously and flushed into the fluvial system. Additionally, changing porewater chemistry altering ionic strength and composition,

pH *etc.* can also trigger the mobilization of aggregated U-colloids and result in their erosion and subsequent downward transport through the peat column.

The physical destruction of U-bearing biomass: Since much of the U is sorbed to semi-decomposed organic matter the physical destruction of the latter by *complete decay* or fire also results in the mobilization of U. Apart from sorbed U, this also releases U that has been accumulated metabolically in plants and other organisms. Triggering events may include the seasonal or permanent lowering of the groundwater table exposing peat to atmospheric oxygen and the associated completion of bacterial decomposition. Decay of peat may also be triggered by pH values rising above a certain threshold (8.2). Drying out of the peat may also lead to *spontaneous combustion* that burns the peat and concentrates contained U in the remaining ash. In the GMB peatland the annual burning of reeds has a similar effect which, however, only affects the reed parts above the water table. Since burning is commonly done in winter the (potentially uraniferous) ash can be washed into the stream by the subsequent spring rains.

The formation of soluble inorganic and organic U-complexes: Depending on the ionic composition of the water, U (as uranyl ion) can form a wide range of highly soluble, often neutral or negatively charged complexes with sulfate, nitrate and carbonate, that hardly bind to any sorbent and thus are highly mobile in the peat-water system. Being contained in frequently used products such as lime (carbonate), fertilizer (nitrate) and gypsum (sulfate) all three U-complex-forming anions are often abundant in natural aquatic systems. Especially in acidic environments, U also forms organic complexes with dissolved organic matter (Dissolved organic matter e.g., humic or fulvic acids) which display a similar high mobility. However, they seldom account for more than 10% of the total U content.

(ii) Factors governing immobilization and remobilization processes

The above discussed processes are strongly controlled by two major aspects, namely water chemistry and hydraulics. The former comprises parameters, such as pH, redox potential (Eh), ionic strength, chemical composition of the water phase in the peat-water system, and mainly control the intensity of the different processes. Hydraulic factors, on the other hand, are of more fundamental importance as they determine where and for how long peat comes into contact with water. With regard to the latter, the duration of water-peat contact is a crucial parameter that indirectly influences water chemistry (e.g., the permanent saturation of organic matter with stagnant water will result in anoxic/reducing conditions) and directly affect U-mobility. The latter is due to processes such as adsorption or precipitation requiring a certain amount of time depending on their kinetics. Therefore, contact time between water and peat determines whether a process can take place, and to what extent. The mode of the water-peat contact will also influence how much of the total water volume may be affected by the im- or re-mobilization processes. Furthermore, the contact mode, e.g., whether peat is in contact with stagnant or flowing water, also determines whether and to what extent concentration gradients at the solid-aqueous interface may be maintained and equilibria be established. This will be discussed in more detail in connection with the hydraulic filter component.

In the following the focus is on summarizing the impacts on U mobility associated with water chemistry including the following parameters: pH, Eh, ionic strength, chemical composition of the water. Since some of the impacts were mentioned in connection with the different im- and re-mobilisation processes some degree of overlap can hardly be avoided.

Impacts of pH: The pH exerts control over a wide range of processes affecting U-mobility including sorption/desorption, precipitation and co-precipitation, dissolution of secondary mineral phases, decay of peat, binding strength of U-organic complexes to mineral sorbents, aggregation and dispersion of colloids, solubility of U-complexes, *etc.* Generally, neutral to weak alkaline conditions prevalent in the GMB peatland favor the electrostatic sorption of U to organic matter and mineral (*i.e.*, inorganic) peat constituents such as clay minerals, iron hydroxides, *etc.* Therefore, lowering of the pH in such systems is likely to increase U mobility by promoting desorption. Depending on the degree of acidification, this may also lead to the dissolution of hydroxide gels and other instable mineral phases. Events that may trigger acidification include the drying out of previously waterlogged peat (indirect acidification through the oxidation of sulfides and the associated generation of sulfuric acid) as well as the input of acidic water from external sources, such as acid mine drainage, acid rain, *etc.* However, decreasing pH-values not only result in U-mobilization but also favor the formation of U-organic complexes and their sorption onto mineral phases such as clay. Also, the optimum for biological U-uptake frequently occurs in acidic conditions.

Impacts of redox potential (Eh): As a redox-sensitive metal, the mobility of U is strongly Eh-dependent. Under oxidizing conditions U is hexavalent and occurs as U-oxide (uranyl ion) which tends to form highly soluble inorganic and organic aqueous complexes that remain dissolved in the water phase. Under reducing conditions, U is tetravalent and forms insoluble species that precipitate out of the water.

Impacts of ionic strength: For U bound to organic complexes, increasing ionic strength somewhat unexpectedly results in decreasing U mobility. This effect has also been found for colloidal U which is mobilized in acidic soils by infiltration of low ionic strength rainwater. For U sorbed to mineral phases and organic matter via electrostatic forces, the opposite effect has been reported, *i.e.*, increasing ionic strength mobilized U, *inter alia*, through metallic ions competing for sorption sites. Increasing ionic strength also has the opposite effect by promoting aggregation, and subsequent gravitational deposition of (U containing) dissolved organic matter, through coagulation and flocculation.

Impacts of chemical composition of the water: The chemical composition of the water phase in the peat-water system mainly impacts on U mobility via constituents with which U can form complexes that are either soluble and thus increase its mobility or are insoluble and therefore promote U retention. This includes inorganic U complexes of which those with sulfate, carbonate, nitrate and chloride display a high solubility under most natural conditions while U complexes with phosphate tend to be much less soluble. Owing to the ubiquitous presence of dissolved organic matter in most natural waters and especially in peatlands, U is likely to form soluble complexes with humic and fulvic acids particularly at low pH. While this generally increases U mobility, in the presence of Ca^{2+} and Al^{3+} ions organic U complexes tend to bind to clay thereby immobilizing U. Furthermore, Ca^{2+} , Mg^{2+} and HCO_3^- have each been found to significantly reduce the efficiency of filtration and flocculation used in water treatment to remove U. Since these ions are naturally produced through the chemical weathering (dissolution) of dolomite (CaMgCO_3), all three ions are abundant in the GMB peatland that is fed by a dolomitic spring.

(iii) Natural and anthropogenic events affecting U mobility in peatlands

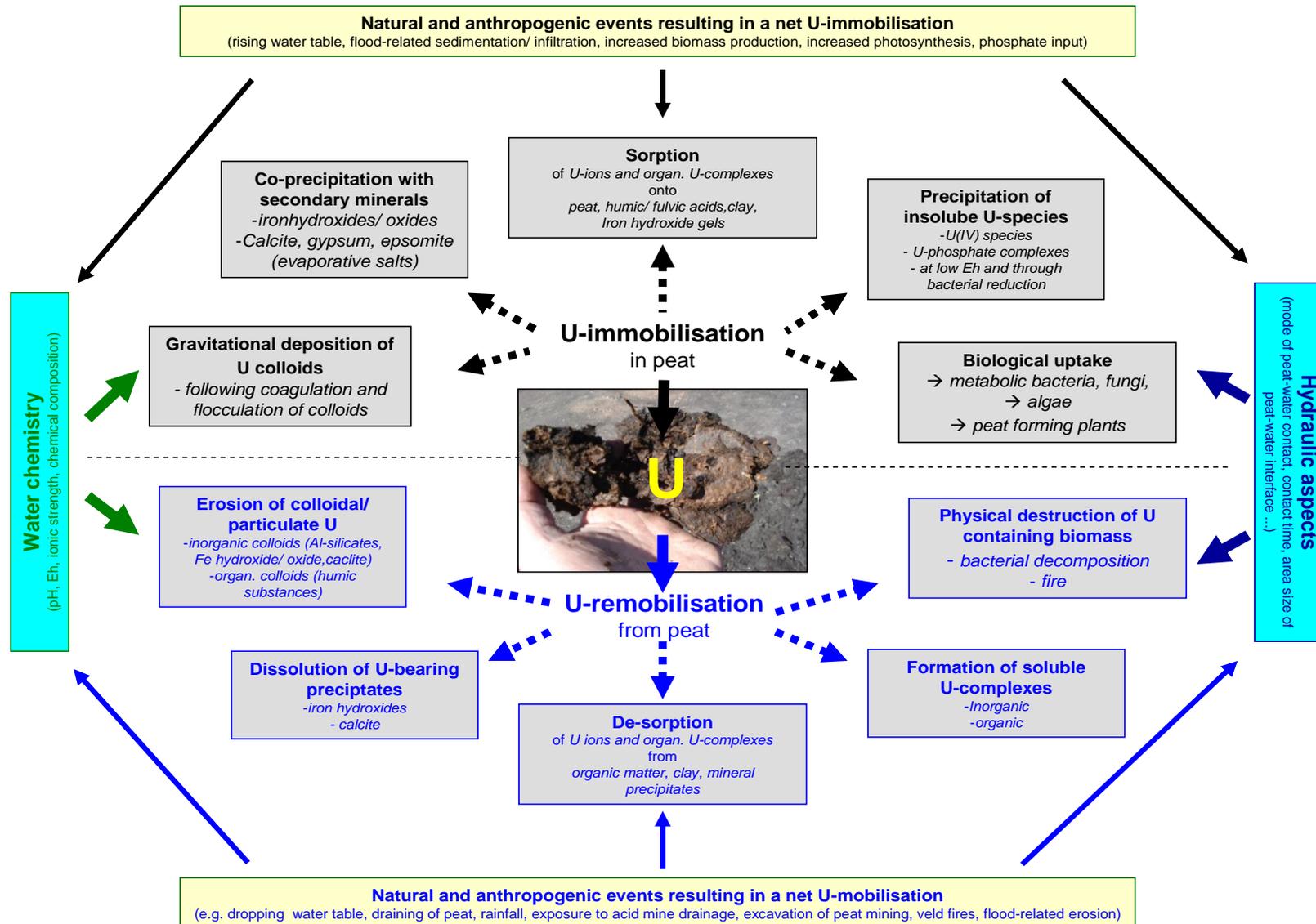
Based on the above processes and governing factors, a range of plausible natural and anthropogenic events are identified that are likely to impact the degree of U attenuation in peat. Natural events

commonly occurring in peatlands include rainfall, flooding, droughts and associated variations of the groundwater table, as well as solar input variations (diurnal and seasonal). Anthropogenic events/impacts, with regard to the study area include the exposure of the peatland to acid mine drainage, elevated levels of mining-related U in (non-acidic) dolomitic water, the annual burning of reeds, the excavation of peat (commercial peat mining), abstraction and diversion of dolomitic water feeding the wetland into an irrigation canal, as well as occasional flooding through re-routing diverted water from the irrigation canal back into the wetland for maintenance purposes.

In terms of effects on the U mobility, these events can be grouped according to the main underlying processes that impact U attenuation, such as oxidization (including subsequent acidification), direct (external) acidification, physical destruction of U containing matter, *etc.* The lowering of the water table during the dry winter months, as a consequence of droughts or of the diversion/abstraction of water, for example, results in the exposure of previously waterlogged peat and organic matter to atmospheric oxygen and the subsequent oxidization of sulfides. Apart from the associated decomposition of organic matter (*i.e.*, reducing sorption potential for U) this results in the formation of sulfuric acid and lowering of the pH, as well as possible dissolution of U-bearing mineral phases. Similar processes may also apply to peat excavated from the wetland and deposited on land. A more direct way of lowering the pH is the input of acidic water from external sources such as acid rainfall or acid mine drainage (AMD) (here termed ‘external acidification’). While rainfall, as well as AMD, lowers the pH, the net effects on U mobilization may be quite different owing to differences in ionic strength and chemical composition discussed earlier.

Figure 1 provides an overview on the processes, governing factors and events, impacting the ability of peat to retain (immobilize) U and those leading to the release (remobilization) of U after the initial sorption.

Figure 1. Overview on processes governing the immobilization and remobilization of U in/from peat including controlling factors and triggering events (chemical component of the U filter model for peat).



2.2. The Hydraulic Filter Component

In order for peat to act as a filter, the U polluted water must somehow come into contact with peat. Regarding the hydraulic properties of *in situ* peat deposits occurring in peatlands a significant body of literature has accumulated over the past four decades or so (e.g., [65-92]). With respect to the hydraulic properties of peat, two distinctly different horizons are important; the acrotelm as upper part of the peat column, consisting of roots and decomposing plant material which is frequently above the water table; and the much denser lower part of the peat (catotelm) that is most of the time covered by water exhibiting anaerobe (*i.e.*, reducing, anoxic conditions). Apart from the hydrochemical different milieus, both horizons display distinctly different hydraulic properties with the loosely structured acrotelm exhibiting a hydraulic conductivity (k_f) that on average is some 10,000 times higher than that of the underlying catotelm (1×10^{-2} vs. 1×10^{-6} m/s) [93]. Holden and Burt (2002) indicate the range of k_f for the acrotelm somewhat wider (10^{-2} – 10^{-6} m/s) but still between 4–6 orders of magnitude (10,000 to 1 million times) higher than the hydraulic conductivity of the underlying catotelm (10^{-8} – 10^{-10} m/s) [74]. Regarding the latter they also point out that depth is not a significant control on hydraulic conductivity of the acrotelm since k_f -values can spatially vary by several orders of magnitude within only a few horizontal or vertical centimeters [74]. For peat-water contact to occur, the following range of different possible hydraulic modes was identified based on literature findings and field observations in the GMB wetland.

2.2.1. Contaminated Surface Water Flows Past the Peat Deposit Without Penetrating to Any Significant Degree (Skimming Over the Surface):

Owing to relatively high flow velocities, surface water exhibits when flowing over peat (e.g., during flood events) or when flowing past bank-forming peat that forms the stream channel, a comparatively short contact period exists for any specific point of the water-peat interface. However, for the peat-water contact area as a whole (e.g., the entire length of the bank-forming or flooded peat), the contact time between stream water and peat may be sufficient to allow for significant U sorption to occur. Under near-laminar flow conditions typically found in low energy wetlands, U sorption would, however, be restricted to a narrow layer of stream water directly in contact with the peat while most of the flowing water body would remain unaffected. Observing that flood events in peatland streams always occur at times of high groundwater table, Evans *et al.* (1999) suggest that the generation of overland and near-surface runoff is controlled by saturation of the catotelm rather than rainfall exceeding the infiltration capacity [82]. By implication, flooding of peatlands adjacent to the stream channel would result in little, if any, stream water percolating through the underlying peat and thus limiting the possible removal of U. While this is true for dissolved U, it may be different for particle-bound U which may be deposited in flooded areas through gravitational sedimentation. Since U mainly arrives in dissolved form at the GMB peatland particulate U transport is of limited importance there. In cases where pools of stagnant water remain after the flooding has subsided, evaporative precipitation of U may, however, be a possible pathway of peat's U pollution.

2.2.2. Contaminated Surface Water Infiltrates into the Peat (Downward Matrix Flow)

Downward vertical matrix flow refers to gravitational infiltration of rain or surface water that percolates slowly through the peat matrix by successively filling interstitial pores on its way to the lower lying water table. This type of diffuse flow through the peat matrix allows for relatively long contact time between polluted stream water and peat and may thus enhance U removal through sorption. However, the possible volumes of water affected are limited by the hydraulic resistance of the peat. Values for the hydraulic conductivity of peat reported in literature vary by up to ten orders of magnitude [83]. This large variation is due to a range of factors impacting the water flow through peat, including the degree of water saturation, the direction of flow (lateral vs. vertical), the composition of the peat (fiber-, clay- and ash-content), the degree of decomposition (the more decomposed, the lower the hydraulic conductivity), the compaction of the peat (deeper peat is more compressed, and thus less penetrable, than shallow peat near the surface), duration of peat's possible drying periods, and the existence of preferential pathways within the peat [4,66,76,80,84-87].

The potential filter effect associated with downward vertical water flow is limited to the relatively shallow upper unsaturated part of the peat (acrotelm) located above the mean annual water table [80]. This zone commonly comprises only a few centimeters but may drop much deeper (during extended dry periods [82]). Percolating surface water reaching the water table is assumed to change to a lateral direction of flow [88].

During high-flow conditions U polluted streams may flood adjacent peat deposits. Owing to the high infiltration capacity of the upper peat layer this is likely to result in stream water percolating through the areas where the acrotelm is not saturated towards the (shallow) water table. With flow velocities in the region of centimeters per day [82], such percolation would allow for sufficient contact time for U sorption to take place given that up to 80% of the dissolved U were found to sorb within the first 15 minutes [53].

A decrease in (saturated) hydraulic conductivity with depth was also found by Price and Whittington (2010), based on column experiments using Canadian *Sphagnum* moss peat. They report a ten times lower hydraulic conductivity already at the rather shallow depth of 25 cm compared to near-surface peat at 5 cm depth ($\sim 2 \times 10^{-4}$ vs. $\sim 2 \times 10^{-3}$ m/s respectively), mainly due to a decreasing size of interstitial pores in the lower lying peat. They also report a drastic decrease in hydraulic conductivity for the near-surface peat by five orders of magnitude after it had been drained, and explained this by merging air bubbles that increase the length of the water flow path through the peat matrix [80]. This is supported by observations of a depressed rate of water table recovery after a prolonged period of low water tables suggesting that peat undergoes physical changes once it dried out [82]. An important consequence of this observation is that drained peat subsequently offers a significant resistance to the infiltration of surface water and would—if the same applies to reed derived peat at GMB—limit infiltration-related U removal after extended dry periods.

2.2.3. Rapid, Downward Concentrated Flow through Peat (Non-Matrix Macropore- and Pipe-Flow)

While the peat matrix generally presents a porous medium that allows for Darcy-type of diffuse water flow, this may be different where preferential pathways exist. In the acrotelm (the upper, aerobic part of the peat that supports plant growth [4]) these preferential pathways may include root channels, animal burrows as well as macropores, while pipes and ash layers may act as preferential flowpaths in the underlying, more dense peat substrate (catotelm). In cases where extensive piping affects peat deposits (e.g., in sloped areas) subsurface water flow through the peat may be rapid with short contact times allowing for little filtering to take place [69,74,82,89-91]. Accounting for approximately 30% of the runoff production within the acrotelm, concentrated (*i.e.*, non-diffuse) flow through macropores is an important flow mechanism in near-surface peat. Although macropores only account for less than 1% of the peat volume Holden and Burt (2002) estimate that they facilitate around 80% of the near-surface water flux in peat [74]. Investigating water flow in pipes developed in shallow peat of the Measnant catchment (Wales) by analyzing over 200 storm events with associated flow rates in stream channels and pipes measured at 17 separate gauging stations, Jones (1979) found that subsurface pipeflow may account for up to 49% of the stormflow and 46% of the baseflow, indicating the significance of the process [74,92] (cited in [82]). While the contribution of pipeflow may be of lesser importance in generally flat topography of the karst fen at Gerhard Minnebron (owing to the lack of sloped terrain), pipes may still form in the near-stream bank-forming peat due to subterranean water flow following the groundwater table dipping towards the stream [93]. While this would restrict the occurrence of pipes to the near surface, Holden and Burt (2002) observed in upland blanket peats of the U.K. that pipes also developed in deeper peat layers well below the groundwater table, preferentially forming at the interface between peat and the underlying mineral substrate. With diameters of 3 to 70 cm and length of up to 150 m pipeflow in deep (water saturated) peat was found to contribute 10% to 30% to the stream flow [74].

2.2.4. Lateral Water Flow through the Peat (Through-Flow)

Where horizontal layers of different hydraulic conductivity exist (e.g., layers of ash, clay, gravel, and bedrock), a preferential lateral water flow through these layers ('throughflow' [88], 'lateral seepage' [73]) is likely to occur. With limited contact of the U containing water to the highly sorptive peat matrix, this layer-bound type of throughflow would result in limited removal of U from the water phase. However, also the peat itself, according to Reeve *et al.* (2001), "usually contain(s) complex sequences of strata that have highly variable botanical, physical and hydraulic properties" [94] and may thus allow for different rates of lateral flow through the peat matrix enhancing U attenuation.

Van Loon *et al.* (2009) determined that exfiltrating groundwater from an adjacent (not subjacent) aquifer entering the peat via upward vertical flow gets redistributed laterally once it reaches the loosely structured, and thus highly permeable, root zone of the near-surface peat (saturated k_f -value: $500 \text{ m/d} = 6.8 \times 10^{-3} \text{ m/s}$) [88]. Apart from the hydraulic conductivity (*i.e.*, resistance to flow) the velocity of the laterally flowing porewater is controlled by the hydraulic gradient (head) driving the flow, and for layer-bound flow, the dip of the layer.

According to Reeve *et al.* (2001), hydrodynamic dispersion associated with the lateral water flow through peat may also drive vertical solute fluxes (e.g., from underlying mineral soils at the bottom of the peat) towards the surface, even in the absence of an upward directed groundwater flow [94]. Reeve *et al.* (2000) suggest that in peatlands where vertical flow of exfiltrating groundwater is limited by mineral soils of low permeability, the lateral flow of water dominates the hydrology in the upper portion of the peat column [95].

Lateral flow or throughflow in peat may also be induced by surface water infiltrating from adjacent stream channels or ponds/lakes into the peat in response to rising surface water levels. This process is reversible and the infiltrated water, temporarily stored in the peat, may be released back into the stream/lake once the water level in the lakes/streams subsides again. Depending on the focal point of investigation, this process is either referred to as ‘bank storage’ (if the stream flow is the main focus) or ‘flow reversal’ if the porewater movement is of interest [77,96].

Owing to pumping regimes by deep level gold mines utilizing day-night difference in electricity tariffs for minimizing their considerable pumping costs, water levels in mining-affected streams often show pronounced diurnal fluctuations of water levels. Associated consequences for the immobilization of U in bank sediments affected by infiltrating water are discussed in Winde and van der Walt (2004) [81].

Investigating the transport of phosphorous (P) in an altered peatland in northern Israel, Sade *et al.* (2010) found that much of the water from a canal running through the peatland infiltrated into adjacent peat via rapid lateral flow in cracks that developed through frequent drying and re-wetting in the upper peat and underlying marl ($k_{\text{sat.}}: 1.7 \times 10^{-3}$ m/s) [97]. Based on differences in flow velocity and chemical conditions between the cracks (rapid flow, oxidizing conditions, low solute concentrations) and the surrounding matrix (slow flow, reducing conditions, high solute concentrations) they propose a conceptual ‘dual-domain model’ for waterborne P-transport. In this model a thin layer of precipitated $\text{Fe}(\text{OH})_3$ covering the walls of the crack acts as a trap for P. Formed by reduced Fe^{2+} that migrates from the matrix pores into the oxidizing cracks such layer could, in theory, also act as a barrier/trap for dissolved U. On the other hand, U may be re-released through the erosion of particles from the Fe-hydroxide layer in the form of particulate U. The higher solute concentrations in the matrix porewater compared to water free-flowing in the canal and in cracks are caused by chemical gradients that drive diffusion of molecules from the cracks to the pores after hydraulic pressure differences between the crack and the matrix that cause advective influx of solutes have equilibrated. The overall water flux is controlled by the (highly variable) hydraulic gradient between the canal water level and the peat [97].

2.2.5. Upward (Non Gradient) Water Flow through Overlying Peat

The upward flow of water through the peat may be associated with a range of different processes involving exfiltrating groundwater, peat porewater, as well as surface water from adjacent water bodies such as streams, ponds and lakes. Hydraulic processes leading to the vertical movement of water against gravitation include the following:

The flow of exfiltrating groundwater from an underlying confined aquifer (e.g., entering the peat via subaquatic springs) [98]. Groundwater that, under artesian pressure, moves upward through the

overlying 3–5 m thick peat deposit to the surface may perhaps occur at the GMB peatland owing to subaquatic discharges from underlying, highly karstified dolomite. However, on site field observations at the GMB peatland suggest that groundwater discharge is localized and confined to subaquatic springs, above which no peat accumulates. This results in well-like, often round holes in the peat layer within which groundwater wells up directly from the dolomitic bedrock to surface. In this situation, it appears unlikely that groundwater also infiltrates into the surrounding peat that offers significant hydraulic resistance. While the groundwater may not filter vertically through the peat it subsequently moves laterally through the near-surface layer draining towards the stream in the centre of the peatland. During this lateral flow U may potentially be removed.

Exfiltrating groundwater entering the peat from a higher-lying, adjacent aquifer sloping towards the peat (*i.e.*, a valley situation) may also move vertically through the peat matrix if the piezometric level is above the peat surface [88]. Owing to the generally flat topography at GMB such water flux would probably be of low intensity. It could be triggered by the higher lying water level in the adjacent river (the Mooi River) that runs parallel to the GMB stream. In which case, disproportionately high, localized groundwater responses to rainfall may occur in the capillary fringe leading to the formation of groundwater mounds (also known as ‘groundwater ridging’) [71,77].

Lateral water flow: In peat areas not permanently fed by groundwater high evapotranspiration losses during the growing season were found to result in falling water tables that temporarily redirect originally lateral water flow to the peat surface [88].

Capillary flow: In the near-surface portion of the peat column capillary effects are responsible for vertical, non-gradient flow of groundwater [80]. Reflecting the varying intensity of evaporation and transpiration such capillary water flux results in diurnal water table oscillations of several centimeters per day [82,99]. In column experiments with Canadian *Sphagnum* peat, Price and Whittington (2010) found that peat porewater, owing to capillary action, moves upwards from deeper storage reservoirs containing some 47 vol.% of water to maintain evaporation from the surface over a 34 day period without exhausting the water contents [80]. While many hydraulic properties of *Sphagnum* peat are not comparable to reed-derived peat found at the GMB wetland, upward movement of porewater, especially during the extended dry periods in winter, is likely to occur there too. An indication of this is, amongst others, the continuous growth of evaporative salt crusts on surface during winter when the groundwater table is low and no rain occurs.

Groundwater ridging: In sloped areas at the edge of the peatland, capillary effects in conjunction with the infiltration of rainwater are suggested to cause disproportionately high increases of the water table known as ‘ground water ridging’ which subsequently lead to the discharge of pre-event water to adjacent streams [15,26,77,100,101]. Other non-Darcy type of vertical, up-gradient water movement may be associated with fluctuating groundwater tables caused by seasonal (*i.e.*, changes in the climatic net-water balance), diurnal (e.g., solar cycle driven oscillation of evapotranspiration, plant growth, *etc.*) or event-related processes, such rainfall, floods and droughts [15].

2.2.6. Significance of the Hydraulic Processes for the Chemical Model Component

Since the concept of U mobility explored in this paper is based on peat-water systems, the conditions under which water comes into contact with peat are of fundamental importance for understanding U attenuation in peatlands. This aspect is covered by the hydraulic component of the conceptual model on the U-retention in peat, and focuses on different possible modes of how peat-water contact occurs. This includes, for example, the relatively slow diffuse flow through the interstitial pore space of the peat (matrix flow), as well as more rapid and concentrated flow over peat and through macropores. Consequences of the different hydraulic modes mainly relate to the associated contact time between peat and water and the size of the contact area. While the latter is relatively large in matrix flow, it is much lower in rapid flow through pipes and macropores. Generally it is assumed that interactions between dissolved U in the water phase and solid peat components, are more pronounced the larger the area of interaction and the longer the peat-water contact time. The latter is of importance with regard to the (often unknown) kinetics of U immobilization and remobilization processes. It may, however, also cease to be relevant if, for example, an equilibrium state is reached that effectively stops the adsorption of U regardless how long peat may be exposed to U polluted water. Such a scenario is likely to be confined to stagnant or very slow moving peat-water systems. In contrast, in systems where water moves comparatively rapid, saturation of the near-interface water layer may be prevented by the ongoing exchange of water. Preventing that ionic saturation acts as a diffusion limiting factor, flowing water may allow for continued U adsorption onto peat or 'leaching' of U from peat. The peat-water contact time has also indirect consequences for the U mobility (*i.e.*, not only with regard to kinetics of certain reaction) since extended water-saturation of organic material, for example, results in anaerobic, reducing conditions that may contribute to U immobilization and *vice versa*. In many instances immobilizing processes, such as precipitation or co-precipitation, are more rapid than remobilization e.g., through the dissolution of precipitates, desorption, *etc.* Therefore, systems with short water-peat contact time may tend to favor a net retention of U.

2.2.7. Summary of the Hydraulic Model Component

Based on literature and observations in the studied peatland, five different peat-water contact modes have been identified significantly varying in associated contact time and area of possible peat-water interaction. Owing to pronounced differences in hydraulic conductivity water movement through the upper, loosely structured root zone of the peat (acrotelm) is up to five orders of magnitude faster than through deeper lying, permanently waterlogged peat. However, owing to horizontal layers of sand, ash and clay, more rapid water fluxes may also occur in deeper parts of the peat column either through these layers (in the case of sand or ash) or at the peat-layer interface (e.g., clay). Moreover, rapid flow also occurs in macropores in the near-surface root zone of the peat and possibly also through pipes which may form in the upper, as well as in the lower parts, of the peat column. Whether piping does indeed occur in the GMB peatland is at this stage of the investigation still uncertain.

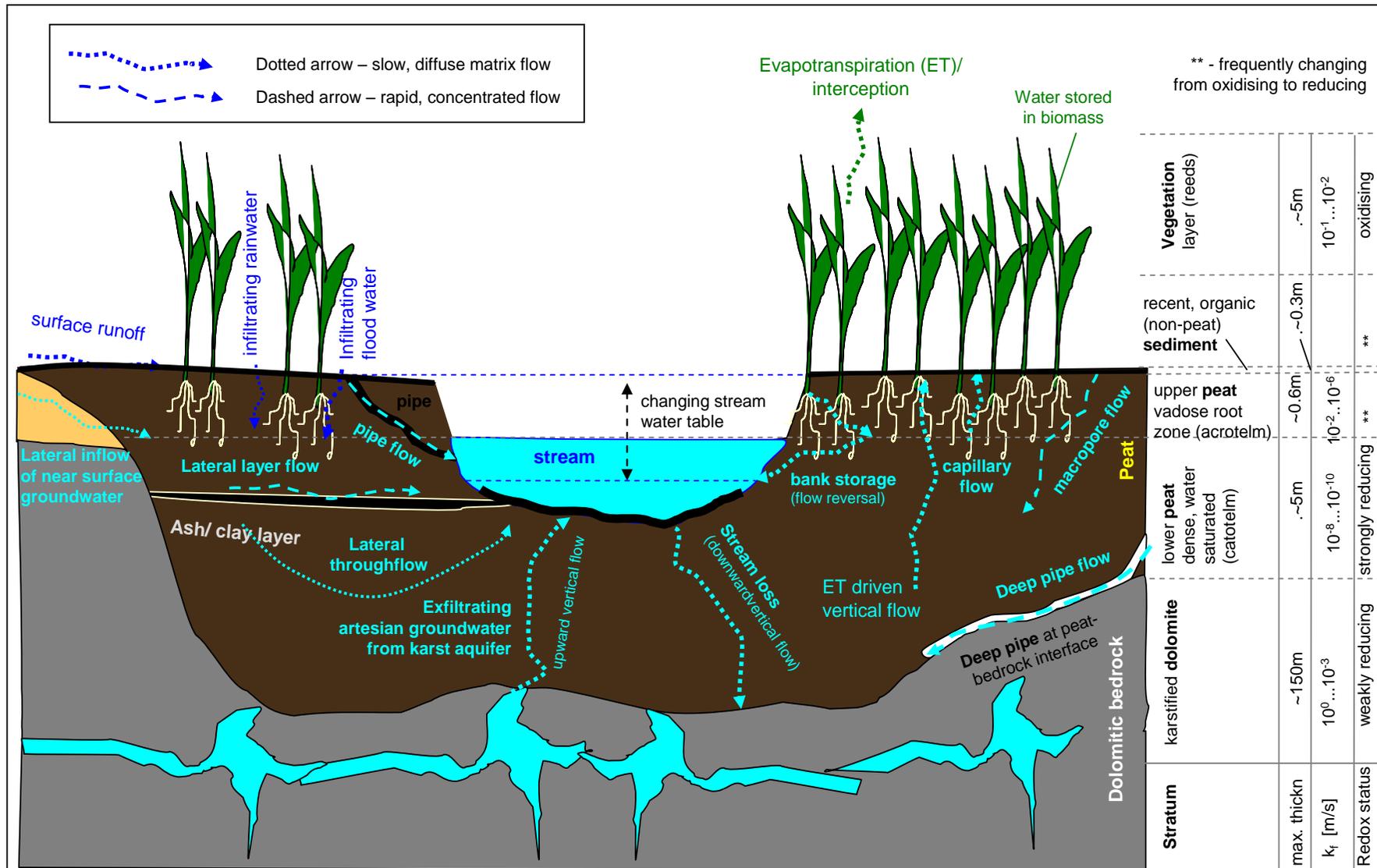
Sources of water in the GMB peatland include:

- stream water infiltrating from the stream channel into the bank peat;
- exfiltrating groundwater moving laterally from shallow aquifers into peat at the edges of the wetland;
- surface runoff from the surrounding catchment entering the margin of the peatland;
- dolomitic groundwater exfiltrating under artesian pressure from the underlying karst aquifer; and
- rainwater directly infiltrating into the acrotelm.

During flood events stream water may also affect peat in areas far from the stream.

In addition to rapid concentrated flow, either horizontally in the stream channel or vertically through macropores and perhaps pipes, a certain degree of slow matrix flow is likely to occur especially in the loosely structured near-surface peat. Apart from gradient-driven downward and vertical flow, this may also include temporal (horizontal) infiltration and exfiltration of surface water following changing stream water levels. In deeper peat vertical (upward) matrix flow may occur as a result of diffusion following evapotranspiration losses on the peat surface. The observed formation of evaporative salt crusts, covering large areas of the peat surface, further points to ground- and or pore-water ascending to surface through capillary forces. The hydraulic properties of the peat and different modes of peat-water contact possibly occurring at the GMB peatland are depicted in Figure 2.

Figure 2. Overview on possible hydraulic processes in the GMB Peatland depicting different modes of surface—and groundwater moving through peat (not to scale) (hydraulic component of the U filter model for peat).



3. Course of Proposed Field and Laboratory Investigations

Based on the above discussed conceptual model, the following 3-phase approach was adopted to obtain site-specific input data into the conceptual model, through a range of different field and laboratory investigations outlined below.

The first phase of the investigation was aimed at characterizing and quantifying *the hydraulic filter component*. In essence that means determining the volume of water that flows through the peatland. Owing to a lack of sufficient flow data for the wetland existing gauging records from the Department for Water Affairs (DWA) for the surrounding region were analyzed in order to establish the possible contribution of the wetland as a whole to the regional system. This was followed by two field campaigns to measure the flow rates at sites near, and in, the wetland for which no flow data were available and to obtain, spatially, more detailed flow estimates. In the final step, the wetland area was screened by measuring water quality parameters (temperature, EC, pH) along horizontal and vertical gradients to detect possible inflow sites of surface- and/or groundwater into the wetland. After establishing a first order approximation of the total volume of water entering and leaving the wetland, and a semi-quantitative apportionment to the different identified sources, attempts were made to determine different peat-water contact modes as described in the hydraulic model component. For this purpose, the hydrodynamics of peat porewater were monitored using quasi-continuous measurements of water levels, and quality parameters, by datalogger controlled *in situ* probes placed in the unmined section of the remaining natural peat.

In the second phase of the investigation, the main objective was to characterize and quantify the *chemical filter component*, *i.e.*, to determine how far peat in the study area under local conditions with regard to chemical water composition, U-speciations and many other site-specific factors controlling the sorption capacity of peat, is indeed able to effectively remove dissolved U from the water column and to retain it. In a first step, U-levels in surface- and groundwater, as well as in sediments and peat samples from the wetland and its surroundings, were analyzed. Based on this, the extent of U-pollution and possibly associated accumulation of U in the wetland sediments and peat was assessed as a first proxy for quantifying the peat filter capacity for U. In a second step of this phase, batch experiments were conducted using sampled peat and two types of typical mine water to determine the U-removal efficiency of peat as well as the remobilization potential.

In the final (third) phase the above results are synoptically integrated into a preliminary, conceptual model, describing the ability of the remaining peat deposit at GMB to act as filter for U-polluted water under current conditions, as well as under a possible post-mine closure scenario, where acidic mine water may flow into the peatland from a vast system of flooded underground mine voids.

4. Summary and Conclusions

Numerous case studies reported in the literature indicate that peat, under natural conditions, acts as a very efficient filter for dissolved U and is able to accumulate the radioactive heavy metal from extremely low (natural background) concentrations in surface and groundwater to levels that may exceed those found in commercially mined, low grade, U ore.

To assess how far local peat at the GMB peatland, under the specific conditions of the study area, may indeed be able to remove U from mining polluted water and thereby protect a downstream municipality, a generic conceptual model on processes and factors governing U attenuation in peat was developed. This model consists of two linked sub-models, namely a chemical filter component addressing the ability of peat to filter and retain U, and a hydraulic filter component that refers to the mode in which U polluted water may come in contact with peat. Based on a significant body of literature, an overview on mechanisms responsible for the removal (immobilization) and subsequent release (remobilization) of U in peat has been compiled that informs the chemical filter component. In a similar manner, the general characteristics of the hydraulic model component were derived.

With regard to the different water-peat contact modes, the associated contact time and the size of the involved reactive surface area of the peat-water interface are of particular importance. They determine whether, and if so, to what extent the various chemical processes governing U mobility in the peat-water system may take place, and what portion of the total throughflow may be affected. In addition, the chemical sub-model also identifies factors such as pH, Eh, ionic strength and others, that determine the occurrence and intensity of the various processes. Finally, based on the conceptual model, a range of plausible natural and anthropogenic events have been discussed that may affect U attenuation in the GMB peatland.

The chemical sub-model contains 10 different processes that govern the attenuation of U peat, all of which are at least to some degree controlled by factors relating to water chemistry. The attenuation of U in peat is ultimately controlled by the net-balance of two different types of processes, namely immobilization and remobilization. The former refers to the removal of dissolved (mobile) U from the water phase either through transforming aqueous U into solid (immobile) phases (phase transition) that then accumulate in peat, or through the incorporation of dissolved U onto existing solid peat constituents by sorption or biological uptake. Immobilization based on phase transitions include the precipitation of insoluble U-species, the co-precipitation of U along with other precipitating secondary minerals, such as calcite and iron hydroxide as well as the gravitational deposition of aggregated U bearing colloids. The latter is somewhat ambiguous as colloids represent a state between solid and truly dissolved U. The remobilization of U from peat also comprises five different processes which either result in the release of U ions or soluble U-complexes back into the aqueous phase (desorption; dissolution of mineral U-phases and formation of inorganic and organic U complexes) or the release of particulate/colloidal U (physical destruction of U-containing organic matter through fire for example and the remobilization of U-colloids/erosion of deposited U bearing particles). Due to the impact of chemical parameters, such as changing pH, redox-potential, ionic strength and chemical composition of the water, these processes can be triggered by a range of natural and anthropogenic events including changing water levels, rainfall, influx of acidic mine water, annual burning of reeds, excavation of peat through commercial mining, *etc.*

In order to verify the applicability of the developed generic model to the local conditions at the GMB peatland a combination of different, site-specific approaches has been designed. For the chemical component, these include an analysis of U concentration levels and geochemical enrichment factors in selected sediment-water systems in and around the wetland, as well as a batch experiment for quantifying the removal efficiency and remobilization rate for two typical U polluted mine waters found in the study area. A similar approach was chosen for the hydraulic component. Based on a range

of identified possible modes of water flow through or over peat, different types of field investigations were designed to characterize and, if possible, quantify the mode and rate of how water comes into contact with the peat and other wetland sediments as potential U filters. This included a statistical analysis of historical flow data, a screening survey of water temperature and EC-levels to detect possible underground inflow of groundwater and quasi-continuous observations of porewater dynamics using electronic *in situ* probes. The results of these investigations are discussed in Part III for the hydraulic component and Part IV for the chemical component of the proposed U-filter model for peat [102,103].

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