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Uranium contamination of soil and groundwater by phosphate fertilizer application

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Acknowledgements

Abstract

Phosphate fertilizers are used all over the world for increasing the fertility of agricultural land. Apart from organic P fertilizers, mineral P fertilizers are most commonly used. They contain between below 1 and more than 100 mg U/ kg. After application and entering the soil zone, this toxic element might finally reach groundwater. Since November 2011, after long discussion, an MCL of 10 µg U/ L was included in the German Drinking Water Directive. However, until now there are no regulations on how much U is allowed to be in phosphate fertilizers. There is not even an obligation of indicating the U contents of commercially available P fertilizers.

Many studies do exist on the sorption of U on different pure or mixed substances and also some long-term field studies. However, there are still numerous unknowns on the fate of U in the subsurface and processes and factors, which control that. So, the main goals of this thesis were to compare different agriculturally used sites with corresponding forest sites by interpreting available long-term soil-, percolation water and groundwater data, to take own soil and water samples to characterize their composition and properties, to conduct various tests with them, to model the speciation in the water samples, and to finally put all these findings together.

For characterizing soils' properties, grain size distribution, pH, carbonate and organic carbon content as well as cation exchange capacity were determined. Distilled water, ammonium acetate at pH 7 and 5, EDTA, hydroxylamine hydrochloride ($NH_2OH*HCl$) and 7 N nitric acid were assessed for their U extraction capability from soils. It was examined whether the specific activity ratio of U-238/Ra-226 can be used for elucidating the origin of U (geogenic, i.e. from P-containing rock, or anthropogenic, i.e. from P fertilizers). From three sites, water samples were taken and analyzed for main and trace elements using IC and ICP-MS, respectively. The results were used for modeling U and P speciation and saturation indices using PHREEQC. Flow-through experiments under saturated conditions using field top- and subsoil samples from one of the study sites, the lysimeter station in Brandis, were conducted using solutions containing 1 mM $NaHCO_3$, 0.168 µM $UO_2(NO_3)_2$, no, 1. 421 or 0.142 mM H_3PO_4 and some of them also 1 mM $Ca(NO_3)$. The applied P concentration was based on the GAP (good agricultural practice) guidelines, and U concentrations were selected according to typical mean contents in P fertilizers. By increasing the contents applied per time, a time shift of 319 days was achieved and consequently a time of 93 years could be performed within 106 days.

From field studies it was found that no general conclusion on the fate of U can be made. Contents in soils varied between 1.3 and 4.1 mg/kg; contents in waters between below detection limit (0.001 µg/L) and 12.9 µg/L. At some sites, concentrations remained constant over time, at others, they increased or decreased. Soil and groundwater U contents did not show the same trend at each study site. The same applies for U contents in groundwater of monitoring wells in the surrounding.

The behavior of U depends on soil properties and composition, as well as fertilization (applied amounts, type of fertilizer, U content, season and frequency of application), climate (e.g. precipitation), ploughing practices (frequency, depth), and others. Distilled water, ammonium acetate (pH 7), EDTA and hydroxylamine hydrochloride mobilize below or around 1 % of total U; ammonium acetate (pH 5) set free between about 2 and 9 %. Even when nitric acid was used, extracted amounts were only between 15 and 40 %. This suggests that U is firmly bound as other studies confirmed. Repeating the ammonium acetate (pH 5) step with the samples from flow-through experiments, recoveries were 5- to 6-times higher. This supports the findings of other scientists that U binding gets stronger over time. Low-level gamma spectrometry could not serve to reveal the origin of uranium because uncertainties were bigger than differences between field and corresponding forest soils. During flow-through experiments, about 99 % of total U was retained even if species modeling suggested uncharged, mobile U complexes to account for a great or the greatest share of total U in most flow-through cells. So, comparability with findings from the field is very limited. The reasons for the effective U retention during flow-through experiments is not yet clear but changing redox conditions in micropore regions of soils, the action of microorganisms and the formation of solubility-controlling phases might play an important role.

Zusammenfassung

Phosphatdünger werden auf der ganzen Welt genutzt, um die Fruchtbarkeit landwirtschaftlich genutzter Böden zu erhöhen. Neben organischen P-Düngern, sind mineralische P-Dünger die am häufigsten genutzten. Sie enthalten zwischen 1 und mehr als 100 mg U/ kg. Dieses toxische Element kann in das Grundwasser gelangen, nachdem es aufgebracht worden und in die Bodenzone eingedrungen ist. Nach langer Diskussion, enthält die deutsche Trinkwasserverordnung seit November 2011 einen Grenzwert von 10 µg U/ L. Jedoch existieren bis jetzt noch keine Grenzwerte für U in Phosphatdüngern. Nicht einmal die enthaltenen U-Gehalte kommerzieller Dünger müssen gekennzeichnet werden.

Es gibt viele Studien zur Sorption von U an verschiedenen reinen oder gemischten Substanzen und Langzeitstudien. Jedoch existieren noch viele Unklarheiten zum Verhalten im Untergrund und beeinflussenden Prozessen und Faktoren. Daher waren die Hauptziele dieser Arbeit mittels Interpretation verfügbarer Langzeit-Boden-, Sickerwasser- und Grundwasserdaten verschiedene landwirtschaftliche Standorte mit entsprechenden Waldstandorten zu vergleichen, Boden- und Wasserproben zu nehmen und deren Zusammensetzung und Eigenschaften zu charakterisieren, Tests mit ihnen durchzuführen, die Speziation im Wasser zu modellieren und schließlich all die Ergebnisse zusammenzuführen.

Um die Eigenschaften der Böden zu charakterisieren wurden Korngrößenverteilung, pH und organischer Kohlenstoffgehalt sowie Kationenaustauschkapazität bestimmt. Destilliertes Wasser, Ammoniumacetat bei pH 7 und 5, EDTA, Hydroxylaminhydrochlorid und 7 N Salpetersäure wurden auf ihr U-Extraktionsvermögen aus Böden geprüft. Es wurde untersucht, ob das spezifische Aktivitätsverhältnis von U-238/Ra-226 genutzt werden kann, um die Herkunft des U aufzuklären (geogen, d.h. aus P-Gestein, oder anthropogen, d.h. aus P-Düngern). Wasserproben wurden von drei Standorten genommen und mittels IC bzw. ICP-MS auf Haupt- und Spurenelemente untersucht. Die Ergebnisse wurden zur Modellierung der U- und P-Speziation und Sättigungsindizes mittels PHREEQC genutzt. Durchflussversuche mit Ober- und Unterbodenproben aus Brandis, einem der Untersuchungsstandorte, wurden unter gesättigten Bedingungen mit Lösungen durchgeführt, die 1 mM $NaHCO_3$, 0.168 µM $UO_2(NO_3)_2$, kein, 1. 421 oder 0.142 mM H_3PO_4 und manche von ihnen auch 1 mM $Ca(NO_3)$ enthielten. Die Konzentration des aufgebrachten P basierte hierbei auf den Vorgaben der „guten landwirtschaftlichen Praxis" und jene des U wurden entsprechend typischer durchschnittlicher Gehalte in P-Düngern gewählt. Durch Erhöhung der pro Zeit aufgebrachten Mengen, wurde ein Zeitraffer von 319 Tagen erzielt; in 106 Tagen wurden 93 Jahre nachgestellt.

Aus Felduntersuchungen wurde deutlich, dass keine generellen Aussagen zum Verhalten von U möglich sind. Die Bodengehalte variierten zwischen 1.3 und 4.1 mg/kg; im Wasser von unter der Nachweisgrenze (0.001 µg/L) bis 12.9 µg/L. An manchen Standorten war die Konzentration über die Zeit konstant; an anderen stieg oder sank sie. Nicht an allen Standorten folgten die U-Gehalte in Boden und Wasser dem gleichen Trend. Gleiches gilt für die U-Gehalte nahe gelegener Grundwassermessstellen.

Das Verhalten von U hängt von den Eigenschaften und der Zusammensetzung der Böden, von Düngung (Menge, Art, U-Gehalt, Jahreszeit und Häufigkeit der Aufbringung), Klima (z.B. Niederschlag) und Bodenbearbeitung (Häufigkeit, Tiefe) ab. Destilliertes Wasser, NH_4Ac (pH 7), EDTA und $NH_4OH \cdot HCl$ mobilisierten unter oder um 1 % des gesamten U; NH_4Ac (pH 5) setzte 2-9 % frei. Selbst mittels HNO_3 wurden nur 15-40 % extrahiert. Daher kann angenommen werden, dass U fest gebunden ist wie andere Studien bestätigen. Die Wiederholung des NH_4Ac (pH 5)- Schrittes mit den Proben der Durchflussversuche führte zu 5- bis 6-mal höheren Ausbeuten. Das unterstützt die Ergebnisse anderer Wissenschaftler, dass die Bindung von U mit der Zeit zunimmt. Gammaspektrometrie konnte die Herkunft des U nicht aufdecken, da die Unsicherheiten größer waren als die Unterschiede zwischen den Feld- und entsprechenden Waldböden. In den Durchflussversuchen wurden ca. 99 % des aufgebrachten U zurückgehalten, obwohl Speziesmodellierung ungeladene, mobile U-Komplexe meist als dominant ermittelte. Daher ist die Vergleichbarkeit mit den Ergebnissen aus dem Feld sehr eingeschränkt. Im Moment ist noch nicht klar, warum U in den Durchflussversuchen so effektiv zurückgehalten wurde. Veränderliche Redoxbedingungen in Mikroporen der Böden, die Aktivität von Mikroorganismen und die Bildung löslichkeitskontrollierender Phasen könnten eine entscheidende Rolle spielen.

List of contents

List of figures

List of tables

List of abbreviations

BDF	"Bodendauerbeobachtungsflächen", i.e. intensive test sites managed by the LfULG
BfUL	"Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft"
BMU	„Bundesministerium für Umwelt" (German Federal Ministry for the Environment)
CEC	Cation-exchange capacity (in $cmol_c/kg$, i.e. centimols of positive charge per kg dry soil material)
DOC	Dissolved organic carbon
EDTA	Ethylenediamintetraacetic acid
EXAFS	Extended X-ray absorption fine structure
FAAS	Flame atomic absorption spectroscopy
FK	Field capacity, i.e. maximal water content in volume % that an undisturbed disturbed soil can hold against gravity, German (according to KA 05): "Feldkapazität"
GAP	Good agricultural practice
IC	Ion chromatography
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
KA 05	Soil mapping handbook used in Germany, "Bodenkundliche Kartieranleitung" in 5. Auflage)
LfULG	Landesamt für Umwelt, Landwirtschaft und Geologie
log k	Dissociation constant
masl	Meters above sea level
MCL	Maximum contaminant level
NDIR sensor	Nondispersive infrared sensor
nFK	Plant-available water (according to German KA 05: "nutzbare Feldkapazität, nFK", i.e. water content between PWP and FK
NP fertilizer	Fertilizers containing nitrogen and phosphate

NPK fertilizer	Fertilizers containing nitrogen, phosphate and potassium
NPOC	Non-purgeable organic carbon
PHREEQC	Geochemical code for modeling speciation in water
ppb	Parts per billion; measure for concentrations, i.e. μg/L or μg/kg
ppm	Parts per million; measure for concentrations, i.e. mg/L or mg/kg
PK fertilizer	Fertilizers containing phosphate and potassium
PWP	Permanent wilting point (German: Permanenter Welkepunkt, PWP"), i.e. water content in a soil in volume % at which plants dry out and cannot recover anymore
SI	Saturation index
SMUL	"Staatsministerium für Umwelt und Landwirtschaft", i.e. German state ministry for environment and agriculture
TIC	Total inorganic carbon
TOC	Total organic carbon
TUBAF	Technische Universität Bergakademie Freiberg
UFZ	"Umweltforschungszentrum", German Center for Environmental Research
Vol.%	Volume percent
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction

1 Introduction

1.1 Motivation and problem description

At the moment, the world population is at about 7.07 billion people (Collins, 2012) and it steadily keeps increasing. It is expected that by the year 2100, there will be 10.1 billion people living on earth (United Nations, 2011). The demand for foodstuffs and energy crops is closely related to this increasing trend. To satisfy the needs of the consumers, farmers have to increase the yield per area by applying fertilizers and pesticides. Fertilizers contain the micro and macro nutrients essential for plant growth. One of the macro nutrients is phosphate. Its main natural source is apatite, a phosphate mineral of magmatic or sedimentary origin.

By nature, this mineral contains uranium and other unwanted toxic trace metals like cadmium. During fertilizer production, these metals are to a greater or lesser extent transferred to the phosphate fertilizer, which is then applied on farmlands (Dienemann and Utermann, 2012b), (Kratz et al., 2008). There phosphate and the associated trace metals enter the soil zone where they are first retarded or are taken up by plants and then, sooner or later, reach the groundwater zone. The transfer into plants is generally not very high but below the limits of quantification (0.025 mg/kg dry matter; Kratz et al., 2008, based on yield data from Kerschberger et al., 1997). However, after having been incorporated into plant tissue, uranium gets enriched in the food chain. The residual U remains stored in the soil or is washed out into the groundwater. Consequently human health is endangered in two ways, one being the consumption of foodstuffs and the other one being drinking water, which in many countries is predominantly produced from groundwater. The principal effects on human health are kidney dysfunctions and an increased cancer risk (Streit, 1991).

As opposed to Cd with a maximum contaminant level (MCL) of 50 mg per kg P_2O_5, until now (summer 2013), in Germany there is still no regulation for U in P fertilizers. Requirements for labeling the uranium contents in fertilizers neither do exist (Behm, 2012). That is because the Federal Government of Germany at the moment does not see a need for action in the context of human toxicity. It says that not the fertilization but the water-bearing rocks mainly determine the uranium concentrations in groundwater. However, instead of giving numbers for the fraction of uranium in ground- and surface waters that stems from fertilization, the government mentions methodological reasons that do not make it possible to directly measure that fraction (Bundesregierung, 2012).

In 2012 ministers and senators of the agricultural departments of the Federal German States asked the Federal Government to publish a report with the U concentrations in phosphate fertilizers. They requested the government to take preventive measures by introducing MCLs and requirements to label U contents in fertilizers to prevent future contaminations. The end of these discussions is still open.

Since 2011 the WHO recommends a guide value of 30 µg/L for U in drinking water (WHO, 2012). In November 2011, after long discussions, the German Drinking Water Ordinance introduced an MCL value of 10 µg/L for German drinking water (Dienemann and Utermann, 2012b). Due to the absence of such a limit, until now this element was not a part of common water analyses (Haferkorn, 2012), (Hübschmann, 2012). It was only analyzed in special cases like in the context of mining or nuclear energy production (Merkel, 2012a). Only for soils, esp. farmlands, longer time series do exist (Haferkorn, 2012). Therefore, with respect to groundwater this work focuses on the present state of the uranium concentration and on prognoses of which development one might expect in future.

1.2 Objectives of the thesis

The objective of the thesis was to investigate the problem of uranium contamination of soil and groundwater as a result of phosphate fertilizer application on farmland. For analyzing this issue, four intensively-farmed sites in Saxony were selected and compared with locations in their vicinity that are used as forests. Available data on soils, water and fertilization practices was interpreted; seepage water samples and undisturbed and disturbed soil samples were taken for conducting various tests with them:

- Undisturbed soil samples
    - Flow-through load tests to see when a uranium-containing solution flowing through a soil column reaches breakthrough. This experiment is a time lapse of the processes that take place in nature and was performed under saturated conditions.
- Disturbed soil samples
    - Characterization of the soils' properties (grain size distribution, cation exchange capacity, pH, total inorganic carbon (TIC), total organic carbon (TOC), total uranium content)
    - Determination of uranium extractable with different extractants
    - Performing gamma spectrometry measurements to determine the total uranium contents of the studied soils and to check whether the U/Ra altered by phosphate fertilizer production can be recognized in farmland soils in comparison to forest soils.
- Water samples
    - Analysis for major and trace elements with special regard on phosphorus and uranium
    - Speciation and saturation index modeling using PHREEQC

In addition to own analyses of samples taken in 2012 and 2013, respectively, water and soil analytical data as well as information on fertilization practices from the sampling sites and their surrounding were interpreted. By that, changes over time could be revealed and used for studying interrelations between different variables ruling the composition of soil and groundwater. Risk assessment and recommendations for the future form the final part of the characterization of the present situation.

2 Fundamentals

2.1 Abundance of uranium in the environment

Uranium occurs at about 3×10^{-4} % on earth (Hoppe, 2012). Different authors speak of between 2.5 and 4 mg/kg in the lithosphere (Dienemann and Utermann, 2012b). That makes it be the 54th most abundant element, more abundant than gold, silver, or mercury (Seilnacht, 2012). The most abundant and most long-lived isotope is U-238, which makes up 99.2742% of total uranium. Besides that, U-235 with 0.7204% and U-234 with 0.0054% are the two other ones that naturally exist (Dienemann and Utermann, 2012b). Uranium ubiquitously occurs in nature stemming from granites and various other mineral deposits. The most abundant mineral is pitchblende, UO_2, which is highly radioactive (Seilnacht, 2012). Uranium enters the environment by leaching from natural deposits, release from mill tailings, combustion of coal and other fuels, emissions from nuclear industry, and the use of phosphate fertilizers, which contain uranium as an unwanted minor constituent.

2.1.1 Uranium in rock and fertilizers

There are two different groups of phosphate-containing fertilizers commonly used in Germany. The first one is mineral fertilizers and the second one is organic fertilizers. Mineral fertilizers are produced from either sedimentary or magmatic apatite rock (Kratz et al., 2008). 87 % of the phosphate rocks used are of marine-sedimentary origin. These marine-sedimentary phosphates as well as the terrestrial sedimentary phosphates generally contain greater uranium concentrations than igneous parent material. This can be seen in Table 1, which lists the ten largest producers worldwide.

Table 1 – U concentration ranges in phosphate rocks of different origin, sorted by type of phosphate and amount of production of the 10 largest phosphate suppliers worldwide (Kratz et al., 2008)

Origin	Mine production in 2002, gross weight [kt]	U concentration range [mg/kg]
Sedimentary phosphate		
United States	35,800	65 - 141
Morocco and Western Sahara	24,000	75 - 130
China	21,000	23 - 31
Tunisia	7,500	32 - 48
Jordan	7,000	46 - 129
Israel	3,500	99 - 150
Syria	2,400	75 - 106
Sedimentary/igneous phosphate		
Brazil	4,700	8 - 220
Igneous phosphate		
Russia	10,500	27 - 85
South Africa	2,800	23

Organic fertilizers are farmyard manure or slurry, i.e. products from animal husbandry, or sewage sludge (Kratz et al., 2008). They are commonly used if agriculture is combined with animal husbandry because it has a twofold benefit: the agriculturist can dispose the animals' feces without having to pay for, and he does not need to buy mineral fertilizers. Table 2 lists the uranium contents of mineral fertilizers and organic fertilizers used in Germany.

Table 2 – Uranium concentration [mg/kg] in P fertilizers commonly used in Germany (modified according to (Kratz et al., 2008); data for mineral fertilizers stems from German fertilizer samples of the FAL ("Bundesforschungsanstalt für Landwirtschaft") sample collection between 2003 and 2007 and various other sources; data for the organic fertilizers stems from the FAL institute of Plant Nutrition and Soil Science fertilizer database. Data is complemented by the compilation of element concentrations in phosphate fertilizers from all over the world by (Taylor, 2013). U content of organic fertilizers refers to dry matter)

Type of fertilizer	Range of P content [% P]	U content [mg/kg]		Number of samples
		range	mean	
Straight P mineral fertilizers				
Soft/ground rock phosphate	0.2-18	0.2-434	92	205
Superphosphate	0.7-13.9	1.0-325	52	37
Triple superphosphate	0.8-22.8	1.2-364	118	38
Mixed-nutrient mineral fertilizers				
Monoammonium phosphate	6.2-23.0	2.9-258	72	18
Diammonium phosphate	4.9-20.2	0.16-194	26	10
NP fertilizer	5.3-25.8	0.03-1888	138	52
PK fertilizer	3.4-20.5	0.3-206	55	49
NPK fertilizer	1.5-21.4	0.04-295	36	164
Organic fertilizers				
Liquid manure (organic cattle breeding)		0.1-2.8	0.35	197
Liquid manure (conventional cattle breeding)	0.14-5.8	0.15-1.4	1.1	28
Sewage sludge	2.1-2.2	0.005-18	3.2	704

For organic P fertilizers, phosphorus and also uranium contents are significantly lower than in mineral fertilizers as shown by the numbers in Table 2. That means that the soil contamination with uranium will be less but also the fertilization efficiency will be lower.

2.1.2   Uranium in soils

U contents in soils typically range between < 1 mg U per kg and > 5 mg U per kg (Utermann and Fuchs, 2008). Its concentration in uncontaminated soils primarily depends on the composition of the soil parent material and the geological and pedological processes that have been acting on the soil. By human activities, uranium contents can reach values of greater than 10 mg U per kg soil. Among these activities are mining, nuclear energy production, fertilizer application on farmlands, or airborne emissions from for example coal power plants (Utermann and Fuchs, 2008). If agriculture is the only human activity considered as impact factor on uranium concentration in soils, a balance can be calculated from P input by fertilization and P output by harvest. Table 3 shows the ranges for U loads for different P fertilizers commonly used in Germany if a P fertilization rate of 22 kg P/(ha×a) is assumed.

Table 3 – Uranium input to farmlands if a P rate of 22 kg/(ha*a) is assumed (ca. 50 kg P_2O_5), according to the good agricultural practice (GAP) (modified according to Kratz et al., 2008)

Type of fertilizer	U input [g/(ha×a)]		
	min	max	mean
Straight P mineral fertilizers			
Triple superphosphate	5.5	48	22
Mixed-nutrient mineral fertilizers			
NP fertilizer	0.05	82	7.0
PK fertilizer	5.1	61	23
NPK fertilizer	0.01	166	8.0
Organic fertilizers			
Liquid manure (conventional cattle breeding)	0.09	55	2.3
Sewage sludge	0.001	19	3.2

In Germany, the fertilization rate is generally lower than 22 kg/(ha*a), the value proposed by the good agricultural practice (Kratz et al., 2008). That is because in the past the fertilization rate was higher so that phosphate could be accumulated in soil, which now still can be used. Economic reasons complement that. Every year, the Julius-Kühn institute calculates the official German P field balance for the German Ministry of Agriculture. The assumptions for these calculations are the average U contents of the phosphate fertilizers given in Table 2, and uranium content in crops of < 0.025 mg U per kg dry matter (limit of quantification in the investigations). The U balance for 1996 was 7.64 g/(ha×a) and that for 2005 amounted 4.40 g/(ha×a) underlining the steadily decreasing trend (Kratz et al., 2008). However, even if the trend is decreasing the U input is still greater than the output by plant uptake, which amounts about 0.1 to 0.2 g/(ha*a). That means that the total quantity of uranium in soil further increases over time. In future, it can be expected that again more phosphate fertilizer will have to be applied than today to provide plants with sufficient quantities of phosphate. That is because in Thuringia and other German Federal States, the phosphorus supply of farmlands steadily decreases since 1990 (Maruschke, 2012). The increase in fertilization rate will at the same time increase uranium inputs in soils and the risk for humans if no counter-measures are taken. One efficient measure would be to introduce an MCL and the obligation for labeling uranium concentrations in fertilizers, as it is already compulsory for cadmium. The call for an MCL and labels on fertilizer products is now supported by the Ministers of Agriculture of the German Federal States (Maruschke, 2012).

2.1.3   Uranium in surface- and groundwater

Uranium concentrations in German rivers and in sea water show relatively little variation. Rivers in Germany usually have uranium concentrations between about 1 and 3 µg/L. In seawater one finds 3.3 µg/L (LfU, 2007). Natural uranium concentrations in groundwater as well as in the unsaturated zone are much more variable ranging over several orders of magnitude. They primarily depend on the mineralogy of the water-bearing rock and are altered by land use and other human interferences (Dienemann and Utermann, 2012b). Table 4 shows uranium concentrations in German groundwaters sorted by the type of rock forming the aquifer.

Table 4 – Uranium concentrations in German groundwaters sorted by type of rock forming the aquifer (LfU, 2007)

Type of rock forming the aquifer	Number of samples	Minimum concentration [µg/L]	50th percentile [µg/L]	90th percentile [µg/L]	Maximum concentration [µg/L]
Acidic magmatic and meta-morphic rocks	627	0.0003	0.03	0.57	35.00
Sands and gravels from North German Plain	790	0.001	0.02	1.20	1134.00
Limestones from "Muschelkalk"	398	0.02	0.80	1.80	11.80
Tertiary sediments	575	0.0003	0.90	3.00	23.00
Sandstones from Lower Trias	402	0.0003	0.30	3.60	71.40
Quartenary sediments from river flood plains	463	0.06	1.30	4.40	58.00
Sandstones and siliceous alter-nations	457	0.0003	0.70	7.20	1450.00
Palaeozoic sedimentary rocks	62	0.0003	0.16	14.90	91.00

Even if some of the waters have maximum uranium concentrations in the mg/L range, the 90th percentile of nearly all of them lies below the German MCL for uranium in drinking water (10 µg/L). That means that only few sites where samples have been taken have such high concentrations. For drinking water production, such wells are often shut down or water treatment measures are taken to lower the uranium concentrations (Dienemann and Utermann, 2012b).

Elevated uranium concentrations in groundwater are not directly related to the U concentrations in drinking water because of different drinking water production and drinking water treatment methods used in Germany (Dienemann and Utermann, 2012b). Most drinking water produced in waterworks in Germany has U concentrations <1 µg/L already before the MCL for uranium had been introduced to the German Drinking Water Ordinance. Therefore, until now there is no danger for public health by drinking water in Germany. The danger could increase in future if no measures are taken to decrease or prevent further U input.

2.2 Health issues and regulations for uranium in drinking water

Humans come into contact with uranium by air, food and water. Intake through air is low and intake by food is between 1 to 4 µg per day. Uranium concentrations in German drinking water are normally very low as addressed in section 2.1.3. However, if uranium is present in the drinking-water source, its concentrations can be higher and water will dominate uranium intake (WHO, 2012).

Uranium has a half-life of 4.5 billion years. Therefore, at U concentrations in drinking water (commonly not higher than 60 µg/L), the radiotoxicity of uranium is much lower than its chemical toxicity (Carroll, 2007). As the uranyl cation resembles the hydrated Ca^{2+} ion, it tends to be stored and accumulated in kidneys and bones where it increases the cancer risk (Streit, 1991). Since 2011, the WHO recommends a guide value of 30 µg/L for uranium in drinking water (before it was at 9 and 15 µg/L, respectively) (WHO, 2012). In the EU Drinking Water Directive, so far no value is defined for uranium (Dienemann and Utermann, 2012b). After many years of discussion, in 2011 an MCL of 10 µg U

per liter was included in the German Drinking Water Directive, 2 µg U / L for mineral water suitable for babies. By now the German Federal Environmental Agency ("Umweltbundesamt", UBA) and the German Federal Institute for Risk Assessment ("Bundesinstitut für Risikobewertung", BfR) do not see any risk for the consumer, neither by food nor by water if the MCL is not exceeded (Umweltbundesamt, Fachgebiet II 3.6 „Toxikologie des Trink- und Badebeckenwassers", 2011).

2.3   The fate of uranium in soil and (ground)water

The electron configuration, $5f^3\ 6d\ 7s^2$, of U is the basis for its reaction and binding behavior. Due to the free valences, U does not occur as free metal in nature but bound in various compounds. The oxidation states of uranium range from +II, over +III, +IV and +V to +VI (Merkel, 2009). In nature, the most important oxidation states are +IV and +VI (Grenthe et al., 2006), +IV being dominant under reducing conditions and +VI under oxidizing conditions. With respect to geochemistry, U(IV) behaves similar to thorium and is nearly insoluble under mildly acidic to alkaline conditions, often precipitating as UO_2 (Schick et al., 2008). Under oxidizing conditions in (ground)water, U in the +VI state primarily forms the linear uranyl molecule, $(O=U=O)^{2+}$, which complexes with ligands like carbonate, hydroxide, and oxalate. These complexes are highly soluble and mobile (Grenthe et al., 2006). Table 5 lists several U(VI) species that might be dominant in groundwater under certain conditions.

Table 5 – U(VI) species that might be dominant in groundwater under certain pH and redox conditions (modified according to Merkel, 2012c)

$(UO_2)^{2+}$
$(UO_2OH)^+$, $(UO_2(OH)_2)^0$, $(UO_2(OH)_3)^-$
$(UO_2CO_3)^0$, $(UO_2(CO_3)_2)^{2-}$, $(UO_2(CO_3)_3)^{4-}$
$((UO_2)_2CO_3(OH)_3)^-$
$(UO_2SO_4)^0$, $(UO_2(SO_4)_2)^{2-}$
$(UO_2H_3PO_4)^{2+}$, $(UO_2H_2PO_4)^+$, $(UO_2HPO_4)^0$, $(UO_2PO_4)^-$
$(UO_2(H_2PO_4)_2)^0$, $(UO_2(HPO_4)_2)^{2-}$, $(UO_2(H_2PO_4)(H_3PO_4))^+$
$((UO_2)_3O(OH)_2(HCO_3))^+$
$(Ca_2(UO_2)(CO_3)_3)^0$, $(CaUO_2(CO_3)_3)^{2-}$
$(Mg_2(UO_2)(CO_3)_3)^0$, $(MgUO_2(CO_3)_3)^{2-}$

However, before uranium enters the groundwater zone, it undergoes different alteration processes in the unsaturated zone. In that zone rock, soil, soil solution and soil air interact and conditions are predominantly oxidizing, making hexavalent U the dominant oxidation state of uranium. U(+VI) is present as the bivalent uranyl ion, $(UO_2)^{2+}$, or forms complexes like $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ or others as shown in Table 5 depending on pH and presence of ligands in the soil solution (Schick et al., 2008). Only the positively charged complexes can be fixed by cation exchange. The negatively charged complexes can be sorbed by organics (Merkel, 2009), Fe/Al oxides and hydroxides (Yamaguchi et al., 2009). Complexes without charge in most cases are mobile due to the limited interaction with surfaces. Human interference in and natural changes of the system can change the binding behavior of uranium in soils. For example, liming or (natural) acidification will cause that sorbed UO_2^{2+} is substituted by Ca^{2+} and H^+ ions, respectively, and consequently released from soil colloids into the groundwater

(Schick et al., 2008). Some of the most central factors influencing the fate of uranium in the soil and groundwater zone are compiled in the following list.

- Properties of the soil
    - Structure (grain size distribution, texture, porosity, permeability)
    - Composition (content of organic matter, (clay) minerals, presence of (free) carbonates, oxides, hydroxides, oxyhydroxides (mainly Fe, Mn and Al), soil moisture)
    - Cation exchange capacity (= the soil's capacity to retain and release positively charged ions; by action of electrostatic forces Cooper, 2009; high for organic matter and clays; low for sandy materials; relatively constant over time, Marx et al., 1996)
- Properties of the soil solution
    - pH
    - Redox potential
    - Ionic strength
    - Composition (presence and concentration of ligands (carbonate, hydroxide, (organic) acids, organics (e.g. humics), phosphate, etc.)
- Further factors
    - Climate
    - Uranium concentration
    - Land use (agriculture, pasture, grassland, forest, etc., tillage (traditional, direct seeding, etc.), liming, fertilization (type and amount of fertilizer; (binding form and concentration of U and P in it), frequency of application))
    - Microorganisms, plants (releasing organic acids, taking up uranium, redox reactions like reduction of U(VI) to U(IV) with subsequent (co)precipitation)

These factors rule the processes that might occur in the subsurface. Figure 1 is a simplified sketch of the system and the processes that might alter the speciation or binding state of uranium.

$CaCO_3$, P_2O_5

H^+ Uptake/release by plants

(Co)precipitation/ dissolution

Complex formation

Mineral formation

H^+

H^+

Ion exchange/sorption (H^+, Ca^{2+})
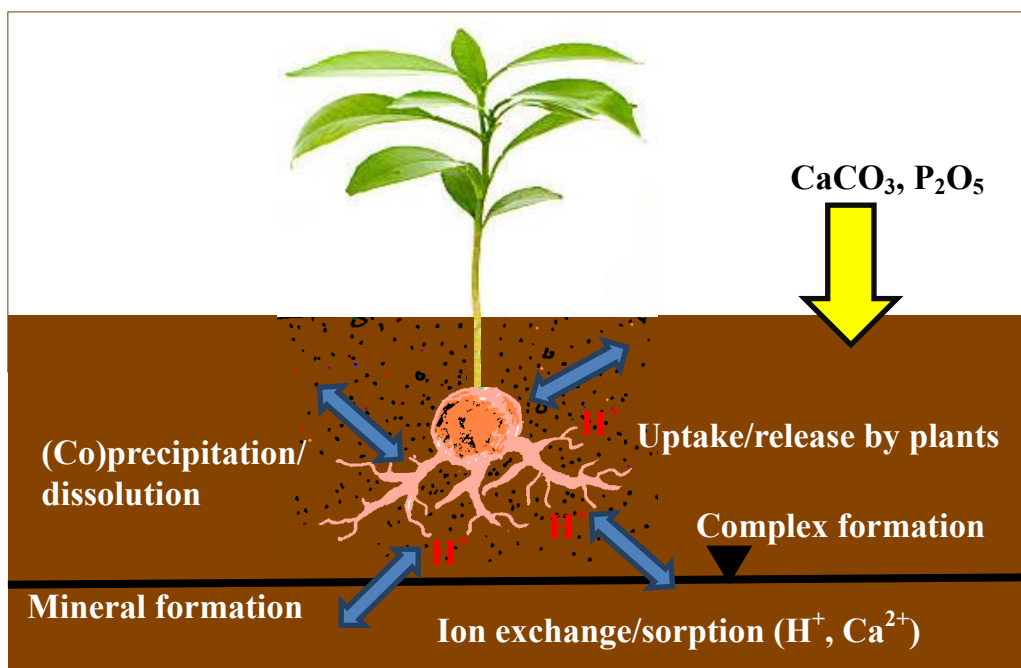
Figure 1 – Processes that might influence the state of uranium in soil and groundwater

2.4 Properties of soils ruling the retention of uranium

After fertilizer application, soils, systems being composed of solid, liquid and gaseous components, are the first environmental compartment being affected. For assessing and understanding processes governing the behavior of uranium in the subsurface, certain parameters characterizing the properties of soils are necessary to determine. Among them are:

- Grain size distribution (for sorption, especially of the finer soil material, i.e. < 2 mm, is relevant as this has a larger surface area and consequently greater sorption capacities per unit weight as compared to coarser material)
- Permeability (influences the fraction of pores filled with water and/or air at a certain water content of the soil)
- Soil solution pH
- Organic matter content (TOC)
- Carbonate content (TIC)
- Cation exchange capacity

In the present work, all of these parameters, except for the permeability, were determined according to the methods presented in section 4.3. As completion of these analyses, extractions using different extractants were used to determine the soil constituents, uranium is bound to and the ease of release of uranium from soil to groundwater and the other adjacent environmental compartments.

2.5 Elucidating the origin of uranium

Uranium-238 is the first member of one of the three natural decay series, the other series being headed by uranium-235 and thorium-235, respectively. Under natural conditions, these three decay chains may be in radioactive equilibrium (EPA, 2012). That means that each radionuclide of such a decay chain decays at the same rate as it is produced, making its activity more or less constant. In the state of radioactive equilibrium, all radionuclides in the series decay at the same rate (EPA, 2012). For equilibrium to be established, two prerequisites need to be fulfilled (ANL, 2005):

1) The half-life of the parent radionuclide must be longer than that of any other radionuclide of the series.
2) Sufficiently long time must have elapsed, i.e. several half-lives of the decay product (daughter nuclide) with longest half-life. That is necessary for ensuring ingrowth of the decay products.

If these two requirements are fulfilled, secular equilibrium is established. This is the case for the mentioned three natural decay chains. If the half-life of one or several of the decay products is similar to that of the parent radionuclide, only transient equilibrium can be reached. In case the half-life of the decay products is greater than that of the parent radionuclide, no equilibrium will be established at all (EPA, 2012). Figure 2 illustrates the statements.
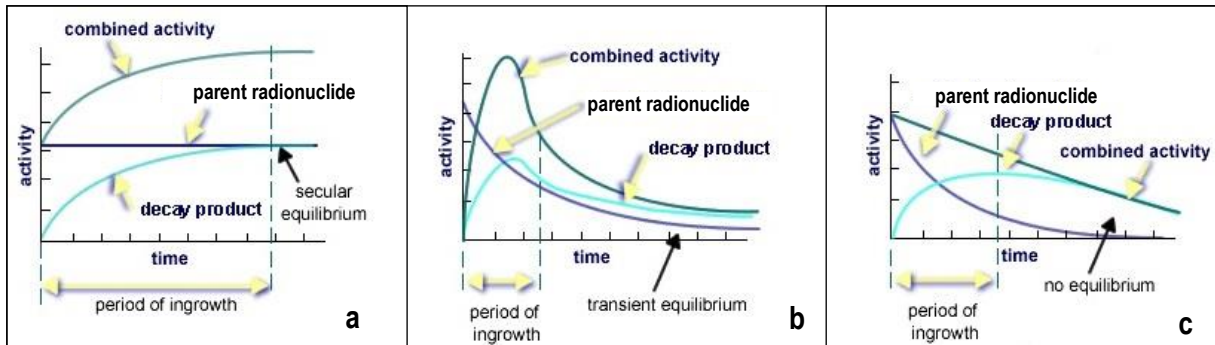
Figure 2 – Options for radioactive equilibria (modified after EPA, 2012. For simplification, all three illustrations assume decay chains with only two steps where the decay product decays to a stable nuclide. a) Secular equilibrium: As the half-life of the decay product is much shorter than that of the parent radionuclide, it generates radiation more quickly. After several half-lives of the decay product, the activities of parent and daughter radionuclide are equal and the activity, i.e. the amount of radiation, is doubled. Beyond this point, decay and production of the decay product are equal. b) Transient equilibrium: As half-lives of decay product and parent radionuclide are similar, initially total activity rises as both radionuclides decay. Eventually, balance (equilibrium) is established. c) No equilibrium: The half-life of the decay product is longer than that of the original radionuclide. Therefore, its activity first increases up to a maximum value and then decreases. The parent radionuclide decays away, and no equilibrium is reached.)

The statements made underline why secular equilibrium normally exists for U-238 and its decay products in uranium-bearing phosphate rock (El Afifi et al., 2009). During rock processing as it is done during phosphate fertilizer production, this equilibrium is broken between different members of the U-238 decay chain (Roselli et al., 2009). It breaks between Pa-234 and U-234, U-234 and Th-230, Th-230 and Ra-226 and Rn-222 and Pb-210. Figure 3 shows the decay chain of U-238.
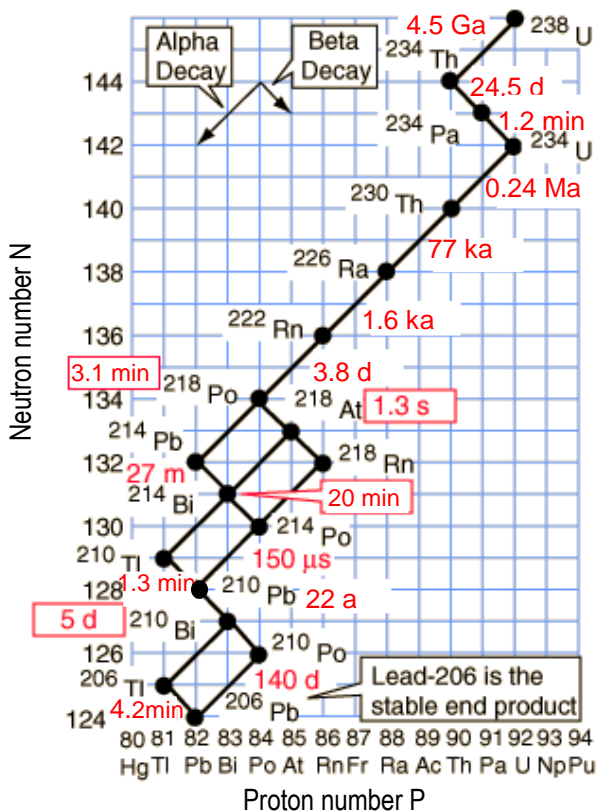
Figure 3 – Decay chain of uranium-238 (Modified after Nave, 2011; Red numbers give the half-lives of the radionuclides. Boxed red values are for half-lives when there are multiple decay paths.)

In addition to the break at different sections of the decay chain, the fertilizer production process causes partitioning of the radionuclides between the products depending on their solubility. Uranium isotopes form soluble compounds with PO_4^{3-} in phosphoric acid; and radium isotopes (chemically similar to calcium) concentrate in phosphogypsum (Roselli et al., 2009). Consequently, the major part of uranium (85-90 %) will be transferred to phosphoric acid and subsequently to the phosphate fertilizer while the greater share of radium remains in phosphogypsum. (Fukuma et al., 2000) studied the distribution of long-lived members of the U-238 and the Th-232 decay series among the products of phosphoric acid production using gamma spectrometry and gross alpha and beta counting. They found that Ra-226, Ra-228 and Pb-210 were predominantly present in the phosphogypsum phase, whereas Th-228, Th-230, Th-232, U-234 and U-238 were enriched in phosphoric acid. (El Afifi et al., 2009) analyzed phosphate rock and phosphogypsum samples, i.e. the source material and the by-product of the phosphoric acid or phosphate fertilizer production process, for their U-238/Ra-226 and U-238/Pb-210 activity ratios. For the rock samples, they found these ratios to be around unity. In the phosphogypsum waste samples, activity ratios were 0.31 ± 0.02 and 0.47 ± 0.16, respectively. In addition to different elements' activity ratios, it is possible to look at the activity ratio of different isotopes of one element, namely U-234/U-238. During phosphate rock processing, this ratio is usually not shifted. Therefore, in rock as well as in phosphoric acid/phosphate fertilizers and phosphogypsum, the activity ratio is around unity (Fukuma et al., 2000), (El Afifi et al., 2009). What shifts this ratio, are prolonged, non-aggressive mineral weathering processes (Zielinski et al., 2000). Consequently, ratios in natural waters can range from 1 to 3 but also from 0.3 to larger than 10. U-234/U-238 in soils will reflect the source of uranium – fresh, non-weathered rock/P fertilizer or weathered minerals. However, since the small activity ratio range for fertilizers and the large one for natural sources overlap, conclusions will be ambiguous. Therefore, to study the origin of uranium (from unprocessed rock or from phosphate fertilizers) in soils in this thesis, not the U-234/U-238 activity ratio was investigated but the activities of the products of the natural U-238 and Th-232 decay chains following the approach described before.

3 Sampling sites

3.1 Criteria for sampling site selection

For sampling, three sites in Saxony and two sites in Saxony-Anhalt, in central eastern Germany, were chosen. They were selected according to the following requirements:

- Land use: agriculture, with intensive phosphate fertilization or at least sufficient according to the good agricultural practice, GAP
- Forest in (close) vicinity, as more or less non-fertilized reference sampling site
- Possibility for taking field and forest soil samples of same/similar geology and soil type
- No other anthropogenic uranium input apart from phosphate fertilizer
- Possibility for taking water samples from the site or close by
- Availability of results from soil and/or water analytics
- Information on land use and fertilization (over several years)

For each of the agriculturally used sites a silviculturally used site in close proximity was chosen as quasi non-fertilized reference. The agriculturally used sites are located in Schmorren, Brandis, Hilbersdorf (all three in the federal state of Saxony), and close to Seehausen (in the federal state of Saxony-Anhalt). From these four sites, the field samples were taken. For finding forest soil sampling sites for the respective field soil sampling sites, the most decisive facts were that they were located in the same or at least a similar geology and that they had soils of the same or at least similar type. The second most important requirement for them was their proximity to the respective agriculturally used site. The fulfillment of most of the other mentioned prerequisites was ensured by selecting sites that are managed by state authorities (BfUL, LfULG) or research institutions (UFZ) with permanent data registration and climate stations etc. on site. The two of the long-term soil investigation sites ("Bodendauerbeobachtungsflächen, BDF", type II, i.e. intensive test sites = "Intensivmessflächen") are managed by the Saxon State Office for the Environment, Agriculture and Geology (LfULG). The lysimeter station in Brandis is managed by the governmental enterprise for environment and agriculture ("Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft, BfUL"). And the lysimeter station "Sauerbach" is managed by the Center for Environmental Research (UFZ) in Halle (Saxony-Anhalt).

3.2 Location in Germany

The GPS coordinates were taken with a Garmin GPS eTrex HCx device. The chosen settings were:

- Position format: Gauss Krueger grid
- Map datum: Potsdam (Bessel ellipsoid from 1841)

The recorded GPS coordinates, given in meters, for the sampling sites can be found in Table 28 in the appendix. Figure 4 shows all sampling points located in the federal German state of Saxony (numbered from 1 to 6). Additionally, all groundwater quality monitoring wells managed by the LfULG in Saxony are shown (marked with small dark blue circles) and all monitoring wells exceeding the limit of determination for uranium, 0.1 µg/L, are highlighted with colored circles as explained in the legend

of the figure. The two sampling sites located in the federal state of Saxony-Anhalt are not shown in the map. They can be found west southwest of Magdeburg – in about 30 km distance from the city.
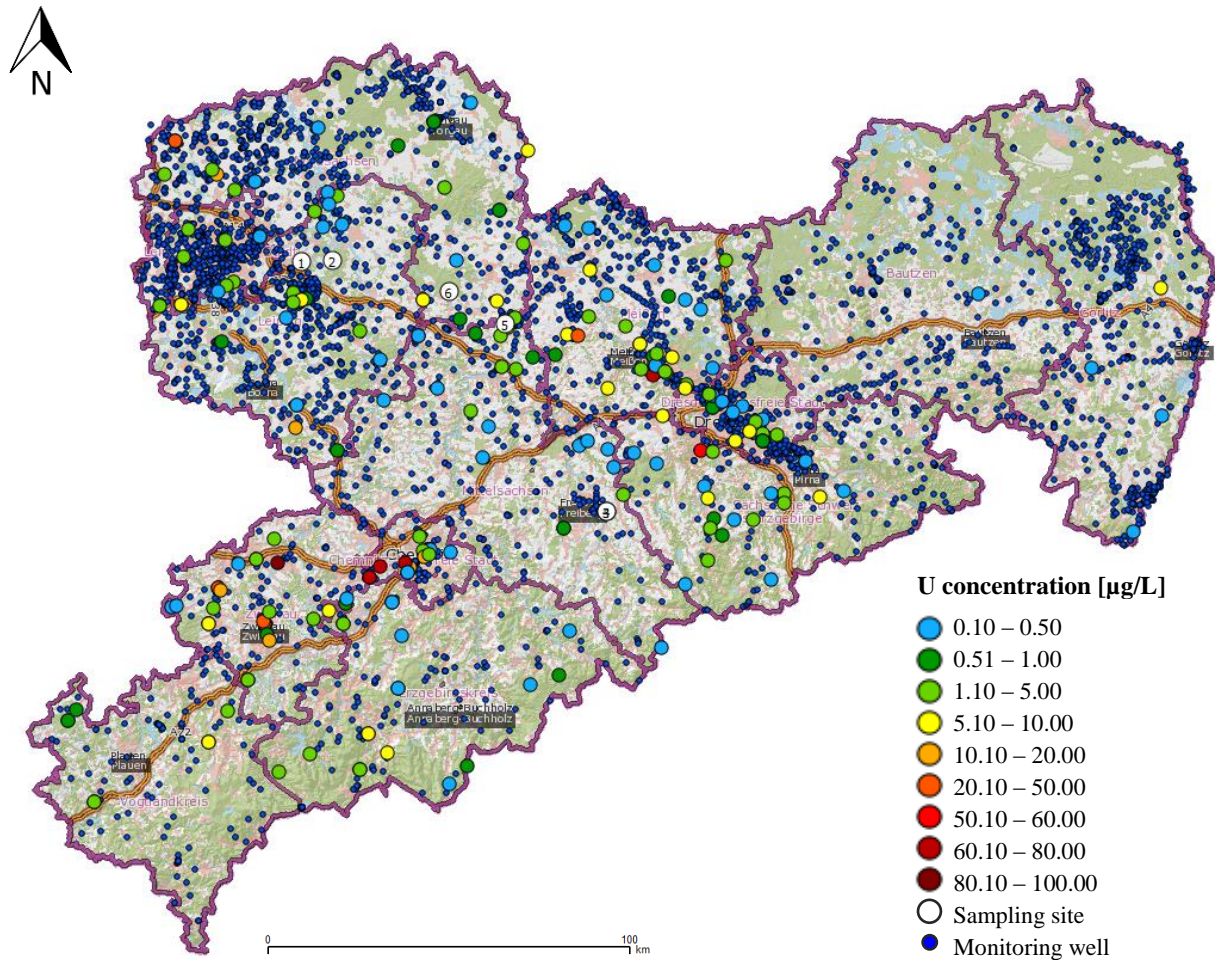
Figure 4 – Map of Saxony showing soil sampling sites (white circles with numbers from 1 to 6 in them; 3 and 4 are very close to each other and therefore plotted one above the other; 1) Brandis lysimeter station, 2) Forest east of Brandis, 3) Hilbersdorf field, 4) Hilbersdorf forest, 5) Schmorren field, 6) Wermsdorf forest), all groundwater quality monitoring wells of Saxony managed by the LfULG (marked with small blue circles) and monitoring wells with U contents exceeding the limit of determination, 0.1 μg/L (marked with colored circles, color explained in the legend)

3.3   Description of the sampling sites

In the following, the four field sampling sites are described in more detail. Table 6 informs about climate, altitude, year of installation and start of continuous measurements. It gives the responsible contact person's name and institution and the equipment on site with the sampled parameters, sampling intervals and pursued research objective. In Table 7 the soils of the sites are described by listing the parent rock or sediment type, the type of soil and stratification, and by characterizing the sampled uppermost horizons. There, also the contaminant retention capability of these soils is estimated by looking at properties like organic matter content, permeability, soil density, and cation exchange capacity. Table 8 finally characterizes the groundwater situation (properties of the aquifer or aquiclude, and depth to groundwater) and evaluates the potential endangering of the groundwater.

13

Table 6 – General description of the field soil sampling sites (Data compilation based on Haferkorn, 2000, Sächsisches Landesamt für Umwelt, 2007a, 2007b, Sächsisches Landesamt für Umwelt, 2009, and Hohlfeld et al., 2012, Kunkel and Sorg, 2011, Pütz, 2012.) BDF sites are of BDF type II, i.e. test sites of intensive investigations that are permanently equipped with measuring instruments logging parameters like precipitation, temperature, water content, etc. over time.)

Site name	Year of instal-lation/start of continuous measurements	Altitude [masl]	Average annual tempera-ture [°C]	Average annual precipita-tion [mm]	Equipment on site, measured and analyzed parameters, sampling, focus of research/investigations	Contact person (institution)
Lysimeter station in Brandis	1976-78/1980	128	9	655	**EQUIPMENT ON SITE** 24 weighable lysimeters from 8 different sites, each site in triplicate (3 m deep, 1 m² surface area, casing made of steel Climate station (precipitation (at ground level and at 1 m via a HELLMANN pre-cipitation collector), automatic climate station, logging all evaporation-relevant parameters every 10 min) Deposition sampler **WATER** Tensiometers and suction cups at 3 different depths, daily determination of amount of percolation water (via lysimeter weight) Sampling once a month during groundwater recharge period (mixed sample from lysimeter bottom)), analysis for NH_4^+, NO_2^-, NO_3^-, P, PO_4^{3-}, SO_4^{2-} **SOIL** Soil analysis from time when lysimeters were installed (analysis for humic matter content, C_{org}, N_{total}, $CaCO_3$, pH (H_2O, KCl)) and assessment of health of growing crops; soil temperature measurement at different depths; registration of cultivation and fertilization practices **FOCUS OF INVESTIGATIONS** Determination of actual evapotranspiration based on daily precipitation, amounts of percolation water and change in soil water storage	Dr. Ulrike Haferkorn (BfUL)

Site name	Year of installation/start of continuous measurements	Altitude [masl]	Average annual temperature [°C]	Average annual precipitation [mm]	Equipment on site, measured and analyzed parameters, sampling, focus of research/investigations	Contact person (institution)
BDF 24 in Schmorren	2000	161	9	589	**EQUIPMENT ON SITE** Climate station with weather shelter (logging of parameters like solar irradiation, humidity and temperature of the air, precipitation, wind velocity and direction) Bulk deposition sampler (Bergerhoff, analysis for main elements and metals) **WATER** Percolation water sampling next to weather shelter every about 2 weeks since 2006 at 45, 65, 145, and 165 cm depth using 4 suction cups at each depth (analysis for pH, conductivity, main cat- and anions, and various metals after 45 µm filtration), determination of water content and water tension in some horizons **SOIL** *Soil chemistry:* mixed soil sampling next to weather shelter and on surrounding field in 2000, 2006 and 2008 from 0-40, 40-52, 52-72, 72-103, 103-153, and 153-175 cm depth (analysis for pH, C_{org}, N_{total}, humic matter content, PO_4, plant-available P and K, and metals (via RFA)); once determination of CEC_{pot}, CEC_{eff} *Soil physics:* temperature logging for selected horizons, once determination of stratification of soil, soil type, grain size distribution, soil density, bulk density, total pore volume, permeability, water holding capacity **FOCUS OF INVESTIGATIONS** Monitoring input of elements and substances from air and precipitation to soils → early warning system for adverse changes in soil composition/properties	Dr. Natalja Barth (LfULG)
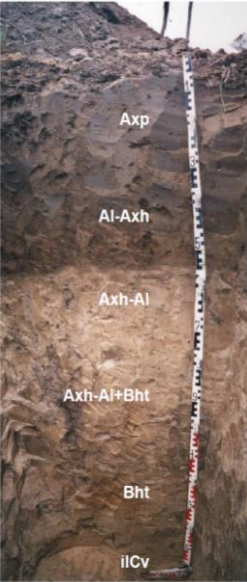
Site name	Year of instal-lation/start of continuous measurements	Altitude [masl]	Average annual tempera-ture [°C]	Average annual precipita-tion [mm]	Equipment on site, measured and analyzed parameters, sampling, focus of research/investigations	Contact person (institution)
BDF 43 in Hilbers-dorf	1995	425	8	628	Same equipment, analyses and goals like at BDF 24, with only these differences: **WATER** Percolation water sampling since 2004 at 40, and 80 cm depth **SOIL** Mixed soil sampling in 1995, 2000, 2006, 2008 and 2009 from 0-5, 5-20, 20-25, 25-45, 45-58, 58-80, 80-100, and 100-120 cm depth	Dr. Natalja Barth (LfULG)
Sauerbach lysimeter station, close to Seehausen	2010/2011	148	9	530	**EQUIPMENT ON SITE** Climate station and three additional precipitation loggers, 10 observa-tion/monitoring wells with automated water level measurements, EC station Lysimeter station with 6 lysimeters from the field close by, sensors at 10, 30 and 50 cm depth (suction cups, matrix potential sensors, tensiometers, TDR probes, heat flux sensors, temperature sensors, CO_2 gas sensor, etc.) **WATER** Percolation water sampling every about 2 weeks since 2011 from 10, 30, 50 cm depth and from lysimeter bottom (150 cm) using SIC suction cup (volume logging, analysis for pH, conductivity, main cat- and anions, TC, TIC, DOC, and N_{total}) **SOIL** *Soil chemistry:* mixed soil sampling from close to lysimeter station in 2011 from 0-26, 26-75, 75-104, 104-170, 170-190, 190-210, 210-250, and 250-270 cm depth (analysis for pH, TC, TIC N_{total}, P, P_2O_5, K_2O, metals like Mn, Fe, Pb, Cd (but not U); determination of CEC_{pot} *Soil physics:* temperature and water content logging for selected horizons, once determination of stratification of soil, soil type, grain size distribution, etc. **FOCUS OF INVESTIGATIONS** Monitoring input of elements and substances from air and precipitation to soils → early warning system for adverse changes in soil composition/properties	Dr. Holger Rupp (UFZ Leipzig/Halle)
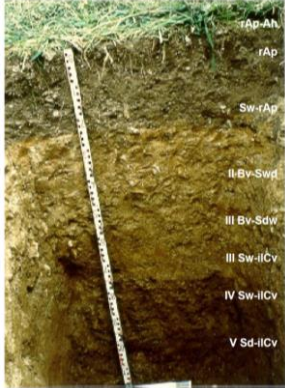
Table 7 – Description of soils at the field soil sampling sites (Only the soil horizons, one above and one below ploughing level, that were sampled are described in the table. At the Brandis site, there are lysimeters from different origins, so-called lysimeter groups. Three of the 24 available lysimeters were chosen for water sampling as their soil type is similar to the sampled field soil that surrounds the lysimeters at the station. The properties of these three lysimeters belonging to three different lysimeter groups are described in the table. The BDF sites are of BDF type II, i.e. test sites of intensive investigations that are permanently equipped with measuring instruments logging parameters like precipitation, temperature, water content, etc. over time. The data compilation in the table is based on Haferkorn, 2000, Sächsisches Landesamt für Umwelt, 2007a, 2007b, Sächsisches Landesamt für Umwelt, 2009, and Hohlfeld et al., 2012, Kunkel and Sorg, 2011, Pütz, 2012. The numerical values for the listed properties are interpreted using Hölting and Coldewey, 2009, Sponagel, 2005 and Blume et al., 2011. The soil science-specific wording and short forms are according to KA 05 Sponagel, 2005.)

Site name	Soil-forming rock/ sediment	Type of soil (according to KA05)	Soil stratification with depth and soil type	Sampled horizons, i.e. topsoil (and horizon below ploughing level)
Lysimeter station in Brandis, lysimeter group 5	Sand loess above fluvioglacial gravelly sand	"Erodierte Braunerde", i.e. eroded oxidized soil	**Bv - Ap** (0-35 cm) Su3/Sl3 **II Cv** (35-175 cm) mSgs **II Cn** (175-300 cm) mSfs	*0-35 cm (Bv-Ap)* Topsoil, impacted by ploughing, low in humic matter (2.1 vol%), very low in carbonate (0.2 mass% C), medium silty sand/medium loamy silt, medium bulk density (1.56 g/cm³), medium to high permeability ($1.8*10^{-4}$ m/s) low to very low water holding capacity (Plant-available water (according to German KA 05: "nutzbare Feldkapazität, nFK") = 16.8 vol%, field capacity (German: "Feldkapazität, FK") = 25.6 vol%, permanent wilting point (German: Permanenter Welkepunkt, PWP") = 8.8 vol%), medium rich in soil skeleton fraction (stones, pebbles, grus, 16 vol%) ➔ Low filter and contaminant retention potential

Site name	Soil-forming rock/ sediment	Type of soil (according to KA05)	Soil stratification with depth and soil type	Sampled horizons, i.e. topsoil (and horizon below ploughing level)
Lysimeter station in Brandis, lysimeter group 7	Sand loess above gravelly morainic loam	"Braunerde-Pseudogley", i.e. oxidized soil, temporarily waterlogged	**Ap** (0-35 cm) Slu **Bv-Sw** (35-50 cm) Sl3 **II Sd** (50-135 cm) Sl4 **III Sd** (135-220 cm) Sl3 **III lCn** (220-300 cm) mSfs	*0-35 cm (Ap)* Topsoil, impacted by ploughing, low in humic matter (2.2 vol%), nearly free of carbonate, loamy silty sand, high bulk density (1.68 g/cm³), low permeability ($1.2*10^{-6}$ m/s), medium water holding capacity (Plant-available water (according to German KA 05: "nutzbare Feldkapazität, nFK") = 21.6 vol%, field capacity (German: "Feldkapazität, FK") = 34.3 vol%, permanent wilting point (German: Permanenter Welkepunkt, PWP) = 12.7 vol%), very low in soil skeleton fraction (stones, pebbles, grus, 2 vol%) → Low to medium filter and contaminant retention potential

Site name	Soil-forming rock/ sediment	Type of soil (according to KA05)	Soil stratification with depth and soil type	Sampled horizons, i.e. topsoil (and horizon below ploughing level)
Lysimeter station in Brandis, lysimeter group 8	Sand loess above gravelly morainic loam	"Parabraunerde-Braunerde", i.e. oxidized soil with some of clay from upper horizons washed out into lower horizons	**Ap** (0-25 cm) Su4 **Al - Bv** (25-70 cm) Su4 **II Bbt** (70-150 cm) Sl3/Sl4 **III Bbt - lCv** (150-300 cm) mSfs	*0-25 cm (Ap)* Topsoil, impacted by ploughing, very low in humic matter (1.6 vol%), very low in carbonate (0.2 mass% C), strongly silty sand, medium to high bulk density (1.59 g/cm³), medium to high permeability ($6.8*10^{-4}$ m/s), medium water holding capacity (Plant-available water (according to German KA 05: "nutzbare Feldkapazität, nFK") = 22.6 vol%, field capacity (German: "Feldkapazität, FK") = 29.3 vol%, permanent wilting point (German: Permanenter Welkepunkt, PWP") = 6.7 vol%), low in soil skeleton fraction (stones, pebbles, grus, 4 vol%) → Low filter and contaminant retention potential *25-70 cm (Al - Bv)* Subsoil, oxidized, partly bleached, nearly free of humic matter (0.4 vol%), strongly silty sand, medium bulk density (1.54 g/cm³), low permeability ($3.1*10^{-5}$ m/s), medium water holding capacity (Plant-available water = 22.6 vol%, field capacity = 29.3 vol%, permanent wilting point = 6.7 vol%), low in soil skeleton fraction (stones, pebbles, grus, 4 vol%) → Very low filter and contaminant retention potential

Site name	Soil-forming rock/ sediment	Type of soil (according to KA05)	Soil stratification with depth and soil type	Sampled horizons, i.e. topsoil (and horizon below ploughing level)
BDF 24 in Schmorren	Periglacial loess loam	"Parabraunerde-Tschernosem", i.e. fertile, oxidized soil, made of carbonate-rich loess forming humic matter rich soil; but upper soil horizons washed out and therefore lowered in humic matter content	 **Axp** (0-40 cm) Ut3 **Al – Axh** (40-52 cm) Ut3 **Axh – Al** (52-72 cm) Ut4 **Axh-Al-Bht** (72-103 cm) Ut4 **Bht** (103-153 cm) Ut4 **ilCv** (153-175 cm) Ut3	*0-40 cm (Axp)* Topsoil, impacted by ploughing, black-grey, low in humic matter (2.1 vol%), very low in carbonate (0.36 mass% C) medium clayey silt with some gravel, high root density, medium bulk density (1.64 g/cm³), low air capacity, i.e. aeration (5.6 vol%), extremely high water holding capacity (Plant-available water (according to German KA 05: "nutzbare Feldkapazität, nFK") = 24.6 vol%, permanent wilting point (German: Permanenter Welkepunkt, PWP") = 11 vol%) *Sampled soil in general* Great effective root penetration depth (153 cm) *Properties of effective root zone* Great base saturation (86-89 %), high CEC (12-18 cmol$_c$/kg), medium to low permeability → Medium filter and contaminant retention potential

Site name	Soil-forming rock/ sediment	Type of soil (according to KA05)	Soil stratification with depth and soil type	Sampled horizons, i.e. topsoil (and horizon below ploughing level)
BDF 43 in Hilbersdorf	Periglacial loess loam and gneiss	"Erodierte Pseudogley-Braunerde", i.e. oxidized soil; temporarily waterlogged; upper horizon impacted by erosion	**rAp-Ah** (0-5 cm) Uls **rAp** (5-20 cm) Slu **Sw-rAp** (20-25 cm) Slu **II Bv-Swd** (25-45 cm) Ls2 **III Bv-Swd** (45-58 cm) Sl4 **III Sw-ilCv** (58-80 cm) Sl3 **IV Sw-ilCv** (80-100 cm) Sl3	*5-20 cm (rAp)/20-25 (Sw-rAp)* Topsoil, impacted by ploughing, brown/dark (grey) brown, rich in humic matter (4.6 vol%), nearly free of carbonate, silty loamy sand with some grus and stones, high to medium root density, some irregular bleaching zones, some rusty spots, low bulk density (1.49 g/cm³), sufficiently high air capacity (12.9/18 vol%), high water holding capacity (Plant-available water (according to German KA 05: "nutzbare Feldkapazität, nFK") = 20-22 vol%, permanent wilting point (German: Permanenter Welkepunkt, PWP") = 15 vol%) *25-45 cm (II Bv-Swd)* Subsoil, oxidized, partly waterlogged, ocher-/light yellowish-brown, very low in humic matter (0.5 vol%), nearly free of carbonate, loam, with some grus and very little stones and sand, low root density, some irregular bleaching zones, some rusty spots and disperse zones, low to medium bulk density (1.4-1.6 g/cm³), low air capacity (9.8 %), medium to high water holding capacity (Plant-available water = 19 vol%, permanent wilting point = 13 vol%) *Sampled soil in general* High effective root penetration depth (80 cm) *Properties of effective root zone* High to medium base saturation (47-66 %), medium to high CEC (9.4-12.5 cmol$_c$/kg) ➔ Medium filter and contaminant retention potential
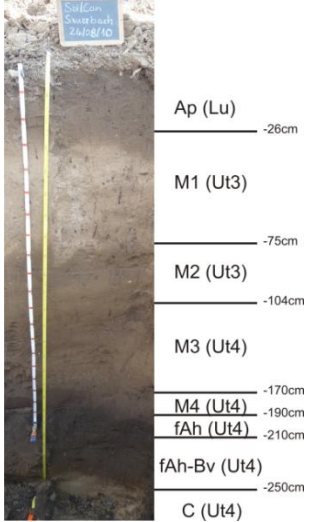
Site name	Soil-forming rock/ sediment	Type of soil (according to KA05)	Soil stratification with depth and soil type	Sampled horizons, i.e. topsoil (and horizon below ploughing level)
Sauerbach lysimeter station, close to Seehausen	Thick layer of colluvial loess loam material above sandstone	"Kolluvisol", i.e. soil material that was transported from another location to the site where it is present now; often by erosion, anthropogenic influence; here: from Holocene	Ap (Lu) -26cm M1 (Ut3) -75cm M2 (Ut3) -104cm M3 (Ut4) -170cm M4 (Ut4) -190cm fAh (Ut4) -210cm fAh-Bv (Ut4) -250cm C (Ut4)	***0-26 cm (Ap)*** Topsoil, impacted by ploughing, dark brown, silty loessic loam, sandy material low in carbonate (1.9 mass% C) mixed with material rich in carbonate ***26-75 cm (M1)*** Subsoil, migrated sedimentary material from Holocene, light brown, medium clayey silt, some bleached zones, medium in carbonate (2.5 mass% C) → Not enough information to evaluate filter and retention potential

Table 8 – Description groundwater situation at study sites (information taken from 1979-1984)

Site name	Description of groundwater situation	Thickness of aquifer/aquiclude	Permeability, k_f	Depth to groundwater	Risk evaluation
Lysimeter station in Brandis	**Aquiclude** (stratigraphy: Saale glaciation sediments), **bordering with unconfined porous aquifer** very close, south of sampling point (fraction of cohesive sediment material of the unsaturated zone: < 20 %, stratigraphy: Elster- and Saale glaciation sediments)	< 2 m	No information	> 2-5 m	**Groundwater not protected** against extensively infiltrating contaminants
Forest east of Brandis	**Unconfined porous aquifer** (fraction of cohesive sediment material of the unsaturated zone: < 20 %, stratigraphy: Elster- and Saale glaciation sediments)	> 10-20 m	No information	> 10 m	**Groundwater relatively protected** against extensively infiltrating contaminants
BDF 24 in Schmorren	**Aquiclude** (extensively distributed, composed of loess, loessic loam, relocated loess, fraction of cohesive sediment material of the unsaturated zone: > 80 %) **covering confined porous aquifer** (stratigraphy: Elster glaciation sediments)	> 5-10 m	$8*10^{-4}$ m/s	> 10 m	**No immediate endangering of groundwater** by extensively infiltrating contaminants
Wermsdorf, forest	**Solid rock aquifer** (without groundwater or only temporarily groundwater-bearing, stratigraphy: sediments from Elster and Weichsel glaciation and Holocene), thickness of covering cohesive material ≤ 2 m	2-5 m	$1-10*10^{-5}$ m/s	No data available	**Groundwater not protected** against extensively infiltrating contaminants
BDF 43 in Hilbersdorf	**Solid rock aquifer**, thickness of covering cohesive material ≤ 2 m; highly metamorphic gneiss ("Freiberger Kerngneis"), only slightly fractured, very little groundwater contained, mostly interflow	No information	No information, but subsurface discharge: 1-1.5 L/(s*km²)	No data available	**Groundwater not protected** against extensively infiltrating contaminants
Hilbersdorf, forest	**Solid rock aquifer**, thickness of covering cohesive material ≤ 2 m; highly metamorphic gneiss ("Freiberger Kerngneis"), only slightly fractured, very little groundwater contained, mostly interflow	No information	No information, but subsurface discharge: 1-1.5 L/(s*km²)	No data available	**Groundwater not protected** against extensively infiltrating contaminants
Sauerbach lysimeter station, close to Seehausen	**Shallow solid rock aquifer** (sandstone) with high salinity; from Upper Keuper ("Rötkeuper, Dolomitmergelkeuper"); covered by cohesive material	> 100 m	No information	About 9 m	**No immediate endangering of groundwater** by extensively infiltrating contaminants
Forest close to Sauerbach lysimeter station	**Shallow solid rock aquifer** (sandstone) with high salinity; from Upper Keuper ("Rötkeuper, Dolomitmergelkeuper"); covered by cohesive material	> 100 m	No data	About 9 m	**No immediate endangering of groundwater** by extensively infiltrating contaminants

4 Methods

4.1 Field work

4.1.1 Undisturbed soil sampling

Ten undisturbed soil samples were taken with steel core cutters at the lysimeter station in Brandis on November 19, 2012. To prevent metal contamination of the samples by the stainless-steel core cutters, liners (length: 6.8 cm, inner diameter: 6.45 cm) made of PVC were used to cover the core cutters' inner walls. Five samples were taken at 12 cm and five at 26 cm depth, each of the numbers standing for the level of the upper edge of the core cutters. After the first five samples from 12 cm depth had been taken, the use of steel core cutters for stabilizing the liners and for preventing cracking of the liners was judged to be unnecessary as the soil was mainly sandy and contained only little gravel and few stones. The five samples from 26 cm depth therefore were taken using only the liners without the stainless-steel core cutters. After sampling, the openings on both sides of the core cutters and/or liners were covered with nylon gauze and then sealed with tape for transport. These undisturbed soil samples were stored cool at about 10°C until the flow-through load tests started. Figure 5 and Figure 6 illustrate the sampling process.

Figure 5 – Undisturbed soil sampling at about 26 cm depth using only PVC liners without steel core cutters

Figure 6 – Leveling top and bottom of a sample from 12 cm depth enclosed in liners and metal core cutter

4.1.2 Disturbed soil sampling

Mixed disturbed soil samples, each of them weighing between 1 and 2 kg, were taken with hand-shovel and spade from four field and four forest sites. Alike the undisturbed soil samples, the disturbed soil samples were taken from above and below ploughing level. Sampling depth was 12, and 26 cm (plus about 6 cm) depth for all field and forest soil sampling sites except for those from Sauerbach. There, sampling depths were 14 and 28 cm (plus about 6 cm). The samples were filled into a plastic bag and labeled with date, site name and sampling depth. They were stored in the laboratory at about 20°C until further treatment. Names, coordinates and altitude of sampling locations as well as sampling dates are listed in Table 28 in the appendix.

4.1.3 Water sampling and in-situ parameters

Percolation water samples were taken at all field soil sampling sites except for that in Schmorren. In Schmorren, throughout the entire period of working on the present thesis, there was not enough water available for analysis. For ensuring comparability, all samples were taken winter or spring, i.e. before fertilizer application. Sampling depths, however, were not the same as suction cups and lysimeter bottoms, respectively, the samples were taken from were not at the same depth.

At the lysimeter stations in Brandis and Sauerbach seepage water samples were taken for main and trace element-, TIC- and DOC analysis. The samples stemmed from the lysimeter bottoms. Additional samples from suction cups that are installed at different depths of the lysimeter walls could not be

taken due to shortage in water. In Brandis, sampling was done on February 28, 2013. Two types of samples were taken from 3 m depth: mixed samples from one month's period from the bottom of ly-simeter # 7/4, 8/6, 5/5; and one "fresh" water sample from the day of sampling from lysimeter # 7/4. January 30, 2013 was the day of sampling at the Sauerbach lysimeter station. There mixed samples (all from 1.5 m depth) from one month's period were taken at the bottom of lysimeter # 1, 2, 4, 5 of the six lysimeters of the hexagon of the lysimeter station using an SIC suction cup. In Hilbersdorf, water samples were taken from a suction cup at 80 cm depth on March 25, 2013. In Schmorren it was not possible to obtain water samples as groundwater recharge there was too little. Therefore, all available water was needed by the LfULG, the authority in charge, for the institution's own analyses. Table 9 informs about how water samples were taken in the field and which methods were used for analysis.

Table 9 – Water sampling, preparation in the field and analytical method

Analytes	Sampling bottle	Preparation	Analytical method
Main cat- and anions	50 mL PE bottles	Filtration	IC
Trace elements	30 mL PE bottles	Filtration, then acidification	ICP-MS
TIC and DOC	100 mL glass flasks	none	Elementar liquiTOC

For filtration, 0.2 μm one-way cellulose acetate filters (Sartorius) were used. Before sampling, bottles, filters and syringes were rinsed with the water to be sampled. ICP-MS analysis samples were acidified to pH < 2 with two drops of semi-concentrated (i.e. ca. 30-33 %) supra-pure HNO_3 per 30 mL sample.

On site, the **in-situ parameters** electrical conductivity, dissolved oxygen content, pH, redox potential and temperature were measured.

For **electrical conductivity** determination, a WTW LF 320 conductivity meter with a WTW Tetra-Con® 325 electrode was used. Before taking it into the field, the electrode's operability was checked with a reference solution (1413 μS/cm at 25 °C). 25°C was chosen as temperature the electrode will automatically correct the read value to, and the instrument-internal cell constant was adjusted so that the reference solution gave this required conductivity for the reference solution.

The **dissolved oxygen** content in water was measured using an HQ40d multi by HACH with an optical LDO (luminescent dissolved oxygen) sensor. Calibration was performed automatically by the device.

For measuring **pH**, a WTW pH 320 device with an EGA 142/TFK Meinsberg gel electrode was used. Two-point calibration was done with buffer solutions with pH 4.01 and 7.00. When not in use, the electrode was stored in a cap filled with 3 M KCl solution.

Redox potential was determined using a PCE-228 pH meter (PCE group) with a WTW SenTix ORP Ag/AgCl electrode. When not in use, it was stored in a cap filled with 3 M KCl solution – just like the pH electrode. Before measurements, the operability of the electrode was checked with a standard solution of 220 mV. In case of too high or too low values, this deviation was subtracted from or added to the readings. The readings of the individual measurements additionally were corrected to the reference temperature of 25°C and the standard hydrogen electrode as reference electrode. pH correction is internally done by the device.

For temperature correction, the following formula based on NERNST equation was used (Hölting and Coldewey, 2009):

$$E_H(25°C) = EMF - 0.198 \cdot (\vartheta - 25)$$

This value then was referred to the standard hydrogen electrode using the following formula (Hölting and Coldewey, 2009):

$$E_H = E_H(25°C) + E_{Ag/AgCl}$$

For thermodynamic modeling (e.g. with PHREEQC), not the E_H value but the pe value is needed. The conversion again is based on NERNST equation (E_H in V) (Merkel et al., 2008):

$$pe = -\log\{e^-\} = \frac{F}{2.303 \cdot R \cdot T} \cdot E_H$$

Simplified (E_H in V) (Merkel et al., 2008):

$$pe = 16.9 \cdot E_H$$

With:
$E_H(25°C)$	Redox potential at 25°C, referred to Ag/AgCl electrode [mV]
E_H	Redox potential at 25°C, referred to the standard hydrogen electrode [mV]
$E_{Ag/AgCl}$	Redox potential of the Ag/AgCl electrode (with 3 M KCl) … 207 mV at 25°C, according to producer (WTW, 2008)
EMF	Reading from the redox electrode [mV]
ϑ	Temperature during measurement [°C]
pe	Decadic logarithm of "electron activity" [-]
F	FARADAY constant [96.484*10³ J/(V*mol)]
R	Universal gas constant [8.314 J/(mol*K)]
T	Absolute temperature [K]

Temperature in the water samples was measured using the conductivity – as well as the pH meter.

Generally in situ parameters were measured simultaneously to the sampling process. At the Sauerbach site, sampling was done by colleagues of the UFZ Leipzig-Halle and samples were subsequently sent to Freiberg per post. There, three days after sampling the cooled samples were processed, preserved and the in situ parameters were measured. Before analyses started, water samples were stored dark and cool in a refrigerator at about 8°C, preserved as described in section 4.3. The same statements apply for the Hilbersdorf site.

4.2 Requesting additional soil and water analytical data

In addition to own sampling and analyses, U concentrations for all water chemistry monitoring wells of Saxony exceeding the detection limit for U as shown in Figure 4 were provided by the LfULG. From this collection of monitoring wells those wells being located close to the sampling points studied in this work were selected for requesting the entire analytical datasets for all years of sampling and analysis. They were used for comparison with the data from the test sites. Table 10 gives an overview of the parameters obtained for the different field sampling sites. For the surrounding of the forest sites, groundwater analytical data was available for examination of changes in water chemistry over time.

Table 10 – Requested parameters for the field sampling sites

Site name (respon-sible institution)	Parameters			
	Soil physics	**Soil chemistry**	**Water chemistry**	**Additional**
Brandis lysimeter station (BfUL)	Soil type, stratification, soil-forming rock/sediment, soil density, coarse pore volume, permeability, water holding capacity	pH (H_2O, KCl), C_{org}, N_{total}, $CaCO_3$, humic matter content	Suction cup sample analysis from 50, 150 and 250 cm depth (ammonium, nitrate, nitrite, P, phosphate, sulfate) Mixed monthly samples from 3 m depth (ammonium, nitrate, nitrite, phosphate, sulfate)	Fertilization (type of fertilizer, time and amount of application), crop type, harvest
Hilbersdorf (BDF 43, LfULG)	Soil type, stratification, soil-forming rock/sediment	pH ($CaCl_2$), C_{org}, N_{total}, phosphate, plant-available P_2O_5 and K_2O, uranium, iron, manga-nese, cadmium, copper, lead, thorium, zinc	pH, conductivity, main anions (chloride, sulfate, phosphate, silica, nitrate, nitrite, fluoride, hydrogen carbonate, carbonate), main cations (calcium, iron, potassium, magnesium, sodium), trace elements (ar-senic, lead, cadmium, uranium), water hardness	Fertilization (type of fertilizer, time and amount of application), crop type, harvest, pesticides (type, time and amount of application) Precipitation (hourly sums) Amounts of percolation water in suction cups over time
Schmorren (BDF 24, LfULG)	Soil type, stratification, soil-forming rock/sediment	pH ($CaCl_2$), C_{org}, N_{total}, phosphate, plant-available P_2O_5 and K_2O, uranium, iron, manga-nese, cadmium, copper, lead, thorium, zinc	pH, conductivity, main anions (chloride, sulfate, phosphate, silica, nitrate, nitrite, fluoride, hydrogen carbonate, carbonate), main cations (calcium, iron, potassium, magnesium, sodium), trace elements (ar-senic, lead, cadmium, uranium), water hardness	Bulk deposition sampler concentra-tions of phosphorus and uranium Fertilization (type of fertilizer, time and amount of application), crop type, harvest, pesticides (type, time and amount of application) Precipitation (hourly sums) Amounts of percolation water in suction cups over time
Sauerbach lysime-ter station (UFZ)	Soil type, stratification	Soil pH, C_{total}, N_{total}, P_2O_5, K_2O, magnesium, boron, bromine, manga-nese, iron, copper, lead, cadmium, aluminium, plant-available (iron, manganese, aluminium), $CaCO_3$, CEC_{pot}	pH, conductivity, some main anions (chloride, sulfate, nitrate, nitrite), main cations (calcium, potassium, magnesium, sodium), P_{total}, trace elements (arsenic, lead, cadmium, uranium), total carbon, inorganic carbon, dissolved inorganic carbon, N_{total}	Current fertilization (type of ferti-lizer, approximate amount of appli-cation), crop type

4.3 Laboratory work

Table 11 gives an overview of the experiments conducted for the different types of samples in the laboratory. Gamma spectrometry measurements were done at the Institute for Applied Physics of the Technische Universität Bergakademie Freiberg (TUBAF). Grain size analyses were carried out at the sediment laboratory of the Institute for Geology of the TUBAF. Soil samples were sieved to smaller than 2 mm for sequential extractions at the Institute for Mineralogy of the TUBAF. There, plastic sieves were available so that metal contamination of the samples could be prevented. All other experiments and analyses were conducted in the water chemistry laboratory of the Hydrogeology department of the Institute for Geology of the TUBAF. In the following sections, all experiments and analyses are explained in greater detail.

Table 11 – Laboratory tests conducted with the different types of samples

Type of sample	Analyzed for	Method/ instrument used
Undisturbed soil samples from Brandis lysimeter station (12 and 26 cm depth)	Uranium breakthrough	Flow-through apparatus driven by peristaltic pump (Ismatec, IPC), shown in Figure 8
	U and other elements' concentration in percolates	ICP-MS (Thermo Scientific X Series 2 Quadrupole ICP-MS, combined with a CETAC ASX-520 autosampler)
Disturbed soil samples (from 12 and 26 cm, or 14 and 28 cm depth, i.e. above and below ploughing level)	Grain size distribution	DIN 18 123 (only sieve sizes 63 μm (wet sieving by hand), 200 μm, 630 μm, 2 mm (dry sieving with sieving machine, Retsch, VIBROTRONIC, type VE 1) used), in combination with particle size analyzer (FRITSCH, Analysette 22, compact) testings
	pH of soil solution	DIN ISO 10 390
	Carbonate content	"Carbonate bomb" according to G. Müller
	TIC and TOC	LiquiTOC II (Elementar Analysesysteme GmbH)
	Cation exchange capacity (CEC)	DIN EN ISO 11260, but analyzed with IC instead of FAAS or ICP-AES (see Table 29 and related comments in the appendix)
	U distribution among soil fractions	Sequential extraction with subsequent ICP-MS analysis
	Origin of uranium (assessment of radionuclides U-238, Ra-226 and Th-232)	Gamma spectrometry using an HPGe detector
Fertilizer samples	U-238-, Ra-226- and Th-232 activity	Gamma spectrometry using an HPGe detector
Water samples	Main cations and anions	Professional IC 850 (Metrohm)
	Trace elements	ICP-MS
	TIC and DOC	LiquiTOC (Elementar Analysesysteme GmbH)

4.3.1 Flow-through experiments

The flow-through experiments were conducted using 10 undisturbed soil samples from the agriculturally utilized land at the lysimeter station in Brandis. Five of the samples stemmed from above ploughing level and five from below, i.e. from 12 and 26 cm downwards, respectively. Figure 7 shows the components the flow-through cells used. The three parts are the liner's mantle, one cap at the top and another at the bottom. They all are made of PVC. The caps contained filter frits (see Figure 7b) to prevent the soils from being washed out. O-rings at the inner walls of the caps were used for sealing the cell. Flow-through cells 1 and 2 were not tight by the O-ring alone. Therefore, they additionally had to be tightened with Teflon tape so that no percolating water could escape from the system.
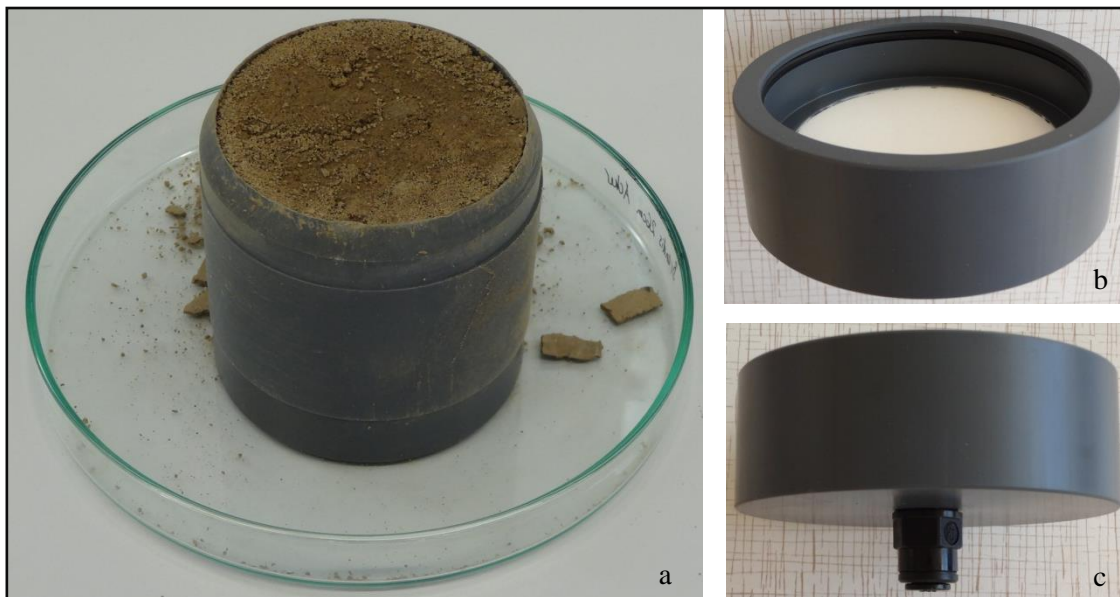
Figure 7 – Components making up the liners enclosing the undisturbed soil samples during flow-through experiments (a) Liner's mantle with the soil sample, b) Cap of liner with filter frit and O-ring inside, c) Bottom of liner with black hose nozzle; cap and bottom of each flow-through cell are built in the same manner using the same components)

The ten flow-through cells were installed in such a way that they could hang, using clamps and a long, horizontal metal rod (see Figure 8). To stabilize the cells, four u-channels, two at the top and two at the bottom were used and connected by threaded rods. Flow-through was from bottom to top to enable entrapped gas to be released as saturated conditions were intended for simplifying the system. To mimic natural percolation processes, the liners were turned upside down. Consequently, flow-through was from the top to the bottom of the soils like in nature. No reference column containing no soil was used because sorption of the percolating solution on the Teflon system and the PVC liners can be assumed to be negligible (Merkel, 2012b).

Figure 8 – Setup for flow-through experiments (left side of the picture: 5 L storage glass bottles (labeled with I to V), upper part of picture: dark grey PVC flow-through cells (labeled with 1 to 10, 1-5 being from upper soil level, 6-10 from lower soil sampling level), below: white Teflon collecting vessels (labeled with 1 to 10 according to corresponding flow-through cell), in foreground: peristaltic pump with pumping tubes and hose connectors. Teflon tubes throughout the system for connecting the individual units.)

Five 5 L-storage glass bottles were placed next to the liners. Each of the bottles supplied two liners with one of the solutions listed in Table 12.

Table 12 – Composition of solutions of storage bottles used for flow-through experiments (Phosphate concentration was selected assuming groundwater recharge as 50 L/(m²*a) (a reasonable value for the area of Brandis where the samples were taken) and P input by fertilization according to GAP (22 kg P/(ha*a). Uranium input by P fertilizers was set to 20 g/(ha*a). To understand where the assumed concentrations come from, see Table 2 and Table 3. Na-HCO$_3$ and Ca(NO$_3$)$_2$ concentrations were chosen as within the range typical for groundwaters below arable land.).

ID	Cells supplied	Concentration of contained components			
		NaHCO$_3$ [mM]	UO$_2$(NO$_3$)$_2$ [µM]	H$_3$PO$_4$ [mM]	Ca(NO$_3$)$_2$ [mM]
I	1, 6	1	0.168 (= 40 µg/L)		
II	2, 7	1	0.168 (= 40 µg/L)	1.42 (= 44 mg P /L)	
III	3, 8	1	0.168 (= 40 µg/L)	1.42 (= 44 mg P /L)	1
IV	4, 9	1	0.168 (= 40 µg/L)	0.142 (= 4.4 mg P /L)	
V	5, 10	1	0.168 (= 40 µg/L)	0.142 (= 4.4 mg P /L)	1

Every 18 days, it was necessary to refill the storage glass bottles. To simplify handling and to ensure constant concentrations of the flow-through solutions throughout the experiment, stock solutions were prepared. Their compositions can be seen in Table 13. For correctly determining the volume of the solutions filled into the 5 L glass bottles, scales were used.

Contained compound	NaHCO$_3$	UO$_2$(NO$_3$)$_2$	H$_3$PO$_4$	Ca(NO$_3$)$_2$
Concentration	1 M	0.168 mM	1.421 M	1 M
Needed stock solution volume	250 mL	250 mL	100 mL	100 mL
Mass or volume needed for stock solution preparation	21.0025 g	0.0211 g	9.66 mL	23.6150 g
Volume of stock solution to be added to the 5 L bottles (bottle ID in brackets)	5 (I-V)	5 (I-V)	5 (II, III), 0.5 (IV, V)	5 (III, V)

The solutions percolating the flow-through cells were collected in Teflon vessels with volumes of about 420 and 950 mL, respectively. Teflon was used to prevent sorption. Before the experiments started, the vessels were first washed with nitric acid and then with distilled water to remove possibly sorbed ions. To avoid evaporation, the glass storage bottles as well as the Teflon vessels were covered using Parafilm or Teflon caps. However, contact to ambient air and temperature in the laboratory was not actively prevented. A peristaltic pump was used for adjusting flow-through to the desired value. Teflon tubing connected the different units of the system – glass storage bottles, the peristaltic pump, the flow-through cells containing the soils and the Teflon vessels. Colored tape was used to indicate which glass storage bottle belonged to which piece of tubing. The specifications of the system are listed in Table 14.

Table 14 – Specifications of the flow-through system

Component of flow-through system	Dimensions	Material	Additional
Liners of flow-through cells	Length: 76.5 mm Inner diameter: 63 mm Outer diameter: 70 mm	PVC	
Caps of cells (at top and bottom)	Suitable for tightening liners using one O-ring (71 x 2 mm), and Teflon tape if needed	PVC	Contain filter frits (16-40 μm pore size)
Filter frits	Pore size: 16-40 μm Fitting in the cells' caps	Glass	
Teflon tubing	Inner diameter: 2 mm Outer diameter: 3 mm	PTFE (Teflon)	Purchased from Klaus Ziemer GmbH
Peristaltic pump	Flow rate: adjusted to about 0.1 mL/min	-	2-stop tubing (Ismatec) inner diameter: 1.02 mm, wall thickness: 0.86 mm, material: TYGON R3607 Hose connector: material: PP
Collecting vessel	About 420 (for # 3-9) and 950 (for # 1, 2 and 10) mL (as these vessels were suitable and available in the department)	PTFE (Teflon)	Washed with semi-concentrated HNO$_3$ and then DI before experiments started

Before the experiments with the actual solutions from Table 12 started, flow-through cells were percolated with demineralized water for about 24 hours. After that period, samples were taken for IC-, ICP-MS- and TIC/DOC analysis to determine major and trace cat- and anions as well as inorganic and organic carbon content of the seepage water. This seepage water can be assumed to have the same or

at least very similar composition as precipitation in nature that has entered the soil. Then the demineralized water was replaced by the solutions listed in Table 12. After two days of washing out the demineralized water and replacing it by the solutions from the storage bottles, the collecting vessels were emptied and the experiments with the solutions from the storage bottles started. From that point on, samples for ICP-MS analysis were taken every nine days and samples for IC- and TIC/DOC analysis were taken every 18 days. Collecting vessel pH was measured every three days, i.e. each time when they were emptied, cleaned with distilled water and dried with paper. When IC- and TIC/DOC samples were taken, in addition to pH also redox potential was measured. During sampling, collecting vessel emptying and cleaning, the pump was kept running and percolating solutions were collected in glass beakers for disposal. During preparation of fresh storage bottle solutions, pumping was interrupted. ICP-MS samples from the 5L storage bottles were taken every now and then for quality check.

4.3.2 Processing disturbed soil samples

After all samples had been taken, at the latest after 11 days, representative mixed sub-samples were won. This was done by crushing bigger lumps of the original 1 kg soil samples in the plastic zipper bags by hand, mixing and homogenizing them. Then about 100 g of each of them were filled on glass Petri dishes. These Petri dishes were put into a compartment drier at 40°C for 3-4 days. It was foregone heating the samples up to 95 or even 120°C – temperatures that are commonly used for drying – as this would change the partitioning behavior of uranium between the fractions. Uranium would especially be redistributed towards the fraction that is bound to iron and manganese oxides (Qiao et al., 2012). In case the dried soils still contained bigger lumps of soils, these were crushed by hand. For sequential extraction, soil samples were sieved with a PVC sieve (analytical sieve according to ISO 565/3310-1 (frame and bottom of sieve made are of plastic)) to < 2 mm, homogenized.

This gentle heating was used for the material for sequential extractions, TIC/TOC analysis, determination of cation exchange capacity and carbonate content and soil pH determination. For grain size analysis and gamma spectrometry, soils were dried at 105°C and then sieved using a metal sieve with a slot width of < 2 mm. For these kinds of analyses, this treatment can be expected to have no adverse effects on the results (Schneider, 2012), (Unterricker, 2012).

4.3.3 Grain size distribution

Grain size analysis was done based on DIN 18 123, where wet and dry sieving is combined. This method was complemented by and compared with the results obtained with a particle size analyzer (FRITSCH, Analysette 22, compact). The individual steps of the sieving analysis were:

- Weighing in at least 200 g of dry soil (300 g in case of material rich in gravel), noting down exact mass
- Wet sieving with 63 μm sieve
- For further treatment, differentiation between:

Material < 63 µm (clay and silt)	Material > 63 µm (sand and gravel)
Flushing it into 10 L plastic buckets	Dry sieving analysis using a sieving machine (Retsch, VIBROTRONIC, type VE 1) and sieves with the following slot widths:
Letting material settle to the ground until the water in the bucket was fairly clear	- 2 mm (gravel, as samples were free of stones)
Draining greatest share of the water from the bucket using a flexible rubber hose and the effect of gravity	- 630 µm (coarse sand) - 200 µm (medium sand) - 63 µm (fine sand)
Flushing the soil and remaining water into porcelain bowls and putting them into a compartment drier at 105°C until all water had been evaporated	In brackets, the grain size fraction remaining on top of each sieve is written. Determining the mass of the material on top of the sieves (by mass difference between mass of soil plus
Weighing the dry soil material (weight difference between filled and empty bowl)	sieve minus sieve mass alone)

The percentages of the individual grain size fractions were determined by referring the mass determined for each grain size fraction to the mass of the originally weighted-in sample and by multiplying the result by 100 %.

For the particle size analyzer procedure, the dry original soil material was sieved with a 200 µm sieve for matters of protection of the analyzer. 5 g of this fine dry soil material were weighted in into a glass beaker and mixed with tap water. 3 mL of 0.45 g/L pyrophosphate, a dispersion agent, were added and samples were agitated for several minutes in an ultrasonic bath to support dispersion. The suspensions were mixed using a dropping pipette and around 10 mL (actual volume depending on the amount of water added to the soil samples) of them were introduced to the analyzer.

The measurement principle of the instrument is that the samples introduced to the system are transported with tap water that circulates through the system. Together with automatic stirring and ultrasonic dispersion this causes mixing. A laser beam being send through the system is being refracted depending on the grain size of the particle it hits. As the background is measured, its signal can be subtracted from the detected signal of the sample to be analyzed. And so, the grain size distribution of the fine fraction of the sample material can be determined.

For some samples, grain size distribution curves obtained from repeated measurements differed very much. It was assumed that this might be caused by baked material and consequently non-representative material from sieving the original samples to smaller than 200 µm. Therefore, a second test series was started. 2.5 g of the original samples were first mixed with water and 3 mL of 0.45 g/L pyrophosphate and put in an ultrasonic bath for about 10 minutes. Then the soil-water mix was poured through a 200 µm sieve and the mix flowing through the sieve was used for the actual analysis using the particle size analyzer as explained before.

4.3.4   Soil pH

Soil pH was determined according to DIN ISO 10 390. In the course of this method, the air-dry fine soil sample were mixed with a $CaCl_2$ solution. This is said to be a better depiction of real soil pH than the use of KCl or distilled water (Blume et al., 2011). The following bullet points describe the procedure in detail:

- Weighing in 10 g of air-dry fine soil (i.e. grain size ≤ 2 mm)
- Mixing with 25 mL of 0.01 M $CaCl_2$ in a glass beaker
- Covering the glass to prevent evaporation, occasionally swinging it (every 10 minutes done here with glass stick)
- Letting it sit for at least 30 min
- Calibrating pH meter (using buffer 4.01 and 7.00)
- Measuring pH with pH probe
- Rinsing electrode with 0.01 M $CaCl_2$ after each measurement

4.3.5   Carbonate content

For that purpose, the so-called "carbonate bomb" according to G. Müller was used. It is shown in Figure 9. The principle of the test is that inorganic carbonate reacts with HCl to form CO_2, which is subsequently released as gas. The carbonate bomb reads this pressure increase like a manometer does and finally gives the carbonate content in % $CaCO_3$. For calibration, first a reference material that contains 100 % calcite must be analyzed. If the analytical result using the "carbonate bomb" deviates from 100 %, a factor has to be used for correcting the results of the subsequently analyzed soil samples.
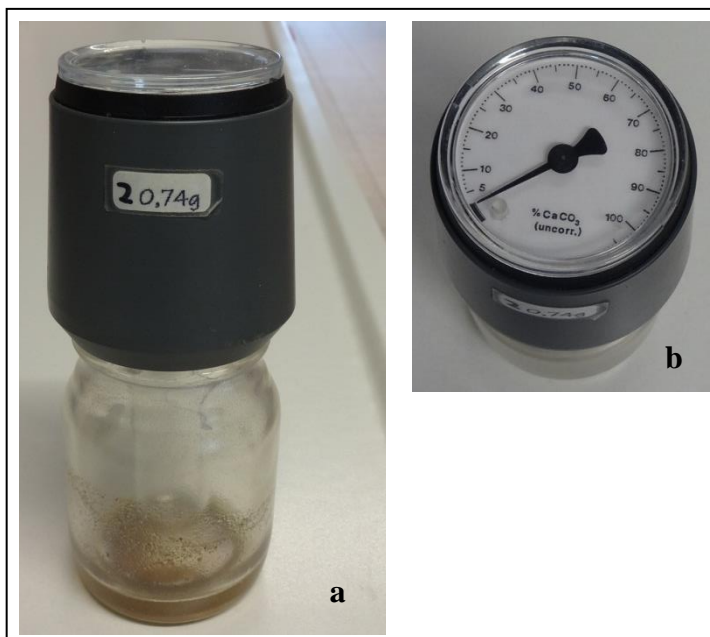
Figure 9 – Carbonate bomb according to G. Müller (a) bomb filled with soil and acid, after mixing, b) display of carbonate content of sample)

The procedure (same for reference material as for soil samples) is as follows:

- Weighing in 0.74 g of sample material into the cleaned reaction vessel
- Filling in 6 N HCl up to the marked level in the tube attached to the cap of the reaction vessel
- Closing reaction vessel (has to stand vertically)
- Lifting reaction vessel, turning and shaking it
- Reading carbonate content in % (after 1-15 minutes)
- Opening, cleaning and drying reaction vessel

4.3.6 Carbon content (TC, TIC and TOC)

Carbon content of soils was determined with the solid module of a LiquiTOC II instrument (Elementar Analysesysteme GmbH). The principle of the analyzer is that the soil sample is oxidized at high temperature of up to 1100°C and generated CO_2 is measured using a CO_2-sensitive NDIR detector. A flow of oxygen that permanently goes through the system removes atmospheric CO_2 that would alter the results of the analysis. The measuring range of the instrument depends on the substance and ranges between 1 μg and 100 mg C absolute. Sample weight should be between 0 and 1000 mg. Consequently, carbon can be detected from low ppb to % C level, according to the manufacturer.

Before actual sample analysis, a calibration was performed using different masses of a standard soil from the producer with 4.1% C. For quality check, between measurements, this soil was analyzed again and checked if it still gave the carbon contents from before.

For analysis of the individual soils, first, they were analyzed for total carbon (TC) by high-temperature oxidation in the analyzer at about 800°C. The generated CO_2 was measured with a CO_2-sensitive sensor (NDIR detection). For that purpose, about 80 to 100 mg of dry, < 2 mm, homogenized soil sample material, sieved with a plastic sieve, were weighed in quartz cuvettes and put into the analyzer. After TC analysis, 5 g of each soil were reacted with 20 mL of 2 N HCl in a glass beaker. The residue was dried in a drying chamber at 105°C. By that the inorganic carbon was purged as CO_2 and only the organic carbon (TOC) remained. The dried reaction product was then analyzed for total organic carbon (TOC) using the same instrument and principle. Change in sample mass by adding HCl was taken into account. Total inorganic carbon (TIC) was determined by subtracting TOC from TC contents.

4.3.7 Cation exchange capacity (CEC)

Determination of the effective CEC was done according to the German version of EN ISO 11260:2011 – "Determination of effective cation exchange capacity and base saturation level using barium chloride solution". The Soil Science Society of America recommends this method as it is highly repeatable, precise and a direct measure of the CEC of a soil (Cooper, 2009). In the United States the ammonium acetate method has been widely used for decades and therefore large amounts of CEC data do exist. Nevertheless the method was not used as it buffers the soil to be analyzed to pH 7 and consequently greatly overestimates the CEC especially for acidic soils (Cooper, 2009).

In natural soils, the cation exchange sites are commonly occupied not by one but by several types of cations. For determining the CEC using the $BaCl_2$ method, all cations present on the soil's surface are first being replaced by barium. This is done by three times applying a 0.1 mol/L $BaCl_2$ solution to the soil. Then exchange equilibrium is established with a 0.01 mol/L $BaCl_2$ solution and after that a known excess of 0.02 M $MgSO_4$ is added. This causes precipitation of insoluble $BaSO_4$ and occupation of all exchange sites with Mg. According to the DIN standard, the decrease in magnesium concentration is finally analyzed with flame atomic absorption spectrometry (FAAS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES). In the present soil testings, cation chromatography (IC) analysis was used instead. Details on methodology and calculations for determining the CEC (in cmol+/kg, i.e. centimols positively charged ions per kg) are given in Table 29 and related comments in in the appendix). Specifics on IC analysis can be found in section 4.3.10.

4.3.8   Extraction of uranium from soils

For evaluating the environmental impact of metals present in soils, it is not sufficient to determine the total concentration of that metal in the soil. Instead it is necessary to determine how and how strong the metal is bound to the solid surfaces, how mobile and bioavailable it is, and how easily it can be released to surrounding media (Stead et al., 2012). Based on the approach by (Tessier et al., 1979), numerous sequential extraction procedures have been developed to determine the binding forms of metals (Stead et al., 2012). They differ in the number of steps, the types of binding forms assessed, the extraction solutions used, the solid-to-extracting-solution ratio, pH, temperature, the reaction time and other features of the experimental procedure and sample preparation like drying, sieving, etc. What they all have in common is that different chemical extractants in order of increasing destructive ability are successively added to the sample being tested (Stead et al., 2012). After a certain period of shaking, during each step the solution is separated from the solid sample, filtered and analyzed for the metal of interest by ICP-MS or other means. For each following extraction step, another extrant is added to the solid sample either after having washed the sample beforehand or not. Extractable fractions that the samples are commonly analyzed for are:

- Water-soluble or exchangeable
- Bound to carbonates
- Bound to iron/manganese oxides
- Bound to organic matter
- Reducible
- Oxidizable
- Acid-soluble or residual.

The results obtained with sequential extractions are operationally defined, i.e. depend on sampling as well as sample preparation rather than being phase-specific (Stead et al., 2012). Results from one sequential extraction analysis are not directly comparable with those of other ones and an approach that worked fairly well for a certain metal in a certain soil cannot automatically be expected to also work for other metals and soils. Therefore, (Stead et al., 2012) recommend an adaption of the procedure to the aim of the study, the metal of interest and the soil under investigation.

During laboratory experiments of the present thesis, severe problems were encountered during sequential extraction analysis. For some of the samples, after the first two extraction steps, it was not possible to separate solid and liquid phase even after half an hour of centrifugation at about 4000 r.p.m. using an MLW T54 centrifuge manufactured by "Medizintechnik Leipzig". Samples did not get compacted but remained extremely sensitive to being swirled up even when being treated with great care. Due to the great losses in soil mass that would be associated with that, it was decided to substitute single extractions for sequential extractions. In Table 15, single and sequential extractions are contrasted with central advantages and disadvantages.

Table 15 – Comparison between single and sequential extractions (own findings combined with information from Rao et al., 2008 and Eichfeld, 2004)

Single extractions		Sequential extractions	
Advantages	**Disadvantages**	**Advantages**	**Disadvantages**
Less loss in soil material	More soil material and centrifuge tubes, etc. needed	Better comparability between extraction steps as same soil sample is used	Loss of soil material during each step
Greater time-flexibility (order of extraction steps free to choose; even parallel performance possible)	Lower phase specificity (minerals' surfaces not attacked by previous extractants)	Greater phase-specificity (increasing vigorosity of reactants)	Greater time consumption as washing is needed after each step → re-adsorption problems might arise
Order of extractants' vigorosity can be defined after experiments			Part of extracting solutions from previous steps remains in tube during following steps
Errors during one extraction step do not affect subsequent ones			Order and kinds of extractants differ from author to author (carbonate-bound, organically bound, Fe/Mn oxides) → question on legitimacy of combining different author's approaches
			Errors associated to repeated centrifugation, filtration and washing of same sample

From this comparison, it becomes clear that neither sequential nor single extractions are without drawbacks. Both alternatives are operationally defined and incomplete, with results depending on the properties of the soil and the metal being studied. For the present thesis, the available soil mass was not a restrictive factor because enough material was present. As it was intended to combine the approaches from different authors to consider the fractions that are probably of greatest interest for studying how uranium is bound in the assessed soils, it was decided to use single extractions.

The extraction procedure used is shown in Table 16. It is primarily based on the sequential extraction approach by (Qiao et al., 2012), which was optimized for radionuclides like uranium and considers the fractions that are likely to be of interest for uranium retention in soils. Different from several other procedures based on (Tessier et al., 1979) not $MgCl_2$ or NaOAc and HOAc but NH_4Ac-HAc is used for extracting the exchangeable metal fraction. This seems to be decent because the other extractants mentioned will cause suppression effects during ICP-MS detection of uranium in the extraction solution (Stead et al., 2012). ICP-MS technology has improved and the mentioned effects have become less significant as they were when (Stead et al., 2012) wrote their paper. However, great chloride concentrations might still be a problem since chloride precipitates on the cones and consequently worsens the signal (Merkel, 2012a). The subsequently required sample dilution will not cause problems for the uranium detection as its detection limit is 0.0001 ppb. Yet it might be a problem for other elements like phosphorus that have higher detection limits (Merkel, 2012a). Besides the mentioned reasons, NH_4Ac is suitable also because it better mimics the processes taking place in farmland soils where plants release organic acids and other organic compounds while $MgCl_2$ concentrations are comparatively low.

Table 16 – Sequential extraction scheme used in this work (The method was largely derived from the procedure used for uranium by (Qiao et al., 2012) in accordance with (Schultz et al., 2000). Only the bound-to-organic-matter fraction was not determined with H_2O_2 but with $(NH_4)_2$-EDTA (according to Zeien and Brümmer, 1989), the final aqua regia step was omitted, and the volumes of reagent and solution were modified. For the HNO_3 step, two different experimental setups were assessed: 1) The soil samples together with 20 mL of HNO_3 were filled into 100 mL Erlenmeyer flasks, covered with watch glasses and one to three of them were put on magnetic stirrers with heating – first with magnetic stir bar and then without. 2) The soil samples together with 20 mL of HNO_3 were filled into 50 mL crimp neck headspace borosilicate glass vials capped and with a cannula in the septum for enabling the gas being developed to escape the vial. The second setup was examined as the results from the first one were inhomogeneous with temperatures not being similar in the different Erlenmeyer flasks due to differing glass bottom geometry and repeated measurements differing by more than factor two.)

Fraction	Extracting reagents	pH	Temperature [°C]	Contact time [h], sample agitation	Reagent/sample ratio [mL/g]	Reaction vessel	Source
Water-soluble	DI water	pH of soil sample solution	20 (room temperature)	2, horizontal shaking	10 (20mL solution, 2 g dry sample)	50 mL PP centrifuge tubes	(Qiao et al., 2012)
Exchangeable (physically sorbed species)	1M NH$_4$Ac	7 (adjustment with 25% NH$_3$ solution)	20 (room temperature)	2, horizontal shaking	10 (20mL solution, 2 g dry sample)	50 mL PP centrifuge tubes	(Qiao et al., 2012)
Bound to carbonates	1M NH$_4$Ac	5 (adjustment with 65% HNO$_3$)	20 (room temperature)	2, horizontal shaking	10 (20mL solution, 2 g dry sample)	50 mL PP centrifuge tubes	(Qiao et al., 2012)
Bound to Fe-/Mn oxides (chemically sorbed species)	0.04M NH$_2$OH*HCl	1.5 (adjustment with 65% HNO$_3$)	20	16, horizontal shaking	10 (20mL solution, 2 g dry sample)	50 mL PP centrifuge tubes	(Waterlot et al., 2012), (Eichfeld, 2004)
Bound to organic matter	0.025M (NH$_4$)$_2$-EDTA	4.6 (no pH adjustment needed)	20 (room temperature)	1.5, horizontal shaking	25 (50mL solution, 2 g dry sample)	50 mL PP centrifuge tubes	(Zeien and Brümmer, 1989)
7M nitric-acid leachable (moderately soluble minerals)	7M HNO$_3$	No pH adjustment, pH was at about -0.8	80 (on a magnetic stirrer with heating / in a sand-water bath in a metal bowl on a heating plate)	6, swirling up / joggling every about 15-20 min	10 (20mL solution, 2 g dry sample)	100 mL Erlenmeyer flasks covered with watch glasses / 50 mL crimp neck headspace borosilicate glass vials, capped, with a cannula in the septum	(Qiao et al., 2012)

The procedure by (Qiao et al., 2012) was modified by changing the extractant used for determining the organic matter fraction and by omitting the final aqua regia step. Instead of using hydrogen peroxide (H_2O_2) for extracting the organic fraction, NH_4-EDTA was used like this was done by (Zeien and Brümmer, 1989). That was because H_2O_2 (as well as NaOCl), the options used for organically-bound uranium (and iodine) extraction, act non-specifically and incompletely (Schultz et al., 1998). As (Schultz et al., 1998) states, NaOCl does not only destroy organic matter but also dissolves carbonates and is therefore not recommended for carbonate-bearing materials. For hydrogen peroxide (Eichfeld, 2004) highlighted its poor selectivity as a matter of concern. (Qiao et al., 2012) pointed out that it is not clear whether the oxidation of organic matter or the oxidation of U(IV) to U(VI) is responsible for the mobilization during this step when using H_2O_2. Even if the oxidation of U(IV) is not likely to be an issue as U can be expected to be oxidized in the soils investigated, (Merkel, 2012a) emphasized the problem of incompleteness of the reaction. Instead, NH_4-EDTA will more completely crack all organics due to the formation of strong complexes (Merkel, 2012a). The aqua regia step was skipped because the silicate-bound uranium that would be determined by that is not of interest in this study as it is not likely to be released to the environment.

The actual procedure can be summarized by the following bullet points.

- Weighing in 2 g of the fine air-dry soil material (duplicates for some samples)
- Filling them into 50 mL PP centrifuge tubes (for HNO_3 step: 100 mL glass Erlenmeyer flasks / 50 mL crimp neck headspace borosilicate glass vials)
- Adding 20 mL (50 mL for EDTA step) of extracting solution
- Shaking the samples for the time given in Table 16 in a horizontal shaker (instead: swirling up / joggling in the case of the HNO_3 step)
- Centrifuging them for 25 min at about 4000 r.p.m. (MLW T54, "Medizintechnik Leipzig")
- Sucking off the solution using a syringe with a cannula (after having flushed syringe and cannula with distilled water and having dried both by mechanical agitation)
- Filtrating the liquid sample with 0.2 μm cellulose acetate filters
- Acidifying the samples to about pH 2 with 2 drops of semi-concentrated suprapure HNO_3, i.e. 30-33 %, per 30 mL of sample (No acidification done for EDTA and HNO_3 step extracts because EDTA will precipitate at low pH Hoffmann, n.d. and clog tubing and nebulizer of the ICP-MS Kummer, 2012 and the HNO_3 extract already is acidic.)
- Analyzing the liquid extracts with ICP-MS (Thermo Scientific – XSeries 2) – after having diluted them in case this was needed (for details see section 4.3.10)
- Subtracting the blanks from the extraction solutions from the ICP-MS results of the individual extraction steps before using them for interpretation

During steps one to three, all samples were shaken for the same time without time buffer for sample centrifugation (only 6 samples possible at a time) and filtration afterwards. Therefore, contact time for some of them was not only 2 h, but maybe up to 3.5 h. For the subsequent steps, samples were treated in a more equal way. The shaking of only six samples was started at the same time and a 30 min time shift was inserted between them.

For the nitric acid step, crimp neck headspace borosilicate glass vials were used. They were put on a sand-water bath in a common pot. The pot was set on a heating plate and temperature was controlled with a thermometer. Samples were swirled every 15-20 min and places of the samples in the pot were shifted every now and then.

After having finished the flow-through experiments described in section 4.3.1, the PVC liners were disassembled and soils were used for extraction experiments. The procedure was the same as described

before – with the exception that only two extractants were used: 1 M NH$_4$Ac at pH 5 and concentrated NaOCl diluted 1:10 without pH adaption (the solution itself had a pH of 11.5). Shaking time for both experiments was two hours. Ammonium acetate at pH 5 was chosen as extractant as it released medium amounts of total U and as it correlated with total U contents. NaOCl was selected because it is a strong oxidizing agent.

4.3.9 Low-level gamma spectrometry

Low-level gamma spectrometry measures the gamma radiation emitted by a sample. Measurements were done using a 38%, i.e. 38 % relative photo-peak efficiency, n-type high-purity germanium (HPGe) detector. The detector consists of a high-purity germanium monocrystal, whose germanium has a comparatively high density and consequently an elevated absorption coefficient for gamma radiation of equal to and higher than a photon energy of 20 keV. Due to this high sensitivity, this method is suitable for analyzing low-radioactivity environmental samples. Several nuclides can be quantitatively measured at the same time without destroying the sample. What furthermore makes the method attractive is the simple and user-friendly handling during which no chemical sample pre-treatment or sample splitting is needed (Schlenker, 2002).

Before the actual analyses, about 100 g of the dried, smaller than 2 mm soil material was filled into round 77 mL plastic boxes, about 70 mm in diameter and 20 mm in height, and sealed with tape to prevent contact to the atmosphere. Then the samples had to be stored for at least one week for radon daughter nuclide ingrowth. For the individual measurements, each with a counting time of about two days, one sample at a time was put on the HPGe detector. To determine if products of the natural U-238 and Th-232 decay chains are in radioactive equilibrium or if this equilibrium is disrupted, a fertilizer sample from one of the sampling sites (there were no samples available from the other sites), and forest and field soil samples from the sampling sites were analyzed for the activities of U-238, Th-232, Ra-226 and also for Cs-137. For interpretation in this work, the activity ratio between Ra-226/U-238 is of main interest. Cesium was introduced to the upper soil horizons during the nuclear weapon testings in the 1960s and 1970s and during the Czernobyl accident in 1986. As it is of purely anthropogenic origin and its entry can be described by a known input curve, Cs-137 is a suitable tracer for environmental processes. In this work, it serves for assessing if forest soils are non-disturbed or if they encountered tillage or other soil-structure disturbing treatment. According to sufficiently high gamma emission energy (intensity), the following gamma lines were used for interpretation with the program GammaVision (EG&G ORTEC, 1994):

-   For U-238
    o   64.0 keV (Th-234), 1001.7 keV (Pa-234)
-   For Ra-226
    o   186.8 keV (U-235/Ra-226), 296.2 keV (Pb-214), 610.3 keV (Bi-214), 1120.8 keV (Bi-214), 1763.8 keV (Bi-214)
-   For Th-232
    o   912.0 keV (Ac-228), 969.6 keV (Ac-228), 239.6 keV (Pb-212), 584.2 keV (Tl-208), 2612.6 keV (Tl-208)
-   For Cs-137
    o   662.0 keV (Cs-137)

Pb-210 was not considered because radon at the one side degasses from phosphate rock during processing (Fukuma et al., 2000) and on the other side is introduced to the soil via precipitation.

The measured peaks belonging to the selected gamma lines were integrated with the software GammaVision (EG&G ORTEC, 1994) to obtain the activities of the radionuclides. For calculating the specific activities from that, the activities were referred to previously measured specific activities of standards (calibration with them), the sample's mass, the measurement time, the geometry of the round plastic box used for the measurements and a factor that considers the weakening of the gamma signal with increasing gamma ray energy.

4.3.10 Water sample analysis

In addition to the seepage water samples taken from the lysimeters in the field as described in section 4.1.3, further water samples were taken from the flow-through experiments described in section 4.3.1. Moreover, samples from extraction experiments and CEC determination were analyzed.

Trace element analysis was done using an **ICP-MS** instrument by Thermo Scientific – XSeries 2. Prior to analyses, 10 mL of the filtered and acidified samples (2 drops of semi-concentrated suprapure HNO_3, i.e. 30-33 %, per 30 mL of sample) were filled into 15 mL centrifuge tubes made of PP. Either this was done without diluting them or after having diluted them – in case of high concentrations that would harm the detector. Then 100 μL of internal standard were added. This standard contained 50 μg/L Ge, 10 μg/L Rh and 10 μg/L Re in concentrated (i.e. 65 %) suprapure HNO_3. Only the treatment of the EDTA extraction samples deviated from that approach. For these samples the internal standard was mixed in the same way as mentioned above with the difference that distilled water was used rather than HNO_3. This is because EDTA is poorly soluble at low pH (exact value depending on the metal being complexed by EDTA (Hoffmann, n.d.) and precipitation would harm the ICP-MS (Kummer, 2012). Detection limits are given in *FOLDER 1* in the digital appendix.

In the field, samples for **analysis of main cat- and anions** using **ion chromatography (IC)** had been filtered and filled into 50 mL PE bottles. For analyzing the samples for major anions, these samples remained unacidified. For cation analysis, acidification with 2 M suprapure HNO_3 to pH between 3.5 and 2.5 was necessary. This was checked using indicator strips (Macherey-Nagel). In case sample dilution was necessary, this was done with distilled water and considered by a dilution factor.

Analysis of major anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) was done using a 881 Compact IC pro (Metrohm) with a separation column of type FGC 1 AN-P (125 mm long, 4.6 mm inner diameter) and a guard column of type FGC 1 AG-P (150 mm long, 4.6mm inner diameter) both manufactured by FRANK GUTJAHR Chromatographie. A mixture of 3.5 mM Na_2CO_3 and 0.5 mM $NaHCO_3$, prepared in degassed (with N_2) distilled water, was used as eluent. Flow rate was 1.0 mL/min. Detection limit for the different anions is 0.01 mg/L.

For major cation (Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}) analysis, a Professional IC 850 (Metrohm) with the separation column Metrosep C4 – 150/4.0 (i.e. 150 mm long, 4 mm wide) and the guard column C4 Guard was used – both manufactured by Metrohm. The eluent composition was 2 mM HNO_3 with 0.7 mM dipicolinic acid. Flow rate was 0.9 mL/min. Detection limit for lithium, sodium and magnesium is 0.01 mg/L; for calcium it amounts 0.02 mg/L and for potassium 0.05 mg/L.

For anion as well as cation analysis, an autosampler (858 Professional Sample Processor) was used. Results were interpreted using the software MagIC Net 2.2. For calibration, external standards with known ion concentrations were measured. The detector used was a conductivity detector.

Total inorganic carbon (TIC) and **dissolved organic carbon (DOC)** were determined using a **LiquiTOC analyzer** (Elementar Analysesysteme GmbH), which has a detection limit of 0.1 mg C/L. For calibration, external standards were used. In the case of TIC analysis, a sodium carbonate stock solution of 1 g C/L was diluted in several steps to cover the concentration range of interest for the water samples to be analyzed. For dilution, degassed (for expulsing dissolved CO_2) distilled water was used. The stock solution used for calibration for DOC analysis was a potassium hydrogen phthalate solution of 1 g C/L. Depending on the TIC and DOC concentrations in the individual samples, different infrared (IR) ranges were chosen (IR 1 for 0…49 mg C/L, IR 2 for 50…300 mg C/L) for analysis. All samples were measured in the infrared ranges 1 or 2 for TIC and for DOC analysis. Injected volumes amounted 9.97 mL, 4.98 and 2.38 mL, respectively. Before DOC analysis, the TIC samples were filtered using 0.2 μm cellulose acetate filters.

4.4   Modeling U and P speciation and saturation indices in water

For analyzing the speciation of uranium in the environment, according to (Merkel, 2012c) calculations using geochemical codes are practically the only option. That is because sophisticated species-analytical techniques like EXAFS and XANES cannot be used if U concentrations are as low as in natural waters. According to (Kruse, 2012), for identifying an individual species, this species needs to account for about 10 % of all constituents contained in the sample. However, geochemical modeling does not give unambiguous reproducible results either. The modeled speciation differs significantly depending on the geochemical code and database used. Not only the log k values of the aqueous and crystalline phases considered vary, but also the number and types of species taken into account by the individual databases is not the same. In many cases dissociation constants have not been determined under conditions resembling those in the environment but for industrial purposes (much higher uranium concentrations of 10^{-2} to 10^{-6} mol/L, different pH values, etc.). It is not yet clear to what extent those results can be transferred to natural systems where U concentrations are in the nmol/L range (Merkel, 2009). The situation is most problematic for data for surface complexation and ion exchange (Merkel, 2012c). Using geochemical models, one therefore has to compile or complete datasets for uranium by deleting certain data and by adding other. Greatest difficulties are caused by the decision on which thermodynamic data to select or to deselect under which conditions (Merkel, 2012c).

For modeling uranium speciation in the water samples, in this thesis **PHREEQC for Windows (Version 2.18.00)** was the geochemical code used. The databases that were compared with respect to the thermodynamic data for uranium and U species considered are:

minteq.v4.dat	NEA.dat
llnl.dat	PCHatches.dat
The chemical-thermodynamics-of-uranium book by (Grenthe et al., 1992) (The updated and extended edition of the book did not contain uranium-phosphate complexes data that differed from the first edition of the book. Therefore, it is not mentioned here.)	

Only species containing hexavalent uranium and one or more phosphate species were taken into account to address the issue of uranium input to water by phosphate fertilizer application. Data was compiled, experimental conditions noted (only possible for the thermodynamics book, Grenthe et al., 1992), and sources were mentioned. All this information can be found in *EXCEL 1* in the digital appendix. For modeling various thermodynamic databases were examined for the species containing U(VI) and phosphate they consider and for the log k and delta H values they give for these species. **Llnl.dat** was finally selected as database used for modeling. A few additional aqueous species $(Ca_2(UO_2)(CO_3)_3, Ca(UO_2)(CO_3)_3^{2-}, UO_2HAsO_4, UO_2H_2AsO_4^+, UO_2(H_2AsO_4)_2)$ were added as can be seen in the PHREEQC input files in *FOLDER 2* in the digital appendix.

In addition to speciation, saturation indices (SI) for potentially forming or existing phases were calculated. In case an index is 0 ± 0.5, the phase is assumed to be in equilibrium with the solution. When SI values are $\leq$ -0.5, the solution is assumed to be undersaturated with respect to the phase in question; when SI values are ≥ 0.5, the solution is assumed to be oversaturated with respect to the phase.

4.5 Statistical data evaluation

4.5.1 Data preprocessing and utilized software

For statistical data evaluation, SPSS for Windows (standard version, 11.0.0 from 2001) was used. All soil data from own analyses and also received data from the responsible institutions of the individual sites was put into a master table. Missing values were replaced by "-999". Values below detection limit were replaced by "0.3 multiplied with the detection limit".

The parameters considered were:

- CEC, pH, TIC, TOC
- Results from grain size analysis (percentage of clay, silt and sand mass of fine material's mass (< 2 mm), percentage of fine material (< 2 mm), clay and silt of total soil)
- Results from extraction experiments of uranium from soils (U concentration in µg/kg dry soil) using the extractants
  - Distilled water
  - Ammonium acetate (pH 7)
  - Ammonium acetate (pH 5)
  - Hydroxylamine hydrochloride
  - Ethylenediaminetetraacetic acid
  - Nitric acid
- Data from the LfULG, BfU and UFZ (pH, PO_4 content (% of dry soil), P_2O_5 (mg/100g), extractable P_2O_5 (mg/100g), Corg (% of dry soil), Al, Cd, Cu, Fe, Mn, Pb, Th, U, Zn (in mg/kg))

The utilized master table can be found in the digital appendix as *EXCEL 2*. The percentages of the different soil fractions were taken from the grain size distribution curves of the individual soils given in *EXCEL 3* in the digital appendix. The amount and temporal resolution of available data was different for the four field sampling sites. It was lowest for Brandis and highest for the BDF sites. Sampling depths and sampling depth intervals were different depending on the site. For making the data of the different sites comparable, it had to be adapted to the same depths by calculating means. However,

there were also numerous missing values. Therefore, the parameters that contained missing values could not be included in the cluster analysis but only be used for rank correlation analysis. Missing values would cause the software to omit the respective parameter.

4.5.2   Checking for normal-distribution

The individual parameters were checked for normality using the nonparametric Kolmogorov-Smirnov test. The parameters are normal-distributed if the result for the significance level (0.05) is exceeded. In case the value is smaller than 0.05 and consequently significant, the distribution of the values of the parameter significantly differs from normal distribution (Paeschke, n.d.).

4.5.3   Spearman rank correlation

Spearman rank correlation analysis of all parameters with each other was done according to the following points:

- Bivariate, two-tailed correlation analysis
- Level of significance of the results of the analysis: < 0.05
- 16 cases, one from surface soil and one from subsoil of both, the field and the forest site

4.5.4   Cluster analysis

Moreover, a cluster analysis was conducted with the following settings:

- K-means clustering (i.e. partitioning rather than hierarchical)
- Using only parameters that have complete datasets (i.e. sampling depth (cm), CEC, pH, TIC, TOC, results from grain size distribution analysis and sequential extraction)
- Predefined number of clusters (2 to 10 clusters were checked)

The level of significance of formed clusters (i.e. for checking if the determined cases are significantly different from each other) was chosen as < 0.05. The most suitable number of clusters was determined by checking the significance of the clustering for the individual parameters. For that purpose, the results from clustering (using 2 to 10 clusters) were defined as new parameters in the input file for SPSS. Then, the nonparametric Kruskall-Wallis test was performed for all considered parameters, using the cluster membership as grouping variable (Lund and Lund, 2013). The best classification was finally determined by counting the number of parameters the classification was significant for (i.e. $<$ 0.05); the maximum number of parameters indicated the best classification to be found. It was aimed to minimize the number of classes.

4.6 Assessment of quality of water analyses

For checking the reliability of the results from water chemical analyses, ion balance and electrical conductivity were calculated using **PHREEQC for Windows (Version 2.18.00)** with the database **llnl.dat** and **phreeqc.dat**, respectively. The relative difference between both is calculated by PHREEQC using the following formula:

$$Relative\ difference\ [\%] = \frac{(measured\ EC - calculated\ EC)}{measured\ EC} \times 100\ \%$$

If the calculated balance is negative, there is an excess in anions; if it is positive, there is an excess in cations. As aqueous solutions do not have a charge, charge imbalances indicate erroneous results. For acceptable analyses, the analytical error, i.e. the charge imbalance, should be less than 5 %. The calculated electrical conductivity (EC) should not deviate from the measured conductivity by more than about 5 %.

The calculation of EC was done using the database phreeqc.dat rather than llnl.dat because the latter database does not offer that option.

Various elements were determined with ICP-MS as well as with IC. For modeling and analytical error assessment, the following results were used for the flow-through experiment samples:

- Main cations (Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+) and main anions (Cl^-, F^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) from IC analysis
- Trace elements (Fe, Mn, Cd, U, As) from ICP-MS analysis
- Hydrogen carbonate (HCO_3^-) as C from TIC analysis
- pH, pe (corrected), temperature

As in the percolation water samples some elements' concentrations were elevated (e.g. Zn in Brandis between 18 and 41 mg/L), the following concentrations were additionally considered for modeling:

- B, Si, Zn, Pb, Ba, Ni, Cr, V, Al, Cu, Sr.

The input files for modeling (named *PHREEQC 1*) can be found in the digital appendix.

4.7 Estimating uranium input by fertilization

In this work, the main input of U to the studied field soils is assumed to be by phosphate fertilization. From the responsible institutions of the sampling sites, information on fertilization for all field study sites was obtained. This information comprised the type of fertilizer used, the amount applied and the point of time of fertilization. However, the exact composition of these fertilizers was not known as labeling in Germany is still not regulated by law (see section 1.1). Therefore, typical ranges for the concentration of uranium, phosphorus and other elements of interest (in mg/kg fertilizer) in these fertilizers had to be utilized. The comprehensive data compilation by (Taylor, 2013) formed the basis. For risk assessment, minimum, maximum and mean uranium concentrations in each individual fertilizer

46

were determined from the data compilation. Only for the Sauerbach site, a sample of the presently used fertilizer was available for analysis of the U content. Additional deposition sampler data was only available for the Schmorren site.

For Sauerbach, the actual U concentration of the fertilizer and for the other sites, the typical ranges were then multiplied with the applied amount of fertilizer in kg/(ha×a). In case, the applied fertilizer was an organic fertilizer, a dry matter content of 7.5 % was assumed as suggested by internal calculations of the LfULG. The uranium input was then converted to the soil horizon above ploughing level (in mg/kg dry soil). This was done by dividing the uranium input (in g/(ha×a)) by the thickness of the soil horizon above ploughing level and the density of the soil. The result was then obtained in µg/kg dry soil.

For assessing the effect of phosphate fertilization on soil and groundwater, in addition to fertilization, concentrations and concentration development of soil and groundwater constituents relevant in this context (e.g. U, P, Cd, As) were interpreted. For Hilbersdorf and Schmorren, data availability was encompassing. For Sauerbach and Hilbersdorf, however, water and soil analytical results did not cover all relevant constituents (especially uranium).

5 Results and interpretation

From here on, the studied soils are represented by abbreviations consisting of letters and numbers. The first two letters represent the site:

- Br = Brandis, Sc = Schmorren, WD = Wermsdorf, HD = Hilbersdorf, SB = Sauerbach.

The third letter stands for the German words for field (A – "Acker") or forest (W – "Wald"). And the number characterizes the sampling depth (12, 14, 26, or 28 cm below surface + about 6 cm further down from each of these depths). For example, the abbreviation "BrA12" represents the field soil sample from 12 (+ about 6) cm depth in Brandis.

5.1 Properties of studied soils at time of sampling

5.1.1 Grain size distribution

Figure 10 displays the grain size distributions determined with dry and wet sieving together with soil pH and effective cation exchange capacity of the analyzed soils. It illustrates that most soils are composed of more than 95 mass % fines, i.e. clay, silt and sand with < 2 mm grain size. Only WDW12, HDA12, HDA26 and HDW26 contain considerably more coarse material that is > 2 mm. In these four soils, gravel makes up between 22 and 52 mass %. For most soils, clay and silt contribute the most to the < 2 mm fraction. Only in case of BrA12, BrA26, BrW12 and HDW26 the fraction of sand is greater than that of clay and silt.
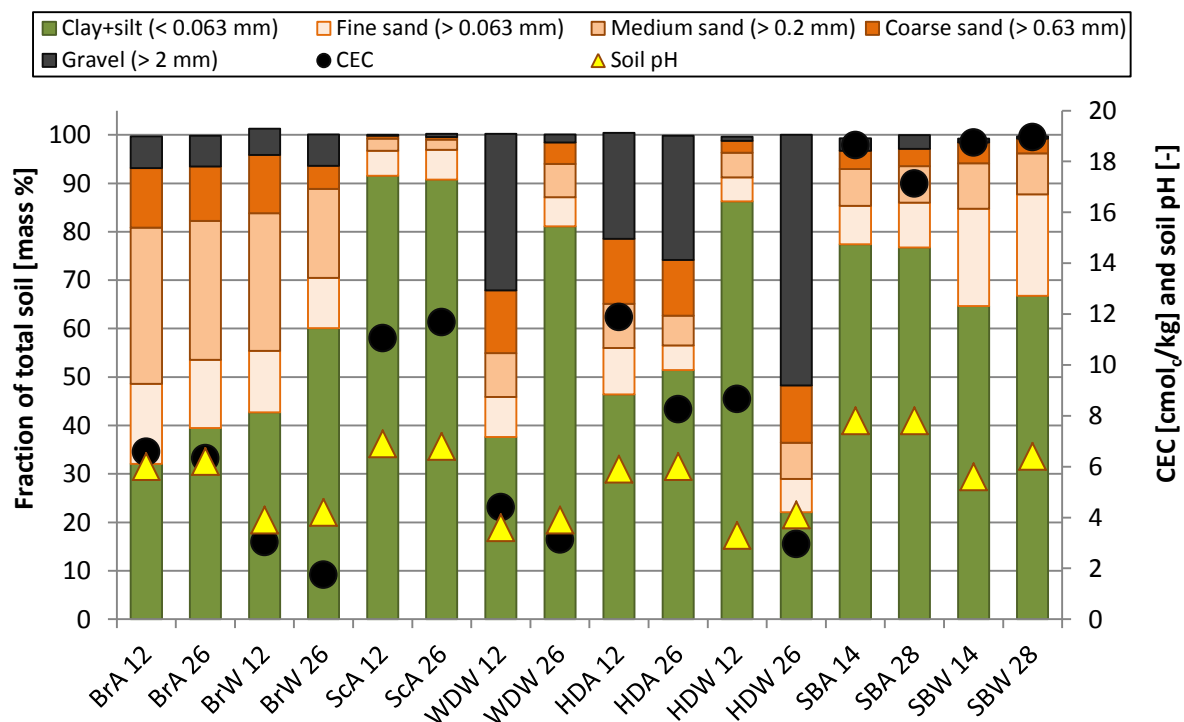
Figure 10 – Grain size distribution (determined with dry and wet sieving), CEC and pH of the field and forest soils

The combined plot of the grain size distribution, CEC and soil pH shows that these properties are interrelated. High CEC in most cases goes in hand with elevated pH and/or great fine clay contents. This positive correlation in the results from rank correlation analysis as described in section 4.5.3 and 5.2.2. Together with the organic matter content, these properties are most important for the retention of uranium in soil.

Figure 10 does not differentiate between clay and silt as they were only determined as sum during sieving analysis. For analyzing the clay content, additional particle size analyzer measurements were conducted. These results were in agreement with those from sieving analysis for some soils; for others they deviated considerably. Therefore, particle size analyzer measurements were repeated up to six times for some of the soils if results differed too much. From the repetitions, means were calculated. When results differed too much from the other repetitions and did not seem reasonable, they were excluded from mean calculation.

Material losses during sieving analysis for most soils were less than 0.5 mass % of the weight of the sample analyzed. Only for the Sauerbach soils losses amounted between 3 and 5 mass %. The Sauerbach soils contain between 97 and 99 mass % fine soil material. It is likely that the fine material losses occurred during wet sieving. There more than 15L of water were needed to separate the < 63 µm material from the > 63 µm material. Then the solid particles did not settle within a reasonable time frame in the 10 L baskets. So, when sucking up the supernatant from the baskets after more than one week of letting the particles settle down, the fine material still floating was abstracted with the water. For correcting these losses, the weight difference was added to the clay fraction.

The difference between the results for the sum of clay and silt, and for fine sand from sieving analysis and particle size analyzer results amounted:

- Less than 5 % for
    - BrA12, BrA26, BrW12, WDW12, HDA12, HDA26, HDW26, SBA28, SBW14, SBW28
- Between 5 and 10 % for
    - BrW26, SBA14
- More than 10 and less than 20 % for
    - ScA12, ScA26, WDW26, HDW12

For evaluating the composition of the fine material, results from particle size analyzer were used as they are more reliable in that range and were repeated several times for checking reproducibility. The sum curves of the grain size distribution of all soils can be found in *EXCEL 3* in the digital appendix. For contaminant retention, the fine material fraction is most relevant (key words: sorption processes, permeability, filter potential). The composition of the fine material of the studied soils is illustrated in Figure 11. The x and the y axes give the content of clay and silt in mass % of fine soil. The sand content is the difference of these two. The closer a point plots to one of the corners of the triangle, the more it contains of the constituent depicted in that corner. Points lying in the middle of the triangle flag soils consisting of equal shares of each of the three components clay, silt and sand. Their soil type would be called loam.
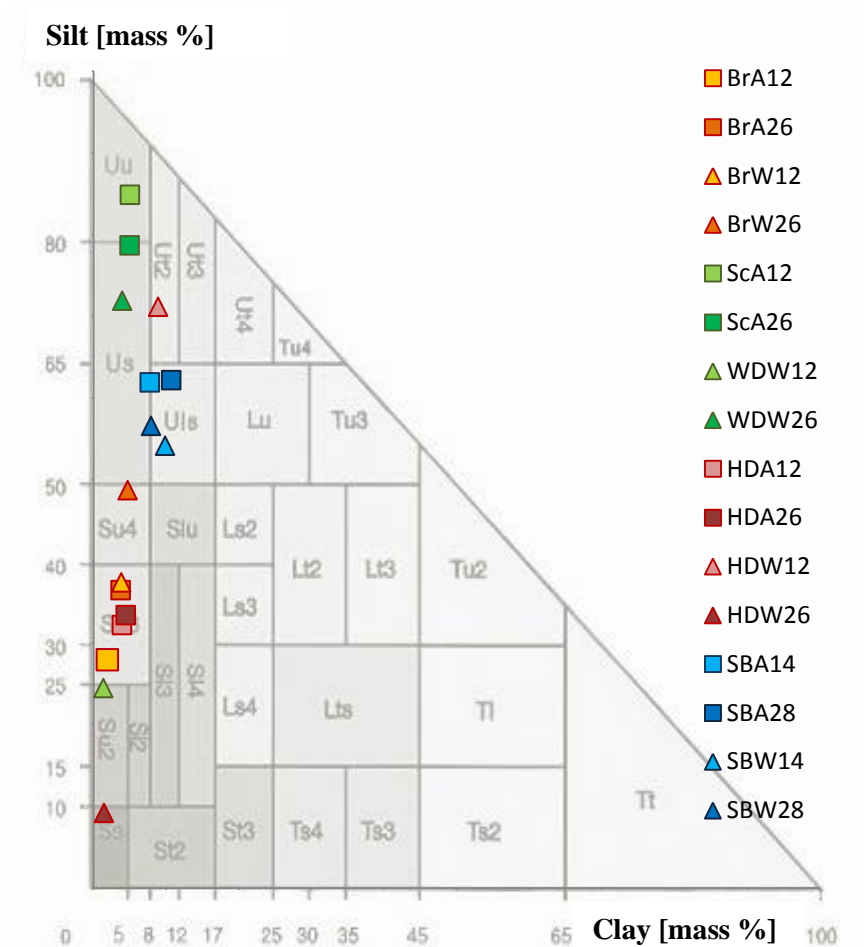
Figure 11 – Grain size distribution diagram (according to KA05, page 142; clay and silt are given in mass % of fine soil; sand is given as difference of both; abbreviations stand for: capital letters: major constituents, lower-case letters: minor constituents; S… sand, T… clay, U… silt, L… loam (mix of sand, silt and clay in equal shares), numbers represent the intensity of a certain admixture: 2… weakly, 3… medium, 4… strongly; e.g. Su4 … strongly silty sand)

All of the studied soils plot more or less close to the left margin of the diagram. They all contain less than 11 mass % of clay in the fine soil fraction. The shares of silt and sand vary over wide ranges: between 9 and 85 mass % and between 10 and 89 mass %, respectively. So, two major groups can be distinguished: silts and sands – with different amounts of admixtures of the other components clay, silt and sand.

The group of silts is formed by:	The group of sands is formed by:
- ScA12, ScA26, WDW26	- BrA12, BrA26, BrW12, BrW26
- HDW12	- WDW12
- SBA14, SBA28, SBW14, SBW28	- HDA12, HDA26, HDW26

Most soils more or less fulfill the prerequisite intended during sampling site selection: for one location, field and forest soils are of the same soil type to make them comparable. Only WDW12 and HDW12 do not properly go in line with that requirement. BrW26 and HDW26 are still within the range of being similar to the other soils of their location. Therefore, sites can be seen as more or less comparable and suitable for studying the fate of uranium in the subsurface.

5.1.2   Soil pH

Soil pH of the analyzed soil samples is shown in Figure 12. Topsoil means 12 or 14 plus about 6 cm sampling depth; subsoil samples are from 26 or 28 plus about 6 cm depth. At all sites pH of field soils is 2 to 3 units higher than pH of the respective forest soils. Differences between topsoil and subsoil are negligibly small (0-0.2) for field soils. For forest soils pH of subsoil is between 0.3 and 0.8 pH units higher than pH of topsoil.
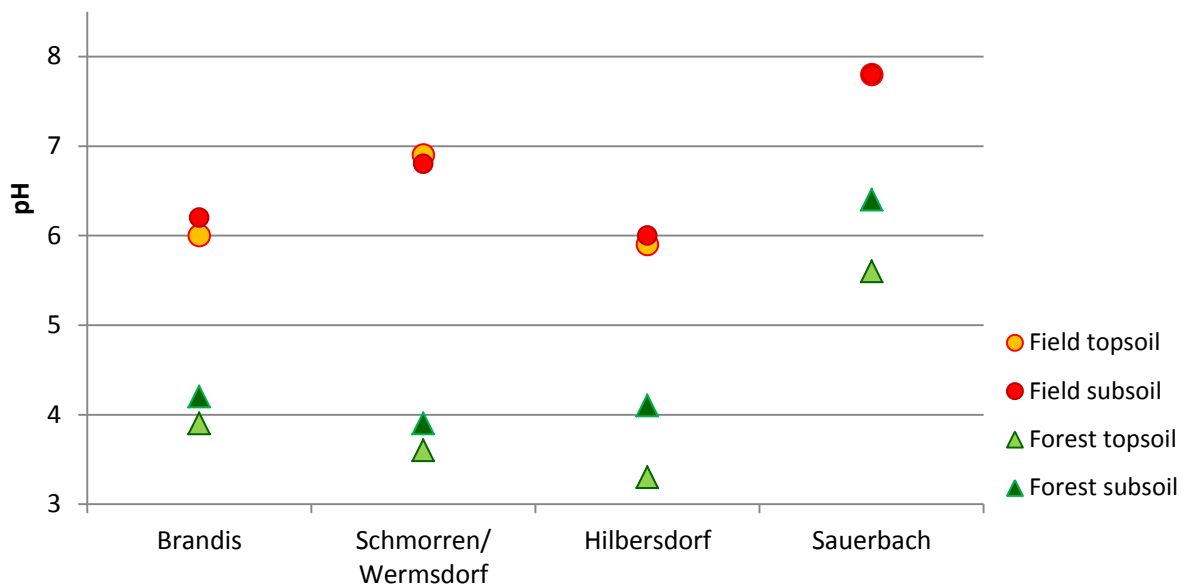
Figure 12 – Soil pH of sampling sites (determined with 0.01 M CaCl₂ according to DIN ISO 10 390; topsoil means 12 or 14 (+ about 6) cm sampling depth; subsoil means 26 or 28 (+ about 6) cm sampling depth. As far as possible, forest samples were taken close to the field soil samples, or at least in the same geology in the vicinity.)

Highest pH values were determined for the Sauerbach site, lowest for Hilbersdorf and Brandis. Schmorren/Wermsdorf lies in between. These differences result from the rock type the soil developed from (greater or smaller buffer pH capacity), vegetation on site (coniferous tree or deciduous tree) producing greater or smaller amounts of acid during degradation, land use (arable land is commonly limed if pH is too low, forests are so less commonly), weather and climate conditions (temperature, precipitation, evaporation, etc.).

For the field soils in Schmorren, Hilbersdorf and Sauerbach determined pH values were close to those obtained from the responsible institutions' data. The difference was always smaller or equal to 0.3 pH units. The only exception was the field soil in Hilbersdorf where the pH determined by the LfULG was 1.5 pH units higher, i.e. pH was 7.5 rather than 6 – the pH determined in the present analyses. This difference might be due to errors during analysis or due to liming of the field soil or other activities not long before the time of sampling.

5.1.3 Carbonate content

Analysis of carbonate contents using a "carbonate bomb" showed that all soils, except SBA14 and SBA28 possess carbonate contents smaller than 5 mass % $CaCO_3$ which is the detection limit of the device. For SBA14 and SBA28, 16 and 18 mass % $CaCO_3$ were determined. Therefore, all soils were afterwards additionally analyzed using a LiquiTOC analyzer as explained in section 4.3.6.

5.1.4 Carbon content (TC, TIC and TOC)

For most sites, the content of organic matter is much higher than the inorganic matter content as can be seen in Figure 13. BrA12 and WDW26 are nearly free of inorganic carbon (TIC). All the other sites are very low in inorganic carbon. Only SBA14 and SBA28 show higher TIC values. HDA12 and HDW26 lie in between. Two important factors controlling the TIC content in soils are the parent material (solid rock or sediment) the soil developed from, and liming of the soils or application of carbonate-containing fertilizers. The parent materials the soils formed from are described in detail in Table 7. For the sites in Brandis and Schmorren/Wermsdorf, this material is sandy and loamy with loess contents that had already been washed out to a great share. In Hilbersdorf, it is a mixture of loess loam and gneiss, which is characterized as nearly free of carbonate by the LfULG. The reason why the Hilbersdorf topsoil still contains a TIC content of 0.9 % C is because of regular application of calcium ammonium nitrate, a nitrogen fertilizer consisting of calcium carbonate and ammonium nitrate. The soil at the Sauerbach site consists of clayey, silty loam, medium to low in carbonate. In addition to natural carbonate stock, the site is regularly fertilized with calcium ammonium nitrate increasing the carbonate content of the soil.
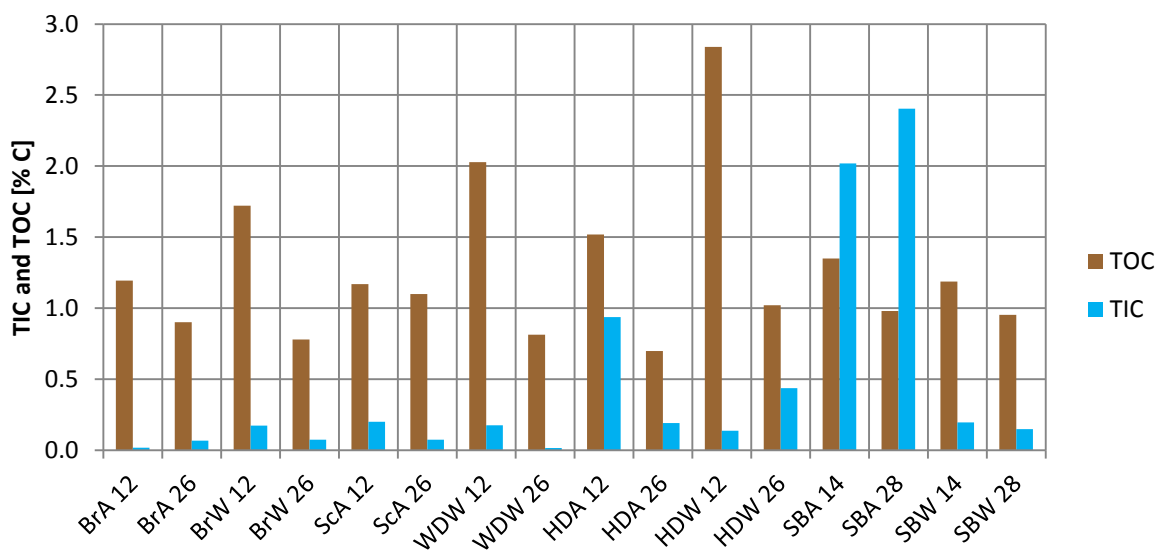
Figure 13 – TIC and TOC contents of the sampled field and forest soils

For evaluating the carbonate contents, in Table 17 they were classified according to the scheme suggested in the German Soil Mapping Handbook, KA05.

Table 17 – Carbonate contents of the analyzed soils (classified according to KA05, page 169)

Carbonate content in words	Range [mass % CaCO_3]	Soil belonging to that group
Free of carbonate	0	-
Very low in carbonate	< 0.5	BrA12, BrA26, WDW26
Low in carbonate	0.5 … < 2	BrW12, BrW26, ScA12, ScA26, WDW12, WDW26, HDA26, HDW12, SBW14, SBW28
With some carbonate	2 … < 4	HDW26 (maybe loess not completely washed out there)
With medium amount of carbonate	4 … < 7	-
With considerable amount of carbonate	7 … < 10	HDA12
Rich in carbonate	10 … < 25	SBA14, SBA28
Very rich in carbonate	25 … < 50	-
Extremely rich in carbonate	50 … < 75	-
Carbonate	≥ 75	-

Organic matter content was also evaluated using KA05 (page 166). All of the sampled soils except WDW12 and HDW12 belong to the same group: soils low in C_{org}. They all have organic carbon contents between 0.5 and 2 mass% C. The other two soils can be classified as possessing medium amounts of C_{org} (between 2 and 5 mass% C).

5.1.5 Cation exchange capacity (CEC)

For evaluating the cation exchange capacity of the individual soils, both the effective (at the present soil pH) and the potential (maximum number of cation exchange places, at pH 8.2 according to KA05, page 368) CEC were considered. CEC_{eff} was determined as described in section 4.3.7; CEC_{pot} was calculated from CEC_{eff} using a pH-dependent conversion factor according to KA05, page 370. The calculations can be tracked in *EXCEL 4* in the digital appendix. Figure 14 displays the results from the calculations and gives the ranges for evaluating the CEC_{pot} according to (Senatsverwaltung für Stadtentwicklung und Umwelt Berlin, 2006). From that it can be seen that for all soils, except SBA14 and SBA28, the maximal achievable cation exchange capacity, CEC_{pot}, is not reached because actual pH is lower than 8.2. It also becomes clear that the lower pH, the greater the difference between CEC_{pot} and CEC_{eff}. So increasing the pH by liming or other activities would at the same time cause an increase in CEC_{eff} towards CEC_{pot}. In the present study, however, only the actual situation is looked at and consequently CEC_{eff}. For some soils, especially HDW12, it is even not realistic to discuss scenarios with CEC_{pot} as an increase from pH 3.3 to pH 8.2 which would be necessary for reaching CEC_{pot} is not likely.
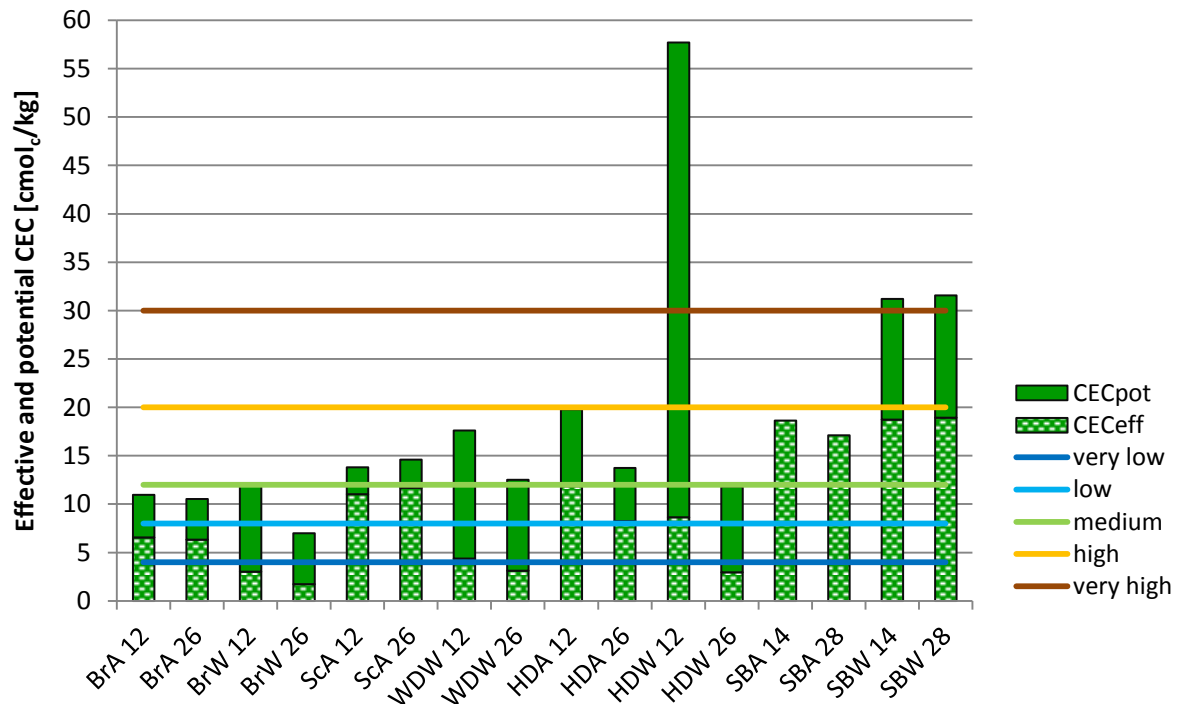
Figure 14 – Effective and potential cation exchange capacity of sampled soils (conversion from CEC_{eff} to CEC_{pot} according to KA05, page 362 and 370; the ranges for the evaluation of the potential cation exchange capacity are given as colored horizontal lines; above 30 $cmol_c$/kg CEC_{pot} is extremely high)

According to (Senatsverwaltung für Stadtentwicklung und Umwelt Berlin, 2006), the effective cation exchange capacity of the studied soils can be classified into the following groups:

- Low (4… < 8 $cmol_c$/kg)
    - BrA12, BrA26, BrW12, BrW26, WDW12, WDW26, HDW26
- Medium (8… < 12 $cmol_c$/kg)
    - ScA12, ScA26, HDA12, HDA26, HDW12
- High (12… < 20 $cmol_c$/kg)
    - SBA14, SBA28, SBW14, SBW28

None of the soils has a very low or very high CEC_{eff}. The actual values effective of the cation exchange capacities among others result from the following soil properties:

- Grain size and specific surface area
    - The smaller the grain size, the greater the specific surface area
    - So, CEC increases along the order: sand, silt, clay
    - Humic matter content (C_{org} in general; the higher the content, the greater the CEC)
- (Clay) mineralogy
    - Kaolinite, chlorite, illite, smectite, vermiculite
- pH
- Degree of weathering of the soil

5.1.6 Total uranium and acid-extractable uranium

U totals in mg/kg of the analyzed soils were calculated from the respective activities in Bq/kg determined with gamma spectrometry (see *EXCEL 5* in the digital appendix). These totals were used for referring the U contents extracted during the individual extraction steps to. Highest U contents were extracted when nitric acid was used as extraction solution. This step was done twice as the first attempt lead to non-reproducible and very inhomogeneous results. During the experiment, some of the samples started to boil even if temperature of the individual heating plates was set to the same level, and same amounts of solution and soil were used. The reason for temperature not being the same in the individual Erlenmeyer flasks that were used can be seen in the different geometry and degree of rounding of the bottom of the vessels that were supposed to be the same. In addition to problems during experiment execution, the utilized acid was prepared in an improper way – it was only 4.55 N instead of the intended 7 N due to errors in the calculations for solution preparation. So, the step was repeated as explained in detail in section 4.3.8. The results from the 4.55 N HNO_3 step as well as those from all the other steps can be assessed as numeric values in *EXCEL 6* in the digital appendix.

Figure 15 shows the uranium contents extracted with 7 N HNO_3 from the sampled field and forest soils as fraction of total uranium in mg/kg.
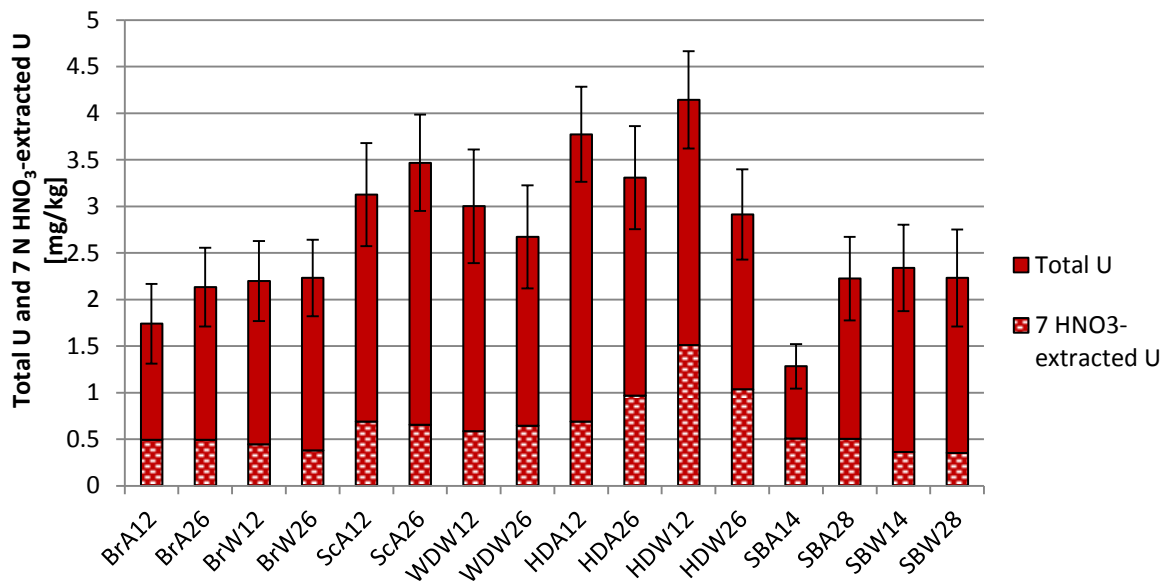
Figure 15 – 7 N HNO_3-extracted U as fraction of total U determined with gamma spectrometry (both in mg/kg dry soil; error bars for total U stem from gamma spectrometry measurements. Errors for U extraction can be assumed to be in the range of 8 to 10 % as determined by Kalembkiewicz and Sitarz-Palczak, 2005 and Rauret et al., 1999)

Regarding total uranium concentrations of the different sites, two groups can be formed:

- Brandis and Sauerbach
  - U contents between 1.3 and 2.3 mg/kg
  - Lowest U content in field topsoil; similar or same contents in the other soils of the site
- Schmorren/Wermsdorf and Hilbersdorf
  - U contents between 2.7 and 4.1 mg/kg
  - Differences between field and forest, topsoil and subsoil

The reason for U totals being different for the individual sites can be seen in the respective parent rock or sediment material the soils developed from. (Kok and Schnug, 2008) give typical ranges for U in soils in Germany depending on parent material and land use (see Table 30 in the appendix). These ranges match those determined in this work. (Kok and Schnug, 2008) came to the same conclusion that the results presented in Figure 15 suggest: differences between uranium contents in field and forest soils are mostly smaller than the errors related to the measurements; in some cases U contents in field soils exceed those in forest soils in other cases it is the opposite way. The errors for U totals are shown as error bars in Figure 15. They range between 0.2 and 0.6 mg/kg. In Brandis and Schmorren/Wermsdorf, none of the differences is greater than the corresponding error. In Sauerbach, only field topsoil U content is considerably lower than that of the other soil samples of the site. In Hilbersdorf, forest (and field) topsoil U content is higher than that in forest subsoil.

Generally as a result from fertilization, one would expect higher U totals in field soil than in forest soil and higher totals in field topsoil than in field subsoil. The actual results, however, deviate from these expectations. In Brandis and Schmorren/Wermsdorf, the reason for that can be seen in low fertilization, low U contents in P fertilizers applied, long time that has elapsed since last fertilizer application, and in the soils' properties (Brandis soil is dominated by sandy material with low sorption potential.). Therefore, field U contents are similar to those of the quasi-background U content in the respective forest soils. The Sauerbach and Hilbersdorf site in the following will be addressed in greater detail.

U extracted with 7 N HNO_3 amounted only between 15 and 40 % of total U, i.e. between 0.4 and 1.5 mg/kg (without considering the error bars). This is very low when considering that 7 N HNO_3, a strong acid of high concentration, was used, temperature was set to about 80°C and contact time was 6 hours. Even though, the step has not been very effective. This might either be because uranium is very strongly bound and the acid's concentration has not been high enough, or, more likely, that the experimental procedure had not been appropriate. Reasons for the poor efficiency of the step might be:

- Binding strength of U in the soils:
  o The share of U not extracted with 7 N HNO_3 might be strongly bound in insoluble silicate minerals, which even are not destroyed by aqua regia but only by HF digestion.
- Experimental procedure:
  o Temperature was maybe not constantly at 80°C but sometimes/often below (checking problematic due to the use of an open system without proper insulation and only 1 thermometer; see photography of the experimental setup in the digital appendix). Sometimes temperature was also above 80 °C and the sand-water mix started to boil
  o Incomplete contact between solid and liquid (no shaking was possible as vessels were open to allow the developing CO_2 from carbonate decomposition to escape; instead the utilized headspace vials were only swirled every 15-20 min)
  o Non-suitable vessel geometry (neck too narrow)
  o Contact time too short
  o Nitric acid too diluted (for comparison: during aqua regia digestion according to DIN ISO 11466, a commonly used method, 1 g dry soil with 6 mL HCl (38 %, i.e. 12.4 N) and 2 mL HNO_3 (65 %, i.e. 15.6 N) are heated up in a sand bath to 115°C for 2 hours and are then filled up to 50 mL with HNO_3 after having cooled down)

The fraction of U extracted with 7 N nitric acid positively correlated with phosphorus, the metals U, Th and Zn as well as with the organic carbon content (see section 5.2.2). That suggests that phosphorus, probably as phosphate, as well as organic carbon strongly bind uranium and can be decomposed, at least partly, by nitric acid. It also indicates that not only U but also Th and Zn are introduced to soil with phosphate fertilizers.

5.1.7   Origin of uranium

Figure 16 illustrates the specific activities for U-238 and Ra-226 at the studied field and forest sites determined with low-level gamma spectrometry. As explained in section 2.5 the basis for the assessment of the origin of U had been that during fertilizer production, U is transferred to the fertilizer to a great share, whereas Ra gets depleted in the fertilizer. So, in field soils one would expect greater specific activities for U-238 than for Ra-226. This effect should be higher in topsoil than in subsoil – if at all visible in subsoil. In forest soils, however, both activities should be more or less the same, i.e. in secular equilibrium.
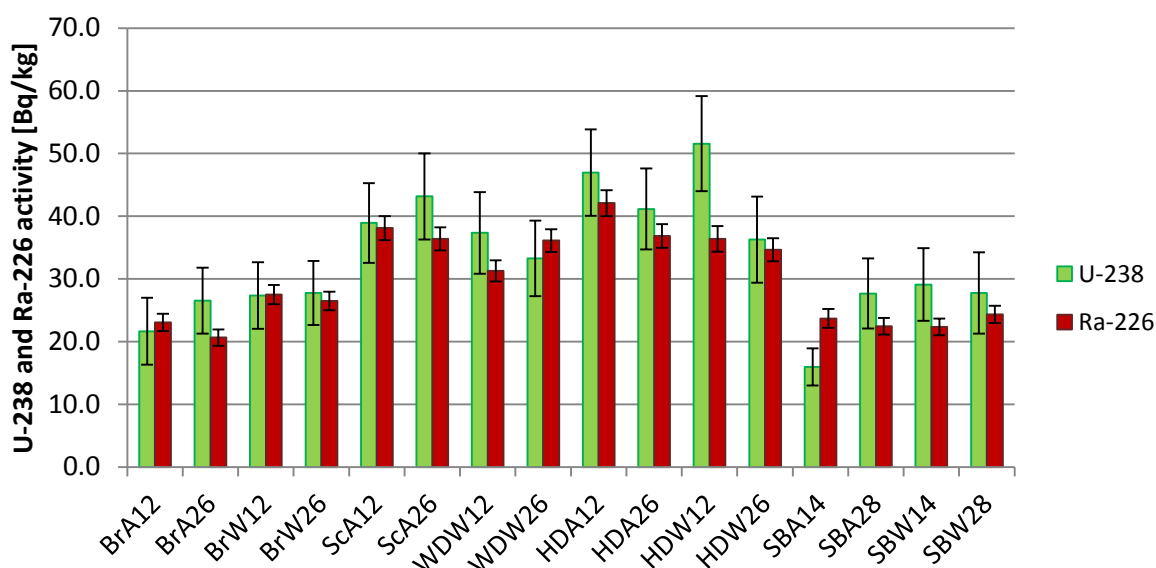
Figure 16 – Specific activities of U-238 and Ra-226 of analyzed soils determined with gamma spectrometry (activities and error bars were determined using the software GammaVision EG&G ORTEC, 1994)

From Figure 16 one can see that in most of the soils, specific activity of uranium is not significantly different from that of radium as the corresponding error bars overlap. U-238 and Ra-226 specific activities are more or less the same in BrA12, BrW12, BrW26, ScA12, ScA12, WDW26, HDW26 and SBW28. So, it is likely that these sites did not encounter considerable uranium input. In Brandis and Schmorren either the amount of fertilizer applied has been low, long time has elapsed since last fertilizer application, or the fertilizer used was low in uranium. Fertilization practices will be discussed nearer in section 5.4.

In fact, activity differences are only significant in HDW12 (U is higher), SBA14 (Ra is higher) and SBW14 (U is higher). From all sampled soils, SBA14 is the only one in which a significant radium excess could be determined. In some of the soils, activity differences are not significant but tendencies towards uranium excess can be seen: BrA26, ScA26, WDW12, HDA12, (HDA26) and SBA28.

The consequence of the observations is that if sufficient amounts of fertilizer with considerably high U concentrations have been applied for several years/decades, it is likely that uranium specific activity in soil increases relative to radium specific activity (for fertilizer and U input, see section 5.4). However, there can be exceptions from that trend (e.g. SBA14 in this study). What adds to the problem of possi-

ble exceptions is that not only in field soils a shift towards U activity might be observed. This shift might also be seen in forest soils as the present analyses showed. So, interpretation of the specific activity ratio of U-238 and Ra-226 becomes more difficult and simply assessing the U-238/Ra-226 specific activity ratio seems not sufficient. (Schlenker, 2002) studied the distribution of radionuclides in forest soils using gamma spectrometry. She studied the correlation between radionuclide contents and parameters characterizing the investigated soils (grain size distribution, mineralogical composition, (organic) carbon content, etc.). She found that in forest soils, uranium, unlike radium, is enriched in the upper soil horizons where organic matter content is highest. The activities of both radionuclides develop towards an equal activity level with increasing depth, i.e. there secular equilibrium is approached. In agreement with other studies she came to the following explanations:

- U forms metal-humic matter complexes with humic acids and fulvic acids.
- If humic matter content is low, uranium binding is dominated by sorption on clay minerals.
- Ra and Th do not form complexes with humic matter and are therefore not enriched in topsoil.
- Ra-226 and Th-232 are preferably sorbed by clay minerals.

(Schlenker, 2002) evaluated the content of organic carbon to be the most decisive factor controlling radionuclide distribution along the soil profile. According to her, time-dependent dislocation within (forest) soils, studied with Pb-210 dating, depends on the following factors:

- Thickness and properties of the humic- and organic matter-bearing horizons
- Factors of the site influencing decomposition and dislocation of organic matter (e.g. acidity of the soil, microbial activity, soil type, constitution of parent material being decomposed to organic matter (type of vegetation)).

If the thickness of the organic matter-bearing layer is great and decomposition and dislocation processes are low, soils can act as long-term storage for radionuclides. In section 5.2 and 5.4 further factors probably impacting U content in soil will be addressed and assumptions will be deepened.

5.1.8   Extractable uranium and binding in soil

In section 5.1.6 it was mentioned that 7 N HNO_3 could only extract between 15 and 40 % of total uranium of the studied soils. For all the other extractants used, recovery was even less. It amounted between 0.02 and 8.6 % of total uranium of the individual soils and between 0.5 and 235 µg/kg dry soil, respectively. In Figure 17, the extracted amounts are given as stapled columns in percent of total uranium (determined with gamma spectrometry) in the respective soils. The diagram also shows total uranium contents in mg/kg as points with the corresponding error bars.
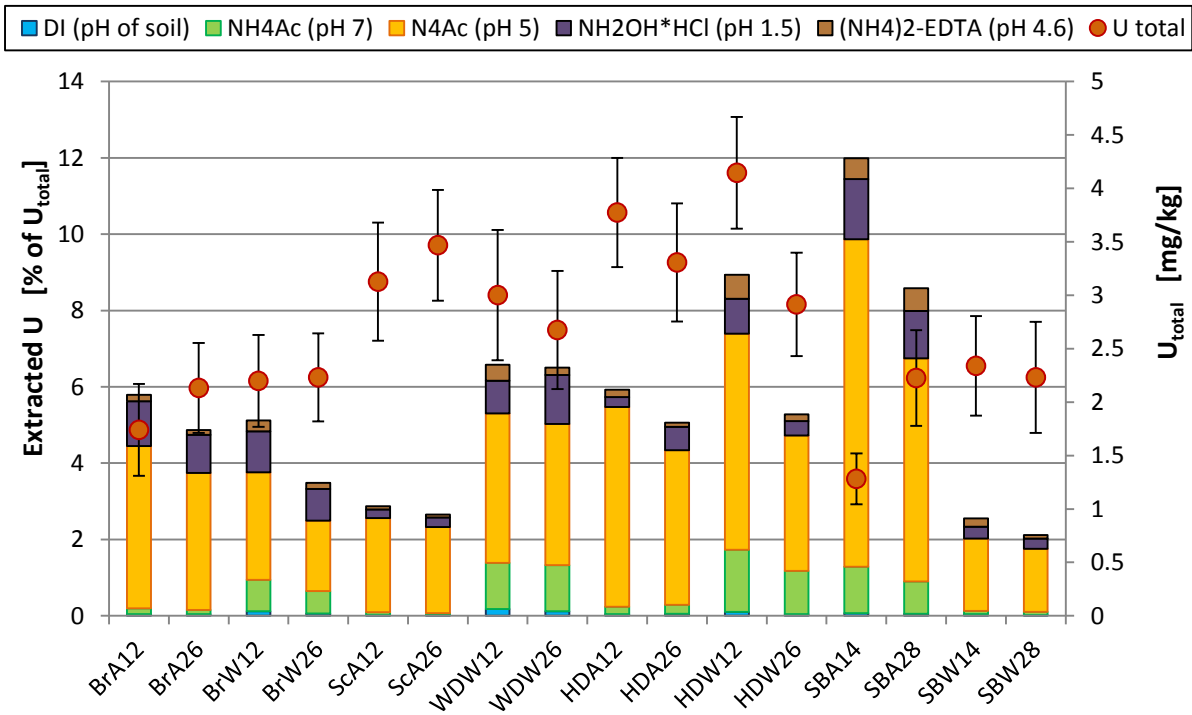
Figure 17 – Uranium extracted during the individual extraction steps in % of total U as stapled bars on the primary y axis together with total uranium contents in mg/kg dry soil with the corresponding error bars (determined with gamma spectrometry) on the secondary y axis.

In Figure 17, it can be seen that there is not always a direct relationship between total U contents and the fraction that is extractable. Greatest amounts of extracted U are not necessarily related to highest U totals. In Sauerbach, field topsoil U total concentration is considerably lower than that in subsoil or forest soil, but extractability is highest. In Schmorren, the trend of U totals is opposite to that of the extractable fraction, i.e. low total contents correspond to great extractability. In Brandis, U totals are essentially the same but extractability varies. For the soils in Hilbersdorf high total U contents correspond to high extractable fractions. The main reason for the differences is probably the parent rock material the soils developed from. The higher the content of silicate minerals and other poorly soluble minerals is, the lower is the extractability.

Table 18 summarizes the results from uranium extraction from the studied field and forest soils. Extractants are sorted by order of increasing uranium release.

Table 18 – Results from uranium extraction experiments (Total uranium was determined with gamma spectrometry. pH, contact time and temperature are given for characterizing the individual extraction steps. Soil properties correlating with the respective steps were determined with Spearman rank correlation analysis as addressed in section 5.2.2. Parameters in brackets indicate that the level of significance of 0.05 was slightly exceeded.)

Extractant	Order of increasing U release	Extracted U [% of U_{total}]	Extracted U [µg/kg]	pH	Contact time [h]	Temperature [°C]	Correlating soil properties (+ … positive; - … negative correlation)
Distilled water	1	0.02-0.2	0.5-5.3	pH of soil itself	2	20	CEC_{eff} (-) pH (-)
0.025M $(NH_4)_2$-EDTA	2	0.07-0.6	2.1-26.2	4.6	1.5	20	TOC (+)
0.04M $NH_2OH*HCl$	3/4	0.2-1.6	7.1-37.8	1.5	16	20	Cd (+)
1M NH_4Ac	3/4	0.08-1.6	1.8-67.5	7	2	20	(CEC_{eff}) (-) pH (-)
1M NH_4Ac	5	1.7-8.6	36.9-235	5	2	20	Pb, Cd, U_{total} (+) (Fe, Cu) (+)
7N HNO_3	6	15.5-39.9	352-1511	Not adjusted → about - 0.8	6	Ca. 80	PO_4, P_2O_5, plant-available P_2O_5 (+) Th, Zn, U_{total} (+) C_{org} (+)
4.55N HNO_3	7	20.5-76.0	480-2106	Not adjusted → about - 0.7	6	Ca. 80	(Al, U_{total}) (-, +)

The amounts of U extracted in the different steps can be divided into four groups depending on the amount of U that has been extracted:

- < 1 % … with DI and EDTA, respectively
- Around 1 % … with $NH_2OH*HCl$ and NH_4Ac (pH 7)
- < 10 % … with NH_4Ac (pH 5)
- > 15 % … with HNO_3

Spearman rank correlation analysis revealed that there is a positive correlation between some of the extraction steps as shown in Table 19.

Table 19 – Results from Spearman rank correlation analysis of the extraction steps (A "+" sign in a green field means positive correlation. No highlighting means no correlation. Significant level is 0.05)

Extraction step	Distilled water	EDTA	NH$_2$OH*HCl	NH$_4$Ac (pH 7)	NH$_4$Ac (pH 5)	HNO$_3$
Distilled water		+	+	+	+	
EDTA	+		+	+	+	
NH$_2$OH*HCl	+	+		+		
NH$_4$Ac (pH 7)	+	+	+		+	
NH$_4$Ac (pH 5)	+	+		+		+
HNO$_3$					+	

From Table 19, from the extracted amounts of U and the correlation results (Table 18) and from the binding forms initially intended to attack by the different extraction steps (Table 16), the following assumptions seem reasonable:

- The distilled water step as well as the ammonium acetate (pH 7) and the EDTA step release the share of U that is relatively easy to mobilize.
- The hydroxylamine hydrochloride step has probably either not been very effective or not specific (for U and/or the oxide-bound fraction) because it released only very little U and did not correlate with anything but the Cd concentration of the soil.
- Greatest amounts of U were released by nitric acid, followed by ammonium acetate (pH 5). They seem to be the most effective extractants used at the boundary conditions of this thesis. Due to the correlation with other metal concentrations and the phosphorus content of soil, it is likely that these extraction steps attack the more strongly bound uranium partly or to a great share stemming from phosphate fertilizers and maybe associated to or bound in phosphate minerals or amorphous precipitates in soils.

Looking back to Table 18, it is surprising that the individual extractants acted as incomplete as they did. Even nitric acid, a very strong acid, did not extract more than 76 or 40 % of total U. Similar results were obtained in (Qiao et al., 2012) the publication most of the extraction procedure was inspired by. The authors did sequential extractions with reference soils and sediments. Not only the total extracted amounts, but also the U amounts extracted by the individual extractants were in most cases similar to the results of the present work. From an IAEA reference soil, the authors extracted 46 % of total U; and from an NIST sediment 52 % could be extracted. The incomplete release of U was ascribed to binding of U in the crystal lattice of minerals or the formation of inert and/or refractory compounds.

It would be good to compare the obtained extraction results with those of other studies. However, the comparison of different studies is possible only in a very limited way (Zewainy, 2008). That is because of four main reasons:

- In the present work, extractions were not done in a sequential way always using the same soil sample for each step.
- Extraction results are operationally defined as already emphasized in chapter 4.3.8, i.e. the results depend on the properties and the composition of the analyzed soils, the extractants used, on the methodology and also on the boundary conditions.
- Depending on the source of uranium, the time since application and the conditions during application, it will be more or less available.
- The composition of the soil solution (especially the concentration of phosphate, carbonate, calcium, etc. and properties like pH and the redox potential) will influence processes like ion exchange, complexation, precipitation, mineral formation and others.

Therefore, even if exactly the same extraction procedure is used, results can differ significantly. In the following, one example (the work by Huhle, 2007) is given, where similarly to this thesis, the U content of a field site is compared with that of a forest site. Topsoil contents from 20 cm depth are compared with subsoil contents from 50 cm depth. As opposed to this work, no U totals were determined by (Huhle, 2007). In her work, extracted U was expressed as percentage of the U released by aqua regia digestion. To make the numerical results more comparable, as far as this is possible, the amounts of U extracted in the different steps of the present thesis were calculated as percentage of nitric acid-extracted U. In (Huhle, 2007), extractions were done sequentially; in the present thesis as single steps. Also the extractants used were different. For making comparisons possible, the steps shown in Table 20 were set to be more or less equal.

Table 20 – Overview of the extraction steps in (Huhle, 2007) and the present thesis used for results comparison.

Step number	(Huhle, 2007)	Present work
1	Ammonium nitrate (soluble U)	Distilled water
2	Ammonium acetate (readily mobilizable fraction)	Ammonium acetate (pH 7)
3	EDTA (organically bound U)	EDTA
4	Ammonium oxalate buffer (occluded to crystalline iron oxides fraction)	$NH_2OH*HCl$
5	Aqua regia	Nitric acid

The results from the aqua regia and nitric acid step, respectively, are shown in Table 21. For (Huhle, 2007), only one value is given for each soil; for this work, the ranges of the analyzed soils are shown.

Table 21 – U extracted from field and forest soils with nitric acid (present thesis) and aqua regia (Huhle, 2007), respectively, in mg/kg

Analyzed soil	(Huhle, 2007)	Present work
Field topsoil (20 cm)	0.96	0.47-1.53
Field subsoil (50 cm)	0.58	0.49-1.04
Forest topsoil (12 or 14 cm)	0.53	0.36-1.51
Forest subsoil (26 or 28 cm)	0.35	0.35-1.04

So, the acid-extractable amounts of U are in a similar range in the soils of both works with the trend to lower contents in (Huhle, 2007) as compared to the present thesis. Table 22 shows the results of the mobilized U using different extractants of both works. The comparison of the extracted amounts of U is based on Table 20.

Table 22 – Comparison of the extraction results of (Huhle, 2007) with those of the present thesis in % of acid-extractable U (Topsoil in Huhle, 2007 means 20 cm depth; subsoil means 50 cm depth – as compared to 12 or 14 and 26 or 28 cm depth in the present thesis. Step 4 in the forest subsoil was identified as outlier by Huhle, 2007 and is therefore not considered here; n.d. means not detectable. The numerical values of this thesis are given in *EXCEL 6* in the digital appendix.)

Extraction step	Analyzed soil	Depth	Extracted U in (Huhle, 2007) [% of U_{total}]	Extracted U in the present thesis [% of U_{total}]
1	Field	Topsoil	0	0.08-0.17
		Subsoil	0	0.10-2.14
	Forest	Topsoil	0	0.27-0.91
		Subsoil	0	0.14-0.49
2	Field	Topsoil	10	0.36-3.06
		Subsoil	8	0.28-3.76
	Forest	Topsoil	2	0.52-6.16
		Subsoil	n.d.	0.52-5.03
3	Field	Topsoil	2	0.37-1.37
		Subsoil	3	0.37-2.66
	Forest	Topsoil	2	1.38-2.16
		Subsoil	3	0.50-0.94
4	Field	Topsoil	55	0.67-4.20
		Subsoil	74	1.36-5.48
	Forest	Topsoil	55	2.02-5.31
		Subsoil	outlier	1.07-5.33

From Table 22 it can be seen that some of the extractants in (Huhle, 2007) released more U and some of them less than in the present work. The orders of magnitude, at least, in step 1 to 3 agreed in both works. In step 5, however, (Huhle, 2007) extracted more than 10-times more U. So, the extractant used there was much more efficient in mobilizing U than the one used in this work. It is surprising that in (Huhle, 2007), not any U could be extracted in the first extraction step, because in the present work, even distilled water released some U. The reason for that is not clear. It might be a matter of detection limit of the analytical method used. What both works have in common is that sometimes, extracted amounts were higher in subsoil and sometimes in topsoil even if acid-extractable quantities were mostly higher (and sometimes about equal or slightly smaller) in topsoil than in subsoil. That might be a combined effect of the U content in parent rock, external U input, physical and chemical soil properties, microbial activities, etc. So, even if there were numerous similarities in both works, both in methodology as well as in the results, they are not directly comparable.

In the studied soils, a negligible fraction of below 1 % of U in soil was determined to be **water**-soluble. As correlation analysis revealed, this fraction increases with decreasing pH of the soil and with decreasing cation exchange capacity (see Table 18). Among the reasons for the correlation with pH is probably pH-dependent speciation and competition by ions being released to solution or being sorbed to soil. The CEC controls how much U can be bound to the soil by cation exchange. For some of the soil sampling sites, CEC is higher in the field and for some in the forest (see Figure 14). The water-soluble fraction follows that trend. In Brandis, in Schmorren and in Hilbersdorf (there, only in

topsoil), the water-soluble amount in forest soils is 1.5- to 10.1-times that of field soils. In Sauerbach and in Hilbersdorf subsoil, it is the other way round. There, 10 to 118 % more U was extracted from field soils as compared to forest soils.

The amounts of U extracted with **diammonium EDTA** are similarly small, i.e. below 1 %, as those of the distilled water step. This is somewhat surprising as EDTA is known as a very strong complexing agent commonly used for extracting organically-bound metals. The positive correlation with the total organic matter content mentioned in Table 18 supports that. As U has a great tendency to binding to organic matter (section 2.3) one would expect greater extracted amounts. (Wang and Yu, 1992) did U extraction experiments with DTPA (diethylene triamine pentaacetic acid), which is chemically similar to EDTA. The authors state that complexes with UO_2^{2+}, the U species dominant under oxidizing conditions, are not stable due to the geometry and the low effective metal charge of the uranyl cation. They conclude that these are the reasons for the non-effective extraction, which in their tests at least accounted for 9-13 % of total U in the studied radionuclide-contaminated soils. The results of the present work cannot be compared to those of (Qiao et al., 2012), because they used a different, a two-step extraction, first H_2O_2 with HNO_3 at pH 2 and 80°C, followed by extraction with ammonium acetate in nitric acid at 20°C. Like for the distilled water-extractable fraction, in Brandis, in Schmorren and in Hilbersdorf, also EDTA-extractable fraction is higher in forest soils than in field soils (21 to 426 %) – Sauerbach again being the exception from this trend (U extraction 144 to 551 % higher in field soil).

Even if pH with 1.5 was very low and the contact time of 6 hours was rather long, **NH$_2$OH*HCl** did not extract more than about 1 % of total U. (Qiao et al., 2012) extracted 4-16 % of total U from the reference soil and sediment, respectively even if they did a sequential extraction and 3 steps already passed before that of Fe/Mn oxides. Nothing else than the cadmium concentration in the studied soils (positively) correlated with the U extracted in this step. So, under the present soil conditions, NH$_2$OH*HCl was neither effective ($\Leftrightarrow$ extracted amount of U) nor specific ($\Leftrightarrow$ correlation results). Originally, this extractant was intended to specifically release the fraction of U bound to iron and manganese oxides. This fraction, besides the oxides- and the clay mineral-bound fractions, is commonly one of the greatest in soils (Scheffer et al., 2010). So, either in the studied soils, not much U was actually bound to Fe and Mn oxides or the extractant has not been suitable. For answering this question, RFA analysis or other structure-analytical methods would be needed. Even if the fraction is low, differences can be seen between field and forest soils. In Brandis, in Sauerbach and in the subsoil of Hilbersdorf, the extractable amount of U is 9 to 406 % higher in field soil than in forest soil. In Schmorren and in Hilbersdorf topsoil, it is opposite (factor 3.4 to 5.0 between field and forest).

For the effectiveness of **ammonium acetate**, pH seems to be a decisive parameter. While at **pH 7**, at the maximum only 1.6 % of total U got extracted; at **pH 5**, it were 1.7-8.6 % at, apart from this, same conditions. This can be explained by the findings by (Wang and Yu, 1992): when solution pH is high, U tends to form complexes with carbonate ions like $(UO_2(CO_3)_3)^{4-}$. These complexes seem to resist complexation with acetate. So, maybe this effect can already be seen at pH 7. Looking back to Table 16, one can see that the ammonium acetate at pH 7 was supposed to release the exchangeable/ physically sorbed species, whereas at pH 5 it should attack the "carbonate-bound" U. Correlation analysis gave different results for the pH 7 extraction as compared to that at pH 5 (see Table 18). At pH 7, released U correlates negatively with the cation exchange capacity and pH – like the distilled water step. This suggests that ammonium acetate at pH 7 attacks only the fairly loosely bound uranium. At pH 5, extracted U positively correlates with the concentrations of different metals, namely Pb, Cd, U$_{total}$ (from gamma spectrometry), Fe and Cu. That shows that the extractant did not specifically act on uranium. In some of the soils (especially in Hilbersdorf), metal concentrations were comparatively high. It is likely that (a share of each of) these metals reacted with ammonium acetate resulting in lower U

recoveries. The fact that the extracted fraction of total U of the pH 5 step does not correlate with the carbonate content of the soil indicates that this step is not specific for releasing carbonate-bound U. Concerning the extracted amounts from forest and from field soils, results look different – depending on pH. At pH 7, it is the same as in the EDTA step: greater recoveries in forest soils as compared to field soils (factor 4.7 to 22.7 between forest and field) and opposite trends for Sauerbach (factor 10.3 to 15.1 between forest and field soil). At pH 5, however, results show the same trend as for the hydroxylamine hydrochloride-extractable fraction. In Brandis, in Sauerbach and in the subsoil of Hilbersdorf, the extractable amount of U is 14 to 353 % higher in field soil than in forest soil. In Schmorren and in Hilbersdorf (topsoil), it is the other way round (8 to 65 % higher U extraction in forest soil as compared to field soil).

As expected, greatest shares of U were extracted using **nitric acid** (see section 5.1.6). What made this step effective was probably the combination of an aggressive, oxidizing strong acid with a rather long contact time of 6 hours and high temperatures of about 80°C. As the first attempt using 4.55 N nitric acid had not been reproducible (temperature and contact time not equal, one of glasses was probably U-contaminated leading to unrealistically high U recoveries), it is not considered for interpretation. Recoveries using 7 N HNO_3 were far from 100 % recovery, ranging from 15.4 to 39.9 % of total U.

Now, after the different extraction steps have been discussed, the individual sites will be looked at in greater detail. What is of special interest in the following is the difference between the extracted amounts from the more and from the less available fractions of field soils as compared to forest soils. The numerical results used as a basis for the interpretations can be found in *EXCEL 6* in the digital appendix. Figure 18 is a similar plot like that in Figure 17 with the difference that not relative U extraction in % of U_{total} is depicted, but absolute U extraction in µg/kg dry soil together with U totals. It will make it easier to follow the site-wise statements in the following.
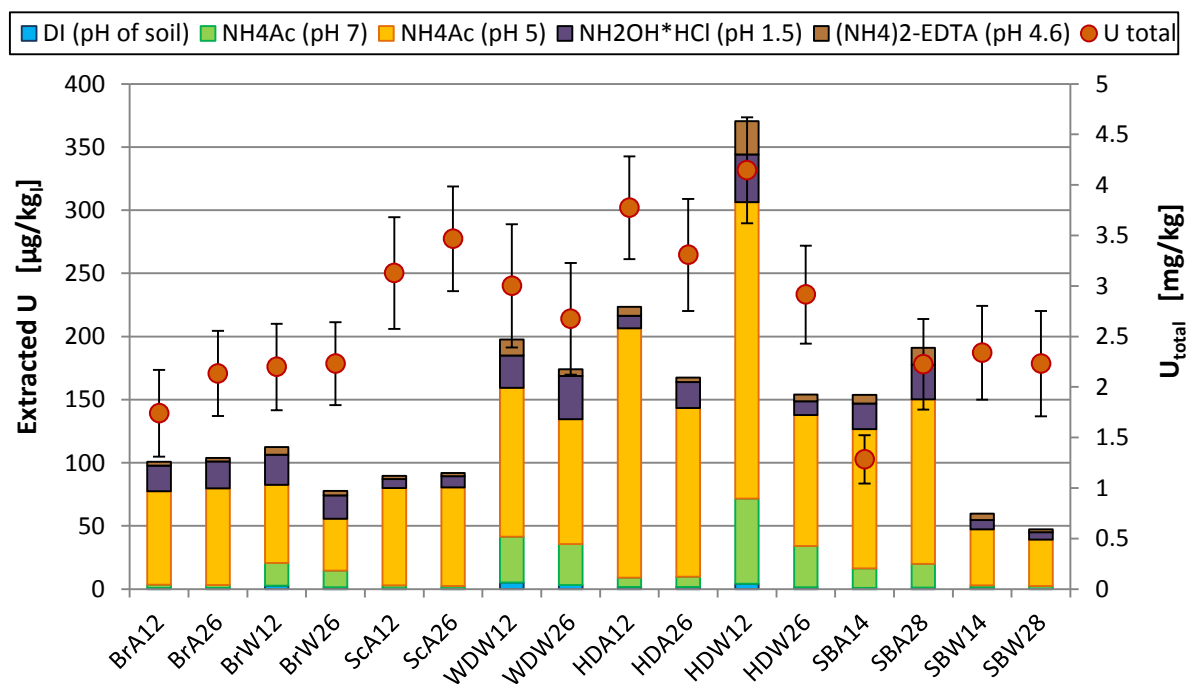
Figure 18 – Uranium extracted during the individual extraction steps in µg/kg dry soil as stapled bars together with total uranium contents in mg/kg dry soil with the corresponding error bars, determined with gamma spectrometry

Brandis

Total U contents are similar (see section 5.1.6). However, U seems to be more available in forest soils as compared to the corresponding field soils there. Recoveries in the distilled water-, ammonium acetate (pH 7)- and EDTA extraction steps were higher in forest soils than in field soils. Recoveries in the ammonium acetate (pH 5)-, hydroxylamine hydrochloride- and 7 N nitric acid steps were higher for forest soils than for field soils.

Schmorren/Wermsdorf

Total U contents in the field soil samples are higher than or similar to the corresponding forest soil samples (see section 5.1.6). U extraction lead to higher recoveries for forest soils as compared to field soils with only one exception: the 7 N HNO_3 step. There, 13 % more U was extracted from field topsoil as compared to forest topsoil – at similar U totals. So, at the Schmorren/Wermsdorf site, U is also more available in forest than in field soil.

Hilbersdorf

U totals of the field and forest soils in Hilbersdorf are in a similar range when the error of the analytical results is taken into account (see section 5.1.6). Only forest topsoil U content is significantly higher than forest subsoil content. Forest (top)soil U seems to be more available than U in field soil because relative U extraction is higher for all extraction steps except that of nitric acid. In subsoil differences in extracted U relative to total U are not so pronounced. In some extraction steps, more U was extracted in forest soils (ammonium acetate (pH 7), EDTA, nitric acid step) and in others, extraction recoveries were higher in field soils (distilled water, ammonium acetate (pH 5), $NH_2OH*HCl$ step). That means that availability is not significantly different. The reason for some extractants mobilizing more U from the one soil than from the other is probably a result of the soil properties, the specifity and power of the extractant and the binding form of U in the soil.

Sauerbach

U totals are nearly the same in all Sauerbach soils except for the field topsoil (see section 5.1.6). There, the U content is significantly lower. However, in contrast to all the other soil sampling sites, in Sauerbach relative as well as absolute U extraction in all extraction steps is (much) higher for field soil than for forest soil. Recoveries from field soils are between 1.4- and 15.1-times that of forest soils depending on the extraction step. That means that U in field soil can be mobilized much more easily than U from forest soil in Hilbersdorf. The reason for that probably lies in differing properties of the field and forest soils in Sauerbach and different binding forms of U. Looking back into the soil characteristics described in the previous chapters, the following differences can be seen: Clay and silt contents and soil pH are higher in field soil (see Figure 10) and total inorganic carbon content is about 12-times higher in field soil than in forest soil (see Figure 13). So it is likely that these properties have an impact on the availability and extractability of U by complex formation, sorption processes or others. As addressed earlier in this chapter, another possible cause could be the source of U (geogenic from indigenous rock or anthropogenic by fertilization) and the (short) time that elapsed since (last) fertilizer application. These factors probably also have an impact on the binding form of U in soil.

Summarizing the extraction results one might come to the conclusion that the hazard of U release from soil is very low. However, in a second set of extractions the fraction of total U being released was much higher. The ten field top- and subsoil samples from Brandis that had been flown through in the experiments described in chapter 4.3.1 were used for two different extractions using:

- 1 M Ammonium acetate (pH 5)
- Concentrated sodium hypo chlorite (NaOCl) solution, diluted 1:10 (pH 11.5, not adjusted)

The experimental procedure was the same as outlined in section 4.3.8. In addition to ammonium acetate, which had already been used for the first set of extractions, NaOCl was selected due to its strong oxidizing potential. That was done because during flow-through experiments, no U breakthrough was reached and this was assumed to possibly have been caused by reduction of U(VI) to U(IV) with subsequent precipitation.

Table 23 summarizes the relative U extraction using NH_4Ac. In the first set of extractions (i.e. without additional U application), extracted U is expressed as percentage of total U contents. These were determined using low-level gamma spectrometry. For the Brandis flow-through samples, the additional application of U was calculated by multiplying the U load [µg/L] with flow-through [mL/min] and the duration of the experiments [min] and referring it to the mass of the samples (see *EXCEL 6* in the digital appendix). It was calculated that 1.76 mg/kg were applied on the soils assuming that loss by flow-through was negligible with less than 1 % of the applied concentration (see chapter 5.8).

Table 23 – U extracted from Brandis field soil using 1 M NH_4Ac (pH 5) in % of U_{total} (from gamma spectrometry) without additional U input and with additional U input from U-bearing solutions during flow-through experiments (In the case of the flow-through samples, U_{total} refers to the Utotal from the Brandis field samples that were not used for flow-through plus the amount of U (1.76 mg/kg) additionally applied during flow-through experiments. For Brandis subsoil without additionally applied U, extraction was not repeated. Therefore, no means could be calculated.)

Extracted U [% of U_{total}]	Without additional U application	Flow-through samples, on which U had been applied
Topsoil		
Minimum	4.04	19.05
Mean	4.25	21.21
Maximum	4.47	23.25
Standard deviation	0.30	1.67
Subsoil		
Minimum	-	17.64
Mean	3.59	20.98
Maximum	-	24.90
Standard deviation	-	2.58

From Table 23 one can see that relative U extraction was about 5- to 6-times higher for the soils from flow-through experiments as compared to those without additional U application. That means that U was more readily available when U had "freshly" been applied.

For interpretation, the following remarks are central. In Brandis, U contents in field and forest soils are basically the same (see section 5.1.6). Greater U input by phosphate fertilization took place in the 1980s; in 2000 and in 2008, only minor amounts of fertilizer had been applied. So, the time since last fertilization is fairly long and recently applied amounts were not very high. According to (Taylor and Kim, 2008), the binding form of U in soil changes over time in such a way that it becomes less available; a transformation from the more available fractions (exchangeable and carbonate-bound in their

case) to the more resistant fractions (bound to/in oxides, organics and non-silicate minerals) takes place. In their study, about one month after U application, the proportion of the more available fractions had returned to the level of the non-treated soil. The proportion of the less available U had doubled or even tripled. (Cheng et al., 2004) highlight that first U gets sorbed to solid surfaces and that it takes more time for (co)precipitates and minerals to form. (Taylor and Kim, 2008) discuss two possible explanations for the shift towards less available fractions:

- Over time more U relocated from the more available fractions to being bound by humic materials, humic-iron, clay-humic and humic-silicate complexes.
- The greatest share of U is and remains complexed by the organic fraction, but the binding strength to the organic matter increases with time.

Several years elapsed since last application of greater amounts of U to the studied field soils. Therefore, it is likely that since then the binding strength of U increased and the availability decreased. So, it is not surprising that U recoveries were small during U extraction from these soils.

Flow-through experiments were run continuously. They were only interrupted for a short time for activities like filling up the storage solution bottles. That means that the soils in the liners were permanently percolated by the flow-through solutions supplying "fresh" uranium and the other components of the solutions (see the table above Figure 19). The field soils, in contrast to that, encountered only pulse-wise U input by phosphate fertilizer application. The permanent supply of "fresh" flow-through solution to the liners and the relatively short duration of the experiments (107 days in total) might have been one of the reasons that prevented stable mineral phases from being formed – at least to such an extent as this maybe was the case for the field soils. And therefore, U in the flow-through soils was more fairly available, i.e. less strongly bound and extraction recoveries using ammonium acetate were 5- to 6-times higher than those of the field soil samples.

As already mentioned, in addition to ammonium acetate, sodium hypo chlorite, NaOCl, was one of the extractants used during extraction of U from the soils of the flow-through cells. Figure 19 illustrates how much of total uranium was extracted from the Brandis flow-through soil samples using ammonium acetate and sodium hypo chlorite, respectively. Above the plot, the composition of the solutions used for flow-through is given in a yellow table.

Bottle ID	NaHCO$_3$ [mM]	UO$_2$(NO$_3$)$_2$ [μM]	UO$_2$(NO$_3$)$_2$ [μg/L]	H$_3$PO$_4$ as P [mM]	H$_3$PO$_4$ as P [mg/L]	H$_3$PO$_4$ as PO$_4$ [mg/L]	Ca(NO$_3$)$_2$ [mM]
I	1	0.178	40				
II	1	0.168	40	1.421	44	135	
III	1	0.168	40	1.421	44	135	1
IV	1	0.168	40	0.142	4.4	13.5	
V	1	0.168	40	0.142	4.4	13.5	1

Figure 19 – Uranium extracted from Brandis flow-through samples with ammonium acetate (NH$_4$Ac) at pH 5 and with sodium hypo chlorite (NaOCl) at pH 11.5 in % of total U (determined with gamma spectrometry).

What can be seen is that U extraction was 50-90 % higher when NaOCl was used as extractant as compared to when NH$_4$Ac was used. That underlines that sodium hypo chlorite is a much stronger extractant due to its oxidizing capabilities. However, also differences between top- and subsoil were greater for NaOCl as compared to NH$_4$Ac. For checking the reproducibility of the extractions, liner # 3 and # 9 (belonging to solution # III and # IV, respectively) were analyzed in duplicate. For ammonium acetate, differences between the duplicates were 0.16 % and 0.72 % for # 3 and # 9. For sodium hypochlorite, differences were 1.53 % and 1.07 %. As these differences are rather low, they are not further considered and means are used in Figure 19.

However, the systematic difference between top-and subsoil for NaOCl extraction seems to be significant. Looking back into the previous chapters, in which the properties of the studied soils were described, one will figure out that Brandis top- and subsoil differ in nothing but the total organic carbon content. So, the EDTA step, which was supposed to release the organically-bound U, should have extracted more in topsoil than in subsoil (see Figure 17). As this step had not been effective, no difference between topsoil and subsoil can be seen. However, during extraction with ammonium acetate at pH 5, U release was about 20 % higher in topsoil than in subsoil supporting the observed trend in Figure 19. It is not clear why this trend cannot be seen for all soils treated with NH$_4$Ac in Figure 19. It might be a result of the different composition of the flow-through solutions as well as the inhomogeneity of the soils.

5.2 Statistical analysis of present soil properties

5.2.1 Normal-distribution

From all soil parameters, the following are normal-distributed:

- CEC, pH, TOC
- Parameters from grain size distribution analysis (percentage of clay, silt and sand mass of fine material's mass (< 2 mm), percentage of clay and silt of total soil's mass.
- All U concentration results from uranium extraction from soils

The following parameters are not normal-distributed:

- The percentage of fine material (< 2 mm) of total soil's mass
- TIC
- All parameters received from the institutions responsible for the test sites (pH, phosphate content (% of dry soil), P_2O_5 (mg/100g), extractable P_2O_5 (mg/100g), Corg (% of dry soil), Al, Cd, Cu, Fe, Mn, Pb, Th, U, Zn (all in mg/kg))

As some parameters are not normal-distributed, non-parametric tests had to be used for statistical analyses.

5.2.2 Spearman rank correlation analysis

All results from Spearman rank correlation analysis can be found in the appendix. The most relevant ones for understanding the behavior of U in the subsurface are listed in Table 24. They are referred to and used for interpretation in several sections of chapter 5.

Table 24 – Results from Spearman rank correlation analysis of soil properties determined in own analyses or obtained from the authorities responsible for the soil sampling sites (The level of significance was defined as 0.05.)

Correlation between…	Correlating parameters	Positive	Negative
Uranium concentration	Nitric acid-extractable uranium	X	
	pH results from responsible institutions	X	
	Phosphorus content (as phosphate, P_2O_5 and plant-available P_2O_5)	X	
	Organic matter content (Corg)	X	
	Metal concentrations (Cd, Cu, Fe, Mn, Pb, Th, Zn)	X	
Phosphate concentration	Nitric acid-extractable uranium	X	
	pH results from responsible institutions, Corg	X	
	P_2O_5 and available P_2O_5 content	X	
	Metal concentrations (Cd, Cu, Fe, Mn, Pb, Th, U, Zn)	X	
P_2O_5 content	CEC, pH, TIC	X	
	pH results from responsible institutions, Corg	X	
	Phosphate and available P_2O_5 content	X	
	Metal concentrations (Cd, Cu, Fe, Mn, Pb, Th, U, Zn)	X	
Available P_2O_5 content	Nitric acid-extractable uranium	X	
	pH results from responsible institutions, Corg	X	
	Phosphate and P_2O_5 content	X	
	Metal concentrations (Cd, Cu, Fe, Mn, Pb, Th, U, Zn)	X	
Metal concentrations (Cd, Cu, Fe, Mn, Pb, Th, U, Zn)	With each other	X	
U concentration extracted with 7 N nitric acid	U concentration extracted with ammonium acetate (pH 5)	X	
	Phosphate and extractable P_2O_5 content	X	
	U concentration	X	
	Organic matter content (Corg)	X	
	Metal concentrations (Th, Zn)	X	
U concentration extracted with EDTA	TOC	X	
	U concentration released during extraction using distilled water, ammonium acetate at pH 7 and 5, respectively	X	
U concentration extracted with hydroxylamine hydro-chloride (NH_2OHHCl)	U concentration released during extraction using distilled water, ammonium acetate at pH 7, and EDTA	X	
	Cd concentration	X	
U concentration extracted with ammonium acetate (pH 5)	U concentration released during extraction using distilled water, ammonium acetate at pH 7, EDTA, and 7 N nitric acid	X	

Correlation between…	Correlating parameters	Positive	Negative
U concentration extracted with ammonium acetate (pH 7)	pH		X
	U concentration released during extraction using distilled water, ammonium acetate at pH 7 and 5, respectively, and hydroxylamine hydrochloride	X	
U concentration extracted with distilled water	CEC, pH		X
	U concentration released during extraction using ammonium acetate at pH 7 and 5, respectively, hydroxylamine hydrochloride, and EDTA	X	
U concentration determined with low-level gamma spectrometry	U concentration released during extraction using ammonium acetate at pH 5, 7 N nitric acid	X	
	Phosphate and extractable P_2O_5 content	X	
	Organic matter content (Corg)	X	
	Metal concentrations (Th, U, Zn)	X	

5.2.3 K-means cluster analysis

A total number of 5 clusters was the lowest number optimal to represent the parameters to be grouped. At a level of significance of < 0.05, this grouping was significant for four parameters:

- TOC
- The percentage of fine soil material (< 2 mm) of the total dry soil
- The extracted uranium concentration (in µg/kg dry soil) from the total dry soil from the ammonium acetate (pH 5) and from the 7-molar nitric acid extraction step.

That means, the classification into the five groups was ruled by the available and the acid-soluble fraction of uranium in soil, and by two parameters obviously controlling the retention of uranium in soils: the organic matter content and the content of fine soil material (< 2 mm).

Cluster membership:

1   ScA12, ScA26, WDW26
2   BrW26, SBW14, SBW28
3   HDA12, HDW12
4   BrA12, BrW12, WDW12, SBA14, SBA28
5   BrA26, HDA26, HDW26

Some of the clusters are formed by or dominated by one site (e.g. # 3 by Hilbersdorf); others contain only one sampling depth (e.g. # 5 with 26 cm). The third group consists of only one type of land use (# 2 - forest) and the last type of clusters is a mix of different depths, sites and land uses (# 4). So, there are several similarities between the soil sampling sites but also many differences.

However, when critically examining the meaningfulness of the cluster analysis, one will first come to the conclusion that the soils have greater differences than similarities. From the 16 parameters assessed during cluster analysis, only 4 were relevant for forming the clusters. Soils are complex, dynamic, multi-parameter systems. That is why it is difficult to compare them. Yet, the four parameters used for cluster forming seem to be suitable and relevant for comparisons.

5.3   Quality of water sample analyses

Ion balances of the percolation water samples of the different field soils were in the following ranges:

- Brandis   0.4 … 3.8 %
- Hilbersdorf   3.6 %
- Sauerbach   5.3 … 6.3 %

That means, for Brandis and Hilbersdorf the value is below ±5 % as given as a requirement for analytical results of sufficient quality. In Sauerbach, it is a bit higher than 5 %, which is not good but still acceptable. In Brandis, however, there was one sample for which the analytical error was 49.7 %. This error was probably a result of technical problems during IC analysis. Due to the great error, it was excluded from interpretation.

The difference between EC calculated with PHREEQC (database phreeqc.dat) and the measured EC expressed as percentage of the measured EC as explained in section 4.6 is as follows:

- Brandis   Measured EC 5.1 to 7.9 % higher than calculated EC
- Hilbersdorf   Measured EC 0.9 % higher than calculated EC
- Sauerbach   Measured EC 30.1 to 48.0 % smaller than calculated EC
                                           Measured EC 21.4 % higher to 40.2 % smaller than calculated EC

That means, only for the one sample in Hilbersdorf the requirement of a relative difference < 5 % is met. For the Brandis water samples, it is elevated by a few %, i.e. the measured EC is higher than the calculated. That might be because the database phreeqc.dat does not contain all elements that are present in considerable concentrations in the samples. And also not the complete analyses were used as input for modeling but only those of highest concentration and probable relevance for U speciation.

For the four Sauerbach samples analyzed, two error ranges are given because anion IC analysis had been repeated, first without dilution; then with 1:5 dilution. In the first modeling attempt, Ca analytical results had been used from IC analysis; in the second attempt from ICP-MS analysis. However, in either case the calculated conductivity was higher than the measured one. Only for one sample in the second attempt it was the other way round. There the nitrate concentration had been more than two-times lower than that of the other samples, which was probably not correct. However, the charge balance is more or less acceptable. That means that in Sauerbach some cat- and anions were probably highly overestimated during analysis.

The ion balance of the flow-through samples was 0 ± 5 % in most cases. It was only slightly higher for few samples. Very high errors of up to 10 % were the exception. In case of elevated errors, possible causes were searched. As none of the results deviated considerably from the other ones of the respective flow-through cell, they were evaluated as plausible and used for interpretation.

The electrical conductivity of the samples from the flow-through experiments was not measured and could therefore not be compared with the one calculated with PHREEQC.

5.4   Percolation water composition

Percolation water samples were taken at all field soil sampling sites except for that in Schmorren (see chapter 4.1.3). In Schmorren, throughout the entire period of working on the present thesis, for analysis there was not enough water available. It was not even possible to use water analytical results from the LfULG for speciation modeling with PHREEQC, because none of the datasets after the only fertilizer application in 2009 was complete. Some of the constituents important for the present work were not included (phosphate, hydrogen carbonate) or were below a rather poor detection limit (e.g. iron with concentrations always, i.e. also before 2009 below 0.1 mg/L). Therefore, Schmorren site was not modeled with PHREEQC. The species distribution of U and P of all other field sites is shown in Figure 20 and Figure 21, respectively. For generating the stapled columns, all P and U species with concentrations higher than 10^{-11} mol/L and 10^{-14} mol/L, respectively, were considered. In Figure 21, the y axis starts at 75 % to make the different lower-concentration species better visible.
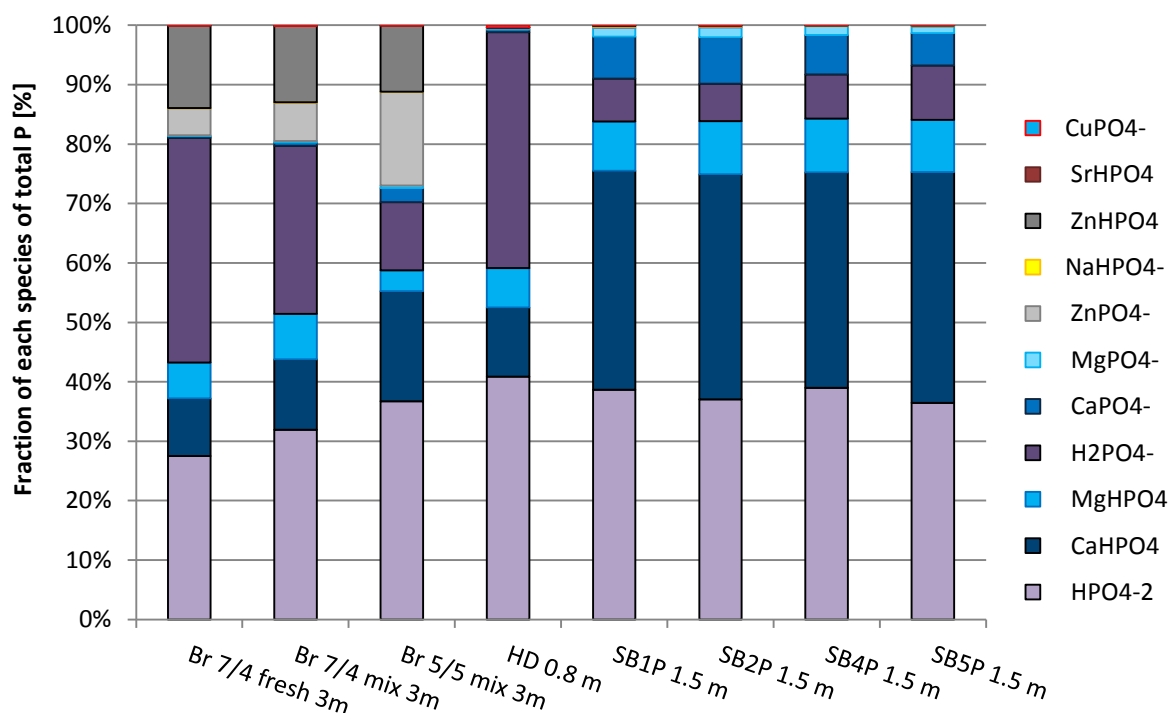
Figure 20 – Phosphorus species distribution in the percolation water samples from the sampling sites in Brandis, Hilbersdorf and Sauerbach (For modeling the software PHREEQC, database: llnl.dat, was used. Br stands for Brandis; the number behind represents the lysimeter. HD means Hilbersdorf and SB Sauerbach. The number behind SB stands for the lysimeter. Sampling depths are given in meters after the sample ID.)

At all sites, P predominantly occurs as free deprotonated phosphoric acid, i.e. as HPO_4^{2-} and $H_2PO_4^-$, or as metal-phosphate- or metal-hydrogenphosphate complexes. In the different Sauerbach lysimeters, P species distribution is nearly the same: the two most dominant species are HPO_4^{2-} and $CaHPO_4$, each with about 35 to 40 % of the total molarity of P. The second most species there are $MgHPO_4$, $H_2PO_4^-$ and $CaPO_4^-$ at about 5 to 10 % each. $MgPO_4^-$ accounts for about 2 %. The other species make up less than 1 %. The reason for the Ca- and Mg-containing species to occur at considerably higher concentrations as compared to the other sites can be seen in the concentrations of these ions. In Sauerbach, P-, Ca-, and Mg concentrations are 2- to 4-times higher.

In Hilbersdorf, in addition to HPO_4^{2-}, $H_2PO_4^-$ is the second dominant species, both with about 40 % of total P. $CaHPO_4$ makes up about 11 % and $MgHPO_4$ about 7 % of total P. The negatively-charged species (about 80 % of total P) will probably be bound by surface complexation to surfaces like iron or manganese oxides and hydroxides. The uncharged species (about 18 % of total P) will probably be very mobile in water without interacting or only interacting by inner-sphere surface complexation.

In the Brandis percolation water zinc concentrations, probably stemming from corrosion of the lysimeters' casings, are extremely high with 18 to 41 mg/L. Therefore, in these waters, two additional Zn complexes occur with about 5 to 15 % of total P. The interactions with charged and uncharged surfaces are similar to those discussed for the other sites.
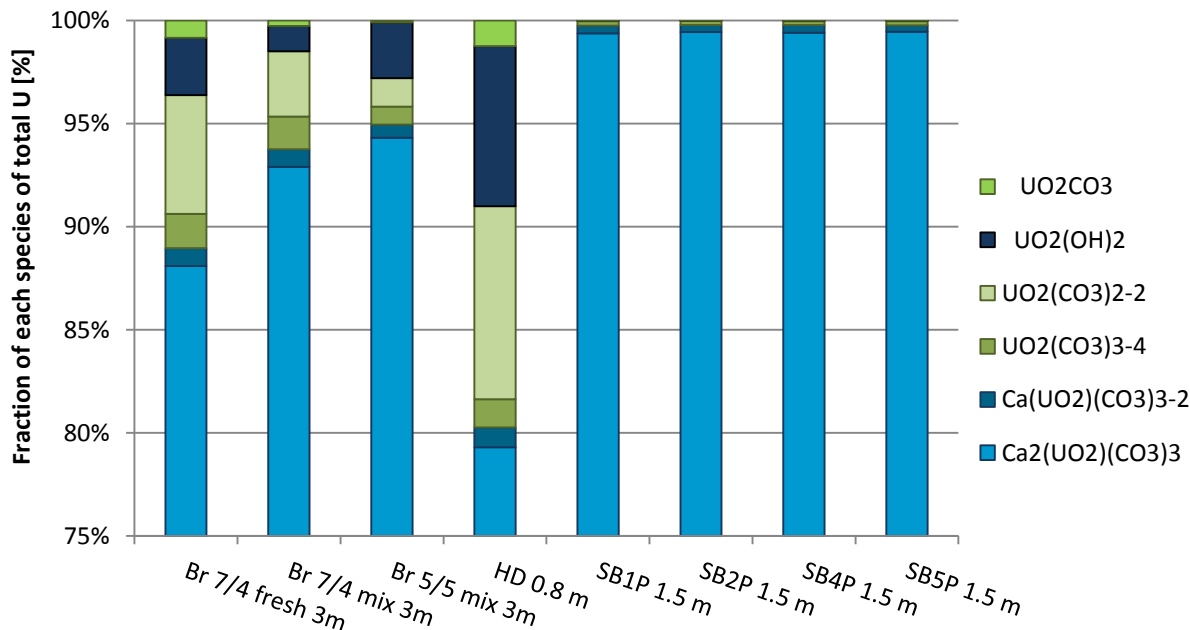
Figure 21 – Uranium species distribution in the percolation water samples from the sampling sites in Brandis, Hilbersdorf and Sauerbach (For modeling the software PHREEQC, database: llnl.dat, was used. Br stands for Brandis; the number behind represents the lysimeter. HD means Hilbersdorf and SB Sauerbach. The number behind SB stands for the lysimeter. Sampling depths are given in meters after the sample ID.)

According to the modeling results, in the sampled groundwaters U only forms complexes with carbonate-, hydroxide- and calcium ions to a considerable extent. Concentrations of complexes with F, P or S are diminishingly small.

The most dominant species at the Sauerbach and the Brandis site is the uncharged complex of $Ca_2(UO_2)(CO_3)_3$. In the percolation water of the Sauerbach lysimeters, it even accounts for close to 100 % of total U. Due to the fact that this species has no charge it will nearly not interact, but it could be retained by specific surface complexation, which is said to depend on pH and the concentrations of dissolved carbonate, U(VI) and Ca (Romero-González et al., 2007), (Davis et al., 2004).

In Brandis, the second most abundant U species is $UO_2(CO_3)_2^{2-}$ or $UO_2(OH)_2$, depending on the lysimeter, making up less than 5 % each. Other species occurring at a few or less than one percent are $UO_2(CO_3)^{4-}$, $Ca(UO_2)(CO_3)_3^{2-}$ and UO_2CO_3. All of them are either uncharged or negatively charged. That means they do not considerably interact with negatively charged surfaces like clay minerals by cation exchange. However, they can be attracted by (positively-charged) surfaces like iron or manganese oxides and hydroxides and be bound by surface complexation.

In Hilbersdorf, distribution among the mentioned species is more equalized. Like at the other two sites, $Ca_2(UO_2)(CO_3)_3$ is the most dominant species with about 78 % of the total molarity of U. But also $UO_2(CO_3)_2^{2-}$ and $UO_2(OH)_2$ occur at about 10 %.

So, in all percolation waters sampled the uncharged U species represent between 87 and close to 100 % of total U. Therefore, U can be assumed to be highly mobile; only specific surface complexation might cause some retention.

5.5 Solubility-controlling phases in the sampled percolation waters

Saturation indices (SI) of phases that might form were calculated with PHREEQC. All Minerals which do not form at ambient temperature and pressure or whose formation kinetics is too low were excluded by a priori knowledge (although they are calculated by PHREEQC). Only those who likely may form were considered. When SI was in the range of 0 ± 0.5 (considering analytical uncertainties of pH and concentrations as well as uncertainties of log K values) these minerals were assumed to be solubility-controlling. The complete list of calculated SI values can be found in *EXCEL 7* in the digital appendix.

According to the definition, if a saturation index is at about zero, the corresponding phase is in equilibrium with the surrounding solution. In case, SI is below zero, water is undersaturated with respect to the mineral and the mineral would dissolve if it was added to the solution. When SI is above zero, water is supersaturated with respect to the phase, i.e. it contains more ions than should be in solution if the phase was in equilibrium with the solution. Reasons why it might still not form can be slow kinetics, unfavorable pressure or temperature, or inhibitors like some trace elements (Merkel, 2013d).

All waters are highly **supersaturated** with respect to several clay minerals. From those, two groups can be formed:

- Ca-, Mg-, K-, Na- and H-nontronite, i.e. Fe^{3+}-rich smectites
    - SI between 7.9-12.6, i.e. $10^{7.9}$- to $10^{12.6}$-times supersaturated
- Ca-, Mg-, K-, Na-, H-beidellite, Ca-, Mg-, K-, Na-montmorillonite, illite, kaolinite
    - SI between 1.2 and 4.5

In addition to clay minerals, there are also other phases that are (highly) **supersaturated at all sites**:

- Al (hydr)oxides: boehmite and gibbsite (SI between 0.5 and 2.2)
- Fe (hydr)oxides: hematite and goethite (SI between 2.4 and 8.9)
- Eskolaite (Cr oxide): SI between 3.1 and 10.9
- Oxides containing two different metals
    - Delafossite, ferrite-Cu (Cu + Fe): SI between 0.7 and 6.2
    - Ferrite-Zn (Fe + Zn): SI between 3.1 and 7.8
    - Trevorite (Ni + Fe): SI between 2.2 and 6.1
    - $ZnCr_2O_4$: SI between 12.4 and 20.4
    - $CdCr_2O_4$: SI between 1.2 and 6.9
- Fluorapatite ($Ca_5(PO_4)_3F$): SI between 3.7 and 10.9

In addition to the minerals that are highly supersaturated at all sites, there are also minerals that are supersaturated only at some sites and undersaturated or close to SI = zero, i.e. in equilibrium with the surrounding solution, at other sites. In case SI for a certain mineral is 0 ± 0.5, in the following it is assumed that this mineral controls solubility in the water sample if this mineral is known by a priori knowledge to form under ambient temperature and pressure conditions. Figure 22 shows the saturation indices of the minerals close to or at saturation in the sampled waters of Brandis, Hilbersdorf and Sauerbach. The upper (+ 0.5) and the lower limit (- 0.5) for the saturation criterion are included.
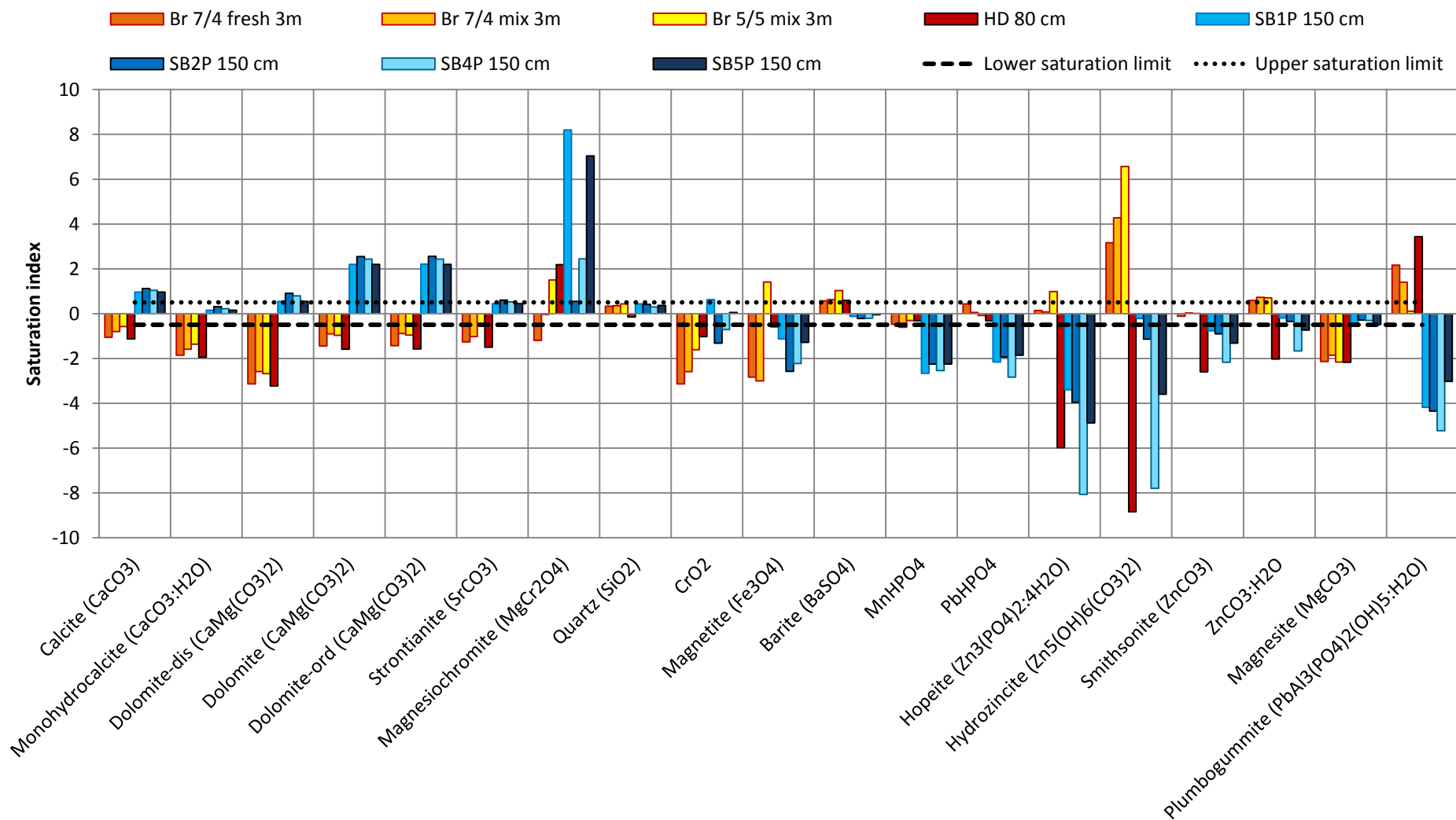
Figure 22 – Saturation indices of solubility-controlling phases of the sampled percolation waters of the Brandis lysimeters (Br 7/4 freshly taken, Br 7/4 and Br 5/5 mixed samples from 1 month's period), from Hilbersdorf (HD) and from the Sauerbach lysimeters (SB1P, SB2P, SB4P and SB5P). The upper and the lower limit (-0.5 and 0.5) define the boundaries of satura-tion, i.e. the equilibrium between solid phase and solution.

In Brandis and Sauerbach multiple water samples were taken from different lysimeters. In some cases all samples of a site showed the same trend (over-, undersaturated or saturated). In other cases trends were different. That is because waters from these sites did not have exactly the same composition.

In Sauerbach, several Ca-containing minerals are (heavily) oversaturated, i.e. ion concentrations needed for mineral formation are by far high enough but minerals do still not form. For dolomite this can be explained by very slow kinetics (Merkel, 2013a). Magnesiochromite is also highly oversaturated in most Sauerbach samples. Only in one Sauerbach sample, it seems to actually have formed because SI is below 0.5. Other minerals that are likely to control solubility in some or all water samples are monohydrocalcite, dolomite in the disordered modification, strontianite, quartz, CrO_2, barite, hydrozincite, $ZnCO_3 \cdot H_2O$ and magnesite. However, in case of dolomite, quartz and magnesite kinetics of formation is probably too slow.

In Brandis, phases that are more or less in equilibrium with solution or are at least likely to develop from a thermodynamical point of view are quartz, barite, $MnHPO_4$, $PbHPO_4$, hopeite, smithsonite and maybe $ZnCO_3 \cdot H_2O$ and plumbogummite.

In Hilbersdorf, the relevant phases are quartz, magnetite, barite, $MnHPO_4$ and $PbHPO_4$. Quartz and magnetite, however, might probably still not form because kinetics is low.

In summary, one can say that various carbonate, sulfate, and phosphate minerals as well as (hydr)oxides are likely to be solubility-controlling at the three sampling sites. None of the U minerals contained in the llnl.dat database of PHREEQC seems to precipitate under the given conditions. With the exception of plumbogummite, probably no clay minerals formed even if several of them were (highly) oversaturated (see *EXCEL 7* in the digital appendix). Generally, one would expect them do precipitate as secondary weathering products of other minerals under normal pressure and temperature conditions. However, maybe kinetics is too slow.

5.6 Effect of phosphate fertilization on soil and groundwater

5.6.1 Brandis

In Figure 23 data on fertilization and uranium content of the Brandis field soil is compiled. No soil or water analytical data for uranium was available from previous years. Phosphorus analytical data was only available for water, not for soil. It was analyzed once a month in times of groundwater recharge, sampled from the lysimeters' bottoms at 3 m depth. For lysimeters 7/4 and 8/6, there was additional phosphorus analytical data available from suction cup sampling at different depths. In 2013, during water analysis of this work, uranium as well as phosphorus was around or below the detection limits of ICP-MS (10 µg/L for P, 0.001 µg/L for U) and IC (10 µg/L for P). This data is therefore not included in Figure 23. The reason for the very low U concentrations in the lysimeters might be sorption to FeOOH or $Zn(OH)_2$ which probably formed on the walls of the highly corroded lysimeters.

The diagram shows how much phosphorus in mg/kg is introduced to the soil (given as minimum, mean and maximum P input based on fertilizer data compiled by Taylor, 2013) by P fertilization. In 1982, 1983, between 1990 and 1999, from 2001 until 2007 and since 2009 no P fertilizer has been

applied. In all years, except 2008, the fertilizer used had been superphosphate; in 2008 it was an NPK, a mixed-nutrient fertilizer.

Water analytical data on P concentration in the three sampled lysimeters of the station is also included in the plot. First samples had been taken and analyzed in 1993. Therefore, no information on P is available from before. The diagram shows P concentrations determined from the mixed water samples taken monthly at the bottom of the lysimeters at 3 m depth. For lysimeters 7/4 and 8/6, in addition to that also P concentrations from water samples taken with suction cups from 50, 150 and 250 cm depth are included. All these monthly concentrations were converted to annual means for this plot. Total U concentration from own analysis (using from gamma spectrometry) of the surrounding soil of the lysimeter station in 2013 is also included. Summed up U input by fertilization to the topsoil impacted by ploughing was calculated as between 1.5 and 750 µg/kg since 1980 (see *FOLDER 3* in the digital appendix), i.e. between 0.08 and 39 % of total uranium presently determined in the soil samples analyzed in 2013. It would have been interesting to compare the concentrations from 2013 with soil data from longer ago to see if and how much it actually increased. It is very likely that it increased and not all U was washed out into groundwater.

P at least seemed to be retained to a great share by soil or be taken up by plants. In Figure 23 it can be seen that P fertilization did not always result in an increase of the P concentration in groundwater. Only after fertilizer application in 2008 it seems like P concentration in water increased nearly by factor three. This effect could not be seen in 2000. Instead of resulting in an increase in P in water, P concentration in water already increased tremendously from about 0.3 to above 5 mg/L the year before. In 2000, it dropped to about 0.6 mg/L and in 2001 even to below 0.2 mg/L. It is not clear whether these are real effects or if analytics were erroneous. It was not possible either to obtain information on which phosphorus data is normalized to phosphate and which to P. In some cases it even seemed like both options were mixed in the datasets. As no water analytical data was available from the 1980s, unfortunately, it could not be examined if P fertilization that was done yearly in that time, affected P concentration in water considerably. Since 1993 P concentrations at the bottom of the lysimeters was at a rather low and more or less constant level of below 0.2 mg/L, close to the detection limit. Due to the lack in data before 1996, the decrease in P concentration in the suction cups since 1996 cannot be explained.
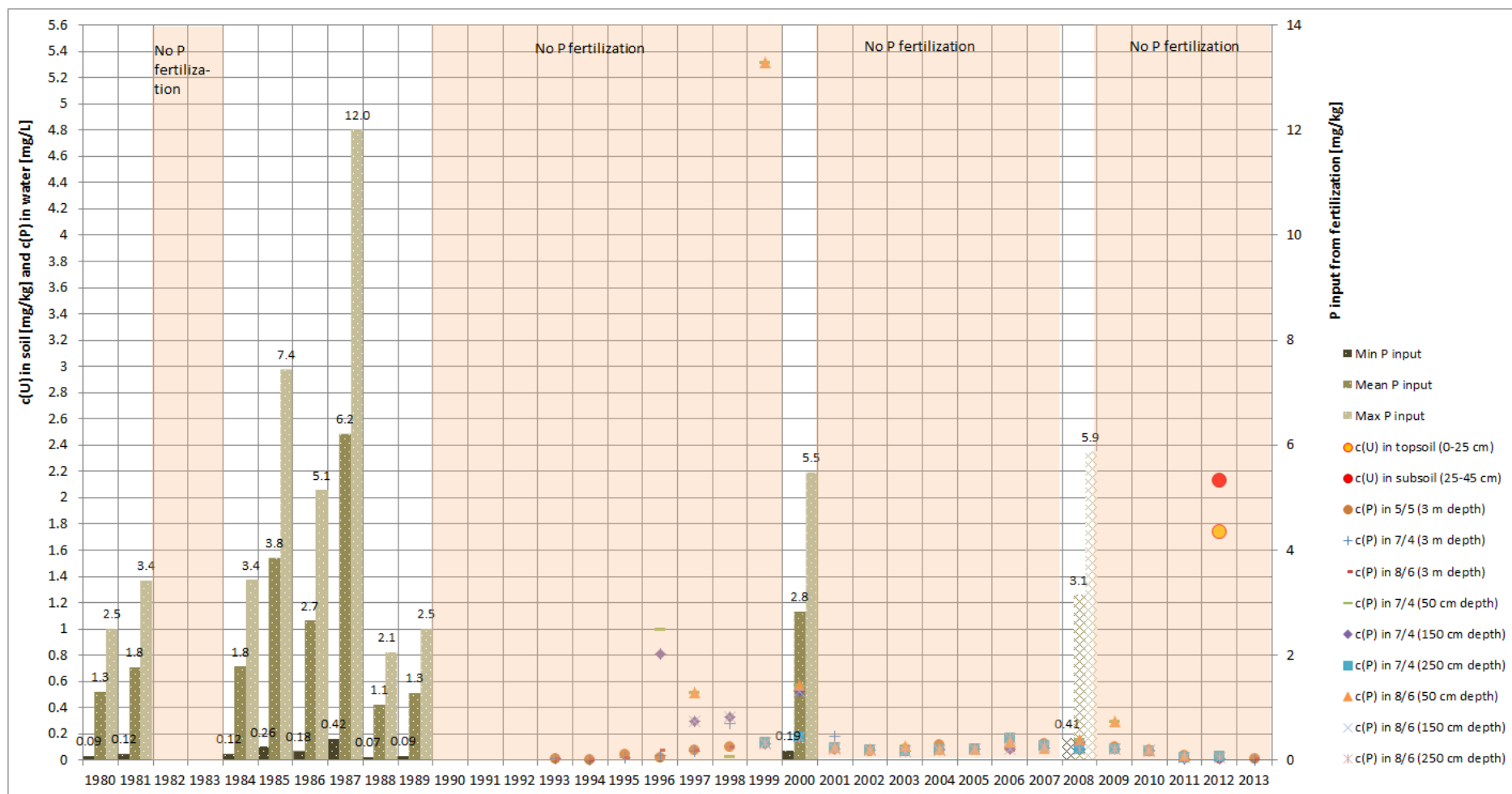
Figure 23 – Phosphate fertilization, uranium concentration in soil (at 0-25 and at 25-45 cm depth, in mg/kg) and phosphorus concentration in percolation water (at 50, 150 and at 250 cm depth, in mg/L; sampled with suction cups) at the field soil sampling site in Brandis over time (P input by fertilization (in mg/kg) is plotted as columns with a different pattern for each type of P fertilizer. Columns for NPK fertilizer are filled with diagonally crossed lines and for superphosphate they are beige-brown with white dots. For each year, minimum, mean and maximum values are given based on the typical ranges for P in these fertilizers (according to Taylor, 2013). The quantities of P input are given as numbers above the columns. No P fertilizer had been applied in 1982, 1983, between 1990 and 1999, from 2001 until 2007 and since 2009. Uranium concentration in soil is plotted as orange and red points for topsoil and subsoil, respectively. P concentration in water is given from analysis of percolation water from the bottom of the three lysimeters (5/5, 7/4, 8/6) from 3 m depth as well as from suction cups from 50, 150 and 250 cm depth of lysimeter 7/4 and 8/6. Water analytical data had been given as monthly means. It was converted to annual means for this plot.

5.6.2 Schmorren

For the Schmorren site, data on fertilization was available from 2000 to 2011. From 2000 to 2008, not any phosphate fertilizer had been applied as shown in Figure 24. Within the regarded time frame, the site was only P-fertilized in 2009 and 2011. In 2009, 170 kg/ha of an NPK fertilizer was used – a mineral mixed-nutrient fertilizer with generally medium uranium contents (Taylor, 2013). In 2011, 20 kg/ha of organic fertilizer (manure from cattle breeding) were applied. They are nearly free of U and therefore did not introduce considerable quantities of U to the soil. Doing the conversions as described in chapter 4.7, the total uranium input to the soil horizon above ploughing level can be estimated as:

Minimal: 0.001   Mean: 0.9   Maximum: 7.6   µg/kg dry soil

As the field soil did not face any phosphate fertilization within the time frame of soil analyses (2000-2008), it was not possible to check if there is a relation between fertilization and U content in soil.

However, what can be seen from Figure 24 is that uranium concentration in soil in 2012 (own analysis with gamma spectrometry) was higher than that of any analysis before. From 2000 to 2008, concentrations ranged between 1.6 and 2.6 mg/kg in subsoil and between 1.8 and 2.8 mg/kg in topsoil. In 2012 U contents were at 3.5±0.5 and 3.1±0.6 mg/kg, respectively. That means, within about 10 years it rose by more than 1 mg/kg, i.e. by about 50 %. This is a tremendous increase, which indicates that the potential of the soil for contaminant retention is very low.

U concentration in water does only partly follow that dramatic trend. Data from the different suction cups scatters over wide ranges and does neither follow a decreasing nor an increasing trend with depth. In some years, U concentration is higher at shallower depth and in some years at greater depth. With the exception of the three lowest values in 2010 and 2011 (two of them are below the detection limit of the LfULG with 0.5 µg U/L), the water analytical data seems to follow an increasing trend. In 2006, when analytics started, U concentration was at 1.3 µg/L. In 2012, it had increased by a factor of about three to 4.1 µg/L. Like in soil, this is a considerable increase that should be seen as a warning signal. The observations are especially dramatic as mineral fertilizer had only been applied once within the entire period of 12 years for which data was available. Maybe the application of manure in 2011 impacted U mobility in soil by increasing the organic matter content.

For proper risk assessment, it would have been necessary to also have data on the fertilizer's composition or a sample of the fertilizer used that could be analyzed for determining the exact composition. As this was not the case, only typical ranges of U in this kind of fertilizer could be used. The great increase in U content in soil suggests that U concentration in the fertilizer had been in the upper range of typical concentrations. What is not clear in Figure 24 is why U content in soil as well as in water increased since 2006 even if no fertilizer had been applied. It might be that U was released from fertilizers that had been applied on the field before it was used as intensive test site and samples were taken for analysis. Maybe the utilized fertilizers were of low solubility and U was released very slowly as it is the case for some kinds of P fertilizers (Kratz and Schnug, 2008).
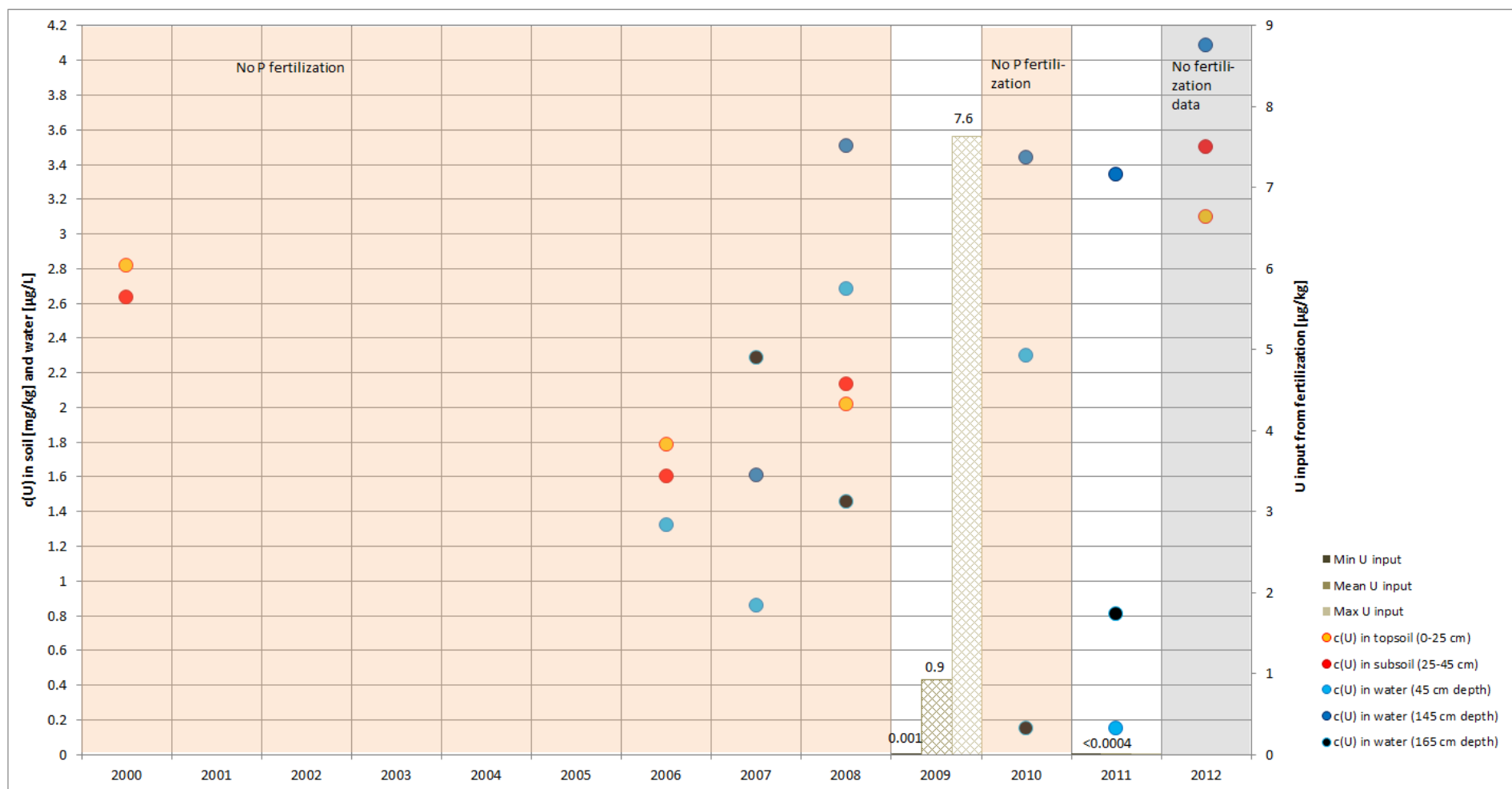
Figure 24 – Phosphate fertilization with NPK fertilizer, U concentration in soil (at 0-25 and at 25-45 cm depth, in mg/kg) and in percolation water (at 45, 145 and at 165 cm depth, in mg/L; sampled with suction cups) in Schmorren over time (U input by fertilization (in µg/kg) in 2011 by manure was negligible. Minimum, mean and maximum U input from fertilizer was calculated based on typical ranges in the utilized fertilizers (according to Taylor, 2013). The quantities of P input are given as numbers above the columns. No P fertilizer had been applied between 2000 and 2008 and in 2010; no fertilization information is available for 2012. Uranium concentration in soil is plotted as orange and red points for topsoil and subsoil, respectively. U concentration in water is given from analysis of percolation water from suction cups installed at 45, 145 and 165 cm depth. U concentration data in water had a resolution of 14 days sampling intervals in case enough percolation water was available. From that, monthly and then annual means were calculated for this plot.

5.6.3   Hilbersdorf

In Figure 25 uranium input to soil in µg/kg by phosphate fertilizer application is depicted together with uranium concentration in topsoil (0-25 cm depth), in subsoil (25-45 cm depth) and in seepage water (40 and 80 cm sampling depth, sampled with suction cups).

Before 2003, different kinds of P fertilizers have been used – manure from cattle breeding in 1996, 2000 and 2005, PK fertilizer in 1997 and 2001, NPK fertilizer in 1999, and "Thomas phosphate" (by-product from steel production) in 1997. From 2008 on, triple superphosphate was applied, with an interruption from 2009 to 2010 where the field was used as pasture with clover cover.

Uranium concentration in soil in 1995 and in 2000 is nearly the same. Concentration in subsoil increased only slightly and concentration in topsoil decreased very little and consequently approached the same level. From the soil analysis in 2006 on, U content steadily increased whereas U input by fertilization decreased to 50 % of the input from 2003-2005. A possible explanation of the increase in U concentration is the fact that the field was not used for farming between 2003 and 2005, but only as clover-covered pasture with fertilization and cattle breeding. Therefore, no uranium and phosphate was withdrawn by harvest, but both entered the soil zone by P fertilization (TSP in 2003 and 2004, TSP and manure from cattle breeding in 2005) and cattle excretions. The increase in organic matter content by omitted harvest and also by the excretions probably also contributed to the increase in uranium content, especially in topsoil. What will probably also have contributed to the concentration increase in subsoil from 2006 on, is the change in ploughing depth. Before 2006 it amounted 15-25 cm, and from 2006 on it was 25-30 cm. Therefore, the border between topsoil and subsoil dropped to greater depth and mixing probably took place.

A point that is not clear is if the type of triple superphosphate (TSP) fertilizer used was the same all the time. It might be that it changed but it was not possible to get this information from the agriculturist owning the field. So it could theoretically be that the TSP applied after 2006 was different from that one before, which would make the increase in U concentration in top- and subsoil after 2006 plausible even if the total amount of P fertilizer applied decreased.
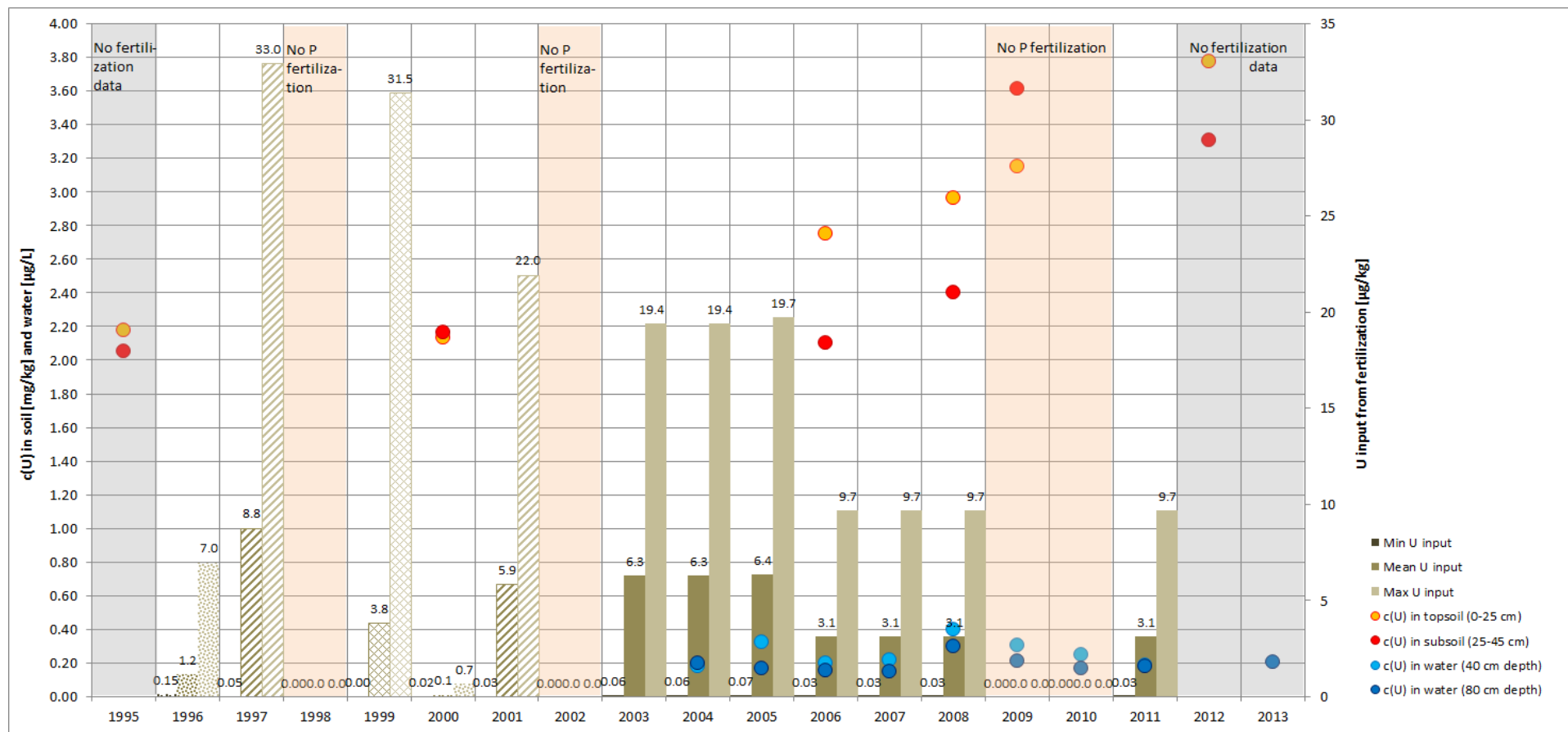
Figure 25 – Phosphate fertilization and uranium concentration in soil (at 0-25 and at 25-45 cm depth, in mg/kg) and percolation water (at 40 and at 80 cm depth, in µg/L; sampled with suction cups) at the field soil sampling site in Hilbersdorf over time (Soil and water data was obtained from the LfULG. Only data from 2012 and 2013 is from own analyses. U input by fertilization (in µg/kg) is plotted as columns – with a different pattern for each type of P fertilizer. Fillings are assigned as follows: triple superphosphate – plain, PK fertilizer – diagonally striped, NPK fertilizer – diagonally crossed lines, manure from cattle breeding – confetti symbols. For each year, minimum, mean and maximum values are given based on the typical ranges for U in these fertilizers (according to Taylor, 2013). From before 1996, no fertilization data is available; in 1998, 2002 and 2009-2010, the field was not P-fertilized. 2009-2010 it was used as pasture with clover for cattle feed. Uranium concentration in soil is plotted as orange and red points for topsoil and subsoil, respectively. U concentration in water is shown as light and dark blue points – light color for 40 cm sampling depth and dark color for 80 cm sampling depth. Time resolution for soil, water and fertilization data is different. Soil analysis results had only been available for some years. Fertilization data was available with exact dates of application and was summed up to annual inputs. U concentration data in water had a resolution of 14 days sampling intervals in case enough percolation water was available. From that, monthly and then annual means were calculated for this plot.).

What cannot properly be seen in Figure 25 is the impact of fertilization on uranium concentration in percolation water. That is because for plotting, annual means were calculated for making it possible to use the same time axis for soil, water and fertilization data. What can be seen is that annual mean concentrations do neither show the same trend as the U input by fertilization nor as U concentration in soil. While U input decreased in 2006 to only half the amount from before that year and U concentration in soil steadily increased, U concentration in water was more fluctuating than following a certain trend. Surprisingly, uranium concentration in water did not follow the decrease in fertilization. However, as U contents at 40 cm depth are mostly higher than and sometimes equal to those at 80 cm depth, it is likely that uranium comes from upper rather than lower soil horizons.

Annual U concentration means smoothen out variation over time. To get an impression of that variation all available analytical results for 40 and 80 cm sampling depth were aggregated to monthly means and plotted in Figure 26.

From that diagram, the much greater variation in U concentration over time becomes clear. Uranium concentration is nearly always below detection limit (0.5 µg/L), but there are also some months in which concentrations were significantly higher than that limit. At 80 cm sampling depth, U could only be detected in water in 2008. At 40 cm depth, U concentration exceeded the level also two-times in 2005, once in 2007, twice in 2009 and once in 2010 making input from fertilization likely.

Comparing the concentration peaks with fertilization depicted in Figure 25, one will notice that there is no direct relationship between both. For example, in 2009 and in 2010, no fertilizer had been applied, but U concentration was higher than in 2011 where the field was being fertilized. So, from fertilization alone one cannot conclude U concentration in seepage water. The variation in U concentration is probably controlled by the interplay between fertilization, precipitation, ploughing, harvest, crop type or use as pasture and other reasons. In the following, this interplay is studied nearer for the highest U peak at 40 cm depth in 2008.
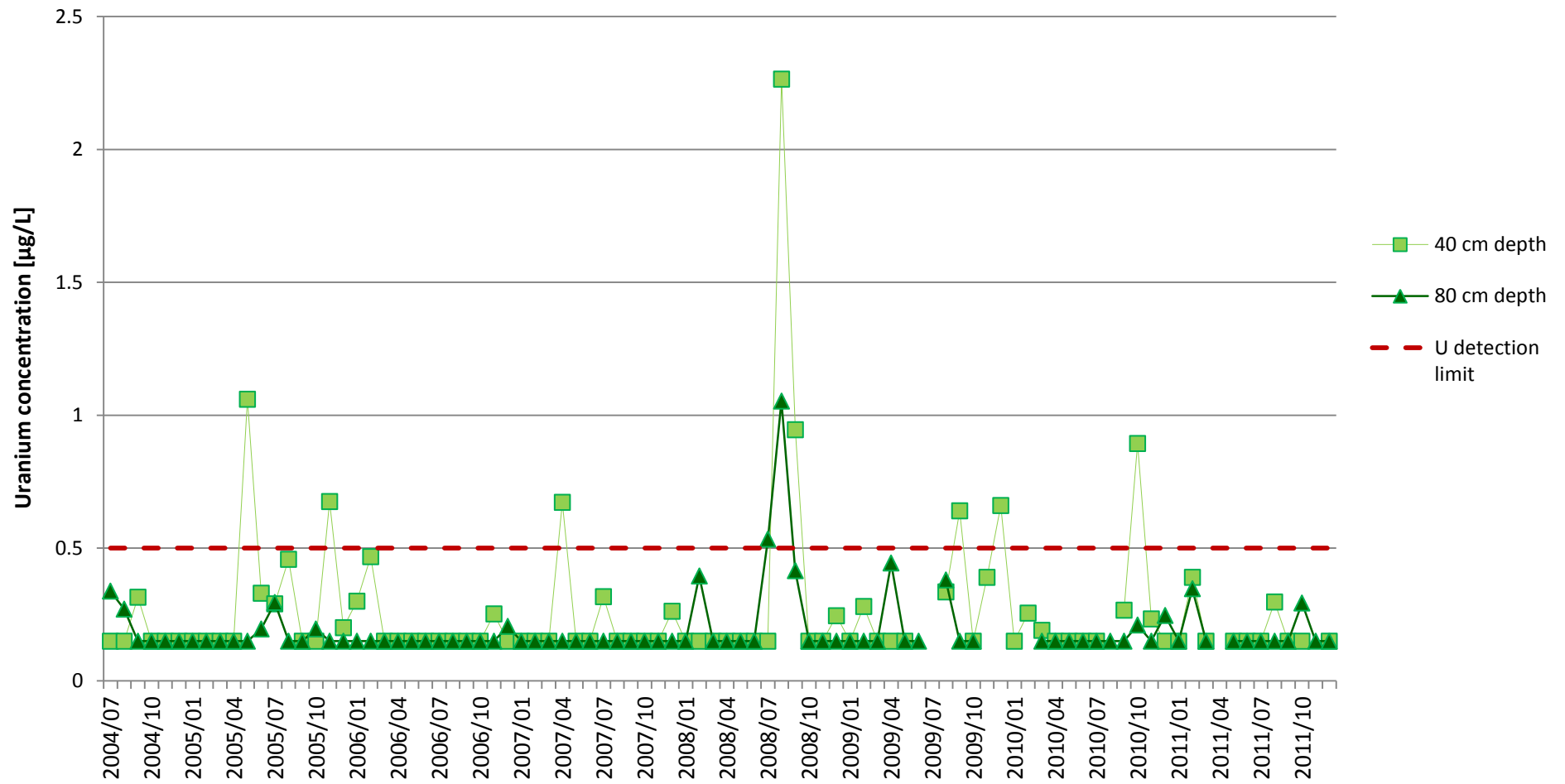
Figure 26 – U concentration of seepage water at the Hilbersdorf site at 40 and 80 cm depth over the entire data registration period of the LfULG (Samples were taken with suction cups. Detection limit of the analyses was 0.5 µg/L and is highlighted as red dashed line. Values below detection limit were replaced by 0.3 multiplied by the detection limit in this plot.)

In the following the situation around the highest U peak in 2008 is looked at in greater detail with higher data resolution. Figure 27 shows monthly means of uranium and phosphorus concentration in seepage water at 40 and 80 cm depth, samples taken with suction cups. To assess possible dilution or washing out by rain water, precipitation was also included in the plot as monthly precipitation sums. For evaluating the quantity of rain that fell, actually measured rainfall at the test site in 2008 was compared with long-term annual means for the DWD (i.e. German Weather Service) station nearby, in Freiberg. Excess precipitation, i.e. months in 2008 in which precipitation was higher than annual means of the DWD station in Freiberg, is colored as stapled column in darker blue. Precipitation shortfall is indicated by white stapled columns in white color filled with light blue dots. In the uppermost part of the diagram, information on fertilization and ploughing (date and depth) is inserted, pointing to the corresponding date with an arrow.

In Figure 27 one can see that P concentration at 40 cm sampling depth is always below or in the range of the detection limit, whereas at 80 cm it is above. U concentration is also mostly below its detection limit or close to it in July. Unlike P, U contents are higher at 40 cm than at 80 cm sampling depth and show greater variation. 100 kg/ha of triple superphosphate was applied on April 28. Probably as a result from that P concentration at 80 cm depth increased by factor two if April (0.09 mg/L) and May (0.18 mg/L) are compared. In June, it already again decreased to the value from April. At 40 cm depth, it remained below detection limit and not sufficient water was available for the analytics, respectively. U concentration did not increase before July/August after ploughing. Soil was shallow-ploughed on August 6, 10-15 cm deep. After that, U concentration increased to 2.3 µg/L at 40 cm depth and to 1.1 µg/L at 80 cm depth. In September, it already decreased to less than half the concentration from August, namely to 0.9 µg/L at 40 cm and to below detection limit at 80 cm depth. P concentration also seems to be affected by ploughing. Between June and August, its concentration at 80 cm depth increased by 56 %. After that it decreased again to reach its minimum in November with 47 % less than the concentration in June.

Because P concentration and maybe U concentration as well (in July it was close to the detection limit) started to increase already before ploughing in August, other influenced seem to also impact concentrations in water. Precipitation is likely to play an important role. So, rainfall data from the Hilbersdorf intensive test site from 2008 compared with the annual means of the German Weather Service (DWD) station in Freiberg not far away was also integrated in Figure 27. It makes clear that the months before fertilizer application, January, March and especially April, had been wetter than the long-term annual mean. After fertilization, precipitation was very low, less than 50 % of the long-term mean. This might have contributed to the decrease in P concentration at 80 cm depth because no additional P was washed out from shallower horizons to greater depth. U concentration did not increase during that time; it remained below detection limit. In August, however, precipitation was very high; the month was moister than the long-term average. That might have caused P concentration at 80 cm depth to increase to a value 20 % higher than the month before. P concentration at 40 cm depth, however, did not increase before September. The reason for that is not clear. The increase in U concentration in August and September was much more distinct than that of P. At 40 cm depth, it rose from below detection limit in July to 2.3 µg/L in August and 0.9 µg/L in September. At 80 cm depth, this effect could also be seen even if not as pronounced as at 40 cm depth. There it increased from close to the detection limit in July to 1.1 µg/L in August.

The reason for the different behavior of U and P can probably be seen in their different chemical properties and the interaction with the individual constituents of soil. P might be precipitated as poorly soluble apatite whereas U will sorb to organics as correlation analysis (section 5.2.2) suggested.
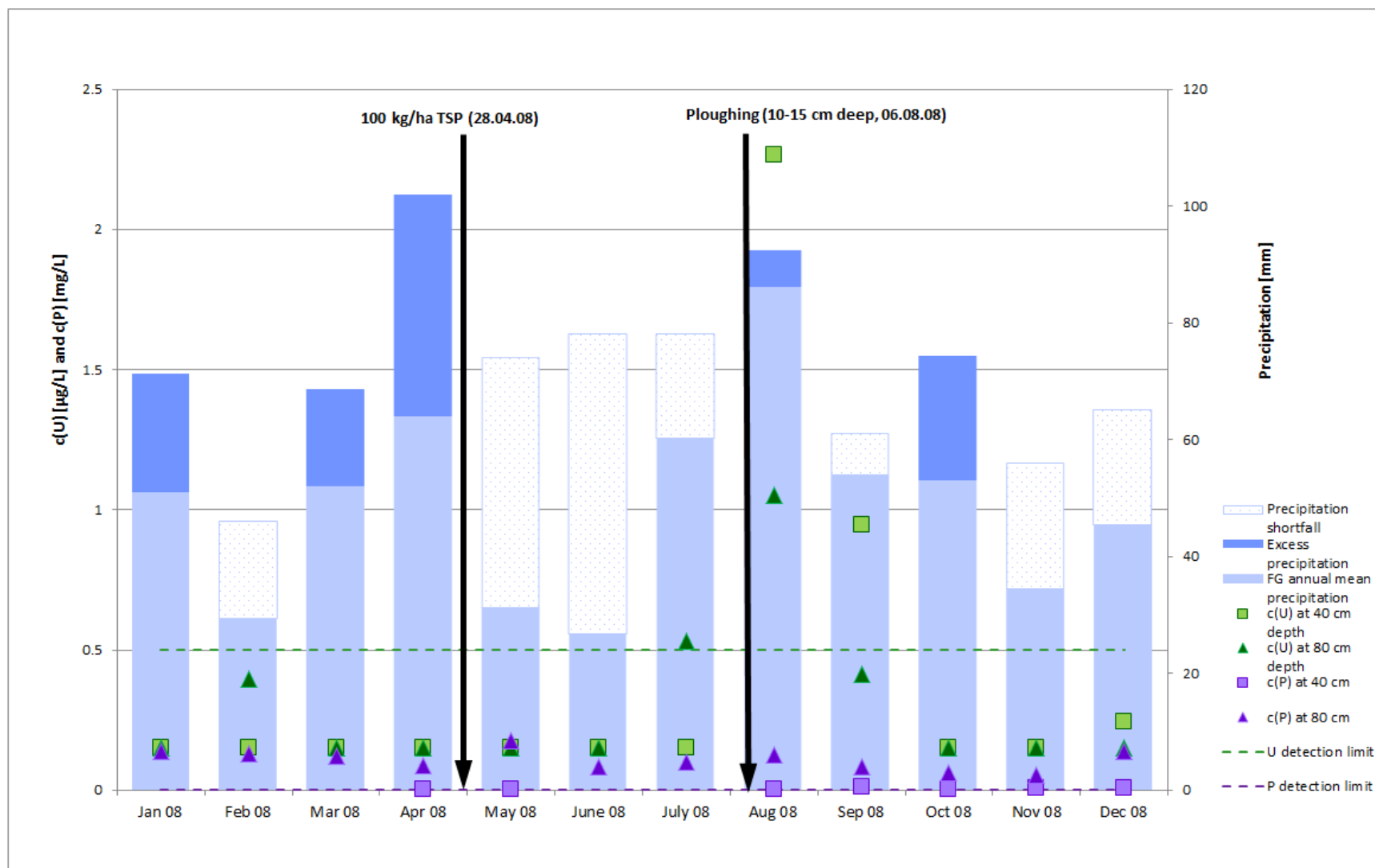
Figure 27 – Hilbersdorf sampling site in 2008 –Impact of precipitation, ploughing and fertilization with triple superphosphate (TSP) on U and P concentration in percolation water at 40 and 80 cm depth sampled with suction cups. Detection limits of the LfULG are depicted as dashed lines (0.5 µg/L for U; 0.01 mg/L for P). Concentrations below detection limit were re-placed by 0.3 · detection limit.

5.6.4 Sauerbach

The lysimeter station close to Sauerbach was established in 2010 and analytics started in 2011. Therefore, no soil or water analytical data is available from before 2011. Since 2011 several parameters and soil and water constituents are regularly being determined. However, several constituents relevant for this study did and do not belong to the analytical program. Neither uranium nor cadmium was analyzed in the water samples taken by the UFZ. In soil, cadmium was determined but uranium was not. Therefore, the effect of phosphate fertilization on uranium content in soil and water cannot be assessed here. What can be calculated, however, is the actual uranium input to soil per year because for the Sauerbach site a sample of the presently applied fertilizer was available for analysis. It was analyzed for its uranium activity using gamma spectrometry and the result was converted to the corresponding U concentration. From that the uranium input to soil per year since 2011 was calculated. Figure 28 shows the annual input in µg/kg together with the present uranium content in topsoil (1.8 mg/kg, at 12 + about 6 cm), in subsoil (2.2 mg/kg, at 26 + about 6 cm) and in water. Uranium content was deduced from gamma spectrometry measurements. Concentration in water stems from ICP-MS analysis of water samples from the bottom (150 cm depth) of four of the six available lysimeters of the lysimeter station. From the analyzed concentrations, minimum (6.8 µg/L), mean (10.2 µg/L) and maximum (12.9 µg/L) is shown in the diagram.
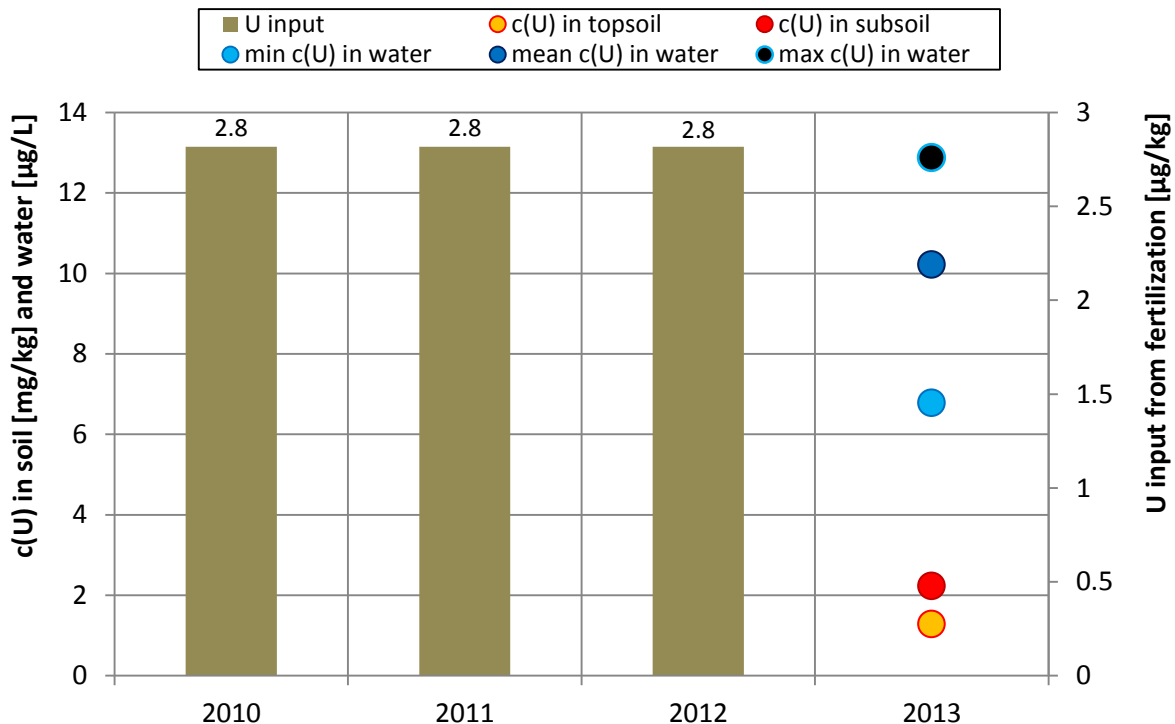
Figure 28 – Annual U input to soil in Sauerbach in µg/kg since 2010 and U concentration in topsoil (12 + about 6 cm) and subsoil (26 + about 6 cm) [mg/kg] from own analysis (converted gamma spectrometry results) and in percolation water [µg/L] from the bottom, i.e. from 150 cm, of four of the six available lysimeters at the Sauerbach site.

The type of fertilizer applied was a triple superphosphate with a low uranium content of about 56 mg/kg (determined with gamma spectrometry) as compared to other P fertilizers of the same type. Typical triple superphosphate fertilizers can contain between about 1.2 and 364 mg U/kg; mean con-

centration of various different samples was determined as 118 mg/kg (Taylor, 2013). As 169 kg/ha of this fertilizer have been applied per year, annual uranium input is 2.8 µg/kg to topsoil. Actual U content in topsoil (12 + about 6 cm) and in subsoil (26 + about 6 cm) is 1.3±0.2 and 2.2±0.4 mg/kg, respectively. That means annual input is circa 460 and 785-times lower, i.e. it amounts 0.2 or 0.1 % of present U content in soil. Consequently, U input to soil is negligible for the considered time span.

For comparison: in the corresponding forest soil, U contents were similar with 2.3±0.5 and 2.2±0.5 mg/kg for topsoil and for subsoil, respectively. That means there is no enrichment in field soil. It is not clear why U content in field topsoil is lower than in field subsoil and in forest top- and subsoil. What is not clear either is the input of uranium to the site before 2010. It is likely that this productive site has been used for agriculture for about 50 years (Rupp, 2013). If fertilization had been the same as at present, input would have been about 140 µg/kg in topsoil, i.e. 5 to 10 % of the present content. These are only speculations that even do not seem likely because U concentration in field soil is equal to or even lower than in the corresponding forest soil.

However, the rather high U concentrations in percolation water ranging between 6.8 and 12.9 µg/L open another hypothesis for discussion. It might be that U in that soil was net retained as complete as in the soils of the other sites but that it formed soluble complexes with carbonate that were washed out into groundwater. In section 5.1.4 it was pointed out that the total inorganic carbon content in Sauerbach is much higher than that of the other sites. It had been evaluated as "rich in carbonate" according to KA05 (Sponagel, 2005). This would support the theory. In fact, the analyzed concentrations give rise to concern as in some of the lysimeters they already exceed the MCL for U in drinking water (10 µg/L). So, one should either change the type of fertilizer or apply less of it to prevent further concentration increase in groundwater.

5.7 Changes in U and P in groundwater in the vicinity of the study sites

In chapter 5.4, the concentration development of U and P in seepage water of the soil sampling sites was addressed. In the vicinity of the sites, there are several monitoring wells managed by the LfULG (for the sampling sites in Saxony) that contain detectable uranium concentrations (detection limit of the LfULG analyses: 0.1 µg/L). They are highlighted with colored dots (coloration depending on the U concentration) in Figure 4. The analytical results of the ones that are in the vicinity of the soil sampling sites of this thesis were requested from the LfULG. For the Sauerbach site that is managed by the UFZ, uranium was not included in water analyses. Therefore, only the development of P can be examined here. So, for the sites in Saxony the development of U as well as that of P over time is now looked at in detail. And for the Sauerbach site, this study only includes P over time. In the diagrams, one can always see a "1" behind the individual years. This stands for the season of sampling (spring = 1, summer = 2, autumn = 3, winter = 4) lasting from March to May, June to August, September to November, December to January. The reason why most diagrams only show "1" is only a result from scale definition. Not all samples were taken in spring. The entire datasets can be found in *EXCEL 8* in the digital appendix.

5.7.1 Brandis

Groundwater analytical P and U data from the surrounding of the lysimeter station for some monitoring wells is available since 1992, for most of them since 2000 as shown in Figure 29 and Figure 30. The phosphate concentration in groundwater is shown in Figure 29. In the diagram, one can see a clear drop in U concentration after 1997. Before 1996, data from only one monitoring well is available. Analyses of its water gave very high phosphate concentrations of up to 5.2 mg/L. Since 1996 data from another monitoring well is available. It is about ten-times lower than that from the previously mentioned one. From 1999 on, data from several more monitoring wells is available. According to (Clasen, 1991) (page 340), these concentrations are in the normal range of groundwaters (tens to hundreds of µg PO_4 /L). The data does not show a clear de- or increasing trend but scatters throughout the years. The reason for the very high concentrations in the first part of the 1990s could be high fertilization rates on the surrounding arable land (for comparison: in Brandis, fertilization was very high and intense in the 1980s).

Since the end of the 1990s, phosphorus concentrations in some of the wells remain at a constant, rather low level of below or around the detection limit of 0.01 or 0.02 mg PO_4/L. Others have a decreasing or increasing trend or scatter without showing any tendency. In some monitoring wells, phosphorus concentrations are high with about 60 µg/L. It is very likely that these high concentrations stem from fertilization in the area.

In Figure 30, with respect to U concentrations, two groups of waters can be formed. The first group is formed by the monitoring wells with low and relatively constant uranium concentrations below 2-3 µg/L. The second group consists of two monitoring wells with higher U contents:

- In "Naunhof - Lindhardt Straße, B 20412/66", U concentration is at between 8 and 18 µg/L.
- In "Naunhof, Straße WWII, B 4/94", it ranges between 3 and 10 µg/L.

They are in the range of or even higher than the MCL of the German Drinking Water Directive of 10 µg/L. Both monitoring wells are located in the SSW of the lysimeter station and are shown as yellow and green dot in Figure 4. In 2000 and 2001, respectively, when sampling and analysis started, U concentrations were highest. Since then, they constantly decreased. This might either be because of the decrease in P fertilizer application in the surrounding or because of application of P fertilizer with lower U concentration. When looking back to Figure 23, one can see that in Brandis both reasons did apply: fertilization intervals got bigger and intensity and U concentration lower.
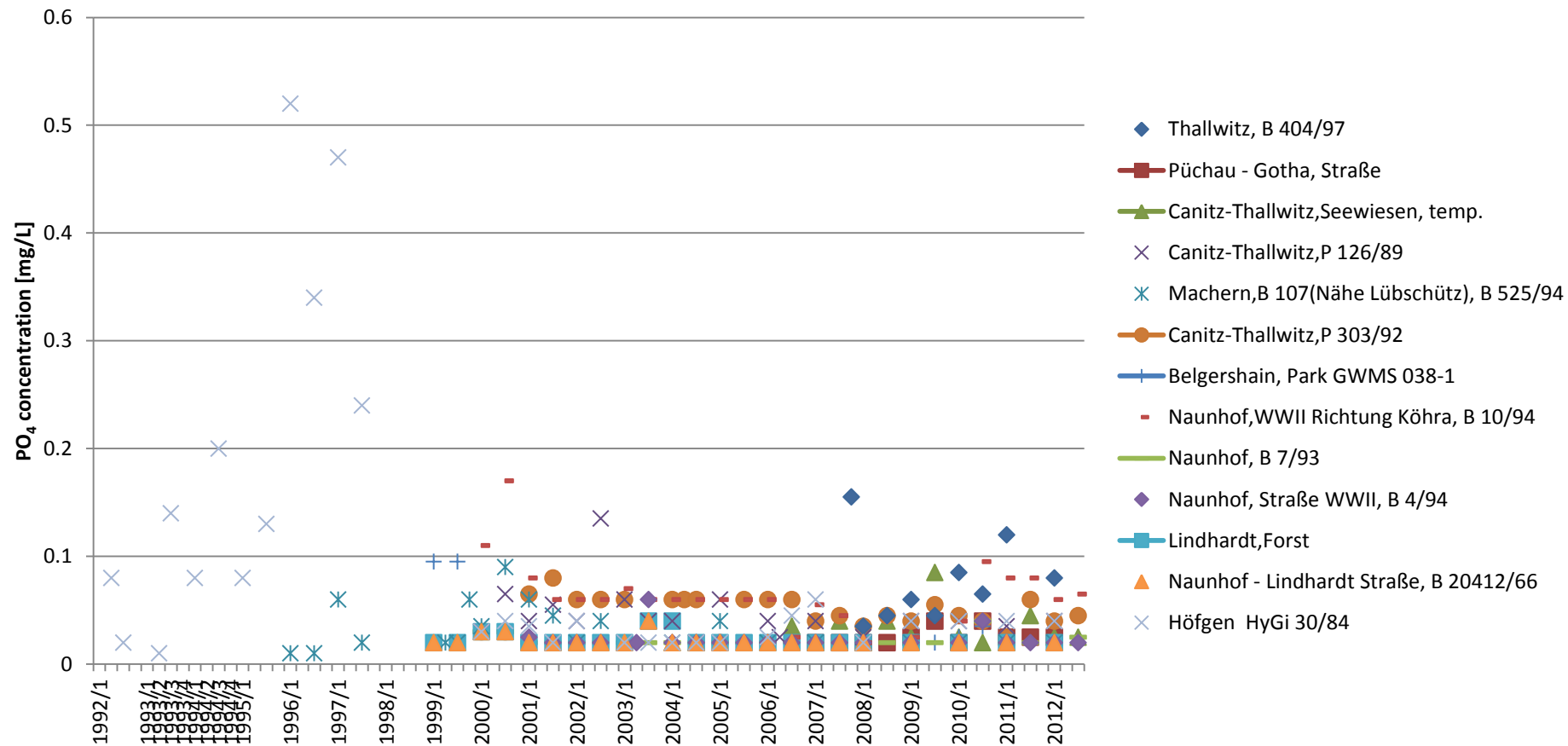
Figure 29 – PO₄ concentration over time in the monitoring wells in the surrounding of the lysimeter station in Brandis
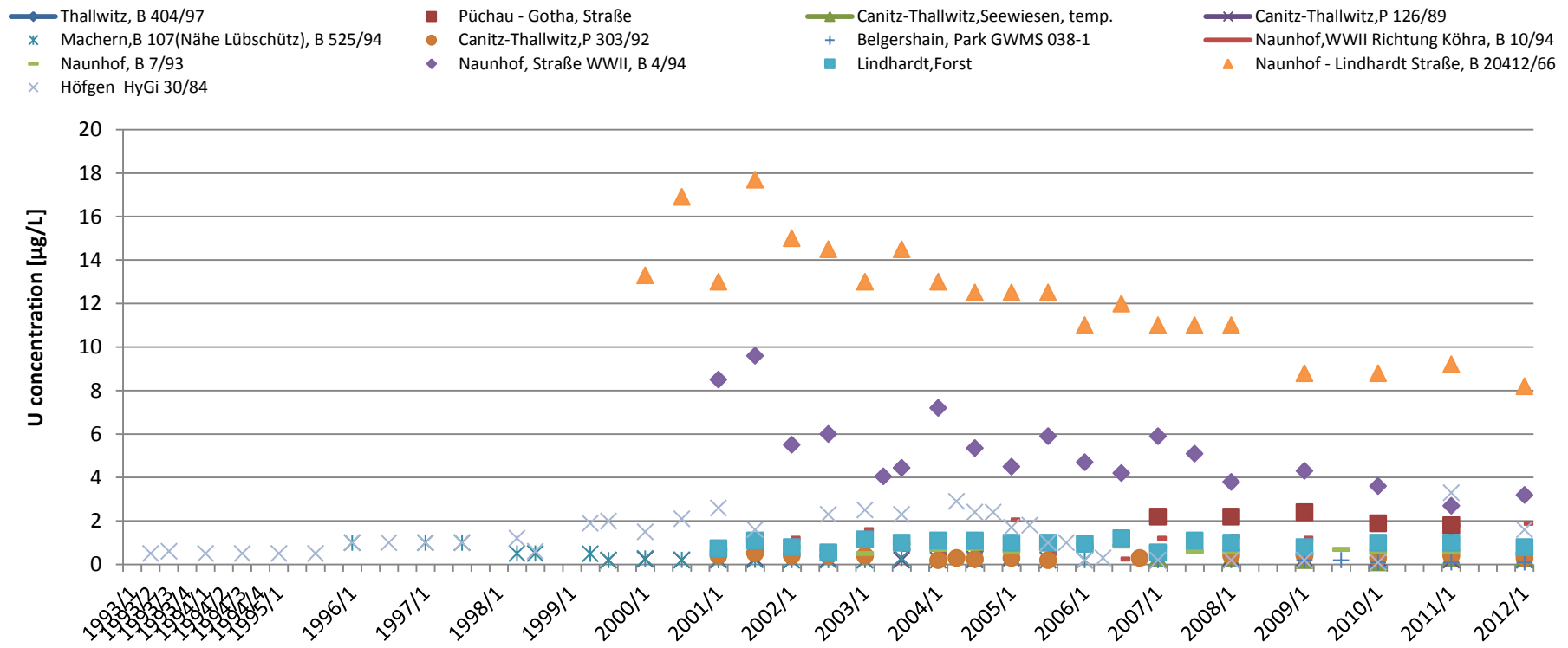
Figure 30 – U concentration over time in the monitoring wells in the surrounding of the lysimeter station in Brandis

5.7.2 Schmorren field

The phosphate concentrations in groundwater from monitoring wells in the surrounding of the Schmorren field soil sampling site are in a much lower range than most of those in Brandis (see Figure 31). Natural groundwaters contain tens to hundreds of µg PO_4 /L (Clasen, 1991, page 340). So, the monitoring wells in Figure 31 are in the lower range of typical concentrations. Like in Brandis, there is no clear trend but concentrations scatter. For four of the five monitoring wells considered here, phosphate concentrations are in the range of 20 to 75 µg/L. The waters with the higher contents could be impacted by fertilization but with either high dilution effects or low P application rates. In the monitoring well "Naundorf, Br. HYP NfOs1/2002, Stauanlage Naundorf", concentrations are always in the range of or below the detection limit of 0.01-0.02 mg PO_4/L. So, this well it is likely that this well is not affected by phosphate fertilization.
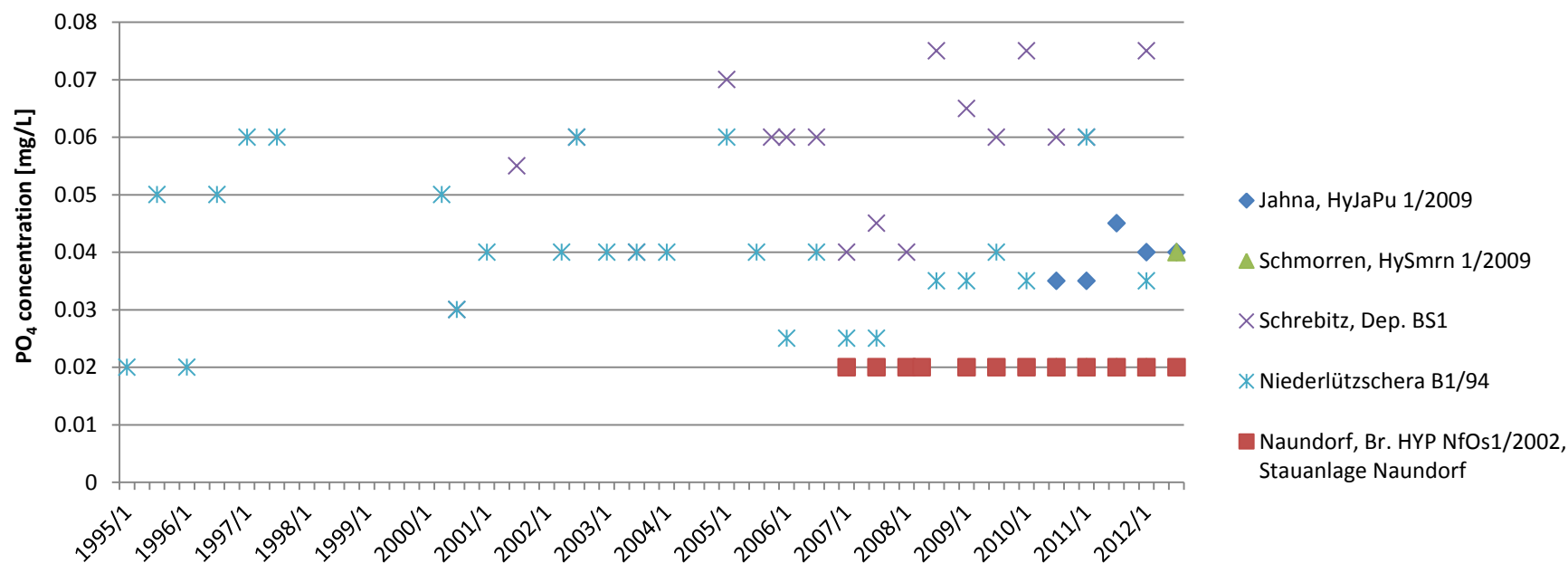
Figure 31 – PO$_4$ concentration over time in the monitoring wells in the surrounding of the Schmorren soil sampling site

In the Schmorren surrounding, four of the five monitoring wells exceeding the detection limit of the LfULG for U show rather low U concentrations of below 3-4 µg/L (see Figure 32). In "Niederlützschera B1/94" and "Schrebitz, Dep. BS1" in the SSW and WSW of the Schmorren test site, respectively, U concentration is about constant. In "Jahna, HyJaPu 1/2009" and "Schmorren, HySmrn 1/2009" in the NE and SSE, there seems to be an increasing trend. Analytics there started not before 2011, there are only two values available that do not allow time series analyses. In "Naundorf, Br. HYP NfOs1/2002, Stauanlage Naundorf" in the NNW, however, the trend also points towards U increase in groundwater since 2006/2007. But it seems to stagnate or even decrease since 2010 at about 7 µg/L, which is already very close to the MCL of the German Drinking Water Directive (10 µg/L). In Figure 24, one can see that the field in Schmorren was subjected to P fertilization in 2009. This is likely to have been the trigger for the abrupt U concentration increase in groundwater. After 2009, no additional P fertilizer was applied as far as it is known at present.

Comparing Schmorren with Brandis, one can say that like phosphate, also uranium concentrations are lower in Schmorren than in Brandis. This difference probably results from differences in fertilization as well as in the contaminant retention capabilities of the soils as mentioned in Table 7.
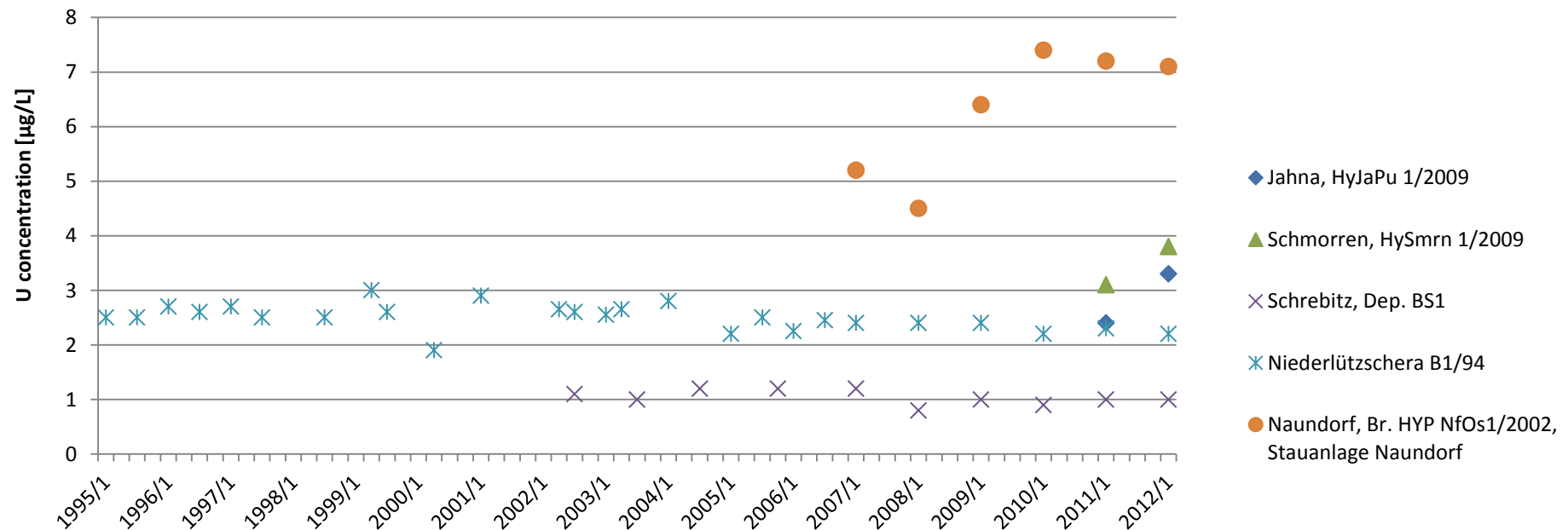
Figure 32 – U concentration over time in the monitoring wells in the surrounding of the field site in Schmorren

5.7.3 Wermsdorf forest

In two of the three monitoring wells, phosphate concentration lies in the range or below its detection limit of 0.01-0.02 mg PO$_4$/L (see Figure 33). Only in "Calbitz, HyCal 1/2007", it keeps steadily increasing since 2008 – the start of sampling and analytics there. It even rises to an enormously high level of 2.2 mg/L where it seems to remain in 2012. So, the well seems to be severely impacted by P fertilizer application or other P sources.
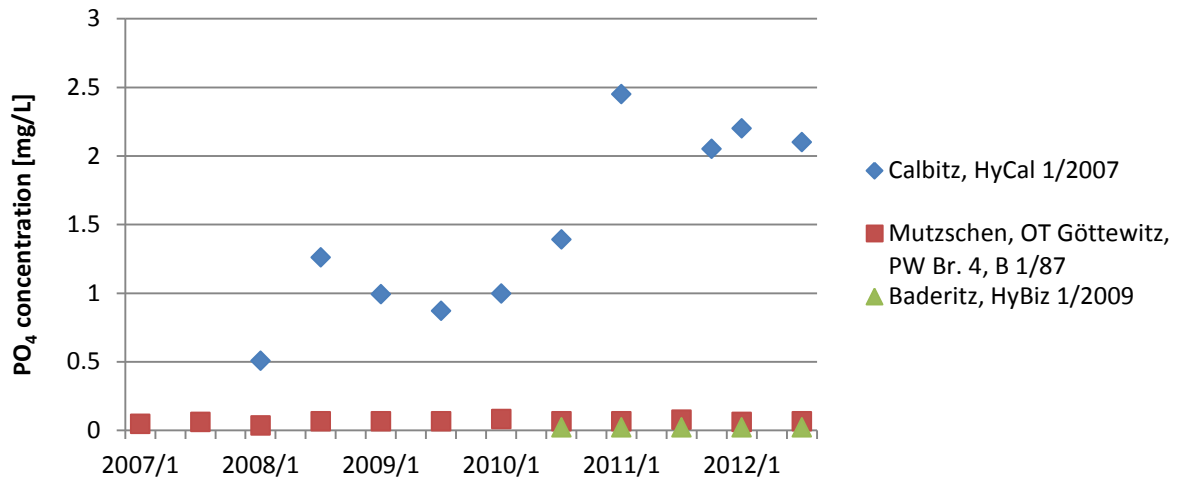
Figure 33 – PO$_4$ concentration over time in the monitoring wells in the surrounding of the Wermsdorf forest site

In the surrounding of the Wermsdorf forest site, U concentration in groundwater is more or less the same over time without indicating an in- or decreasing trend since 2007 (see Figure 34). The time since the monitoring well in "Baderitz, HyBiz 1/2009" started to be in operation is too short for assessment. The constancy in U content supports the assumption that the forest site either did not encounter P fertilization or P fertilization with low U contents (see P concentration increase in "Calbitz, HyCal 1/2007" in Figure 33).
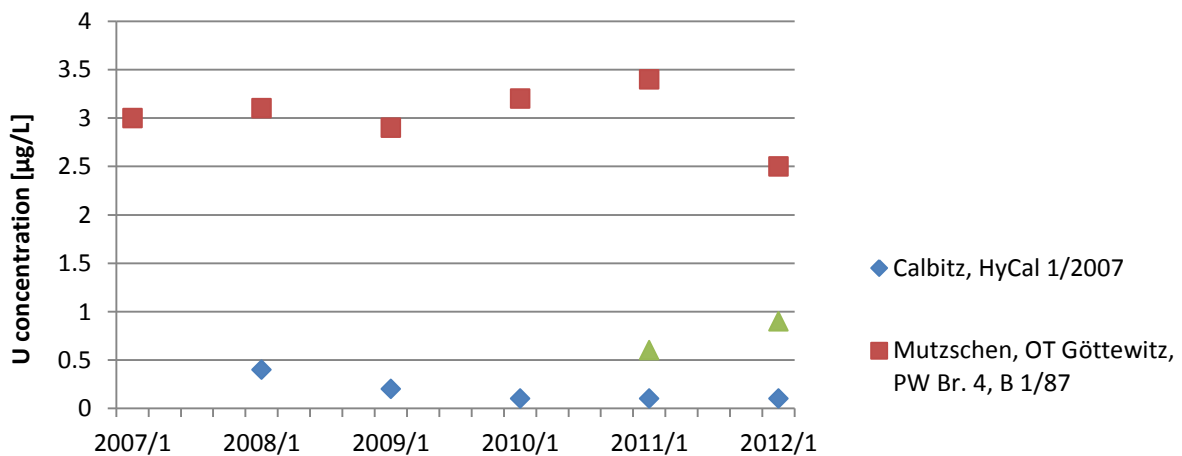
Figure 34 – U concentration over time in the monitoring wells in the surrounding of the Wermsdorf forest site

5.7.4   Hilbersdorf

Phosphate concentration in "Linda, B 17/07" is very low, in the range of the detection limit of 0.01-0.02 mg PO_4/L as shown in Figure 35. In "Naundorf, Gippenhäuser, HyFr 101/89", in 2010, concentration was high (0.25 mg/L) in 2010 and decreased abruptly since 2011 – the level where it remained until now. This might either be a real observation or an erroneous result. In "Oberschaar, Hy OrhaFr 1/2011", data is only available since 2011 and therefore too short for time series analysis.
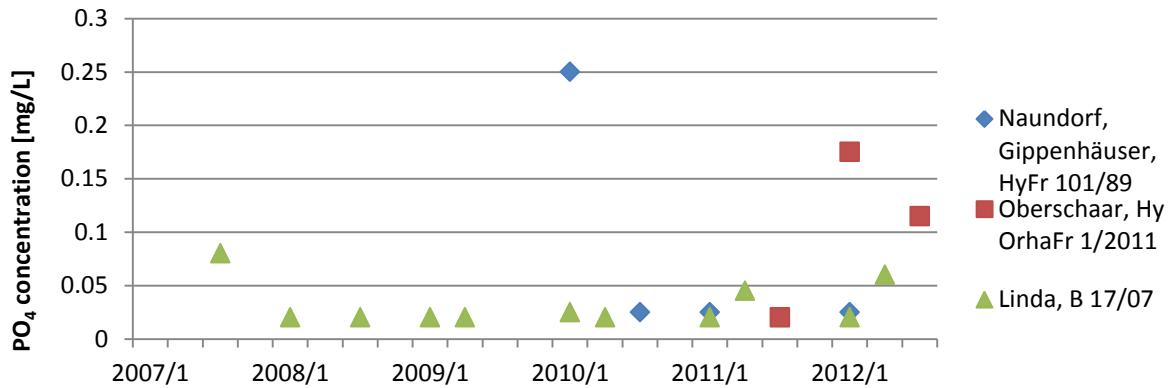
Figure 35 – PO₄ concentration over time in the monitoring wells in the surrounding of the Hilbersdorf site

Figure 36 shows the U groundwater analytical data of the three monitoring wells in the surrounding of the Hilbersdorf site. Generally, U concentrations are very low as compared to the other, previously mentioned sampling sites. In Hilbersdorf, contents are in the range of the Wermsdorf forest site of below detection limit (0.1 µg/L) to below 3 µg/L. That means they are all clearly below the MCL of U in the German Drinking Water Directive (10 µg/L). Two of the monitoring wells were put into operation in 2010. Therefore, only three data points are available since then. They seem to indicate a decreasing trend or a trend approaching a constant value. This cannot be said with certainty due to the short period of time depicted with the analytical data. The third monitoring well, "Linda, B 17/07", is in operation since 2007. Until 2010, it shows a decreasing trend. Since 2010, U concentration did not decrease any more but remained at about 0.5 µg/L.
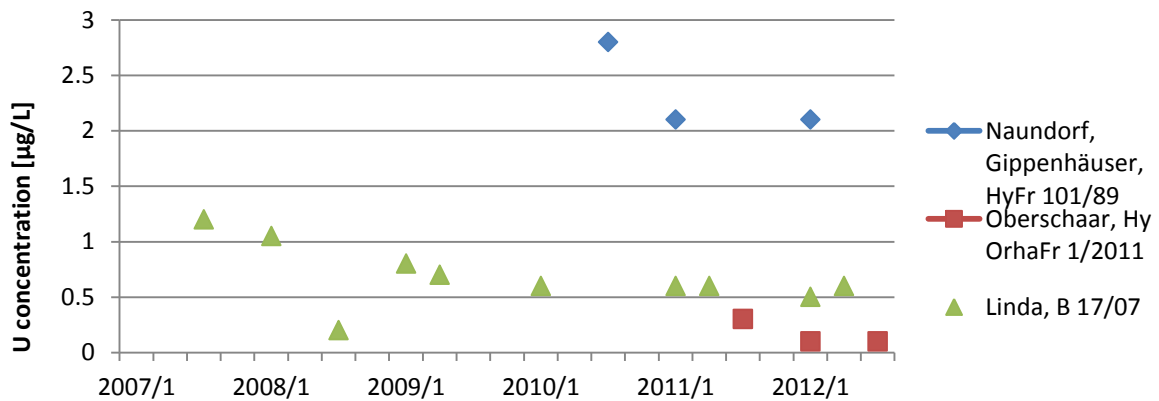
Figure 36 – U concentration over time in the monitoring wells in the surrounding of the Hilbersdorf site

5.7.5   Sauerbach

In Figure 37, phosphate data is shown for two monitoring wells at the lower part of the Sauerbach catchment. These two monitoring wells are therefore impacted by the entire catchment (Musolff, 2013) and not only by the field that was studied in the present thesis. Some of the water constituents differ significantly from those of the waters sampled directly below the lysimeters. For example, nitrate concentrations are lower by factor two to four in the monitoring wells as compared to the lysimeter percolation water (about 40 to 100 mg/L vs. 140 to 230 mg/L).
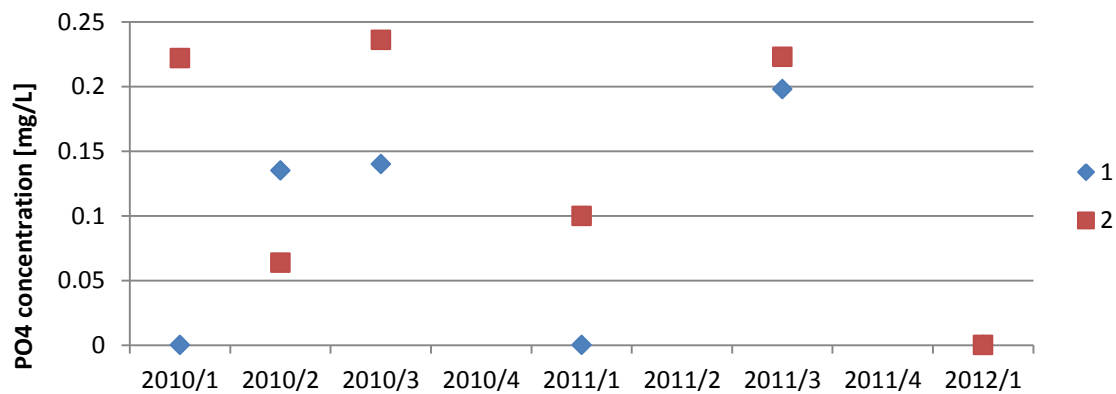
Figure 37 – PO$_4$ concentration over time in the monitoring wells in the surrounding of the Sauerbach site (Well # 1 is in direct vicinity to the lysimeters; # 2 is located a few meters upstream the creek. Detection limit is 0.05 mg PO$_4$/L)

There is no clear trend of the phosphate concentration over time but results scatter a lot. Some of them are below 0.05 mg PO$_4$/L, detection limit of the photometric P determination of the UFZ in Halle. According to (Clasen, 1991) (page 340), these concentrations are in the normal range of groundwaters (tens to hundreds of μg PO$_4$ /L) with 64 to 236 μg/L. So, the monitoring wells are either not impacted by fertilization or encountered considerable dilution.

5.8   Summary of the main results of the study sites and risk evaluation

The central goal of the thesis had been to better understand the fate of U in the subsurface after phosphate fertilizer application. In that frame, especially also risk assessment was of great importance. Therefore, earlier in the present thesis, in chapter 3.3, the sampling sites were described in detail and the risk for soil and groundwater to be contaminated with U by phosphate fertilizers was estimated. At that point, only the given information from the responsible institutions could be used. In the course of this thesis, soil properties were studied in detail using different methods. Groundwater samples were analyzed and from these results and with the help of PHREEQC species distribution was modeled and saturation indices of important minerals were calculated. Additionally available soil and groundwater data from the sites and their surrounding over time was examined and checked for trends. Now all this information, findings and corresponding interpretations are put together in Table 25 and risk evaluation is updated.

Table 25 – Compilation of relevant data for evaluation of risk for contamination of field topsoil and groundwater with uranium (For the properties of the Brandis site, ranges are given describing the properties of the three sampled lysimeters. In brackets reference is given to the chapter where the properties were discussed earlier. Topsoil means at 12 and 14±6 cm depth, respectively. Subsoil stands for sampling depths of 26 and 28±6 cm. TOC stands for total organic carbon.).

Criteria for comparison	Brandis	Schmorren	Hilbersdorf	Sauerbach
SOIL PROPERTIES				
Type of soil (chapter 5.1.1)	Highly silty sand	Silt or slightly sandy silt	Highly silty sand	Slightly sandy silt or slightly loamy, slightly sandy silt
Bulk density [g/cm³] (chapter 3.3)	Medium to high (1.56 to 1.68)	Medium (1.64)	Low at top (1.49); below: low to medium (1.4-1.6)	No information
Soil-forming rock/sediment (chapter 3.3)	Sand loess above gravelly sand or loam	Loess loam	Loess loam and gneiss	Thick layer of colluvial material above sandstone
pH of top- and subsoil (chapter 5.1.2)	6.0 6.2	6.9 6.8	5.9 6.0	7.8 7.8
Fraction of < 2 mm soil material [mass %] in top- and subsoil (chapter 5.1.1)	93 % 93 %	99 % 99 %	79 % 74 %	97 % 97 %
Fraction of cohesive material (clay, silt) [mass %] in top- and subsoil (chapter 5.1.1)	32 % 43 %	90 % 84 %	46 % 51 %	72 % 75 %
CEC_{eff} in top- and subsoil (chapter 5.1.5)	6.6 … low 6.3 … low	11.0 … medium 11.7 … medium	11.9 … medium 8.3 … medium	18.6 … high 17.1 … high
Humic matter content in topsoil [vol. %] (chapter 3.3)	Very low to low (1.6- 2.2)	Low (2.1)	High in upper 25 cm (4.6), very low at 25-45 cm (0.5)	No information
TOC content in sampled soils [mass % C] in top- and subsoil (chapter 5.1.4)	1.19 … low 0.90 … low	1.17 … low 1.10 … low	1.51 … low 0.70 … low	1.35 … low 0.97 … low
Carbonate content in sampled top- and subsoils [mass % C] (chapter 5.1.4)	0.02 … very low 0.07 … very low	0.20 … low 0.07 … very low	0.94 … considerable amount of carbonate 0.19 … low	2.02 … rich in carbonate 2.40 … rich in carbonate
Soil's U retention potential	Very low to low (⇔ poor retention capability)	Low to medium (⇔ l retention capability)	Low to medium (⇔ soluble carbonate complexes in groundwater likely)	Low to medium (⇔ soluble carbonate complexes in groundwater likely)

Criteria for comparison	Brandis	Schmorren	Hilbersdorf	Sauerbach
UPPERMOST AQUIFER/AQUICLUDE				
Descripiton (chapter 3.3)	**Aquiclude**, bordering with **unconfined porous aquifer** very close, south of lysimeter station	**Aquiclude** (out of loess, loessic loam, relocated loess), covering **confined porous aquifer**	**Solid rock aquifer** (≤ 2 m of covering cohesive material; highly metamorphic gneiss, only slightly fractured, very little groundwater contained, mostly interflow)	Shallow **solid rock aquifer** (sandstone) with high salinity; covered by cohesive material
Permeability, k_f [m/s] (chapter 3.3)	No information	$8 \cdot 10^{-4}$ … high, like gravelly sand	Only subsurface discharge is given: 1-1.5 L/(s*km²) … low	No information
Depth to groundwater [m] (chapter 3.3)	> 2-5 … shallow	> 10 … medium	No data because no isohypses possible for solid rock	Ca. 9 … medium
FERTILIZATION				
Annual U input [µg/kg] (min/mean/max) to topsoil (chapter 5.6)	0.004-0.34/1.42-16.80/8.97-106.00; most of it in 1980s; nearly none any more since 1990; only in 2000 and 2008 → first probably high, then diminishing	Nearly none, only in 2009: 0.001/0.93/7.65 → negligible	Nearly every year; depending on year: 0-0.15/0-8.80/0-32.96 → continuous, changing quantity and quality	Probably already for ca. 50 a; actual data only since 2010, annually: 2.82 → medium, maybe constant already for at least 3, or maybe also up to 50 years
Mean annual U input [µg/kg] (chapter 5.6)	0.15/7.63/48.75	0	0.04/3.21/11.97	2.82
Total U input [µg/kg] (chapter 5.6)	Since 1993: 1.46/76.29/487.55	Since 2000: 0.001/0.93/7.65	Since 1995: 0.58/192.57/718.14	Over a period of 52 years: 3.19/313.61/967.41 Assuming same fertilizer as at present: 149.36

Criteria for comparison	Brandis		Schmorren		Hilbersdorf		Sauerbach	
U IN SOIL								
Content in field top- and sub-soil in 2013 [mg/kg] (chapter 5.1.6)	1.7±0.4 2.1±0.4		3.8±0.6 3.3±0.5		3.1±0.5 3.5±0.6		1.3±0.2 2.2±0.4	
Difference between field top- and subsoil (chapter 5.1.6)	Nearly none		Maybe field subsoil higher than field topsoil		Higher in topsoil than in sub-soil		Nearly none	
Difference between field and forest (chapter 5.1.6)	Nearly none		(Maybe) higher in field than in forest		Very small		Nearly none	
Change in U content in field soil (chapter 5.1.6)	No evaluation possible, be-cause only results from own analysis (2013) available		First decreasing (2000-2006) 2.7 → 1.7, Then increase by factor 2! (2006-2008-2012): 1.7 → 2.1 → 3.3 (3.1 in top-soil; 3.5 in subsoil; gamma analysis result)		1995-2000: constant at ca. 2.1 Then increase by 36 (topsoil) or 71 % (subsoil) (2006-2012; before no data): 2.8 → 3.8 in topsoil 2.1 → 3.3 (2012) or 3.6 (2009) in subsoil		No evaluation possible, be-cause only results from own analysis (2013) available	
U EXTRACTABILITY								
7N HNO$_3$-extractable U [% of U$_{total}$] in top- and subsoil (chapter 5.1.8)	Field: 28.4 23.2	Forest: 20.3 17.1	Field: 22.0 18.9	Forest: 19.6 18.9	Field: 39.9 29.3	Forest: 36.5 35.5	Field: 39.7 22.6	Forest: 15.45 15.75
NH$_4$Ac (pH 7)- extractable U [% of U$_{total}$] in top-, subsoil (chapter 5.1.8) … selected because in litera-ture, this extractant is some-times used for evaluating plant-availability	Field: 0.15 0.11	Forest: 0.82 0.59	Field: 0.08 0.05	Forest: 1.21 1.21	Field: 0.19 0.24	Forest: 1.63 1.13	Field: 1.21 0.85	Forest: 0.08 0.08

Criteria for comparison	Brandis	Schmorren	Hilbersdorf	Sauerbach
U IN WATER				
Present situation in seepage water in 2013 [µg/L] (chapter 5.6)	At 3 m depth: 0.001, 0.004, 0.001, 0.004 → very low, in range of detection limit	Long-term LfULG data at 45, 145 and 165 cm depth: 0.15-2.68, 1.61-4.09, 0.15-2.29 (0.15 = below detection limit)	At 80 cm depth: 0.21	At 150 cm depth: 6.78, 9.14, 12.87, 12.08 → very high
Change in U content in seepage water [µg/L] (chapter 5.6)	No evaluation possible, because only results from own analysis (2013) available	Scatters a lot; but seems to increase from 2007-2012: around 1 → around 3.5 or 4	Not really (2004-2013), always up and down: 40 cm depth: 0.18-0.40 80 cm depth: 0.15-0.30	No evaluation possible, because only results from own analysis (2013) available
Dominant U species in seepage water (PHREEQC modeling, chapter 5.4)	$Ca_2(UO_2)(CO_3)_3$ (88-94 %), $UO_2(CO_3)_2^{2-}$ (1-6 %), $UO_2(OH)_2$ (1-3 %), $UO_2(CO_3)_3^{4-}$ (1-2 %) → mainly uncharged	No water sample available	$Ca_2(UO_2)(CO_3)_3$ (79 %), $UO_2(CO_3)_2^{2-}$ (10 %), $UO_2(OH)_2$ (8 %), $UO_2(CO_3)_3^{4-}$ (1 %), UO_2CO_3 (1 %) → mainly uncharged	$Ca_2(UO_2)(CO_3)_3$ (99 %) → nearly solely uncharged species, but probably overestimated due to erroneous IC analysis
U concentration in groundwater and development over time in surrounding monitoring wells (chapter 5.7)	Some data since 1993, but most data not before 2001: in some monitoring wells **constant** c(U) below 3 or 1 µg/L; **decreasing** trend in 2 wells (from 17 and 9 µg/L, respectively, in 2001 down to 8 and 3, respectively, in 2012)	**Constant** c(U) in 2 wells in surrounding (2.5-3 or 1 µg/L) since 1995 or 2002, respectively, or **increasing** trend since 2007 in another well (from 5 to 7 µg/L); other wells not before 2011 → no trend assessment possible	**Decreasing** trend (from 1.2 to 0.5 µg/L) since 2007 in one monitoring well; from 2.8 to 2.1 and 0.3µg/L to below the detection limit (0.1 µg/L) in two other wells since 2010 and 2011, respectively → seems like a constant level is approached in each well	No data available

As summarized in Table 25 in Brandis, much time passed since last (intense) P fertilizer application. From the lysimeter station there is neither U data available for soil nor for groundwater over time. The samples taken in 2013, however, gave average U contents of about 1.5 to 2.5 mg/kg in soil and very low concentrations (i.e. in the range of the detection limit of 0.001 µg/L) in percolation waters leaving the lysimeters. U in field soil does not differ from that in the corresponding forest soil suggesting that concentration did not significantly increase. soil The lysimeter water sample data, however, needs to be seen with care and is likely to not to reflect the actual situation because the lysimeter walls, made of galvanized steel, are probably corroded as highly elevated Zn contents in the range of tens of mg/L in percolation water indicated. So, iron (hydr)oxides probably formed and effectively sorbed U and other elements effectively reducing concentrations in water. The trend of U in the monitoring wells in the surrounding of the station is constant in some of them and decreasing in others. That observation goes in hand with the decrease in P fertilization of the field adding less U to the local aquifer. U contents in the monitoring wells with decreasing trends had been very high in 2001 with 17 or 9 µg U/ L, close to or above the MCL of the German Drinking Water Directive (10 µg/L). In 2012, it had decreased to 8 and 3 µg/L, respectively – still very high or at least elevated. That means that the site in Brandis is very susceptible to U contaminations. The sandy soil with low organic matter content in Brandis does not retain U in an effective way but a great or even the greatest share reaches the groundwater, which is rather shallow there with only few meters depth. The share of U remaining in soil seems to be more or less immobile; only about 20 to 30 % of U_{total} could be extracted using nitric acid.

In Schmorren, P fertilizer had been applied only once, in 2009, since the beginning of data recording in 2000. The amount is likely to have been low. However, U contents in soil and percolation water increased unproportionally to that input. In soil, U concentration increased by factor 2 between 2006 and 2012, from 1.7 to 3.3 mg/kg in topsoil and 3.5 mg/kg in subsoil. Contents in water scattered much but showed an increasing trend from about 1 to 3.5 or 4 µg/L. In the groundwater of the surrounding monitoring wells, U contents were constant in some and increasing from 5 to 7 µg/L since 2007 in another one. So, either the applied fertilizer contained considerably more U than common fertilizers according to (Taylor, 2013) do, or there was an additional input from other fields or other sources that are connected with the same aquifer. The fact that U content in field soil is slightly higher than that of forest soil supports the assumption that fertilization has caused the increase. All in all, the vulnerability of this soil for U contamination can be evaluated as very high. That is especially because input was low and rare, depth to groundwater is relatively great with > 10 m, and concentration increase is high even though.

In Hilbersdorf, P fertilizer was applied nearly every year, but type and amount varied. In soil, U content was constantly at about 2.1 mg/kg since 1995 until 2000. After that, it increased to 2.8 and then to 3.8 mg/kg in 2006 and 2012, respectively. For percolation water, yet, no trend can be seen. Between 2004 and 2013, U concentrations varied from 0.2 to 0.4 µg/L at 40 cm and from 0.15 to 0.3 µg/L at 80 cm depth. In the surrounding monitoring wells, one can observe a decreasing trend from about 1 to 3 µg/L down to below 1 µg/L. This trend seems to approach a constant level. So, it appears like the soil effectively retains U and prevents it from reaching the groundwater zone. The elevated U contents in field topsoil support the assumption that U stems from fertilizer. It might be bound by organics to some extent as contents there are relatively high. However, surprising is that U contents in forest soil are more or less at the same level as those in field soil. Also the availability, i.e. the extracted amounts using nitric acid and ammonium acetate, respectively, are basically the same. They are about 10 to 15 % higher than those in Brandis and Schmorren and amount about 30 to 40 % and 0.2 to 1.6 %, respectively. So, either U content in forest soil also increased over time by the application of (phosphate) fertilizers in the context of making forests soils less acidic and increasing fertility or by wind-blown

input, or contents there were naturally higher than those of the corresponding field site. This cannot be examined as no soil data over time is available for the forest site.

For the Sauerbach site, fertilization data is only available since 2010. It is likely, however, that it was used for agriculture already for several decades. The fertilizer used at present has a medium U content. For soil, it is the same: U concentration ranges between 1 and 2 mg/kg and there are no significant differences between field and forest soil. Availability, i.e. extracted amounts however, are about 3- to 15-times higher in field soil as compared to forest soil (in topsoil: 40 vs. 15 % of U_{total} using nitric acid; 1.2 vs. 0.08 % using ammonium acetate at pH 7). Moreover, U concentration in percolation water at 150 cm depth is rather high ranging from 6.8 to 12.9 µg U/ L depending on the lysimeter regarded. Even if neither percolation water data over time, nor any groundwater U data is available, it can be assumed that these high concentrations are not natural. It is very likely that phosphate fertilization has caused this increase. And it might have been especially high at this site because of its soil and groundwater composition. The soil there is high in carbonate and pH and at the same time is low in organic carbon, which could act as a sorbent. Groundwater has an elevated salinity resulting in high competition for sorption sites on solid surfaces. Due to the high calcium and carbonate contents in water, the uncharged and consequently very mobile $Ca_2(UO_2)(CO_3)_3$ species accounts for the greatest share of U. It is likely that it does nearly not interact with soil under the present conditions and consequently quickly reach the groundwater zone.

5.9   Flow-through experiments

In the previous chapters the present state of soil and groundwater and the development over time were presented and discussed. The flow-through experiments using Brandis field top- and subsoil are the third part of the assessment of the effect of P fertilization on soil and groundwater. They should serve as a forecast of when and how much U will reach the groundwater zone and how much will be retained by the soils. All calculations, analytical and numerical results can be found in *FOLDER 4* in the digital appendix.

If stop times for storage bottle refilling etc. are subtracted, this experiment lasted for 100 days. The amount of U and P applied on one day of the experiments is equal to that applied during about 319 days in reality – assuming fertilization according to the GAP guidelines as explained in Table 12 in chapter 4.3.1. So, the experimentally depicted time is 93 years. Within that time, breakthrough was reached in none of the columns. On a first sight, this is rather surprising because soil and water analytical results studied in the previous chapters showed a more or less direct effect of fertilization on soil and water. PHREEQC modeling prior to the experiments had suggested that most U species formed would be uncharged and no U minerals would be formed. Therefore, it had been expected that a great share of the applied U would not be retained by the soils.

5.9.1 U, P, and Ca mass balances and concentration development over time

During the actual experiments, however, about 99 % of U was retained in each column (see *EXCEL 9* in the digital appendix), except for cell # 3. The concentration of U in the water flowing out of the flow-through cells into the collecting Teflon vessels over time is shown in Figure 38. In most cells, less than 1 % of the applied U (40 µg/L) were found in the columns' outlets. In cell # 3, about 2 % escaped. As opposed to the other cells, starting at February 7, 2013, U concentration in the outflow water started to rise abruptly. The reason for that is not known. About one month later, it reached a more or less constant level of about 0.75 µg/L until the end of the experiments. However, the corresponding cell of the subsoil, cell # 8 did not follow the same trend but remained at the very low level from the beginning, below 0.05 µg/L.

It might be that some of the cells' U concentrations started to rise in April but this increase is too small and time was too short to say this with certainty. Throughout the entire experiment, none of the cells approached breakthrough, i.e. close to equal input and output U concentrations (40 µg/L).
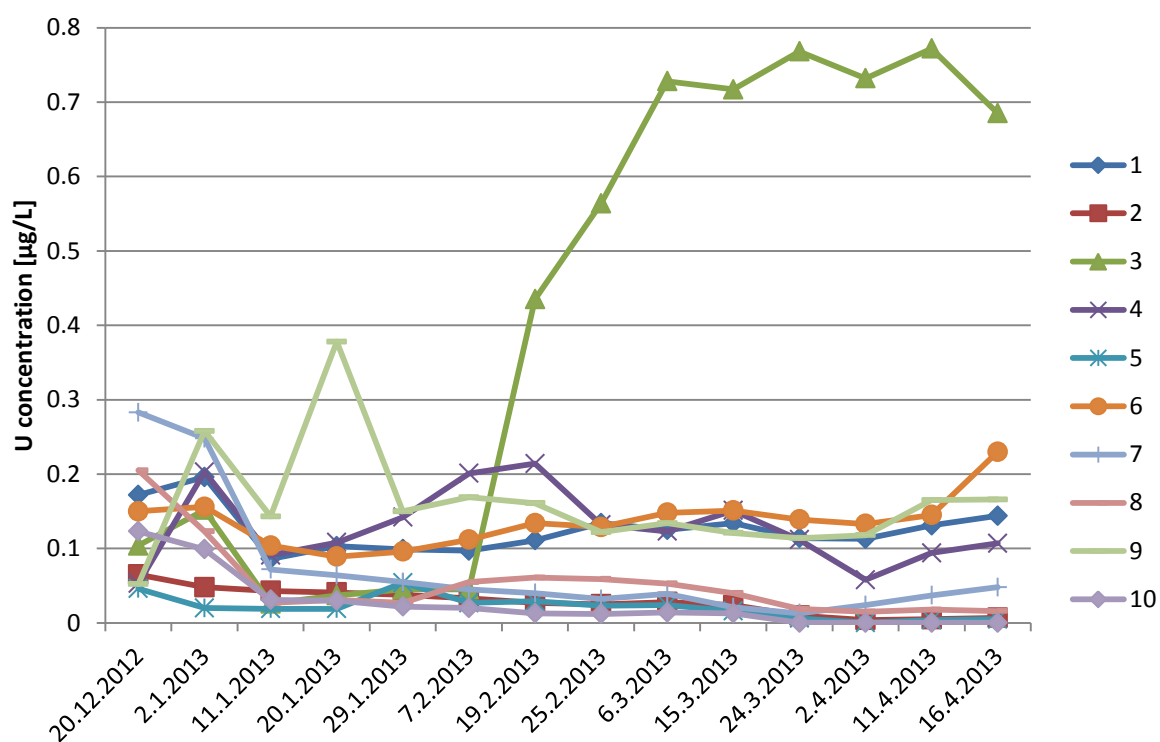
Figure 38 – U concentration in water escaping from the flow-through cells (Sampled in the Teflon collecting vessels as described in chapter 4.3.1. Analyses were done with ICP-MS. Detection limit was 0.001 µg/L.)

In addition to U, mass balances were also calculated for P and Ca. HCO_3^-, the fourth component being contained in the flow-through solutions, is not included in mass balancing as its concentration permanently changes by the interaction with carbonate and atmospheric CO_2.

From the phosphoric acid applied, in total only between 0.1 and 24 % were retained by the soils, i.e. the greatest share remained in the water phase. Retention decreased over time. Figure 39 shows the P mass balances, i.e. input minus output, for the different flow-through cells. The amount of P is referred to the duration of the intervals between sampling and is consequently given in mg/d.

In the first time interval, around December 20, cells were flown through by distilled water to see how much of which element is washed out of the soils. On average, the amount of P washed out of topsoils was twice as high as that of the subsoil samples, namely between 0.20 and 0.31 mg/d vs. 0.10 to 0.14 mg/d. It is very likely that difference results from P fertilizer applied on the uppermost soil horizon.

From the second time interval on, which started on December 20 after sampling, the actual flow-through solutions were used. For better following the interpretations, here again the composition of the applied solutions is given. Solution I was applied on cell 1 and 6; II on 2 and 7, etc.

Solution number	NaHCO$_3$	UO$_2$(NO$_3$)$_2$		H$_3$PO$_4$ as P	as P	as PO$_4$	Ca(NO$_3$)$_2$
	[mM]	[µM]	[µg/L]	[mM]	[mg/L]	[mg/L]	[mM]
I	1	0.178	40				
II	1	0.168	40	1.421	44	135	
III	1	0.168	40	1.421	44	135	1
IV	1	0.168	40	0.142	4.4	13.5	
V	1	0.168	40	0.142	4.4	13.5	1

For P application on the flow-through cells, that means: Cells 2, 3, 7 and 8 were loaded with 44 mg/L P, cells 4, 5, 8 and 10 with 4.4 mg/L and cells 1 and 6 did not receive any P. In Figure 39 one can see that in those cells that did not receive any P, i.e. # 1 and 6, P mass balances were always negative. So, in sum these cells lost phosphorus (between 0.08 and 0.31 mg/d). The total amount of P washed out of cell 1 was 20.5 mg as compared to only 9.9 mg in cell 6. As mentioned before, this is an effect of the difference in total contents in top- and subsoil.

Cells 2, 3, 7 and 8 received 10-times more P than cells 4, 5, 9 and 10. The corresponding mass balances did not constantly differ by factor 10 but varied between a factor of 4 and 15. That means the more P is applied, the more is retained, but this relationship is not linear (probably due to processes like mineral formation, dissolution, complex formation, etc.). Concerning the relative P retention, there is no clear difference between the cells that received 44 mg/L P as compared to those that received 4.4 mg/L. Sometimes relative retention is higher in the first group and sometimes in the second.

If the P mass balance over time is looked at, one will see three phases:

1) 20.12.2012:   No P input → negative P mass balance in all cells; similar range
2) 2.1.2013:   P input started → greatest P retention; between 56 and 79 % of input in cells 2, 3, 7 and 8; between 72 and 88 % in cells 4, 5 , 9 and 10.
3) 20.1. – 16.4.2013: Constant P input (44 vs. 4.4 mg/L) and constant or decreasing absolute retention [mg/d] (at a different level in the cells, depending on input concentration.).

Towards the end of the experiments, in March/April, P mass balances in the individual cells even reached negative values in some of them (# 4, 9 and 10). That means in those cells, output was greater than input (by 3 to 34 % of the input).
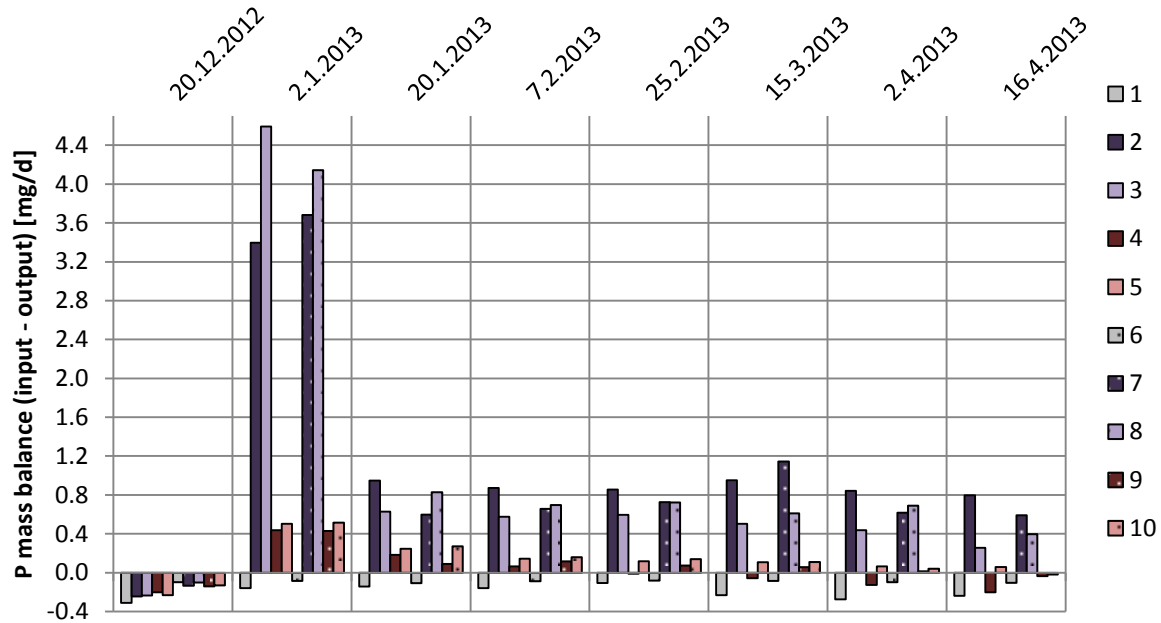
Figure 39 – P mass balance, i.e. input minus output in the ten flow-through cells filled with Brandis field topsoil in mg/d (Soil samples 1 to 5 stem from topsoil; 6 to 10 from subsoil. The solutions applied on the soils are given in the yellow table earlier in this chapter. Solution I was applied on flow-through cell 1 and 6; II on 2 and 7, etc.).

Calcium was only applied on cells 3, 5, 8 and 10 – 40 mg/L on each of them. The other cells did not receive any calcium. Figure 40 shows the Ca concentration of the solutions flowing out of the flow-through cells over time. During IC analysis, some samples from March 15 were mixed up. So, in case it was possible, the missing results were replaced by ICP-MS analytical results modified by a factor that takes into account the average difference between IC and ICP-MS Ca concentrations. From the plot, it becomes clear that without additional Ca application, Ca outlet concentrations range between 5 and 10 mg/L. When 40 mg Ca/L are added, outlet concentrations increase to between 30 and 50 mg/L. They are highest in cells 3 and 8, i.e. the cells to which also the greatest amounts of P (44 mg/L) were added. Second highest concentrations are achieved in cells 5 and 10, in which the applied P concentrations were 10-times lower. So, this difference is probably a result of two main processes:

- Desorption of Ca from soils by being substituted by H^+ that stems from H_3PO_4.
- Dissolution of carbonates contained in the soils by phosphoric acid attack – even if diluted.
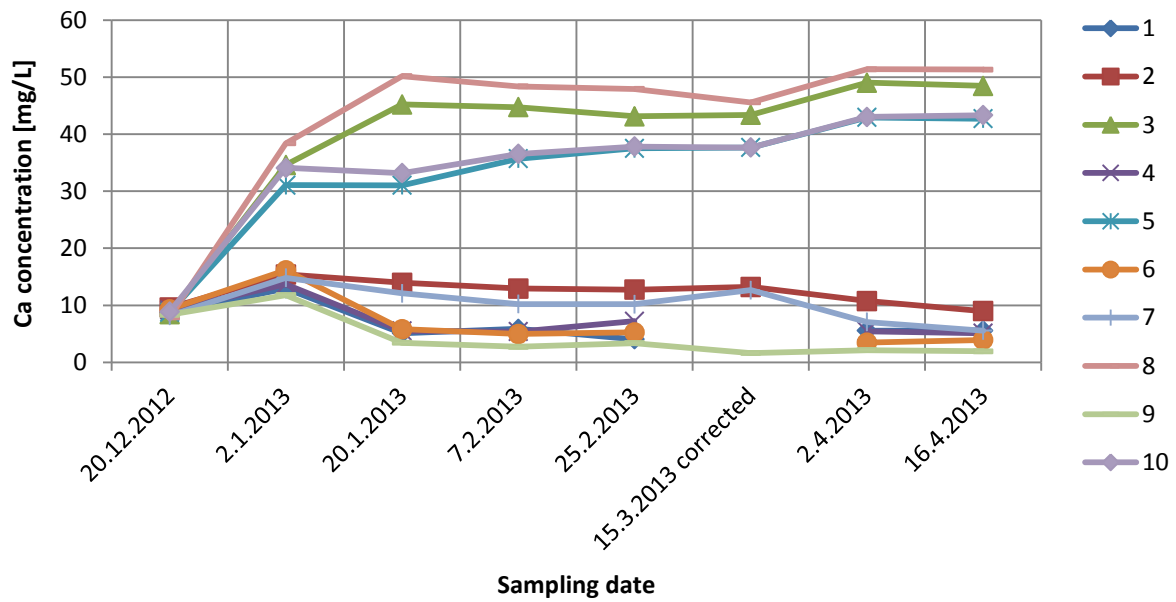
Figure 40 – Ca concentration in the flow-through cells over time in mg/L

The results from the Ca mass balance calculations are shown in Figure 41. From that it can be seen that the Ca balance is negative in all cells except those that receive additional Ca. In cells 5 and 10, mass balance is positive throughout the entire experiments; in cells 3 and 8, it is only positive in the first time interval until the 2.1.2013. Most negative values are obtained for cells 2 and 7 during most of the time. Only towards the end of the experiments, in April, Ca losses were similarly great or even greater in cells 3 and 8. These are the cells on which highest P concentrations (44 mg/L) were applied and consequently pH values were lowest.
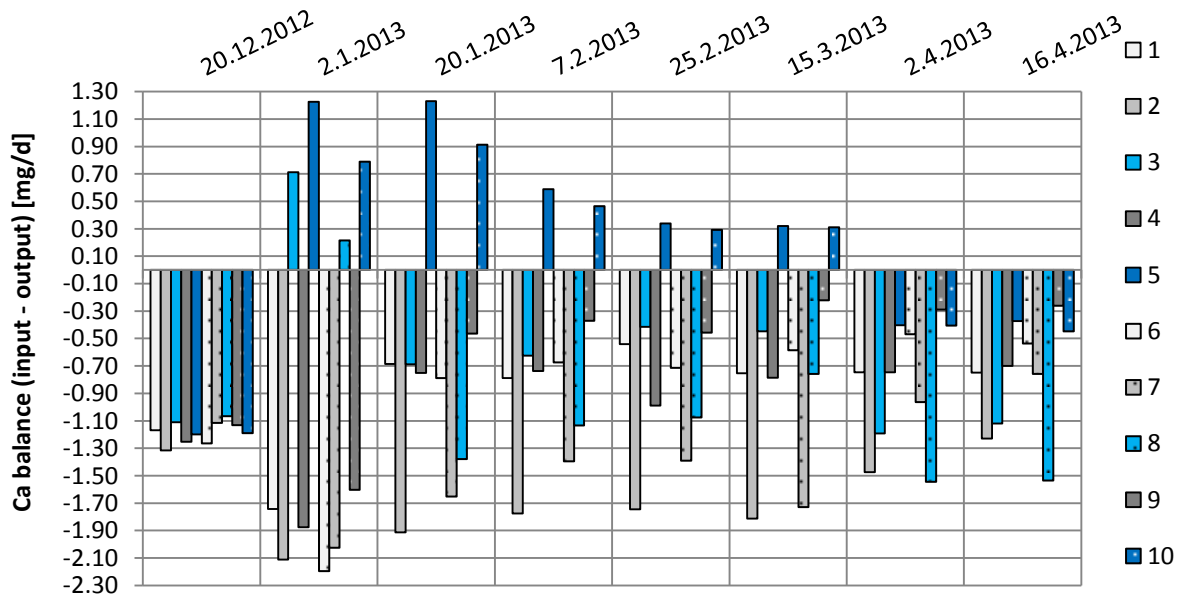
Figure 41 – Ca mass balance, i.e. input minus output in the ten flow-through cells filled with Brandis field topsoil in mg/d (Soil samples 1 to 5 stem from topsoil; 6 to 10 from subsoil. The solutions applied on the soils are given in the yellow table earlier in this chapter. Solution I was applied on flow-through cell 1 and 6; II on 2 and 7, etc.)

5.9.2 Flow-through, pH and redox potential over time

Throughout the entire experiment, in most of the cells flow-through remained constant at between 0.093 to 0.095 mL/min as can be seen in Figure 42. It only dropped in some of the cells, namely cell # 10 (0.095 to 0.092 mL/min), # 8 (0.095 to 0.093 mL/min), # 5 (0.097 to 0.093 mL/min) and # 3 (0.093 to 0.089 mL/min), i.e. between 2 and 4 %. The one very low flow-through in cell # 1 in January was caused by a leakage problem. This is not considered for interpretation and calculations.
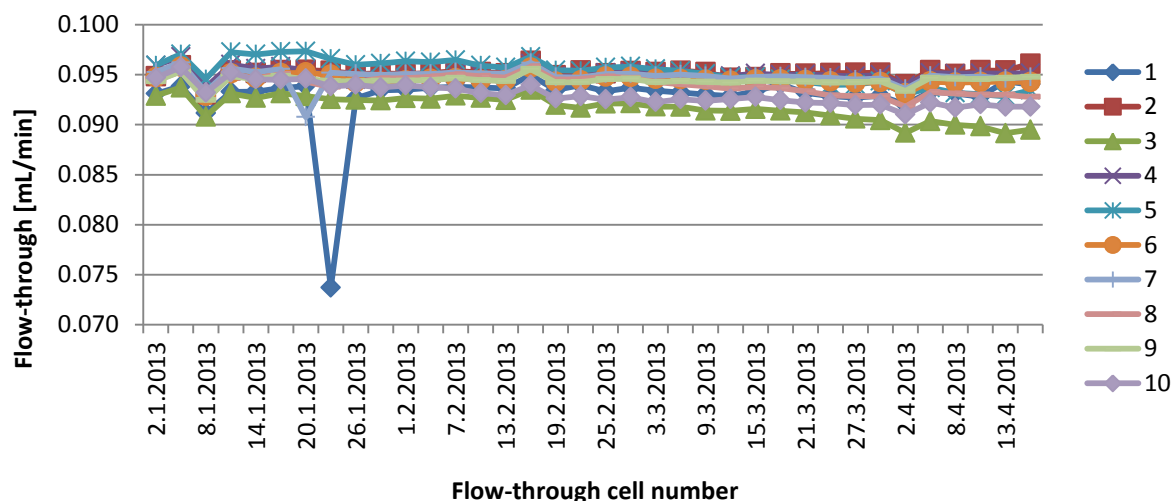
Figure 42 – Flow-through in the flow-through cells over time (Cell # 1 to 5 contain Brandis field topsoil, cell # 6 to 10 contain Brandis field subsoil)

In Figure 43 one can see that pH only slightly dropped in some of the cells. In most of them it remained more or less constant due to pH buffering or due to the fact that the applied solution of the storage bottles (STB I to STB V) was close to that of the respective soil. It is not clear why pH in cell # 7 increased in the beginning of March for some weeks, but it is probably not a reason of erroneous measurements because the pH electrode was the same all the time for all cells and was calibrated before each measurement. So, maybe some reactions in the cells were the reason for the change in pH.
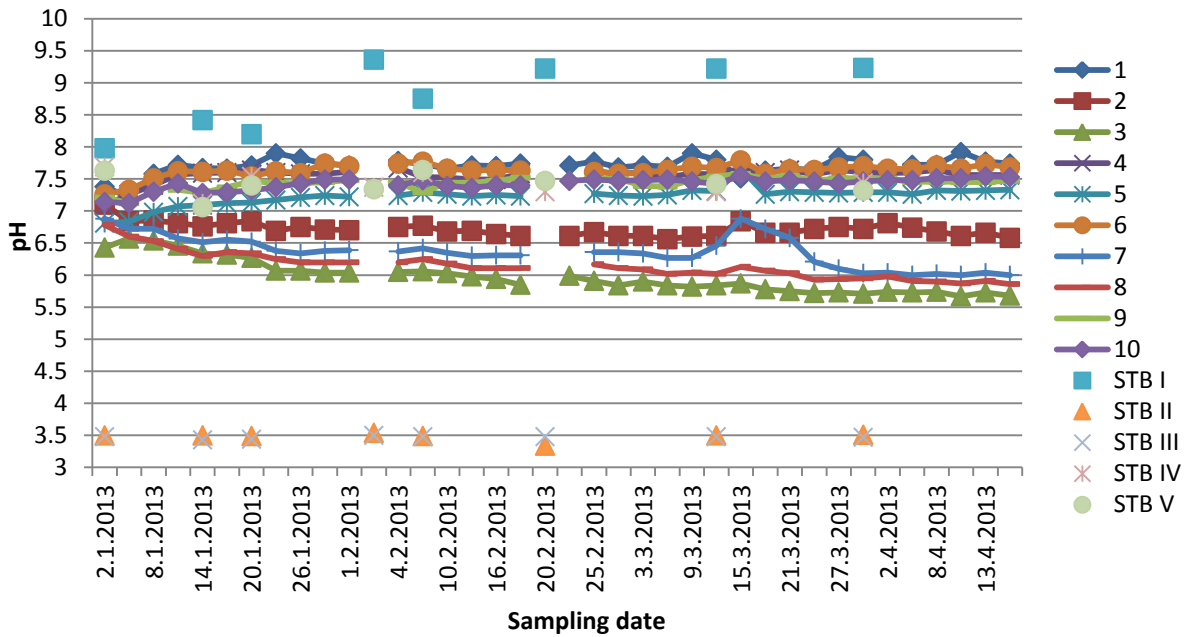
Figure 43 – Development of pH over time in the flow-through cells (Cell # 1 to 5 contain Brandis field topsoil; cell # 6 to 10 contain Brandis field subsoil. The abbreviations STB I to STB V stand for the storage bottles whose composition is explained in Table 12 in chapter 4.3.1.)

For the redox potential, there was no clear trend over time, but results always went up and down. Eh was only determined when IC and TIC/DOC samples were taken. Therefore, the density of measurements is only half that of the pH results. The results probably do not reflect the conditions in the flow-through cells because they were determined in the water collected in the Teflon vessels beneath the flow-through cells. These cells were not close to being completely filled with water during most of the time but contained much air. So, percolation water intensively interacted with air and it is not surprising that redox conditions were always oxidizing. In the flow-through cells, however, it is likely that at least sometimes and in some of the (micro)pores, conditions got reducing. This had not been considered during modeling prior to the experiments but might have caused U(VI) to be (partly) reduced to U(IV) and to be one of the reasons why breakthrough was not reached.

5.9.3 Development of important elements and visible changes over time

To examine if some of the analyzed constituents correlate significantly, a Spearman rank correlation analysis for each individual cell was done. The results from that can be found in *FOLDER 5* in the digital appendix. There are several parameters in each cell that correlate significantly. As each solution (I to V) was applied on two soil samples, one from top- and one from subsoil, correlation analysis results should be the same or at least similar for these two. However, this was nearly never the case. Only in few cases, some of the correlating parameters were the same.

That means that the different soils do not behave in the same or at least similar way even if they stemmed from the same site and same sampling date. This finding underlines that soils are very complex and that their properties can vary even within short distances. For example, differences in grain
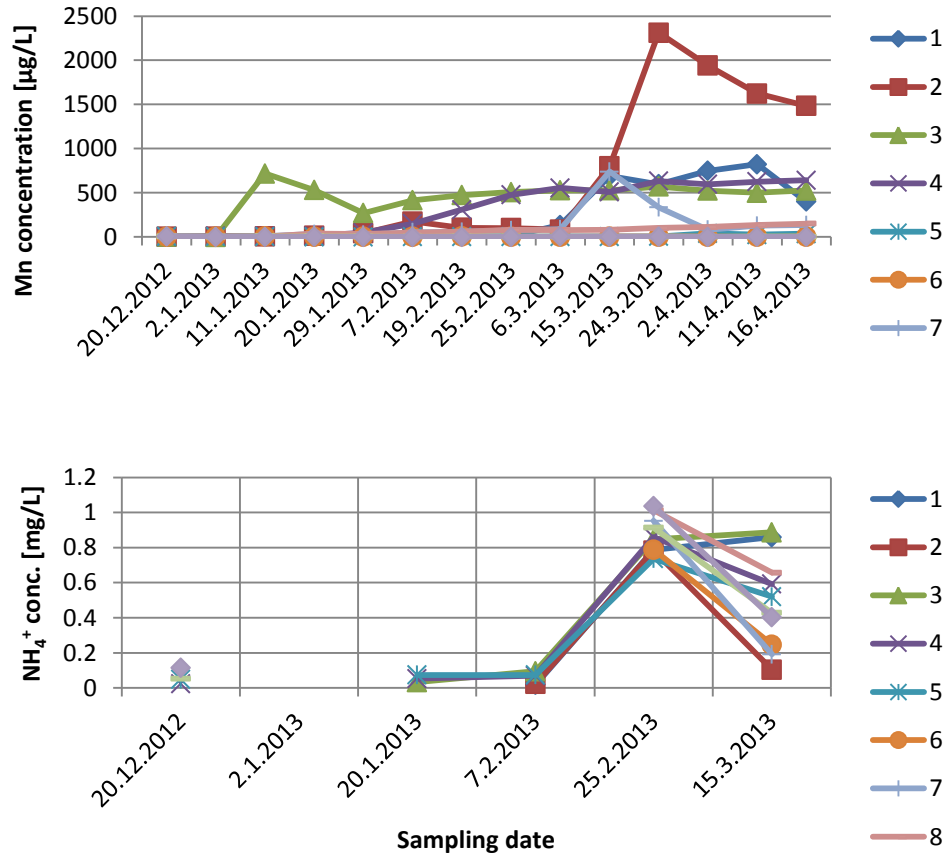
size distribution, porosity and permeability have an effect on the flow conditions, the availability of oxygen and consequently the redox potential and other properties. This might have caused the different reaction on the same treatment.
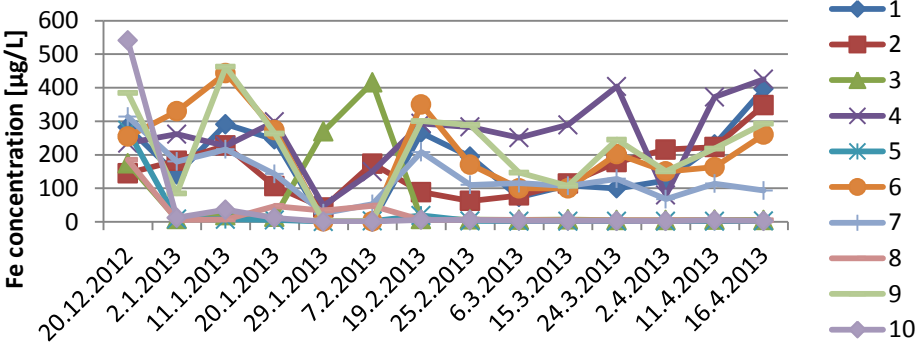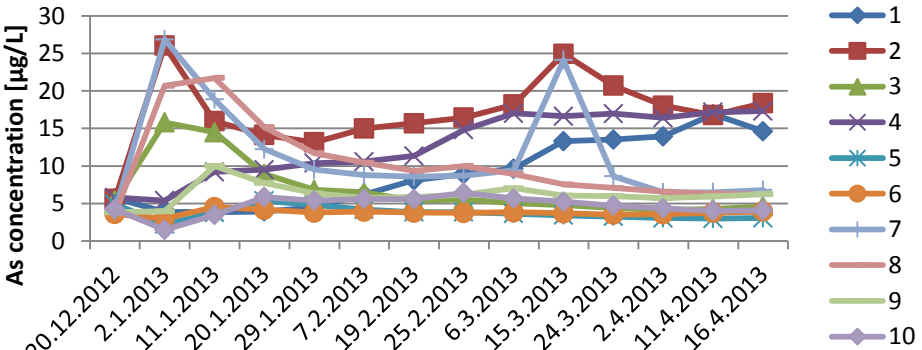
It is very hard or impossible to draw reliable conclusions on what actually happened in the cells and what caused U to be retained so effectively. However, some statements and speculations can still be deduced from analytical results (see Table 26). In addition to the **observations that can be put into numbers**, also **visible changes** were perceived that can only be **subjectively expressed using words**.
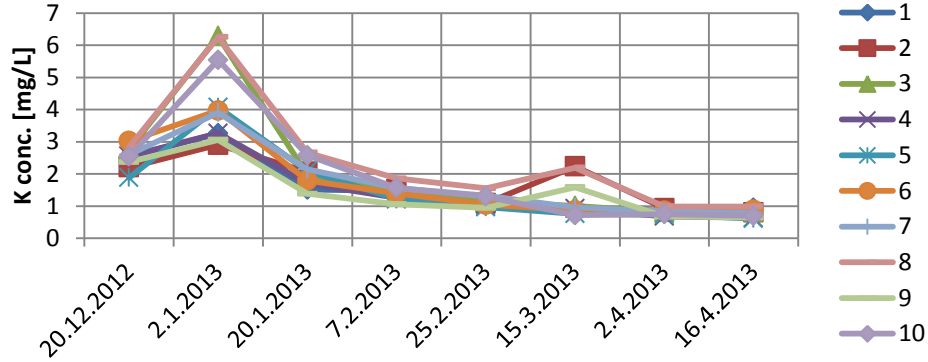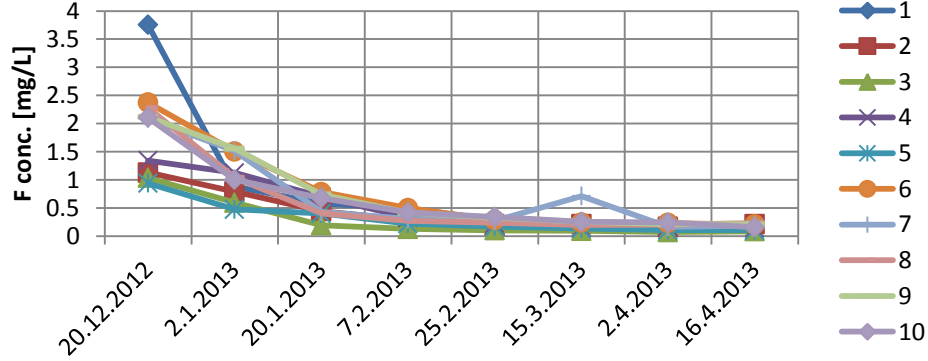
For example, **in the course of the experiments**, blackish, brownish or yellowish precipitates formed in the outlet hoses of the flow-through cells. It might be that these are bacteria, algae, soil particles or a combination of them. The percolate leaving the cells in some cells was very clear; in other cells it was slightly turbid, or extremely turbid and consequently hard to filter. For some cells, this appearance did not change over time; in other cells it changed – either constantly towards clearer or more turbid, or not constantly but sometimes towards more clear and sometimes towards less clear. In some Teflon collecting vessels even some sand, which had left the cells, was collected. In addition to the coloration of the percolation water, gas bubbles regularly developed and escaped from the soils into the outlet tubes. This gas (likely CO_2) can only have been generated in the cells, probably by microorganisms.
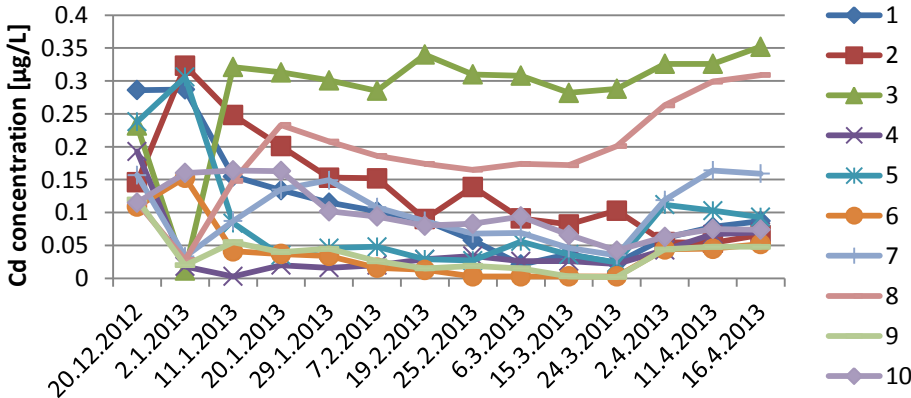
After the experiment was finished, the cells were dismantled. There it was seen that in some cells some fractionation or segregation of bulk material had occurred: fine soil material had accumulated in the inlet part of the flow-through cells, which is located at the cells' bottoms. Flow-through speed was very low and therefore probably did not control this fractionation. So, the reason might be density differences of the contained minerals. In other cells, no fractionation had occurred – in most cases these cells were predominantly sandy with very little clay or silt. Some cells were dryer than others even if flow-through had been nearly the same with differences of only few %. And in the last three samples that were dismantled, cell # 1, 10 and 2, some brownish, blackish or whitish precipitates at the top of the cells were spotted. Their color goes in hand with those of the minerals/precipitates that probably formed in the different cells (see Table 27). It might be that either visible precipitates only formed at the exterior of these three soils, or that it would also have formed at the others if more time would have been given. It might be that contact to oxygen from the atmosphere boosted this visible precipitate formation. All these subjective observations and interpretations can be found in *EXCEL 10* in the digital appendix, together with all numerical results and diagrams of the experiments.

Table 26 – Observations made during flow-through experiments together with some central diagrams and the respective interpretations

Observation	Interpretation
Increase in the Mn, NH_4^+, NO_2^- concentrations over time in some flow-through cells. No NH_4^+ concentration results available for April due to problems with IC analyses (chromatograms were squeezed so that NH_4^+ peaks could not be differentiated from the very high Na^+ peaks) 	Mn is only water-soluble in its reduced form, Mn^{2+}. Ammonium and nitrite are products from the anaerobic reduction of nitrate – mostly done by denitrifying bacteria. The occurrence of these substances is an indication for reducing conditions that probably established in at least some parts of the flow-through cells. It is likely that this development towards more reducing conditions was most pronounced in micropore regions as well as in dead end pores. Dead end pores could either already have existed in the soils or have evolved by precipitation of iron minerals and other solids as coating on the soils. According to (Shang et al., 2011), such micropore regions are the preferential locations for U binding. So, it is likely that at least some of the U(VI) got reduced to U(IV) there.

Observation	Interpretation
Great fluctuation in Fe concentration over time in all cells except for # 3, 5, 8, 10. In cell # 3, it increased until February 7, and then dropped dramatically by about factor 50 to ca. 6 mg/L. In cell # 8, it also dropped after February 7 – from about 40 to ca. 5 mg/L. In cell 5 and 10, it decreased steadily and then remained more or less constant at around 2 and 3, respectively. 	Redox conditions fluctuated in most cells. Generally, when conditions are reducing, Fe becomes more mobile (as Fe^{2+}). When they are oxidizing, Fe is mainly present as Fe^{3+} and precipitates as oxides and or hydroxides acting as effective sorbents for U and other elements (Cheng et al., 2004), (Wang et al., 2011). The solubility-limiting phases of the different flow-through cells over time are given in Table 27. The change in redox conditions might be one of the factors controlling Fe concentration in the waters flowing out of the cells. A second factor likely to have caused the strong decrease after first sampling is cation exchange. During that process, the available Fe probably was replaced by Ca and Na that were added with the flow-through solution and only the less available Fe fraction remained. The reason why Fe concentration was permanently low in cell 3, 5, 8 and 10 is probably that Fe was precipitated as poorly soluble phases.
The soils on which highest P concentrations were applied, released greatest amounts of As. After the initial release maximum, As concentration in water decreased and then increased again. In cells on which no P was applied, As release was constantly low all the time. 	As was mobilized/replaced by phosphate. In cell # 3, 4 and 8, the concentrations of As and PO_4 correlate significantly. In cells 3 and 8, this correlation is negative; in cell 4, it is positive. In 3 and 8, 44 mg/L P had been applied, in cell 4, 4.4 mg/L. So, for the release of As by phosphate, P concentration seems to play an important role. In the diagram left, one can see that As was also set free from the soil in cell # 1 that did not receive any P. It is known that As can also be mobilized by hydrogen carbonate (Zheng et al., 2004). Moreover, reducing conditions favor As release (Bacterial reduction of Fe(III) to Fe(II) causes Fe oxyhydroxides to dissolve.) (Stüben et al., 2003). So, it might be a combined effect in the present experiments.

Observation	Interpretation
K, Mg, F, SO$_4$ release from the flow-through cells decreased with time from some mg/L to about or below 1 mg/L; none of these components had been applied on the soils. Two examples are given below. K concentration in the percolates first increased and then decreased. F first was between about 1 and 3.7 mg/L; in the end in April at about 0.2 or 0.1 mg/L. SO$_4$ decreased from ca. 0.2 to 0.5 mg/L to ca. 0.1 mg/L or to below detection limit (0.01 mg/L) in all cells. 	These easily exchangeable cations were replaced by cations (K$^+$ and Mg^{2+}) from the flow-through solution by cation exchange. At the first sampling in December 2012, K release was lower than in the sample taken in January. That can be explained by the fact that until December 20, distilled water had been applied and after that the actual flow-through solutions. Therefore, ionic strength was much lower in the beginning and consequently competition was lower as well. As the amount of sorbed K is finite, released concentration decreases with time. For Mg, processes and development over time are similar. For F and SO$_4$, the curves showing the concentration development over time have a similar shape with a steadily decreasing trend. This trend is a result of the washing out of soluble quantities, maybe some anion exchange (replacement by phosphate or hydrogen carbonate added with flow-through solutions), or mineral/precipitate dissolution. Fluoride was contained in the soils in considerable concentrations probably as a result from phosphate fertilization, because P fertilizers contain fluoride in the mg/kg range (Taylor, 2013).

115

Observation	Interpretation
Na and Ca concentrations in water leaving the cells' outlets first increased and then remained at a constant level of about that applied on the soils. For some cells it was even slightly higher.	First some of the applied Na and Ca was retained by the soils (by cation exchange releasing other cations like K^+ or Mg^{2+}) until an exchange equilibrium was established. Then soils were saturated with respect to these ions and no more could be retained. Outflow concentrations exceeding inflow concentrations suggest release from the soils themselves. Differences in Mg and Ca concentration between the soils are probably a result of differences in total contents in them.
Nitrate and phosphate are constantly low in the cells on which they were not applied. They first increased and then remained at a constant level in those cells on which they were applied at the level at which they were added. Cl^- concentration was very low (< 1.3 and mostly below 1 mg/L) throughout the entire experiment.	Same statements as for Na and Ca.
Cd concentration develops very unequally in the different cells. Its concentration most of the time is highest in cell 3 and 8 with a constant to increasing trend. It is more or less steadily decreasing or first decreasing and in the end, in April, slightly rising again in the other cells. 	Cd stems from the soils and is released faster or slower in higher or lower concentrations probably depending on the solutions applied as well as on soil properties and the total Cd contents in the soils. Its concentration is highest during most of the time of the experiment in cells 3 and 8 – the solutions containing highest concentrations of phosphoric acid and calcium. H^+ and Ca^{2+} seem to have replaced Cd effectively by cation exchange.

5.9.4 Speciation of U and P over time

For generating the species distribution plots, all species within a range of two to three orders of magnitude difference between most and least abundant were considered. For U, that means that all species down to 10^{-14} mol/L were included and for P all species down to 10^{-11} mol/L. Depending on the flow-through solution applied, different species are dominant. Species distribution in the input solutions very much resembled that of the output. The cells, which received the same solutions, showed similar species distribution over time. Differences between top- and subsoil were not very great. Only in cell # 2 and 7, respectively, the dominant U species is not the same. In cell 2 it is $UO_2PO_4^-$ and in cell 7 it is $UO_2HPO_4^-$. The reason for the differences can be seen in pH, which is higher in cell 2 than in cell 7 (see Figure 43). Apart from this exception, speciation is similar in the flow-through cells receiving the same solutions. Therefore, in the following only the diagrams for topsoil are given. The original data as well as the diagrams for the corresponding subsoils can be found in *EXCEL 11* in the digital appendix.

In nearly all flow-through cells, except # 5 and 10, according to PHREEQC modeling P predominantly occurs as free acid, in the partially deprotonated forms $H_2PO_4^-$ and HPO_4^{2-}, respectively, depending on solution pH. In most cells, these negatively charged species account for > 90 % of total P. Due to their negative charge, they can bind to FeOOH and other (hydr)oxides (Merkel, 2013c). Yet, as addressed in section 5.9.1, in total only between 0.1 and 24 % of the applied P were retained. So, maybe sorption and P mineral formation were too slow. Figure 44 and Figure 45 show two examples for the **P speciation** in one flow-through topsoil cell (cell 3) on which much P (44 mg P /L) and one on which little P (4.4 mg P /L) was applied (cell 4) resulting in lower or higher pH in solution.
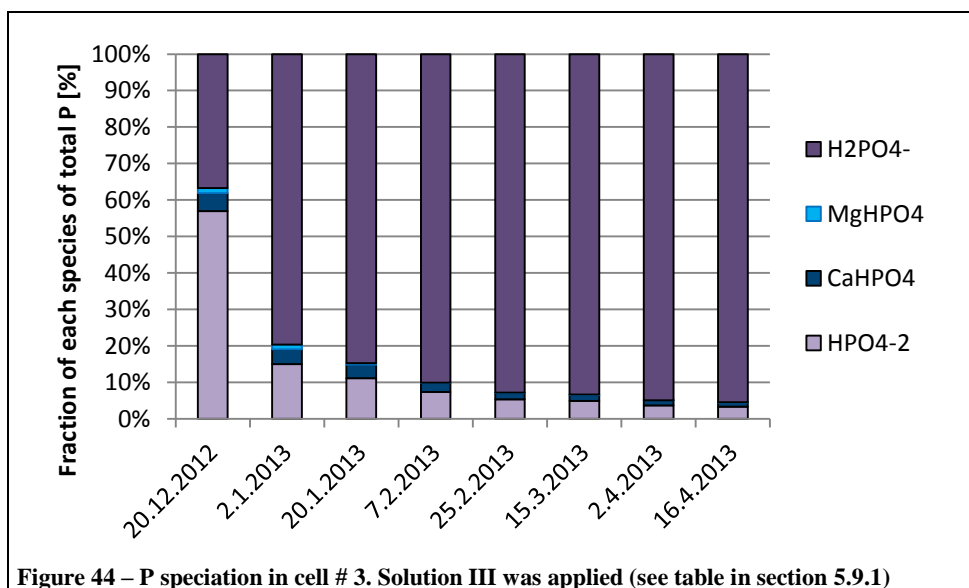
Figure 44 – P speciation in cell # 3. Solution III was applied (see table in section 5.9.1)
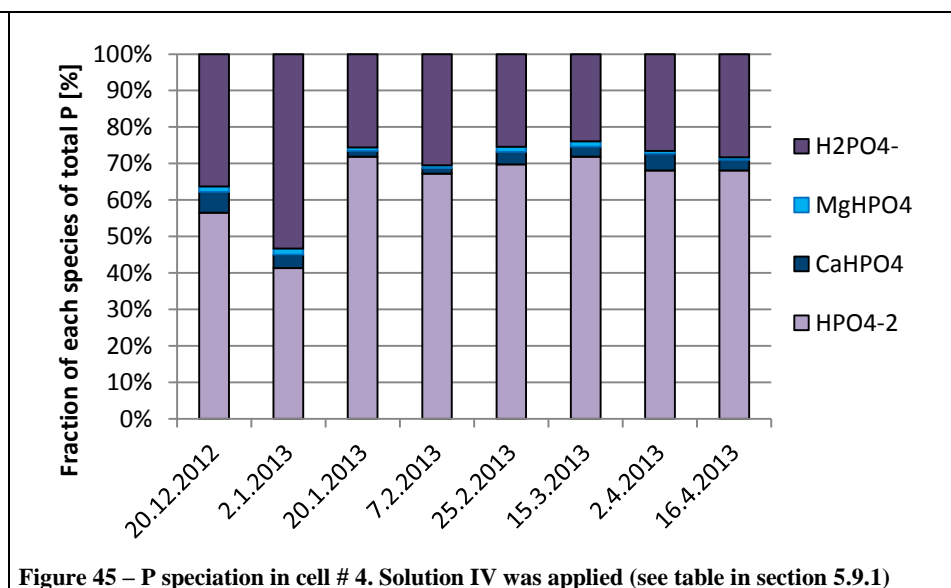
Figure 45 – P speciation in cell # 4. Solution IV was applied (see table in section 5.9.1)

Figure 46 shows the **P species distribution** in cell # 10. In cell 10 and 5 (the corresponding cell that contains Brandis topsoil), the free acid forms of P account for about 85 %. The remaining P is bound to Ca as $CaHPO_4$ and $CaPO_4^-$ or, to a lesser extent, to Mg in $MgHPO_4$, i.e. uncharged complexes that are very mobile and will likely be washed out.
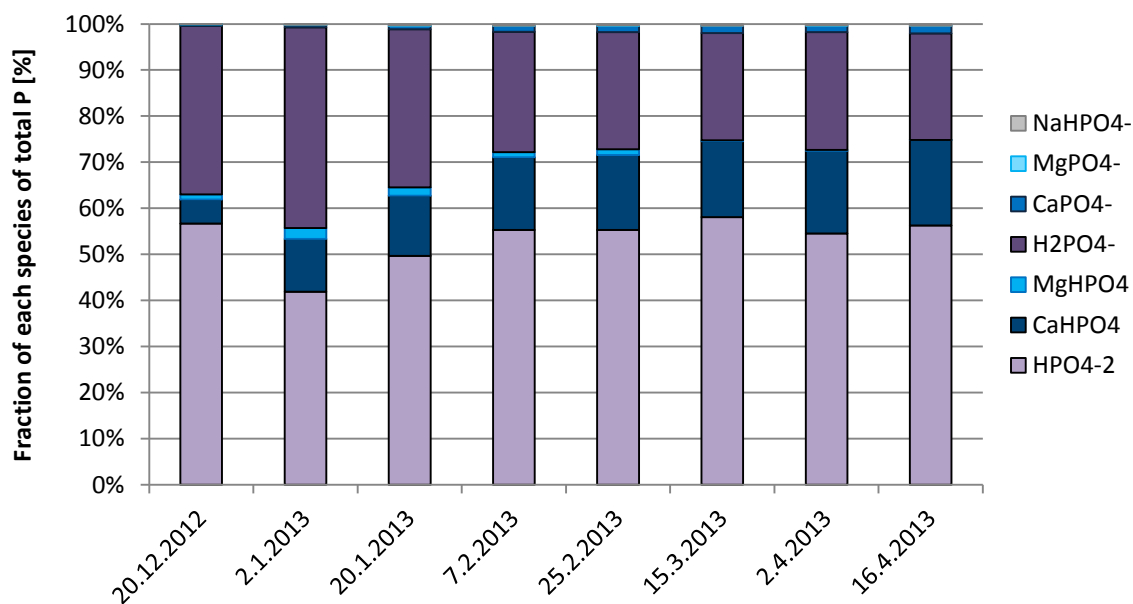
Figure 46 – P species distribution in flow-through cell # 10 over time. Solution V was applied. It was composed of I containing 1 mM $NaHCO_3$ and 0.168 µM $UO_2(NO_3)_2$, 0.142 mM P added as H_3PO_4, and 1 mM $Ca(NO_3)_2$ as shown in the yellow table in section 5.9.1.

From the following **U species distribution** figures over time it can be seen that according to the PHREEQC modeling results U nearly exclusively occurs as uncharged or negatively charged complex. The fraction of positively charged complexes is negligible. Anions predominantly forming complexes with U in the cells are hydrogen carbonate/carbonate (HCO_3^-, CO_3^{2-}), phosphate/hydrogen phosphate/dihydrogen phosphate (as PO_4^{3-}, HPO_4^{2-} or $H_2PO_4^-$) – with protonation depending on pH. In addition to these anions stemming from the applied flow-through solutions, hydroxide ions (OH^-) also form complexes with U. Ca ions are incorporated in ternary calcium uranyl carbonato complexes. In the following diagrams, the species distribution calculated for the samples taken on the 20.12.2012 are relatively similar. That is because during that step, all flow-through cells were loaded with distilled water. After that date, the actual solutions were applied and differences become bigger.

On cell 1 and 6, only uranium and hydrogen carbonate were applied. Figure 47 shows U speciation in cell 1 over time. The dominant species are $Ca_2(UO_2)(CO_3)_3$, $UO_2(CO_3)_2^{2-}$ and $UO_2PO_4^-$. $UO_2(CO_3)_3^{4-}$ and $UO_2(OH)_2$ also occur in considerable concentrations. The carbonate complexes are dominant due to addition of hydrogen carbonate with the flow-through solution at an initial pH between about 8 and 9. Ca and P can only stem from the soil itself as there was no additional input. Ca was probably set free by replacement (cation exchange) by Na, which was added with the applied solution. The variation in the species distribution is likely to be a combined effect of formation of solubility-controlling phases listed in Table 27, more or less available and accessible Ca ions, and degassing/transformation of hydrogen carbonate and other processes in the soil, on its surface and in solution.

Figure 47 – U species distribution in flow-through cell 1 over time. For plotting all U species between 10^{-10} and 10^{-13} mol/L were considered. Solution I had been applied. It contained 1 mM $NaHCO_3$ and 0.168 μM $UO_2(NO_3)_2$.

Cell 2, 3, 7 and 8 are the ones, on which in addition to $NaHCO_3$ and $UO_2(NO_3)_2$, highest P concentrations (44 mg P/ L) were applied. In cell 3 and 8, also 40 mg/L Ca, as $Ca(NO_3)_2$, was added. As can be seen in Figure 48 and Figure 49, Ca did not cause any significant change in U speciation. In both cells, 2 and 3, the phosphate complexes, UO_2HPO_4 and $UO_2PO_4^-$, were the dominating ones (The molarity of added P was 50 % higher than that of added Ca). The only difference between both cells is that in # 2 phosphate complexed with U mainly in its deprotonated form whereas in cell # 3 the simple protonated form, HPO_4^{2-}, was the main ligand. This difference can be explained by the pH, which was lower in cell 3 than in cell 2 throughout the experiment.

Figure 48 – U species distribution in flow-through cell 2 over time. For plotting all U species between 10^{-10} and 10^{-13} mol/L were considered. Solution II had been applied. It contained 1 mM $NaHCO_3$, 0.168 μM $UO_2(NO_3)_2$ and 1.421 mM P, added as H_3PO_4 .

Figure 49 – U species distribution in cell 3 over time. For plotting all U species between 10^{-10} and 10^{-13} mol/L were considered. Solution III had been applied. It contained 1 mM $NaHCO_3$, 0.168 μM $UO_2(NO_3)_2$, 1 mM $Ca(NO_3)_2$ and 1.421 mM P, added as H_3PO_4 .

The P concentration applied on cell 4, 5, 9 and 10 was 10-times lower than that on the previously discussed cells. It amounted 0.142 mmol/L P. That is why in the respective species distribution diagrams U-P species do not account for about 100 % any more (see Figure 50 and Figure 51). Instead in cell 4 (shown in Figure 50) and correspondingly in cell 9, uranyl carbonato, hydroxo and ternary calcium uranyl carbonato complexes also form. There is some variation in the concentration of the individual complexes but in principle it remains the same all the time.

In cell 5 (see Figure 51) and 10, the $Ca_2(UO_2)(CO_3)_3$ complex is the dominant species. Its concentration increases over time whereas the concentration of $UO_2PO_4^-$ and UO_2CO_3 decreases. This can be explained by the fact that Ca ions are not only being bound in aqueous complexes but are also involved in cation exchange processes. Ca^{2+} from solution replaces other cations bound to the solid soil material until exchange equilibrium between soil and solution is reached for the cations involved. As soon as this transient equilibrium is reached, probably already in March/April of the present experiments, speciation does not considerably change any more if conditions and solution composition remain constant. According to PHREEQC modeling, $CaHPO_4 \cdot 2H_2O$, hydroxyapatite, $Ca_5(OH)(PO_4)_3$, and whitlockite, $Ca_3(PO_4)_2$ are oversaturated but probably do not precipitate fast enough in the columns to limit Ca aqueous concentration.

Figure 50 – U species distribution in cell 4 over time. For plotting all U species between 10⁻¹⁰ and 10⁻¹³ mol/L were considered. Solution IV had been applied. It contained 1 mM NaHCO₃, 0.168 µM UO₂(NO₃)₂ and 0.142 mM P, added as H₃PO₄ .

Figure 51 – U species distribution in cell 5 over time For plotting all U species between 10⁻¹⁰ and 10⁻¹³ mol/L were considered. Solution V had been applied. It contained 1 mM NaHCO₃, 0.168 µM UO₂(NO₃)₂, 1 mM Ca(NO₃)₂ and 0.142 mM P, added as H₃PO₄ .

The consequences of these findings on P and U speciation are:

- Only a small fraction, 0.1 to 24 % of P_{total}, is retained during flow-through experiments (see chapter 5.9.1).
- Uncharged U complexes would generally be expected to be very mobile.
- The negatively charged complexes can be sorbed by positively charged surfaces like Fe oxides and hydroxides by surface complexation.

So, the question remains why still nearly none of the applied U (1-2 %) left the flow-through cells throughout the experiment and why only very little of the P that was applied was retained. There are several possible explanations. Among them are the following ones:

- P sorption processes and P mineral formation might have been too slow or inhibited by unfavorable conditions (pe, pH, etc.) or inhibitors like certain trace elements, or by competition by other ions contained in the applied solutions (especially HCO_3^-) (Merkel, 2013c)
- Various charged as well as uncharged complexes might have gotten bound to Fe and Mn (hydr)oxides by surface complexation depending on pH and the concentrations of dissolved carbonate, phosphate, U(VI) and Ca (Romero-González et al., 2007), (Davis et al., 2004), (Cheng et al., 2004), (El Aamrani et al., 2002).
- Bacteria and other microorganisms as well as humic acids could have reduced and consequently immobilized U(VI) to U(IV) in dead-end pores and micropores (Mbudi and Merkel, 2006), (Sachs et al., 2006).
- Precipitation of iron - and other metal (hydr)oxides could have generated surface coatings that might have clogged (micro)pores of the soils or generated new micropores by narrowing existing pores. As these micropore regions are the preferential regions for U sorption (Shang et al., 2011), this would have intensified U binding.
- Clogging by precipitates could also have generated more reduced conditions in some parts of the soils and subsequently have transformed U(VI) to U(IV).

The effective U retention during flow-through experiments is probably a combined effect of the mentioned possible reasons and others that are not mentioned or not even understood yet. For studying surface complexation, batch and column experiments with defined solid phases and solutions at different pH values can be used. In addition to that, other, more sophisticated methods like XAS or XANES can be used to differentiate between mono and bidentate surface complexes (Merkel, 2013b). Fluorescence spectroscopy could also help to understand U binding to different minerals (Wang et al., 2011). However, for using these methods, high concentrations and the dominance of the species of interest are required – conditions that are not close to nature. The activities of microorganisms has not been studied in this thesis either. However saturation indices of possible solubility-controlling phases have been modeled using PHREEQC. The results from that are presented and discussed in the following chapter.

5.9.5 Solubility-controlling phases

Depending on the flow-through cell considered, over time there were different phases that probably controlled solubility. These phases are listed in Table 27 – coloration selected according to colors the mineral phases commonly possess. The complete results with numerical values for saturation indices etc. can be found in *EXCEL 11* in the digital appendix. Like in the waters sampled at the field sites, no clay minerals seemed to be solubility-controlling either due to slow kinetics, inhibitors or other reasons.

According to modeling, relevant minerals were carbonates, (hydr)oxides, (hydrogen) phosphates, and mixed-anion minerals. The metals they contained are Ca, Mg, Fe and Mn. It seems odd that several phosphate minerals are oversaturated or in equilibrium with solution but P mass balance revealed that still nearly no phosphate was retained in the soils (see section 5.9.1). So, maybe mineral formation is too slow or inhibited, or the amount of P precipitated as mineral is too small. None of the phases shown in Table 27 are clay minerals. Generally one would expect them to be among the first phases that form. The reason why they do not form spontaneously here is not clear.

In some of the cells, there are several periods during which no phases are in equilibrium with solution. However, this does not mean that really no phases form. It might be that simply no thermodynamic data exists on some of the phases that form. (Merkel, 2012c).highlights that the availability and the numeric values of thermodynamic data differs depending on which database is regarded. So, the modeling results need to be considered with care. And finally, findings from modeling can only be as good as the input data from water analytics. In the present case, especially the redox potential and pH in the micropores of the flow-through cells might significantly vary over time and be in the reducing range sometimes. The action of bacteria and other microorganisms can trigger and impact redox reactions and consequently alter speciation, cause precipitation or dissolution.

Table 27 – Mineral phases controlling solubility in the flow-through cells over time (The abbreviations stand for:

C	calcite ($CaCO_3$)	FeCa	calcium ferrite ($CaFe_2O_4$),
FeMg	magnesium ferrite ($MgFe_2O_4$)	HAP	hydroxylapatite ($Ca_5(PO_4)_3(OH)$)
HIO	hydrated iron oxide ($Fe(OH)_3$)	MGT	magnetite (Fe_3O_4)
MNP	manganese hydrogen phosphate ($MnHPO_4$)	R	rhodochrosite ($MnCO_3$)
S	strengite ($FePO_4 \cdot 2H_2O$)	W	whitlockite ($Ca_9(MgFe)(PO_4)_6PO_3OH$).

Phases were evaluated as probably solubility-controlling when their SI was 0 ± 0.5.)

Date / cell #	1	2	3	4	5	6	7	8	9	10
20.12.2012		HIO	HAP	HAP	HAP		HAP			
2.1.2013	HIO	HIO	HAP		MNP		HIO	W	HIO	MNP
		S					FeMg		FeMg	
		W					S		FeCa	
							W		MNP	
20.1.2013		HIO	HAP		MNP		HIO	HIO		W
		S	S					S		
		W								
		FeCa								
		FeMg								
7.2.2013	MNP	HIO	S	HIO	W		HIO	HIO		MNP
	MGT	S					S	S		
	HAP	FeCa						HAP		
		FeMg								
25.2.2013		HIO	S	R	W	MNP	HIO	HAP		MNP
		HAP								FeCa
		S								
15.3.2013	HIO	HIO	S	R	C	MNP	HIO	HAP		
		S					S	MGT		
		W					W			
		FeCa					FeCa			
2.4.2013	HIO	FeMg	MGT	HIO	MGT	HIO	HIO		HIO	
	HAP			R			S			
				W						
16.4.2013		FeMg	MGT	R			HIO	MGT	HIO	
									MNP	

6 Conclusions

The intention of the thesis was to study the fate of U in the subsurface after phosphate fertilizer application using samples from four different study sites in Saxony and Saxony-Anhalt. It was intended to identify the origin of U (geogenic from rock vs. anthropogenic from P fertilizers) in the respective soils by assessing the U-238 / Ra-226 specific activity ratio using low-level gamma spectrometry. Finally flow-through experiments were conducted to look at changes in soil and groundwater composition and especially U contents in time-lapse mode.

From studying agricultural and forest soils of the four different sites it was found that no general statements on the fate of uranium can be made. Depending on fertilization practices (type and amount of fertilizer applied, frequency and season of application), ploughing (depth, frequency), properties and composition of soils (grain size distribution, density, mineralogy, porosity, permeability, cation exchange capacity, carbonate and organic carbon content, etc.), and of groundwater (pH, redox potential, ionic strength, main and trace elements, etc.), U will be retained more or less effectively in the unsaturated zone, or seep down into the saturated zone. The time it takes for U to reach the groundwater zone is highly dependent on depth to groundwater and groundwater recharge. All these complex interrelations make it hard or even impossible to directly compare different sites. In case, availability of data is limited, either in quantity or in quality or in both, evaluation and interpretation is even more difficult. So, reliable risk assessment for a certain location is only possible if its properties are well known. For understanding changes in U contents in soil and percolation and groundwater, recording of the input by phosphate fertilization is essential. It is necessary to know how much of which type of fertilizer is applied when, which other treatments (ploughing, application of pesticides, etc.) the soil encountered, which crops were farmed, etc. The cultivation practices sheets by the LfULG can serve as a useful example for data recording.

During extractions with distilled water, ammonium acetate (pH 7), EDTA and hydroxylamine hydrochloride below or around 1 % of total U could be mobilized. Ammonium actetate (pH 5) liberated between about 2 and 9 %. Even using nitric acid, only between 15 and 40 % were extracted. This suggests that U is firmly bound as other studies confirmed (Qiao et al., 2012, Huhle, 2007). Correlation between organic matter content of soils and total and extractable U confirms that organics play an important role for U binding. For the more mobile fractions, CEC and pH seem to be ruling soil properties. Repeating the ammonium acetate (pH 5) step with the samples from flow-through experiments, recoveries were 5- to 6-times higher. This supports the statements by (Taylor and Kim, 2008) and (Cheng et al., 2004) that U binding gets stronger over time.

For revealing the origin of U, examining the U-238/Ra-226 activity ratio using low-level gamma spectrometry was not successful, because uncertainties were bigger than differences between field and forest soils and between topsoil and subsoil.

Flow-through experiments under saturated conditions using field top- and subsoil from the lysimeter station in Brandis, one of the study sites of this work, depicted 93 years within 106 days. About 99 % of total U applied on the columns was retained; no breakthrough was reached. (Barnett et al., 2000) did column experiments with similar U concentrations as in the present work and showed that thousands of pore volumes are needed to reach breakthrough. (Giammar et al., 2012) compared UO_2 dissolution in batch experiment cells, continuously-stirred tanks and plug flow reactors and concluded that oxidative UO_2 dissolution decreases if flow-through is limited. In the present thesis, slow flow-through speed and probably also the presence of microorganisms might have shifted the redox conditions in some parts of the soils towards more reduced ranges. As a consequence U(VI) could have been converted to poorly soluble U(IV) (Mbudi and Merkel, 2006), (Sachs et al., 2006). In some of the studied field soils, however, U was not so effectively retained but U application caused U concentration in percolation water to increase. PHREEQC species modeling based on eH in the outlet indicates that U is mainly present in its oxidized, mobile form as uncharged or negatively charged aqueous complexes there. So, from the difference in U retention it can be concluded that soil column experiments under saturated conditions are not suitable to reproduce processes in unsaturated soils.

7 Recommendations and outlook

During data acquisition, experimenting and interpreting it became clear that if four sites are studied at the same time, this cannot be done in detail for each of them if there are time restrictions. So, it might be better to focus on one or two sites and deepen investigations (groundwater flow-direction, structure, thickness and composition of aquifer, (historic) data on land use over time, etc.).

The choice of the study site(s) is probably the most important step for the success of such an applied research topic. It is essential that the density of relevant data is sufficiently high. And also the period of time since when this data exists is central for doing risk assessment studies and time series analysis. In the present work, the intensive test site in Hilbersdorf was concluded to be the most suitable one. However, it would also make sense to search for further sites that are more strongly fertilized and/or have lower U geogenic backgrounds, because then differences between U contents in field and forest soil would be greater. Under such conditions, i.e. when uncertainties are smaller than differences in specific activity ratios of U-238/Ra-226, it might be possible to successfully trace the origin of U with low-level gamma spectrometry.

The conducted experiments can be improved and/or extended in the following way:

- Assessment of soil properties:
    - Before preparing soils (drying, sieving), it should be clear how much is needed for which experiment. Based on that, drying temperature (40 or 105°C) and sieve material (plastic, steel or copper) can be selected and alteration of the results can be prevented.
    - For soils that are likely to be low in carbonate, the "carbonate bomb" test can be omitted due to its high detection limit of 5 mass% $CaCO_3$.
    - The humus content of soil should be included in the characterization of the composition of the soils. The organic matter content should/could be specified nearer distinguishing between humic matter/acids, fulvic acids, etc. as they play a central role for U binding in soils (Dienemann and Utermann, 2012a).
    - In the present work, the percentage of clay of total soil mass had been determined. The next step should be to analyze which clay minerals are contained in this grain size fraction and at which percentage using XRD.
    - The intervals between grain size classes are much smaller when particle size analyzers are used as compared to those from traditional sieving analysis. So, different grain size classes, i.e. not only those defined by standards, could be calculated and assessed for their correlation with the U extracted during the different extraction steps.
- Extraction of U from soils:
    - Some of the extractants used should maybe be replaced by other, more effective ones because extracted U was very low in this work.
    - It would be interesting to directly compare the differences between the results from sequential U extraction with those from single extractions using same soils and same extractants. If the results are similar or can be correlated with each other, single extractions would be more practical to use.
    - The interaction between soil and solution should be intensified for the 7 N HNO_3 step and temperature constancy has to be ensured to make results comparable. This could be achieved by using wider reaction vessels with insulated walls standing on thermostatically-controlled heating plates.

126

- In case very strong and concentrated acids are used for extractions, glassware should be acid-washed before use. That is especially the case in laboratories where U is regularly used for experiments because glassware formerly used for storing stock solutions in it might not be sufficiently clean after washing without acid. The best option, however, would be Teflon vessels. But they are also very expensive.
- The determination of the ease of U release could be complemented by examinating the actual U binding forms using batch experiments combined with XRF, XAS, XANES, XRD, SEM-XRD, EXAFS analyses, Raman spectrometry and raster electron microscope studies.
- Flow-through experiments:
  - Redox conditions should be prevented from becoming reduced in the cells. This could probably be achieved by either increasing flow-through (For that, the caps of the cells would have to be tightened more properly, e.g. by using multiple O rings per cap) or by letting the pump run intermittently and maybe pump air through the cells in defined intervals. It is likely that faster flow-through would also shorten the time needed for reaching breakthrough. But intermittent flow-through would be more suitable for depicting the soils' unsaturated conditions.
  - Additional microbiological methods should be used for identifying microorganisms in the soils.
  - Mineralogical and structure analytical methods would be a useful extension for determining probably emerging coatings, amorphous precipitates and secondary minerals (compare the fluorescence spectroscopy study by Wang et al., 2011).
  - During flow-through experiments, gas bubbles developed and escaped from the soils into the outlet tubes. The released gas should be analyzed using gas chromatography in order to assess if its source could be microorganisms relevant for the fate of U.
  - For step-wise understanding what causes the differences between flow-through experiments and findings from the field, various parallel tests could be conducted: e.g. adding additional water constituents (e.g. F, which occurs in P fertilizers in the mg/kg range), or modifying temperature and/or pH. For example (Keum et al., 2002) did batch and column U sorption experiments at different pH, temperature and flow-through. U concentrations were similar to those in the present work. At pH 4 and about 10-times higher flow rates, breakthrough was reached within hours. It would be interesting how results are affected by additional constituents in water. For comparison, in the parallel tests one column should also be loaded with a commercial P fertilizer. To see the effect of the various soil constituents on U sorption, some of the parallel-test columns could be packed with pure substances (e.g. quartz, certain clay minerals, etc.) like described in several studies. For example the component additivity approach together with EXAFS and surface complexation modeling of U sorption on Mn oxides pursued by (Wang et al., 2012), would be worth to be extended to other soil components.
- Modeling with PHREEQC:
  - Modeling results using different databases should be compared and checked for plausibility.
  - In the different databases, the number of aqueous species and limiting phases included is limited. It would be constructive to re-determine certain solubility products, formation constants, etc. of further species.

- o The available thermodynamic data should be examined for the boundary conditions at which it was developed (In the present work, this was already done/started for species containing U and P as shown in *EXCEL 1* in the digital appendix). In case these conditions differ too much from the U-release-by-fertilization experiments, these constants should be re-determined.
- Gamma spectrometry:
  - o The method can be used as simple and non-destructive alternative to RFA for determining U totals.
  - o In addition to the U-238/Ra-226 specific activity ratio, U-238/U-234 could be examined for its suitability for revealing the origin of U. The background for that is that P fertilizers have a different U isotope signature than P minerals in soils. However, again the problem for the assessment could be the analytical error, which might be higher than activity ratio differences. So, a gamma spectrometer with lower analytical errors would be very helpful for assessing the activity ratio of U-238/Ra-226 as well as that of U-238/U-234.
  - o In areas that were subjected to the radioactive fallout from the Czernobyl accident, the specific activity of Cs-137 can reveal if a soil encountered ploughing or other disturbance/mixing since 1986. This could help for the selection of suitable forest sites to compare the agricultural soils with.
- Fertilizer samples:
  - o For not having to estimate U inputs to soil using average concentrations of common fertilizers, P fertilizer samples presently applied on the studied soils should be obtained and analyzed. In addition to testing them for their U content, also other relevant components should be considered (e.g. F, Ca).
  - o The binding form of U should be examined and compared so that consequences on the ease of U release could be deduced. According to (Zielinski et al., 1997), the mobility of fertilizer-derived U depends not only on porewater chemistry and soil properties like mineralogy, moisture, pH and texture, but also on the type of fertilizer.
  - o The water-solubility under different pH conditions would be worth to assess as well as the kinetics of that as there are different types of P fertilizers: types that slowly set free the contained U and types from which release is faster.

For practice, the consequences and recommendations are as follows:

- Preventing or reducing further U contamination:
  - To prevent/reduce further U contamination of soils, input should be stopped or at least minimized. This can be done by reducing P fertilization and/or by using P fertilizers with low U contents. For example, organic P fertilizers (e.g. manure and slurry) or mineral fertilizers from the Kola Peninsula contain much less U than other mineral P fertilizers (Taylor, 2013). Another option would be to recycle P, i.e. by regaining it from animal feces and other sources. Depending on the source, U contents of the products would be low by themselves. As P is forecasted to be one of the first resources that will be exhausted, P recycling is probably the most sustainable option.
  - There should be limits on how much U is permitted to be contained in fertilizers and there should also be an obligation for labeling fertilizers with that information. The Commission for Soil Protection of the German Federal Environmental Agency ("Kommission Bodenschutz des Umweltbundesamtes") proposes that U content in P fertilizers should be regulated in the fertilizer ordinance ("Düngemittelverordnung"). According to the proposal, U contents should have to be labeled starting at 20 mg U per kg P_2O_5 and MCL should be at 50 mg U per kg P_2O_5 – equivalent to the regulations for Cd. Moreover, the commission supports formulating common limits and regulations all over Europe for U as well as Cd in fertilizers (Dersee, 2012).
- U and P monitoring, data management and data supply:
  - The existing data on soil, groundwater, land use, climate, etc. should be made easily available for researchers and decision makers. A common online database in which data from all parties involved would be a precious solution. It would simplify and speed up the process of exchanging data. In such a database, relevant metadata like information on sampling (date, time, boundary conditions, in situ parameters, contact person, etc.), perhaps sample processing (sieving, drying, etc.) and on analytics (institute in charge, performing employee, method used, detection limit, etc.) should be contained. Utilized units and species (P vs. PO_4 or P_2O_5) should be unified or at least clearly pointed out. Contact addresses of persons in charge should be easily accessible.
  - Processing of recorded data should be extended, e.g. by generating interactive GIS maps containing most relevant information on the present state of soil and groundwater as well as the development over time.
  - Cooperation and exchange between the different institutions in charge of the research stations (lysimeter stations, intensive test sites, etc.) should be established/intensified. At the moment, each station has an own main research goal, e.g. certain metals, nutrients, or changes in soil water storage. Exchange of water samples and complete analyses could either be valuable already now or in future.
  - For more reliably estimating U input by fertilization, it would be necessary to know P and U contents and composition of the fertilizers actually applied. Having access to samples from these P fertilizers would be an alternative of equivalent value.

- Using U from P fertilizers:
  - o Instead of judging U as solely problematic constituent in P rock, its value as resource for nuclear power generation should be considered. There are attempts and first successful implementations for separating the U contained in P rock during production of P fertilizers (Hurst, 2013), (Wang, 2012). Until 1990, worldwide there were 15 such plants that recovered U from P rock. All of them were closed when U prices dropped dramatically (Merkel and Hoyer, 2012). Whether U recovery from P rock will become economical again or not will depend on U prices on the world market (Srivas, 2012).
- Effect on public health:
  - o According to (IVA, 2009), at the moment there is no acute risk for human health if average diet is assumed. 90 % of ingested U is excreted with feces; the rest leaves the body with urine. So, there is no accumulation in the body. The WHO defined tolerable total amounts of U ingestion: 0.5 µg/kg for soluble compounds and 5 µg/kg in case of insoluble compounds. For a person of 60 kg weight that means that daily intake of 30 to 300 µg is acceptable. In the present work, highest U concentrations were found in one of the monitoring wells in the surrounding of the lysimeter station in Brandis. Between 2000 and 2002 U contents were at about 17 µg/L. If this water was used as drinking water without U removal, less than 2 liters of it would already be sufficient for reaching the lower limit of acceptable U intake.

In the long term, there are two main ways of addressing the problem of U contamination:

1) Extracting the U contained in phosphate rock during phosphate fertilizer production
2) Continue applying U-containing fertilizers and remove possibly elevated U contents in groundwater with water treatment methods

The second option causes nothing but costs and has no economic benefit. That is because U contents in groundwater (some micrograms to tens of micrograms) are not high enough for using the extracted U for nuclear power production. In contrast to that, U in P rock commonly occurs in the range of hundreds of micrograms to hundreds of milligrams, i.e. about two to four orders of magnitude higher. So, due to the higher concentration, the extraction efficiency would also be much higher. In case U market prices keep rising in future, P rock will become an economically beneficial option.

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9 Appendices

9.1 Sampling in the field

Table 28 – Soil sampling in the field (GPS coordinates were determined using a Garmin GPS eTrex HCx device)

Sampling site	Sample type		GPS coordinates		Altitude [m]	Sampling date
	Field	Forest	Easting	Northing		
Brandis lysimeter station (BfUL)	X		4541623	5688174	128	2012/11/19
Forest east of Brandis		X	4547322	5688253	163	2012/11/25
Hilbersdorf (BDF 43, LfULG)	X		4598xxx*	5641xxx*	423	2012/11/23
Hilbersdorf, forest		X	4598xxx*	5641xxx*	423	2012/11/23
Schmorren (BDF 24, LfULG)	X		4579xxx*	5676xxx*	161	2012/11/28
Wermsdorf, forest		X	4569239	5682490	208	2012/11/28
Sauerbach lysimeter station (UFZ)	X		4450980	5771908	148	2012/12/19
Forest close to Sauerbach lysimeter station		X	4451020	5771934	149	2012/12/19

* Coordinates were rounded to full 1000 meters due to reasons of protection of privacy of the land owner

9.2 Determination of cation exchange capacity
Needed chemicals:

Table 29 – Needed chemicals for CEC determination

Chemical contained in solution	$BaCl_2$	$BaCl_2$	$MgSO_4$
Concentration [mol/L]	0.1	0.0025	0.02
Preparation	Dissolve 24.43 g $BaCl_2*2H_2O$ (M=244.26 g/mol) in DI water (20°C); fill up to 1000 mL	Dilute 25 mL of 0.1 M $BaCl_2$ solution to 1000 mL	Dissolve 4.93 ± 0.01 g of $MgSO_4*7H_2O$ (M=246.47 g/mol) in DI water (20°C); fill up to 1000 mL

Procedure:

1) Weighing in 2.5 g of air-dry soil (grain size ≤ 2 mm), pre-treated according to e.g. ISO 111464
2) Filling the soil into a closeable PVC centrifuge tube (50 mL)
   → Mass m_1 (soil + tube + cap)
3) Adding 30 mL of 0.1 M $BaCl_2$ to soil
4) Shaking for 1h
5) Weighing filled tube *(1st time: about 32.5 g; 2nd and 3rd time: about 35 g)*
6) Centrifugation for 10 min at 3000 g
7) Removing supernatant
8) Repeating steps 3) to 7) two more times (after supernatant removal and addition of new solution, tubes will weigh 2.
9) Adding 30 mL of 0.0025 M $BaCl_2$ (concentration in equilibrium solution will be about 0.01 M if 2.5 mL of solution remain in soil sediment)
10) Shaking over night
11) Weighing tubes *(weight should be about 35 g)*
12) Centrifugation for 10 min at 3000 g
13) Decanting supernatant
14) Weighing tube + cap + content (m_2)
15) Adding 30 mL of $MgSO_4$ solution to soil
16) Shaking over night
17) Weighing tube *(weight should be about 35 g)*
18) Centrifugation for 10 min at about 4000 r.p.m. using an MLW T54 centrifuge manufactured by "Medizintechnik Leipzig"
19) Decanting supernatant over a coarse filter paper (7 cm diameter) into an Erlenmeyer flask
20) Determining Mg excess with ICP-MS (c_1)
21) **Testing blanc tube by same explained procedure without soil**

Calculation of Mg excess concentration and consequently CEC:

$$c_2 = \frac{c_1 \cdot (30 + m_2 - m_1)}{30}$$

c_2 corrected c(Mg) in sample [mmol/L]

c_1 measured c(Mg) in sample [mmol/L]

m_1 mass of centrifuge tube with air-dry soil [g]

m_2 mass of centrifuge tube with wet soil [g]

CEC of soil [cmol+/kg, centimols positively charged ions per kg]:

$$CEC = \frac{(c_{b1} - c_2) \cdot V}{m}$$

c_2 corrected c(Mg) in the sample [mmol/L]

c_{b1} c(Mg) in blank solution [mmol/L]

V   volume of solution [L] = 0.03 L

m   mass of air-dry sample [kg] = 0.025 g

- Interferences:
  - Ca from calcite or gypsum
  - Soluble salts
  - Organics

9.3 Typical ranges of U in German top- and subsoils

Table 30 – Typical ranges of U in mg/kg in German top- and subsoils of different land use and soil parent material (modified according to Kok and Schnug, 2008, page 40)

Soil parent material	Relevant for site …	Soil stratum	Land use	Sample number	Minimum	Median	90th percentile	Maximum
Sands		Topsoil	Arable land	41	0.4	0.8	1.4	1.4
		Subsoil		25	0.3	0.7	1.2	1.7
		Subsoil	Forest	222	0.1	0.5	1.0	1.6
		Substratum		26	0.3	0.4	0.9	1.0
Sandy loess		Topsoil	Undifferentiated	93	0.5	1.4	1.8	2.5
		Subsoil		135	0.4	1.2	1.7	2.7
Sandstones		Topsoil	Undifferentiated	26	0.4	1.5	2.0	2.6
		Subsoil		28	0.3	1.5	2.4	2.6
Loess		Topsoil	Arable land	179	0.5	2.0	2.6	3.5
		Subsoil		42	1.0	2.0	2.5	3.1
		Topsoil	Forest	279	0.5	2.0	2.6	3.6
		Subsoil		31	0.4	2.1	2.8	2.9
Acid igneous and metamorphic rocks		Topsoil	Arable land	77	0.5	2.4	4.2	6.0
		Topsoil	Forest	160	0.6	2.4	4.4	7.5
		Subsoil		328	0.7	2.6	4.6	7.2

9.4 Overview over relevant EXCEL files used in the thesis

ID	Content	Folder and file name	Page in thesis where the file is cited
FOLDER 1	Detection limits IC, ICP-MS, TIC/DOC	MSc_digital_appendix\Methodology\Detection_limits+general_info	42
EXCEL 1	Overview over P and U species and constants in different PHREEQC databases	MSc_digital_appendix\Methodology\Flow-through_load_test\PhreeqC_modeling\Final_U-P_thermodynamic_data_compilation	44, 127
FOLDER 2	Folder with PHREEQC input files	MSc_digital_appendix\PhreeqC\Input_files+input_data(Excel)	44
EXCEL 2	Master table for statistical data evaluation of the 4 test sites	MSc_digital_appendix\Results\SPSS_analysis_files\SPSS_input_data\ Sequ.extr.+soil_properties_import-ready	45
EXCEL 3	Grain size distribution curves	MSc_digital_appendix\Results\All_soils_properties\Grain_size-analysis\Final_particle_size_analyzer_results_all_samples_and_fine_soil_plot	45, 49
PHREEQC 1	Quality of water analyses PHREEQC input file	MSc_digital_appendix\PhreeqC\Input_files+input_data(Excel)\ All_sites_BM_EC	47
EXCEL 4	CEC_{pot} and CEC_{eff}	MSc_digital_appendix\Results\All_soils_properties\ CEC_Mandy_Hoyer_with_cation_IC_analysis	53
EXCEL 5	U totals from gamma spectrometry calculations	MSc_digital_appendix\Results\Gamma_spectrometry\Gamma_spectrometry_results\ All_gamma_results_compiled_and_extr._results_normalized_to_them	55
EXCEL 6	All U extraction results	MSc_digital_appendix\Results\All_soils_properties\Sequential_extraction\2013-01-28 Hoyer_seq. Extr_ICP_all_results_final	55, 63, 65, 67
EXCEL 7	Saturation indices of waters from sampling sites, modeled with PHREEQC	MSc_digital_appendix\PhreeqC\Phreeqc_llnl.dat_all_sites-input+output_speciation+SI+EC+interpretation	77, 79

ID	Content	Folder and file name	Page in thesis where the file is cited
FOLDER 3	U input to the different sites over time	MSc_digital_appendix\Test_sites-received_data	80
EXCEL 8	Concentration development of P and U in the monitoring wells in the surrounding of the sampling sites	MSc_digital_appendix\Groundwater_analytical_data_from_state\Sophie_Conradt_Data_on_24GWMs_near_my_test_sites\Compilation_U+P_concentration_at_the_24_LfULG_sites	91
FOLDER 4	Folder with all flow-through results	MSc_digital_appendix\Results\Flow-through_experiments	105
EXCEL 9	U and P mass balance in flow-through cells	MSc_digital_appendix\Results\Flow-through_experiments\U-P-Ca_mass_balance_calculations	106
FOLDER 5	Development of concentration of relevant elements over time in flow-through percolates	MSc_digital_appendix\Results\Flow-through_experiments\Analytics	111
EXCEL 10	Visible changes of flow-through cells over time	MSc_digital_appendix\Results\Flow-through_experiments\Visible_changes_over_time	112
EXCEL 11	U and P speciation and saturation indices of solubility-limiting phases in flow-through cell percolates over time, modeled with PHREEQC	MSc_digital_appendix\PhreeqC\Modeling_results\All_flow-through_results(llnl.dat_output)	117, 122