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EVALUATION OF SOIL EXTRACTION METHODS FOR URANIUM

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES IN THE APPENDIX

1. Introduction

Uranium in soil

The discovery of the uranium (U) is credited to the German pharmacist Martin Heinrich Klaproth during work in his experimental laboratory in Berlin in 1789. U occurs naturally in low concentrations in rock, soil, and water. Note that U is present in most soils at a low concentration, so the mere fact that a soil contains U does not mean that it has been artificially contaminated by U. According to the United Nations (UNSCEAR, 1993) the normal concentration of U in soil is 0.3 to 11.7 mg kg^{-1}.

One important reason, why understanding the behavior of U in the environment is becoming increasingly important because of the high quantity of nuclear waste to be disposed during wars. The military has used depleted uranium (DU) ammunition in recent international conflicts, including: 1991 Iraq/Kuwait (Gulf War I), 1995 Bosnia/Herzegovina, 1999 Kosovo/Serbia, and in 2003 Iraq (Gulf War II) (Bleise et al., 2003), also, most recently, in 2006 in Lebanon (obtained by personal communication with Prof. Dr. Chris Busby in the international symposium protecting water bodies from negative impacts of agriculture" Loads and fate of fertilizer derived uranium. June 4-5, 2007, Braunschweig, Germany). Also the use of P fertilizers raises the background level of U in the environment. For instance, Taylor (2007) concluded that mean level of U increased by about 1.3 mg kg^{-1} for soil sampled about 40 years ago compared with 1992 soil samples as a result of P fertilizers application.

The mobility, bioavailability, and toxicity of U are governed by its chemical form and binding mechanism to the sediments or soils (Elless and Lee, 2002; Filgueiras et al., 2002). Better understanding of different U forms and mechanisms governing the U behavior in soils is useful because it leads to the best possible extraction procedures and the best remediation treatments in U-affected soils. Generally U may be present in soil as soluble, exchangeable, complexed (e.g. the uranyl cation (UO_2^{2+}) complexes with CO_3^{2-}, PO_4^{3-}, SO_4^{2-} and Cl^-), organic matter bound, precipitated and reduced forms, which impact its mobility and fate in the soil environment.

The soluble and exchangeable U forms are weakly bound and likely to be mobilized by slightly aggressive waters. The carbonate phases are those that can be dissolved in acid solution and the iron and manganese phase are sorbed but could be released under reducing conditions (reductive dissolution of the oxide phase) (Elless et al., 1997). The sulfide and organic matter phase (reduced) require strong oxidizing conditions to release U, and the residual phase is unlikely to be mobilized (Grassi et al., 2005).

Mechanisms by which U mobility can be reduced in different environments include; precipitation of U (VI) and less soluble U (IV), extracellular and intracellular microbial uptake of U (VI) and U (IV) in the presence of microbial energy source, sorption of U by organic matter and minerals over a wide range of pH, occlusion of U by clay and Fe oxide coatings, formation of U (IV) oxide surface coating on U (VI), and co-precipitation of U with Fe and Mn oxides and substitution in silicate clays and CO_3 (Duff et al., 2002).

For the non-volatile substances in the soil, like plant nutrients and heavy metals including U, the soil solution is the only transport medium (Castilho et al., 1996). In a separate study, Tyler and Olsson (2001) used the high-speed centrifugation of the soils at moisture content of 60% of water holding capacity (WHC) to study the effects on soil solution chemistry and plant uptake of U by raising the pH of soil samples. They attributed the greatly increased solubility and uptake of U observed with high pH to the formation of highly soluble, negatively charged carbonate complexes with UO_2^{2+} ion. In another study, very little (< 1%) of total U in the soil samples was found in the soil solution (Taylor and Kim, 2007). The results also indicated that the solution UO_2^{2+} concentration was correlated with the P fertilizer application.

Few investigations have been published on the factors affecting the U availability in soil. Soil's chemical and physical characteristics, including pH, redox potential, cation exchange capacity, concentration of CO_2, amount and type of dissolved salts, organic matter content, porosity, and permeability control U behavior and distribution (Langmuir, 1978). There are more factors which affect the U mobility in soils: the presence of phosphate (PO_4^{2-}), $CaCO_3$, SO_4^{2-} and iron oxides in the soil, also its clay content and the microbial activity. Therefore, in determining the mobility, bioavailability, and toxicity of U, it is very important to understand the physical, chemical and microbial characteristics of the contaminated soils (Filgueiras et al., 2002).

Soil pH value

The pH value is an important geochemical parameter and is anticipated to have a significant impact on U leaching, precipitation, and/or mobilization, because it can change U chemical forms in soil, which have different mobility characteristics. U is amphoteric, meaning that it can mobilize at either high or low pH (Grassi et al., 2005).

In acidic environments, speciation is dominated by UO_2^{2+}, the highest soluble U form. At pH > 4, cationic uranyl hydroxide and uranyl carbonate complexes form, of which the later complexes are anionic above pH 9 (Duff and Amrhein, 1996; Davis et al., 1998). Similar results have been found by Lamas (2005). UO_2^{2+} was expected to be the predominant form in the pH range from 3.4 to 4.6 in the investigated forest soils. In contrast, the U-hydroxides, which are strongly adsorbed to soil surfaces and thus are less mobile, predominated at the pH ranged from 6 to 6.5 in the grassland soils. In the lower pH range, increased solubility due to the hypothesized presence of the UO_2^{2+} was not always observed (Vandenhove et al., 2007a).

In alkaline conditions, the U distribution ratio (R_d) was less than 20 when the solution pH was less than 8. As the results of Johnson et al. (2004) revealed, U sorption increased drastically as the soil pH increased. This means that the mobility of U decreased as the pH increased above 8 in alkaline soils. Also, when Echevarria et al. (2001) investigated the influence of soil pH on U sorption ratios (sorption ratios (SR) were computed as the ratio of the concentration of uranium on the soil to the concentration in the pore-water in 1 kg^{-1}) in the presence of 1 mg kg^{-1} U, they found that soil pH was highly linearly correlated with (log SR) as a probable consequence of the existence of different U complexes as a function of soil pH.

On the other hand, results of Zhou and Gu (2005) indicated that the higher the pH, the greater the amount of U extracted by the CO_3 solution. Huang et al. (1998) reported that at pH 9 UO_2^{2+} ions are predominantly in the form of $(UO_2)_3(OH)_7^{-1}$. Zhou and Gu (2005) showed that a much larger amount of U(VI) was extracted by the CO_3 solution at pH 10.4 than by the $NaHCO_3$ solution at pH 8.2. Tyler and Olsson (2001) and Vandenhove et al. (2007a) observed increasing of U solubility with increasing pH, and this increase was found to be linked with the formation of highly soluble negatively charged CO_3 complexes.

Carbonate

Calcium carbonate ($CaCO_3$) is usually used to release U in mines and contaminated sites, and has been mentioned to dissolve unstable precipitated P sources under aerated soil conditions and natural or higher pH (Harmsen and Haan, 1980; Duff and Amrhein, 1996; Mason et al., 1997; Zhou and Gu, 2005). Also, Zhou and Gu (2005) pointed out that solutions of CO_3/ HCO_3 could result a rapid and great increase in leaching and the mobility of U (VI) from the contaminated soil. This stands in contrast to reports by Lamas et al. (2005a) in a comprehensive study of the factors affecting the mobility of U in contaminated soil. They reported that the addition of $CaHPO_4$ alone, or in combination with $CaCO_3$, reduced the U availability in different soils. The addition of lime reduced the U availability in grassland soil. The results revealed that the addition of $CaCO_3$ didn't release U, which was complexed by $CaHPO_4$.

In strongly alkaline conditions, CO_3^{2-} leaching involves the formation of highly soluble U(IV)- and U(VI)-carbonate complexes, which are not likely to absorb strongly to negatively charged surfaces in soil. The recent data suggested that U carbonate ternary complexes might be the principal surface species (Duff and Amrhein, 1996; Bargar et al., 1999, 2000). Some key reactions in this process are:

$$2\,CO_3^{2-} + UO_2^{2+} \longleftrightarrow UO_2(CO_3)_2^{2-} \quad \text{and}$$

$$3\,CO_3^{2-} + UO_2^{2+} \longleftrightarrow UO_2(CO_3)_3^{4-}$$

(Clark et al., 1995).

Zheng et al. (2003) showed that the presence of $CaCO_3$ in soils strongly affects U(VI) sorption. Higher concentrations of soil $CaCO_3$ lead to a pronounced decline of the pH-dependent sorption curve in the neutral pH range because of the formation of a very stable neutral complex of calcium uranyl carbonate in solution.

Iron oxides

Under aerobic conditions, iron (Fe) plays an important role in immobilizing of UO_2^{2+} in the subsurface through sorption. U can co-precipitate with Fe oxides and become bound in the soil. Fe-hydrous-oxides are common in the environment and strongly adsorb both U (VI) and CO_3^{2-}. Fe-oxides grain coatings have been shown to be important metal-ion-adsorbing phases (Hsi and Langmuir, 1985; Coston et al., 1995; Bostick et al., 2002). Iron (hydrous) oxides, including ferrihydrite (Moyes et al., 2000), goethite [FeOOH] (Kohler et al., 1992) and hematite [Fe_2O_3] (Bargar et al., 1999) can strongly sorb U (VI) under neutral to slightly basic conditions. The results of Bargar et al. (1999) are opposite to the predictions that the U (VI)-carbonate ternary complexes should predominate only above pH 6. They mentioned that U (VI)-carbonate complexes were found to be the predominant adsorbed U (VI) species at all pH values. Such complexes may occur on minerals having surface-charging behaviors similar to Fe_2O_3 (e. g., Al-oxides).

U binding by iron oxide minerals appears to occur through inner-sphere surface complex formation involving two oxygen atoms of the FeO_6 octahedron (Waite et al., 1994). Surface complexation modeling of UO_2^{2+} species in carbonate-free solution at pH >5 suggests that monobi- and tridentate uranyl-hydroxyl complexes are responsible for uptake on ferric hydroxides (Fe $(OH_3)\cdot H_2O$). The uptake of U from aqueous solution by iron hydroxides such as FeOOH occurs by surface complexation and ceases when the surface becomes saturated (Moyes et al., 2000). Their results indicated that bi-dentate inner-sphere surface complexes were formed on the iron hydroxides by coordination of two surface oxygens from an iron octahedron in the equatorial plane of the complex.

The ability of different iron oxides to oxidize biogenic uraninite (UO_2) under reducing conditions is extremely different as shown in recent work by Nevin and Lovley (2000), Ginder-Vogel et al. (2006). They demonstrated that uraninite (a sparingly soluble U phase) oxidation by $Fe(OH_3)\cdot H_2O$ is thermodynamically favorable under limited geochemical conditions. Results also revealed that FeOOH and Fe_2O_3 have a limited capacity to oxidize UO_2 while ferrihydrite ($5Fe_2O_3\cdot H_2O$) can lead to UO_2 oxidation. Production of soluble U(VI) is most extensive in the $5Fe_2O_3\cdot H_2O$ system (0.70 μM), with lesser amounts detected in FeOOH (0.50 μM) and Fe_2O_3 (0.38 μM) systems. The extent of UO_2 oxidation by $5Fe_2O_3\cdot H_2O$ increased with increasing HCO_3 and Ca concentration, but decreased with elevated Fe(II)(aqueous) and U(VI) concentrations.

Nitrate, a common co-contaminant with U in aquifer sediments, induces U(IV) oxidation by oxidation Fe (II) with nitrite to Fe (III), which in turn oxidizes U(IV) (Senko et al., 2002, 2005). They suggested that these actions take place as follow:

$$2NO_2^- + 2UO_2 + 6H^+ \longrightarrow N_2O + 2UO_2^{2+} + 3H_2O$$

$$10NO_2^- + 20Fe^{2+} + 33H_2O \longrightarrow 5N_2O + 4Fe5HO_8\cdot H_2O + 30\ H^+$$

$$2Fe5HO_8\cdot H_2O + 5UO_2 + 30H^+ \longrightarrow 10Fe^{2+} + 5UO_2^{2+} + 24H_2O$$

Phosphate

Phosphates (PO_4^{3-}) are among the most insoluble U (VI) compounds, and when phosphate is present in the soil at appreciable concentrations, uranyl phosphate compounds can control dissolved uranium concentrations. The influence of phosphorus compound ligands in soil solution on the mechanisms of U sorption remains thus far unclear, meaning that a lot of research is still needed to understand the relation between the PO_4^{3-} and U mobility. The results from the literature revealed that maximum dissolved U in soil solution concentrations was observed in different soils with low PO_4 level compared to that with a higher level of PO_4^{3-} (Vandenhove et al., 2007a).

Sowder (1998) found that uranyl phosphate phases were markedly resistant to dissolution by deionized water, acetic acid, EDTA, and bicarbonate. Lamas et al. (2005a) demonstrated that the addition of $CaHPO_4$ reduced the available U in different soils near to the background level and also decreased the U-uptake by *Lolium perenne* plants grown in U-contaminated soil. They also suggested the value of 25 mg kg^{-1} water soluble P in the soils as the maximum level of soluble P in soils that have the potential to reduce the U-uptake by plants from contaminated soil.

These results are in partial agreement with those of Rivas (2005). It was reported that the addition of P fertilizer as $CaHPO_4$ to U-contaminated soil sharply reduced the U concentration and uptake by maize and sunflower plants, but it didn't decrease the plant-U concentration and uptake by faba bean plants. Because of the low solubility of uranyl phosphates compounds, the addition of apatite ($Ca_5(PO_4)_3(OH)$) to contaminated soils has been proposed as a remediation strategy (Arey et al., 1999).

The decrease of U concentration in soil solution in the presence of P compounds may be attributed to the precipitation reactions (Koch-Steindl and Pröhl, 2001), or to enhance U sorption on the soil surfaces by formation of ternary surface complexes involving both UO_2^{2+} and PO_4 (Payne et al., 1996).

Clay content

Soil clay content is one of the predominant factors controlling U sorption on alkaline desert soil surfaces (Johnson et al., 2004).A positive correlation was found between the U distribution ratio (R_d, the amount of U absorbed from solution divided by the concentration of U remaining in solution after equilibrium time) and soil clay content. They also mentioned that most depleted U from military use is expected to be on the surface or near surface. UO_2^{2+} sorb at both permanently and variably charged sites of clay mineral surfaces (Turner et al., 1996, Hudson et al., 1999). Bostick et al. (2002) reported that outer-sphere complexes dominate at the permanently charged sites and inner-sphere complexes form at the variably charged, edge sites. Reversible adsorption and the inhibition by weakly coordinating cations have traditionally been used to suggest that outer-sphere complexation is an important adsorption mechanism, similar to labile outer-sphere surface complexes that often form on clay minerals. However, inner-sphere complexes can also be labile and thus cannot be ruled out based on these macroscopic measurements. However, any inner-sphere complex formed must be relatively labile to describe the reversible sorption observed in both batch and flow experiments (Bostick et al., 2002). UO_2^{2+} adsorption in each of the media was remarkably similar despite widely varying mineralogy

(Barnett et al., 2000; Bostick et al., 2002). Weakly negative correlation was found between the clay content of most soils studied by Sheppard and Evenden (1992) and the plant concentration ratio of radish plants, cultivated in U-contaminated soils, also the clay content was negatively significantly correlated with U extracted by $NaHCO_3$, indicating that, as expected, U was less readily extracted when the clay content was high.

Organic matter

UO_2^{2+} has been reported to combine with organic ligands such as soil humic substances, acetate, oxalate and citrate (Ganesh et al., 1997; Huang et al., 1998). As well U has been found in the soils sorbed, chelated or complexed with soil organic matter.

Zhou and Gu (2005) found a strong linear relationship between U(VI) and total organic carbon released from the soil. Therefore, the amount of U(VI) extracted by hydroxide (NaOH) may be attributed to the complexation of U(VI) with soil organic matter. The brown color (in the extracted solution) was due to dissolved soil humic substances at high pH, which caused the deprotonation of the surface functional groups and desorption of soil humic substances. The slow release of the U(VI)-organic matter complexes could be caused by the slow diffusion and desorption rates of the U(VI)-organic matter complexes (Zhou and Gu 2005).

The presence of humic substances could also have enhanced the mobility of U(VI) as a result of its complexation reactions with humic substances. For example, Crancon and Lee (2003) reported that a large fraction of U(VI) was associated with humic materials in various soils.

In an incubation experiment, Lamas et al. (2005b) observed that the addition of different organic materials increased the U extractable by DTPA as compared to non-amended soil. They also mentioned that the different organic amendments have had different impacts on the availability of U following the relative order: amended with legume > amended with straw > non-amended soil. They attributed these increments in the extracted U to the release of low molecular weight compounds, which would mobilize the U absorbed by soil, from the easily decomposed organic materials and to the pH increases.

Organic matter in the soil found to be negatively correlated with extractable U by ammonium acetate (NH_4Ac), and negatively correlated with U concentration in radish plants. Also the organic matter had highly significant positive correlation with background U concentration in soils (Sheppard and Evenden, 1992).

Cation exchange capacity

As a result of the effects of the above factors and because some of the U forms have positive charges; U forms can be adsorbed on a variety of negatively charged soil constituents including clay minerals, oxides and silicates, and organic materials. Johnson et al. (2004) found a positive correlation between the U distribution ratio (R_d) and the cation exchange capacity (CEC) of the soils tested. This phenomenon suggested that the adsorption of U through weak electrostatic bonds with the clay is an important mechanism in controlling U mobility. These results were in a good agreement with the results of Vandenhove et al. (2007a). They observed that the soils, which have high CEC values, exhibit higher U sorption and low U concentrations in the soil solution compared to that with low CEC values.

Sheppard and Evenden (1992) reported that the available U extracted from different soils by NH_4Ac was significantly negatively correlated with CEC of the soil. CEC of the soils was highly significantly negatively correlated with the U-uptake of radish plants. These observations implied that the CEC reduces the mobility of U in soils. Sheppard and Evenden (1992) also observed that there is a positive correlation (r = 78**) between CEC of a soil and its background U content.

Microbial activity

Different interactions have been found between microorganisms and U, including sorption of UO_2^{2+} to the surfaces of bacteria, inhibition of bacterial metabolism by UO_2^{2+}, and secretion of uranyl phosphate by bacteria (phosphate dissolving bacteria). All of these interactions lead to the precipitation of uranyl phosphate. Also these interactions may be affected by another set of factors such as: organic matter and the abundance and form of iron hydroxides present in the environment.

Citrate has been shown to enhance the partitioning of UO_2^{2+} onto FeOOH by up to 90% (depending upon chemical conditions) in the pH range from 3 to 6 (Redden et al., 1998) by formation of a ternary surface complex involving citrate, FeOOH, and UO_2^{2+}. The bacterially mediated degradation of citrate could reverse this enhancement, leading to the release of U(VI) bound to FeOOH. In addition, bacterial cells can directly sorb U(VI) and/or release PO_4^{3-}, which may react with U(VI) to precipitate solid U(VI)-phosphate phases (Bencheikh-Latmani et al., 2003).

Another effect of microorganisms that several microorganisms in common in soil is that they can enzymatically reduce U(VI) to U(IV) under anoxic conditions, and this effect, in turn, affects the mobility and bioavailability of U in soil (Caccavo et al., 1992; Gorby and Lovely, 1992; Tebo and Obraztsova, 1998; Lovley et al., 2000).

Studies presented by Wielinga et al. (2000) using *Shewanella alga* (*S. alga*) as a dissimilatory metal-reducing bacteria (DMRB) demonstrate that amorphous iron hydroxides may compete with UO_2^{2+} as terminal electron acceptor. They reported that when *S. alga*e were added to UO_2^{2+} acetate solution (400 µM), UO_2^{2+} was removed from the solution within 10 hours. Similarly, UO_2^{2+} in the presence on FeOOH (11.1 µM of U/m^2 of solid) underwent a dramatic reduction (>90%) with active *S. alga* cells. In contrast, when $5Fe_2O_3 .9H_2O$ was available (0.67 µM of U/m^2 of solid) only 48% of the initial U(VI) was removed after 10 hours. This means iron hydroxides retard UO_2^{2+} reduction and precipitation, thereby increasing their mobility in soils.

The uptake of U by biomass (bacteria) was highly affected by the pH of the solutions. At pH 6 and 7, significant uptake of U by biomass was measured at about 1.28-3.84 µmol of U per mg of biomass (Huang et al., 1998). The U was removed from solution primarily through extracellular adsorption. It is not clear what the main sorption mechanisms were in this study. PO_4^{3-} and carboxyl groups on the cell surface may serve as sites of U complexation since the two groups and UO_2^{2+} ions all possess predominately negative charges at alkaline pH and positive charges at acidic pH, which should minimize surface sorption of U through charge repulsion (Huang et al., 1998).

On the other hand, the presence of U has an inhibitory effect on the growth of bacteria, such as for instance, *Desulfovibrio desulfuricans* (Tucker et al., 1996). Contrarily the results of Lamas et al. (2005b) implied that there is not any toxic effect of U on microorganisms in soil at the rate of 500 mg kg^{-1} U in soil in an incubation experiment.

Redox chemistry of uranium

Because U has different oxidation states, it can exist in the +3, +4, +5, and +6 valences in different environments. U (VI), (i.e. UO_2^{2+}) and U(IV) (i.e. UO_2) are the most common oxidation states of U in natural environments. The redox potential is one of the most important factors because most of the immobile mineral phases that form when U is in reducing condition (Amrhein et al., 1993; Grassi et al., 2005). U can form a mobile ion or an immobile mineral depending on several key factors. U will exist in the +6 oxidation state under oxidizing to mildly reducing environments. U (IV) is stable under reducing conditions and is considered relatively immobile because U(IV) forms sparingly soluble minerals, such as (UO_2). There is no specific threshold of redox potential for U mobility, because the U mobility is also influenced by other key factors.

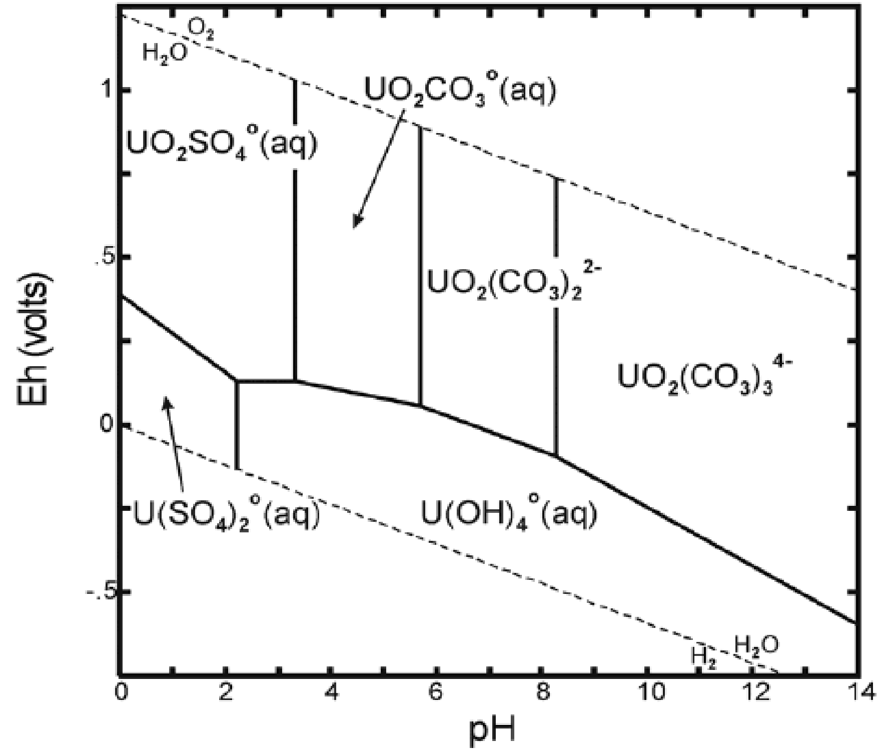

Figure 1.1: Eh-pH diagram showing the dominant aqueous complexes of U [Diagram was calculated at 25 ºC and a concentration of 10^{-7} mol/L total dissolved U in the presence of dissolved chloride, nitrate, carbonate, and sulfate.] (Krupka and Serne, 2002).

Figure (1.1) shows the Eh-pH diagram for the dominant U aqueous species calculated for total concentrations of dissolved U, chloride, nitrate, carbonate, and sulfate of 0.024 (10^{-7} mol/L), 22, 1.7, 67.5, and 108 mg/L, respectively. This figure indicates that sulfate complexes would dominate the aqueous speciation of U at pH values less than 3. At higher pH values, the speciation of U(VI) is dominated by a series of strong aqueous carbonate complexes, which increase the solubility of U at these environmental conditions (Langmuir 1997). Because anions do not readily adsorb to mineral surfaces at basic pH conditions (EPA 1999), the anionic charge of the aqueous U(VI) carbonate complexes at pH values greater than 6 result in decreased adsorption and thus increased mobility of U. Under reducing conditions, the speciation of U(IV) is dominated by $U(OH)_4$ (aq) at pH values greater than 2 even in the presence of the dissolved chloride, nitrate, carbonate, and sulfate (Fig. 1.1) (Krupka and Serne, 2002).

Complexes with sulfate, fluoride, and possibly chloride are potentially important UO_2^{2+} species where concentrations of these anions are high. However, their stability is considerably less than the CO_3 and phosphate complexes (Grenthe et al. 1992).

Lamas et al. (2005b) found that in most cases the aerobic condition increased the available U extracted from contaminated soils (500 mg kg^{-1} U) with different extractants as compared to the anaerobic condition. These increments may be attributing to the formation of soluble UO_2^{2+} cation, which related to the increase of redox potential. Duff et al. (1999) found that most of soluble U(VI) was lost from solution when potential reducing agents were added (alfalfa shoot) to the sediments, meaning that the U(VI) was reduced to U(IV). Upon exposure to air, the precipitated U was readily oxidized. They also noticed that at high Eh and high CO_2 concentrations, dissolved U concentrations were higher than in the low CO_2 concentration due to greater complexation with CO_3. Also dissolved U concentration decreased only under intense sulfate reducing conditions, at low Eh conditions. It appears that U reduction occurred by chemical reduction via sulfide ion.

Uranium in plant

Shahandeh and Hossner (2002) studied the role of soil properties on the accumulation of U in one U tailing soil and 8 cultivated soils contaminated with different concentrations of UO_2^{2+} nitrate (100-600 mg kg^{-1} U). Plants grown in soils with high carbonate U fractions accumulated the most U both in shoots and roots. The lowest plant U occurred in clayey acid soils with high Fe, Mn and organic U fractions. Therefore Fe and Mn oxides and organic materials can play an important role in sorption of U and they can reduce the availability of U for plants. On the other hand, CO_3 has an enhancement effect on the uptake of U by plants.

Vandenhove et al. (2007b) stated that the free UO_2^{2+} cation and uranyl carbonate complexes are most U forms available for root uptake and transfer to the ryegrass shoots and that in some cases uranyl-phosphate complexes are readily transferred. Furthermore, they didn’t find any relation between the U soil-to-plant transfer factors (TF) or U uptake and the U concentration in the soil solution extracted with different extractants (NH_4Ac-pH 7, NH_4Ac-pH 5 and $(NH_4)_2C_2O_4$). These results are in agreement with the observations for beans (*Phaseolus vulgaris*) (Laroche and Henner, 2003).

Plants response may vary when subjected to different U concentrations. Gulati et al. (1980) reported that wheat yield increased significantly with increase of U dose to 6 mg kg^{-1} and then decreased significantly, while tomato yield decreased significantly with the addition of U to soil. According to Vandenhove et al. (2006), exposure to high concentration of U can cause oxidative stress and cellular redox imbalance in plants like beans (*Phaseolus vulgaris*) and also cause severe DNA damage in bean roots. Rivas (2005) found a significantly positive relation between the U concentration in soil and the U concentration in maize, sunflower and faba bean tissues. The results also revealed that the U concentration in soil significantly decreased the biomass production of the three plants. Sheppard and Evenden (1992) compared the U uptake of radish and beans from different contaminated soils with the U extracted by $NaHCO_3$ and NH_4Ac extractants; they found good correlation only between U extracted by NH_4Ac and the transfer factor for plants.

Vandenhove et al. (2006) reported that the capacities of enzymes involved in the anti-oxidative defense mechanisms (such as: GPOD, SPOD, GLUR, SOD, ICDH, G-6P-DH, and glutathione (GSH)) in roots were slightly stimulated with increasing U exposure concentrations. U contents found to be up to 900-fold higher in roots (31-4,916 mg kg^{-1}) as compared to primary leaves (1-16 mg kg^{-1}). Enzyme capacities in leaves were not affected by U treatment. Total and reduced GSH levels were higher in primary leaves of U exposed plants than in control plants. When exposed to 1,000 µM U, level of total and reduced GSH dropped. These results indicate that, for *Phaseolus vulgaris*, the U toxicity threshold is expected to be between 100 and 1,000 µM U (Vandenhove et al., 2006).

It was also reported that the concentration of U tends to reach a constant value in wheat grains in spite of the concentration of U in soil (Pulhani et al., 2005). They also reported that most of the U uptake by plants accumulated in the roots of wheat, and only about 1-2 % was distributed in the grains. The distribution of U concentration in different parts of the wheat plant showed a decreasing trend as root > shoot > husk > grain, calcium exerts an antagonistic effect on the uptake of U (Pulhani et al., 2005).

Extraction of U from soils

There is extensive evidence that neither total nor dissolved aqueous metal concentrations are good predictors of bioavailability and/or toxicity (Adam et al., 2006). Very few investigations have been performed on the extraction of U from the soil. Zhou and Gu (2005), extracted U from U-contaminated soil (pH 4.0) with sodium bicarbonate ($NaHCO_3$) at varying concentrations (0-1 M) and sodium hydroxide (NaOH) under anaerobic and oxic conditions. They reported that the amounts of U(VI) extracted under both anaerobic and oxic conditions by $NaHCO_3$ were increased with an increase of the concentration of $NaHCO_3$ used. The amounts of U(VI) extracted at concentrations of 0.03, 0.2 and 0.5 M $NaHCO_3$ reached values of about 55%, 82% and 93% respectively, of the amounts of U(VI) extracted by 1 M $NaHCO_3$ under anaerobic condition. On the other hand, extraction of U(VI) by NaOH accounted for only 40-50% of the U(VI) extracted by $NaHCO_3$ under similar pH conditions.

Vandenhove et al. (2007b) extracted U with three different extractants from 18 different soils (pH ranged from 4.63 to 7.52), artificially contaminated with 36 mg ^{238}U kg^{-1} dry weight soil. The results revealed that exchangeable U (extracted with 1 M NH_4Ac, pH 7) varied between 0.7 and 20 mg kg^{-1} (about 2% and 55% of the total U content in the soils), whereas the U extractable with NH_4Ac-pH 5 (U bound to CO_3) ranged from 17 to 97% (average: 66 %) of the total U soil content. The high levels of U released following NH_4Ac, pH-5 extraction are probably partially due to the dissolution of surface precipitates. The percentage of U extracted with ammonium oxalate $(NH_4)_2C_2O_4$ (U bound to amorphous phases) ranged from 82 to 100% (average: 89%). They also stated that the soil parameters had no influence on the extractable percentages of U.

U extracted with $NaHCO_3$ and NH_4Ac from wide range of U-contaminated soils (ranged from background level to 10,000 mg U kg^{-1} soil) with different characteristics (wide range of pH from acidic to slightly alkaline soils, clay content from 1 to 33%, and organic matter content from 1 to 41%, Sheppard and Evenden, (1992)). The extraction efficiency of NH_4Ac was lower than for $NaHCO_3$, while a good correlation was only found between U extracted by NH_4Ac and the transfer factor for plants. The results also showed that the extraction efficiency of NH_4Ac increased with higher concentration of U in soils, suggesting that the U became more extractable and therefore more bioavailable (Sheppard and Evenden, 1992).

U was extracted by AAAc-EDTA solution showed better correlation with U uptake by *Lolium perenne* cultivated in four different soils contaminated with four different U rates (0, 250, 500 and 1,000 mg kg^{-1}) than U extracted by DTPA (Lamas, 2005). Both DTPA and AAAc-EDTA extractants have different extracting capability when extracting U from soils. Furthermore, the presence and the type of organic matter in a soil may also affect the amount of U extracted (Lamas, 2005).

The U extracted by DTPA from pure soil (without addition of organic material) was about 0.1% of the total U (500 mg kg^{-1} U) and ranged between 1.6 and 14.3% of the total U for AAAc-EDTA extractant. In soil amended with cereal straw, the U extracted by DTPA ranged from 0.01 to 4 mg kg^{-1} (< 0.8% of the total amount), while in soil amended with alfalfa the DTPA extractable U ranged from 0.04 to 20 mg kg^{-1} (< 4% of the total amount). In the case of U extracted by AAAc-EDTA, the results also revealed that these values reached to 40 mg kg^{-1} (8% of the total amount) in soil amended with cereal straw, and to 55 mg kg^{-1} (11% of the total amount) in soil amended with alfalfa (Lamas et al., 2005).

Not only does the chemical composition of the extractant affect its efficiency to extract U from soils, but also the ionic strength and the extraction ratio. Zheng and Wan (2005) used $NaNO_3$ to extract U from contaminated soil at different ionic strengths (from 0.01 mol L^{-1} to 1.0 mol L^{-1}) and different extraction ratios (from 2:1 to 100:1). They found that both the ionic strength and the extraction ratio have a positive impact on the release of U (VI) from the soil. It is estimated that the maximum U concentration reached about 24% of the total U in soil at the highest ionic strength (1.0 mol $NaNO_3$ L^{-1}), which is still significantly lower than half of that extracted with 0.2 mol L^{-1} $NaHCO_3$ (pH = 10).

Sequential extraction procedures have been used by Zheng and Wan (2005) to identify and quantify the different U (VI) chemical forms in a U polluted soil (206 mg U kg^{-1}). Zheng and Wan (2005) used distilled water for soluble form, $Ca(NO_3)_2$ for exchangeable form, CH_3CO_2H + $Ca(NO_3)_2$ for carbonate form, $Na_4P_2O_7$ for organic matter bound U, $(NH_4)_2C_2O_4$ + $H_2C_2O_4$ to extract amorphous oxides forms and H_2SO_4 + HNO_3 for mineral forms. A ratio of 40:1 was used for all extractions except the last extraction where a ratio of 15:1 was used. It is estimated that about 50% of U in the soil was associated with mineral structure, whereas about 40% U was in the sum of carbonate and organic forms. The percentage of U (VI) in the amorphous form was about 5%, and around the same percentage was accounted for both exchangeable and soluble forms.

Johnson et al. (2004) used another sequential extraction procedure to extract different forms of U from alkaline desert. They used $MgCl_2$ to extract soluble phase, NH_4Ac in acetic acid for $CaCO_3$ form, hydroxylamine hydrochloride for oxide bound U, and finally a mixture of HCl + HNO_3 + HF for the residual form. They noticed that most of the U in these contaminated soils was found in the $CaCO_3$ fraction.

Several leaching solutions have been developed for the remediation of U contaminated soils. These methods base on the use of some strong solutions for leaching U with or without the use of other chemicals as oxidizers which can convert U metal and U (IV) to V (VI), and then form soluble complexes. These solutions include: 0.1 N nitric acid, 2% ammonium carbonate, 5 % sodium hypochlorite, EDTA, 2% citric acid, 0.1 M hydroxylamine-hydrochloride, and sodium citrate-bicarbonate-dithionite (Lee and Marsh, 1992). In general, this approach can remove a higher percentage of U than that removed by bio-available (e.g., plants and microorganisms) (Sheppard and Evenden, 1992).

Other researchers used other leaching solutions to extract U from contaminated soils (remediation). This approach is based on the use of powerful chelators for U, together with redox chemistry, to extract U from soil. Concentrated sulfuric acid and $NaHCO_3$ were used for this purpose as leaching solutions with or without oxidants $NaHCO_3$ and NaOCl (Duff et al., 1998). They reported that leaching soil with 0.05 M NaOCl solution followed by 0.5 M $NaHCO_3$ removed about 70% of the total soil U. These methods showed the potential of these chemicals for release of U from soils.

Fujino et al. (2000) used 1-Phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone as extraction reagent and di-isobutyl ketone as an organic solvent of the U from apatite minerals after treating the apatite with hot concentrated nitric acid, then the organic U phase was measured directly by ICP-AES.

Centrifugation technique of soil solution extraction

The soil solution is the aqueous liquid phase of the soil and its solutes. Soil solution extraction by centrifugation was recommended because it is the only method that is suitable for all soil types (Castilho et al., 1996). Also it is an easy, fast, and cheep method, so it appears the most promising method of extracting the soil solution. There are three main kinds of centrifugation: low speed centrifugation (low force or pressure), high speed centrifugation (high force or pressure) and centrifugation with immiscible liquid. The first two types are based on free drainage of the pore water (soil solution) into a collecting cup. The third is based on the displacement of pore water by an immiscible liquid followed by subsequent collection of the displaced water (Bonito, 2005).

Centrifugation has been widely used for extraction of the soil solution or soil pore water from various soils (Menzies and Bell, 1988; Campbell et al., 1989; Castilho et al., 1996; Taylor and Percival, 2001; Bonito, 2005). Different centrifugation methods have been reported by many authors (Elkhatib et al., 1987; Tyler, 2000; Nambu et al., 2005). Elkhatib et al. (1987) compared two centrifuge methods (drainage and immiscible liquid) and favored the drainage method because its greater efficiency and lower variability between the replications. They recommended the use of soil at field capacity (33 kPa) and centrifuge it for 20 min at a relative centrifugation force (RCF) of 4.8×10^5 for obtaining the soil solution. Tyler (2000) used a sequential centrifugation at 24 -18,900 × *g* RCF to obtain soil solution from calcareous soil at water holding capacity (WHC). Taylor and Percival (2001) employed the drainage centrifugation method at 7,000 rpm for 30 min to obtain the soil solution of the field-moist samples using double 50 ml polypropylene centrifuge tubes. Bonito (2005) used a wide range of centrifugation speed from to 3,000 to 12,000 rpm, and favored the speed of 7,000 rpm for 30 minute as the optimum speed to obtain the soil solution. The results of Perez et al. (2002) showed that the centrifugation speed could significantly impact the composition of the extracted soil solutions.

In the field of U more research is needed to better understand the behavior of U in soils. Knowledge of how different soil characteristics affect the environmental chemistry of U will enable better predictions of the fate and potential hazards of U in soils and should be useful in predictions of the human health problems caused by the accumulation of U in plants. It is important to find a suitable and effective extractant for U as well as other toxic heavy metals.

The main purpose of this work is to study the ability of the most common extractants usually used in soil laboratories to extract the heavy metals from soils with different characteristics to extract U from different soil groups (with a wide range of U concentrations) , and to establish a suitable method to extract U from soils. The ideal extractant for U should be able to extract only the available U from soil and be strongly correlated with U uptake by the plant.

The objectives of this study were:

1) to study the extractability of U from soil samples by common heavy metal extractants, and contrast the similarities/ differences amongst them,

2) to find out which of these extractants will best predict the plant uptake of U and,

3) to study some of the different factors affecting the U extractability and bioavailability for plants.

2. Material and Methods

The current work was carried out at the Institute of Plant Nutrition and Soil Science (PB), Federal Agricultural Research Centre (FAL), Braunschweig, Germany.

2.1 Description of the sample material

Four different soil sample groups were analyzed in this work to cover a wide range of U concentration in soils. Some of them were collected for previously conducted model experiments and the other were collected specifically for this work from U-contaminated sites in Germany and long term fertilization experiments, respectively.

2.1.1 Soil samples originating from a greenhouse pot experiment with different crops

The first group of U-contaminated soils used in this work came from a previously conducted pot experiment by Rivas (2005). It was a mixture of two kinds of soil: a silty-loam sand soil collected from a grassland site and a sandy soil from a forest site at different depths of both soils (0-25 cm and 25-50 cm). They were taken from the experimental site of the FAL, Braunschweig, Germany. Braunschweig (E 10° 27`, N 52° 18`) is located in the Lower Saxony country. The mean annual temperature is about 8.9 ° C; the mean annual precipitation is around 619 mm.

Originally, there were three contamination levels of U (166, 329 and 660 mg kg^{-1} U) plus control without artificial contamination (0.34 mg kg^{-1} U); the addition of P fertilization in the form of $CaHPO_4$ resulted finally in eight different levels of U content. Two P fertilization rates (0 and 1,200 mg kg^{-1} P), two N fertilization rates (250 and 500 mg kg^{-1} N), two S fertilization rates (0 and 50 mg kg^{-1} S) were used. The details of all treatments investigated in this study are presented in Table 2.1.

This greenhouse experiment was conducted on June 25th and harvested on August 4th 2003, three crops were cultivated for six weeks; corn (*Zea mays* L.), sunflower (*Helianthus annuus* L.) and faba bean (*Vicia faba* L.). In the case of faba beans, no nitrogen fertilization had been applied. In the present work these soil samples took numbers from 1 to 44

Table 2.1: The initial uranium (U) and phosphorus (P) contents, nitrogen (N) and sulfur (S) additions to the selected soil samples with different treatments of the pot experiment of Rivas (2005).

	mg kg^{-1}					mg kg^{-1}			
Sample No	**U content**	**N rate**	**S rate**	**P content**	**Sample No**	**U content**	**N rate**	**S rate**	**P content**
				Maize					
1	166	250	0	334	**11**	173	250	50	1,558
2	166	500	0	334	**12**	173	500	50	1,558
3	166	250	50	334	**13**	385	250	0	1,558
4	166	500	50	334	**14**	385	500	0	1,558
4	329	250	0	334	**15**	385	250	50	1,558
6	329	500	0	334	**16**	385	500	50	1,558
7	329	250	50	334	**17**	643	250	0	1,558
8	329	500	50	334	**18**	643	500	0	1,558
9	173	250	0	1,558	**19**	643	250	50	1,558
10	173	500	0	1,558	**20**	643	500	50	1,558
				Sunflower					
21	$0.2 \cdot 10^{-4}$	250	0	1,558	**29**	329	250	0	334
22	$0.2 \cdot 10^{-4}$	500	0	1,558	**30**	329	500	0	334
23	$0.2 \cdot 10^{-4}$	250	50	1,558	**31**	329	250	50	334
24	$0.2 \cdot 10^{-4}$	500	50	1,558	**32**	329	500	50	334
25	166	250	0	334	**33**	643	250	0	1,558
26	166	500	0	334	**34**	643	500	0	1,558
27	166	250	50	334	**35**	643	250	50	1,558
28	166	500	50	334	**36**	643	500	50	1,558
				Faba bean					
37	$0.2 \cdot 10^{-4}$		0	1,558	**41**	329		0	334
38	$0.2 \cdot 10^{-4}$		50	1,558	**42**	329		50	334
39	166		0	334	**43**	643		0	1,558
40	166		50	334	**44**	643		50	1,558

2.1.2 Soil samples originating from an incubation experiment

The second group of uranium-contaminated soil used in this work was derived from a previous incubation experiment under anaerobic conditions carried out by Lamas et al. (2005b). It was a grassland loamy sand soil obtained from the experimental field of the FAL, Braunschweig, Germany, classified as Podzolic Brown earth (organic carbon; 20 g kg^{-1} dry weight (DW) basis and pH 6.2).

The soil had the following combination of treatments without U contamination: a) control without organic materials (given numbers 1-2 in this work), b) with 50 g kg^{-1} DW basis dried legume meal (milled alfalfa plants) (given numbers 3-4 in this work), and c) with 50 g kg^{-1} DW basis cereal straw (given numbers 5-6 in this work). Another set of treatments was repeated with the addition of 500 mg kg^{-1} U_3O_8 (given numbers 7-8, 9-10 and 11-12, respectively).Two replicates were performed for each combination. The green modification of depleted uranium (DU) of finely pulverized U_3O_8, was prepared from UO_2 $(NO_3)_2.6H_2O$, by precipitation with ammonia to $(NH_4)_2$ U_2O_7, then incineration at 720 °C to U_3O_8 following Fleckenstein (1972). This form had a similar behavior of the oxidized DU (Lamas, 2005). This incubation experiment was started on Nov 21st 2000, and continued for 40 weeks. Incubated soil samples were numbered from 45 to 56 in the present work.

2.1.3 Soil samples from different sites around Schneeberg (Saxony)

The third group of the soil samples (14 samples) used in this work was collected from six sites around Schneeberg, Saxony, Germany. The Saxony country is located in the southeast of Germany. The locations, soil types and land use of these soil profiles are summarized in Table 2.2 and some of the chemical characteristics of the soil samples are presented in Table 2.3.

Table 2.2: General characteristics of the soil samples collected from the Saxony country, Germany.

Soil profile	Location	Soil type (FAO-classification)	Profile description and samples No.	Land use
1	Berghotel Steiger, Schneeberg	Gleyo-Orthic Luvisol	Metamorphic rocks, Phyllite **1-topsoil:** stony, friable silt with plough pan at 30 cm depth	field crop: corn
			2-subsoil: stony, silty clay loam	
2	Daniel mine, southwest of Schneeberg	Eutric and typic Cambisols	Metamorphic rocks, Andalusit **3-topsoil:** very stony, clayey silt loam, massive breaking to nut	field crop: potato
			4-subsoil: clay	
3	Dreihäuser Sandberg	Spodo-Dystric Cambisol	Weathered Eibenstock-Granite **Organic layer** (O): 0-10 cm	Forest
			5-topsoil (Aeh): 10-15 cm	
			6-subsoil (Ahe+Ae): 15-25 cm	
			7-weathered B (Bhs+Bsv): 25-55 cm	
4	Eibenstock mountain	Spodo-Dystric Cambisol	Eibenstock-Granite **8-topsoil** (rApd = Plow soil horizon): 0-38 cm	grassland
			9-subsoil (Bvs+Bs): 38-45 cm	
5	Schlunzig, Zwickauer Mulde	Gleyic Cambisol	Flood plain **10-topsoil** (rGo-aAp): 0-27 cm	field crop: corn
			11-subsoil (II rGo-aM): 27-55 cm	
6	Zwickauer Mulde river, north of Zwickau	Gleyic Cambisol	River bank **12-topsoi**l (Ah+M-Ah): 0-35 cm, silty sand	grassland
			13-subsoil (Go-M): 35-60 cm, silty sand	
			14- >60 cm: more sandy than above	

Data in this table were obtained by personal communication with Guenter Rank and Ronald Symmangk, Sächsisches Landesamt für Umwelt und Geologie (LfUG).

Table 2.3: Selected chemical characteristics of soil samples collected from the Saxony country.

Samples	**pH ($CaCl_2$)**	**Total U**	**Total P**	**Total Cd**	**Total As**
		(Aqua regia)			
		mg kg^{-1}			
1	5.47	3.99	1,225	0.65	264
2	5.42	3.54	1,005	0.48	319
3	5.46	2.55	1,244	0.34	52.7
4	5.57	2.39	627	0.11	27.8
5	3.09	1.35	198	0.08	34.5
6	3.17	1.22	122	0.04	10.0
7	4.23	1.39	581	0.04	4.74
8	4.94	1.78	1,712	0.47	17.3
9	5.13	1.49	784	0.13	8.57
10	4.86	9.10	1,146	0.74	80.7
11	4.38	9.14	630	0.77	48.5
12	5.58	56.0	1,283	6.96	111
13	5.37	88.9	1,737	7.43	115
14	5.40	72.7	1,328	4.86	93.5

2.1.4 Soil samples from long-term fertilization trials

The soil samples were collected from two sites of long term fertilizer trials. The first site where 18 samples were collected, is located at the South Field (field No 4, Fig. 2.1) of the Institute of Plant Nutrition and Soil Science (PB), Federal Agricultural Research Centre (FAL), Braunschweig, Germany. Numbers from 1 to 18 were given these soil samples

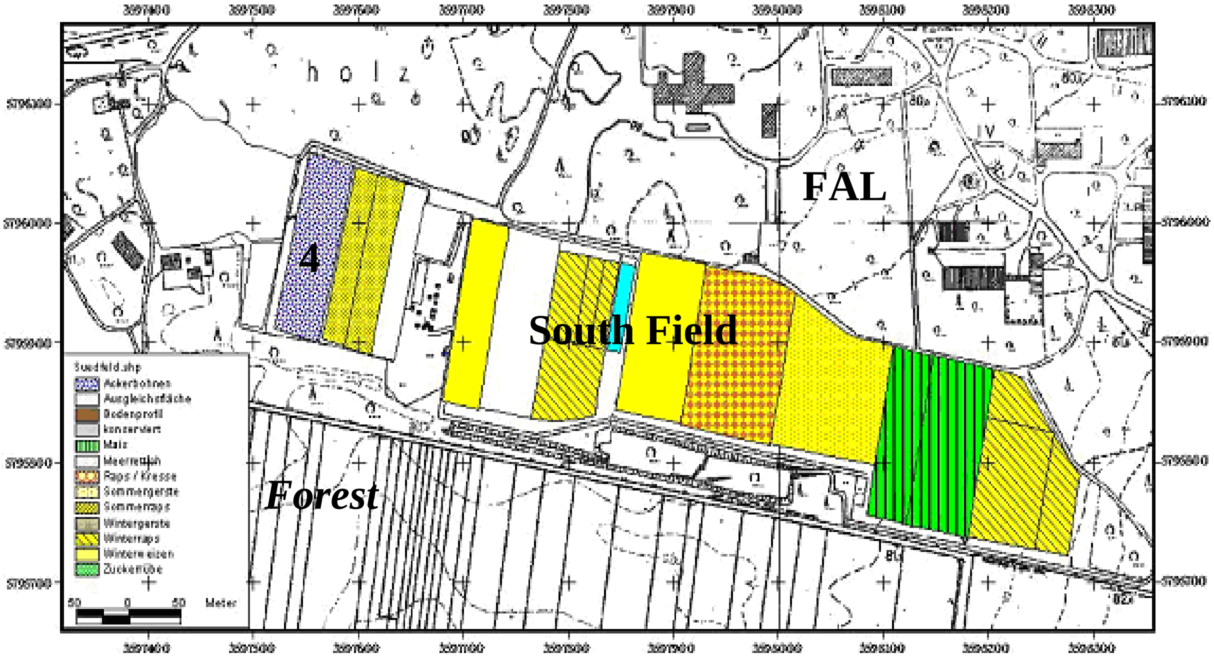

Figure 2.1: The South Field of the Institute of Plant Nutrition and Soil Science (PB), Federal Agricultural Research Centre (FAL), Braunschweig-Völkenrode.

The soil type is a Cambisol with a loamy sand soil texture (<7% clay; >47% sand). Faba bean was cultivated in the field, using reduced tillage treatment. The treatments were: NK (samples No 1-6), NK + FYM (samples No 7-12) and NPK+ FYM (samples No 13-18) each with three replicates (Table 2.4). The samples were taken at two depths: 0-15 and 15-30 cm.

Table 2.4: Treatments in the long term P fertilizer experiment at Braunschweig.

Treatments	**N**	**P**	**K**
		[kg ha^{-1}]	
Mineral NK	0	0	120
Mineral NK + FYM	40	0	120
Mineral NPK + FYM	40	30	120

FYM was added at a rate of 1.2 t ha^{-1}a^{-1}

Six further soil samples were collected from an experimental site at Freising. Freising (E11° 66`, N 48° 38`) is situated in the Bayern country in the far southeast of Germany. The mean annual temperature is about 7.7 ° C; the mean annual precipitation is around 810 mm. These samples had the following treatments: NK (sample No 19), NK + FYM (sample No 20), NK + straw (sample No 21), and three mineral P fertilizers (Super phosphate, Novaphos and Hyperphos (samples No 22-24)). Table 2.5 presents some chemical characteristics of soil samples collected from long term P fertilizer experiments in Freising.

Table 2.5: Selected chemical characteristics of soil samples collected from long term P fertilizer experiment in Freising.

Samples No	**Total U**	**Total Cd**	**Total Ni**	**Total Pb**
		(Aqua regia)		
		mg kg^{-1}		
1	1.29	0.17	37.1	24.3
2	1.20	0.15	33.4	22.6
3	1.09	0.13	32.0	20.1
4	1.40	0.16	34.3	23.3
5	1.19	0.15	32.6	22.9
6	1.17	0.14	33.0	22.3

2.2 Soil sample preparation

The soil samples were air-dried, passed through a 1-mm sieve and stored in a cooling room until the extraction.

To establish the procedure for obtaining the soil solution, some centrifugation speeds and soil water contents were examined as follows:

30 g saturated soil (WHC) centrifuged for 30 min at 3,000 rpm → 3.0 ml water
30 g saturated soil (WHC) centrifuged for 20 min at 7,000 rpm → 4.5 ml water
30 g saturated soil (WHC) centrifuged for 30 min at 7,000 rpm → 4.8 ml water
30 g (at 60% WHC) centrifuged for 30 min at 7,000 rpm → 2.5 ml water

The obtained water percentage of WHC was about 53%, and was about 22% of the total water in the both cases of field capacity (60% WHC) and low speed.

The EC of the soil solution extracted at WHC was 2.91 mS cm^{-1}, while it was 4.75 mS cm^{-1} in soil solution extracted at FC (field capacity).

These results implied that the centrifugation speed is the most influential factor on the soil solution quantity; also the EC is diluted by adding water.

These results recommended that the centrifugation speed of 7,000 rpm for 20 min at WHC is the best procedure to obtain a suitable solution for measuring elements.

2.3 Different methods of U extraction from the soil

The main purpose was to study the ability to extract U with the most common extractants, which usually used in soil laboratories to extract the heavy metals from soils with different characteristics, from different soil groups and to establish a suitable method to extract U from soils.

- Extraction of U from soil by acid ammonium acetate-EDTA (AAAc-EDTA) (Lakanen and Erviö, 1971):

A solution of ammonium acetate (0.5 M), 0.5 M acetic acid and 0.02 M Na_2 EDTA was prepared and the pH was adjusted to 4.65.

5 grams of the soil and 50 ml of the extracting solution were shaken for 1 h at 27 rpm and filtered. The U content in the soil was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-QMS).

- Extraction of U from soil by diethylene triamine pentaacetic acid (DTPA) extracting reagent (Lindsay and Norvell, 1969):

  0.01 M triethanolamine (TEA) and 0.005 M DTPA solution was mixed with $CaCl_2$ 0.01 M solution and the pH was adjusted to 7.3.

  10 grams of soil and 20 ml of the extracting solution were shaken for 1 h at 27 rpm and filtered. The U content in the solution was measured by ICP-QMS.
- Extraction of U from soil by 1N ammonium acetate (NH_4Ac) adjusted to pH 7.0 at a soil/solution ratio of 1:10 (Sheppard and Evenden 1992).
- To avoid the heavy load of organic compounds in these solutions, 25 ml of the supernatant was taken into a ceramic crucible and evaporated on a sand bed at 200 °C then ignited in a muffle furnace at 550 °C for 4 h. After cooling, it was eluted with 5 ml 10 % HNO_3 and completed with bi-distilled water, then filtered with suitable filter paper and stored until measuring.

Centrifugation technique of soil solution extraction

The soils were saturated until reaching their water holding capacity (WHC) with bi-distilled water. About 25 g of moist soil were packed into a small polypropylene tube, which was featured a small hole in its bottom covered with a small piece of filter paper. The prepared tubes were inserted into the centrifuge tubes after a cylindrical polypropylene support was inserted first into the centrifuge tubes. And then centrifuged for 20 min at 7,000 rpm. After centrifugation, the polypropylene tubes containing the soil samples were removed and the soil solutions collected inside the centrifuge tubes were poured off into test tubes.

2.4 Soil analysis

- Soil pH was measured in 0.01M $CaCl_2$ suspension using Hanna pH meter (VDLUFA-Method, Hoffmann, 1991).
- Soil solution pH was measured directly in the soil solution by Hanna pH meter.
- Electrical conductivity (EC) in the soil solution was measured using conductivity-meter (LF 251, Wissenschaftlich Technische Werkstatt (WTW), GmbH, Germany.
- Aqua regia extraction of heavy metals (AbfKlaer, 1992) was carried out as follow: 25 ml of a mixture of 37 % HCl and 65 % HNO_3 (3:1) was mixed with 5 g of soil sample in a round flask overnight. In the next day, the mixture was boiled for 2 h, and transferred into 100 ml volumetric flask after cooling, then filtered and stored. Heavy metals were measured by ICP-

QMS. P content was measured colorimetrically using a Perkin-Elmer 550SE UV/VIS Spectrophotometer.

- Soil available P (CAL) was extracted by Calcium-acetate-lactate (CAL) (Schüller, 1969). P content in soil was measured colorimetrically using a Perkin-Elmer 550SE UV/VIS Spectrophotometer.

2.5 Statistical analysis

Statistical analysis of the data was performed with the SPSS statistical package Version 12, and the linear regression coefficients were determined. All calculations were made at dry weight bases.

2.6 Safety measures

A number of safety measures were employed:

- Staff always wore disposable dust protection masks and latex gloves when attending the U-polluted samples.
- Filtration residues from soil extractions and other contaminated materials like empty containers and used gloves were collected and disposed according to the regulations for low radioactive wastes.

3. Results

The main objectives of the present study were to evaluate some methods, which could be used for extracting and assessing the bioavailability of U in different soils, and to study the main factors affecting the U mobility in a wide range of contaminated soils.

3.1 Extractable U in greenhouse experiment soil samples

In this group of soils, the soil was collected after the growth period of three crops (maize, sunflower and faba bean) in greenhouse pot experiment. The soil had been artificially contaminated with U. The high U concentration in these soil samples gave the opportunity to evaluate the efficiency of the extractants on the extractability of U in different conditions. With the use of these samples it was possible to investigate of some factors affecting the availability of U in soil, and to evaluate the different extractants as plant predictors for U.

3.1.1 Extracting forces of AAAc-EDTA, DTPA, NH_4Ac and soil solution for U from soil

The AAAc-EDTA, NH_4Ac and DTPA extractants had different extracting forces for U from soil. The AAAc-EDTA extractant was the most powerful extractant, while the DTPA was the weakest in the maize soil samples (Table 3.1). The U extractability was found to be a function of the extraction solution. The U extractable by AAAc-EDTA ranged from 13.3 to 103.0 mg kg^{-1} (6.5-31.3% of the total U in soil), while the U extractable by DTPA ranged from 0.02 to 5.4 mg kg^{-1} (0.003-1.7% of the total U in soil) in the case of maize. U extracted by NH_4Ac ranged from 2.5 to 61.9 mg kg^{-1} (1.5-18.8% of the total U in soil) whereas U found to be soluble in soil solution (obtained by centrifugation) ranged from 0.03 to 2.74 mg kg^{-1} (0.0-0.4% of the total U in soil) in the case of maize soil samples (Table 3.1). The same trend was observed also for sunflower and faba bean soil samples. The extracted U with AAAc-EDTA ranged from 0.02 to 167.7 mg kg^{-1} (7.4-190.4% of the total U in soil), the extracted U by DTPA ranged from 0.002 to 8.6 mg kg^{-1} (0.1-2.0% of the total U in soil) and U extracted by NH_4Ac ranged from 0.02 to 73.4 mg kg^{-1} (1.5-22.3% of the total U in soil). The soil solution U in soil solution ranged from 0.004 to 0.82 mg kg^{-1} (0.02-105% of the total U in soil) in the case of sunflower soil samples (Table A.1).

Figure 3.1 illustrates the extractable U with the different four extractants used in this study expressed as a percentage of the original total U in soil for faba bean soil samples. The results showed that the extracted U by AAAc-EDTA ranged from 0.05 to 146.6 mg kg^{-1} (6.9-89.3% of the total U in soil). The extracted U by DTPA ranged from 0.005 to 5.2 mg kg^{-1} (0.1-1.7% of the total U in soil) and from 0.04 to 54.0 mg kg^{-1} (1.3-16.4% of the total U in soil). The soil solution U ranged from 0.004 to 0.49 mg kg^{-1} (0.01-1.1% of the total U in soil) (Fig.3.1). These results revealed that these four extractants were not equally effective for U extraction.

Table 3.1: Extractable U with AAAc-EDTA, DTPA, NH_4Ac and soil solution [mg kg^{-1} and % of the total] in soil from pot experiment with maize in relation to the presence of P fertilizer.

Presence of P	**U level in soil**	**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**	**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**
		mg kg^{-1}				**Relative to total U (%)**			
Without P	166	42.4	1.8	26.3	-	25.6	1.1	15.8	-
		42.3	1.6	24.6	0.21	25.5	1.0	14.8	0.13
		29.8	1.2	19.0	0.30	18.0	0.7	11.5	0.18
		45.1	1.6	21.0	0.23	27.2	0.9	12.6	0.14
	329	103.1	3.8	56.9	0.29	31.3	1.2	17.3	0.09
		79.7	4.8	61.9	0.38	24.2	1.5	18.8	0.12
		95.2	5.4	49.4	0.75	28.9	1.7	15.0	0.23
		62.7	5.0	57.5	0.41	19.1	1.5	17.5	0.12
With P	173	13.3	0.1	2.6	0.06	7.7	0.1	1.5	0.04
		14.2	0.1	2.5	0.04	8.2	0.1	1.5	0.02
		14.0	0.1	2.9	0.03	8.1	0.1	1.7	0.02
		13.9	0.2	3.9	0.10	8.0	0.1	2.2	0.06
	385	25.4	0.3	7.0	0.81	6.6	0.1	1.8	0.21
		29.0	0.3	5.7	0.30	7.5	0.1	1.5	0.08
		26.3	0.3	6.2	1.64	6.8	0.1	1.6	0.43
		24.9	0.3	5.8	1.30	6.5	0.1	1.5	0.34
	643	53.6	0.5	11.2	1.44	8.3	0.1	1.7	0.22
		56.5	0.5	10.5	0.64	8.8	0.1	1.6	0.10
		50.5	0.7	10.7	1.72	7.9	0.1	1.7	0.27
		48.9	0.0	12.1	2.74	7.6	0.0	1.9	0.43

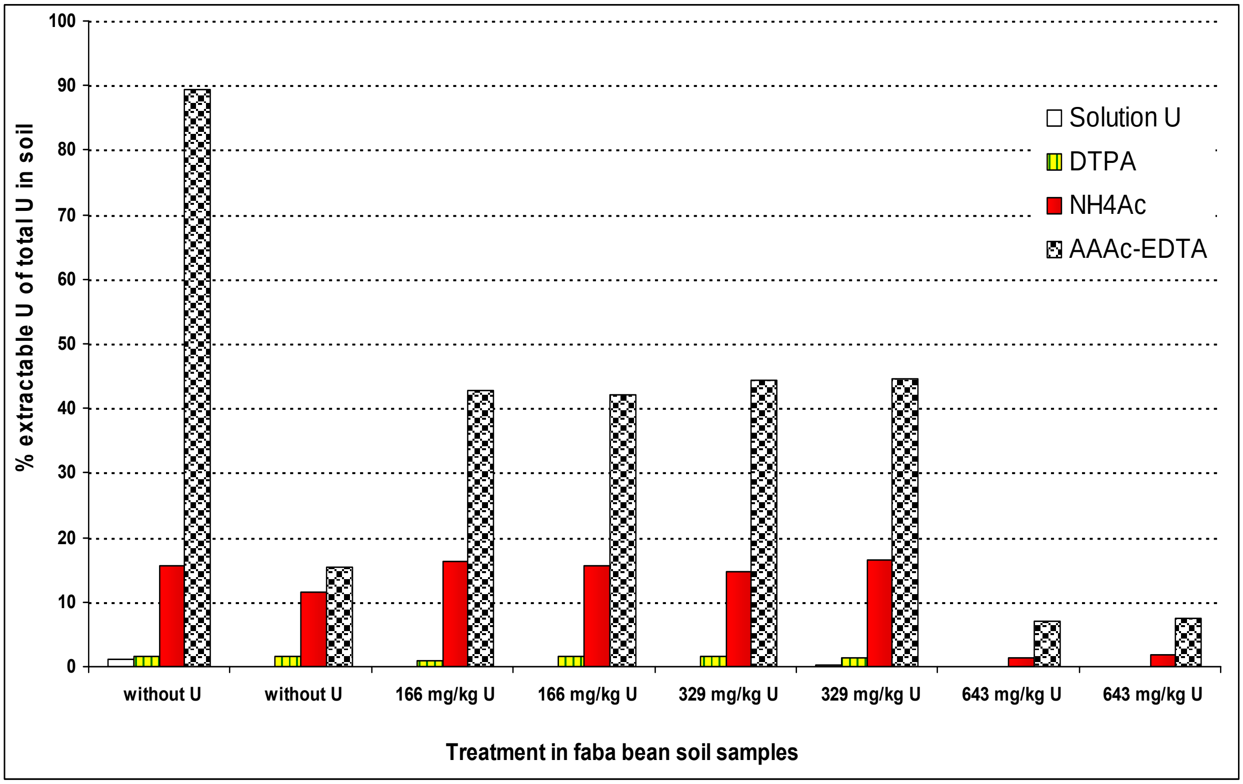

Figure 3.1: Extractable U (AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution) expressed as a percentage of the total U in soil from pot experiment with faba bean.

3.1.2 Effect of total U in soil on the extractability of U

This indicates the four extractants showed similar behavior for all crop soil samples (Fig. 3.2), meaning that the U level in soil influenced the extractable U with the four extractants used in this study. The extracted U by AAAc-EDTA at U level in soil 329 mg kg^{-1} was higher than that extracted from soil that had 166 mg kg^{-1}.This trend was observed in all crop soil samples. In this case the extracted U values ranged from 85.2 to 165.2 mg kg^{-1} for all crops soils at the 329 mg kg^{-1} U level in soil comparing with the range of 39.9-78.0 mg kg^{-1} at the lower U level in soil. The same observation was found in all cases of the other three extractants. The highest value of extracted U by DTPA at U level in soil 329 mg kg^{-1} was 5.8 mg kg^{-1} while the highest value at the level 166 mg kg^{-1} in soil was 1.9 mg kg^{-1}. In the case of NH_4Ac, the extracted U at the U level of 329 mg kg^{-1} was 69.3 mg kg^{-1}, while the highest value at the level of 166 mg kg^{-1} in soil was 30.8 mg kg^{-1}, these values were 0.53 and 0.2 mg kg^{-1} in the soil solution for the higher level and the lower level of U in soil, respectively (Fig. 3.2).

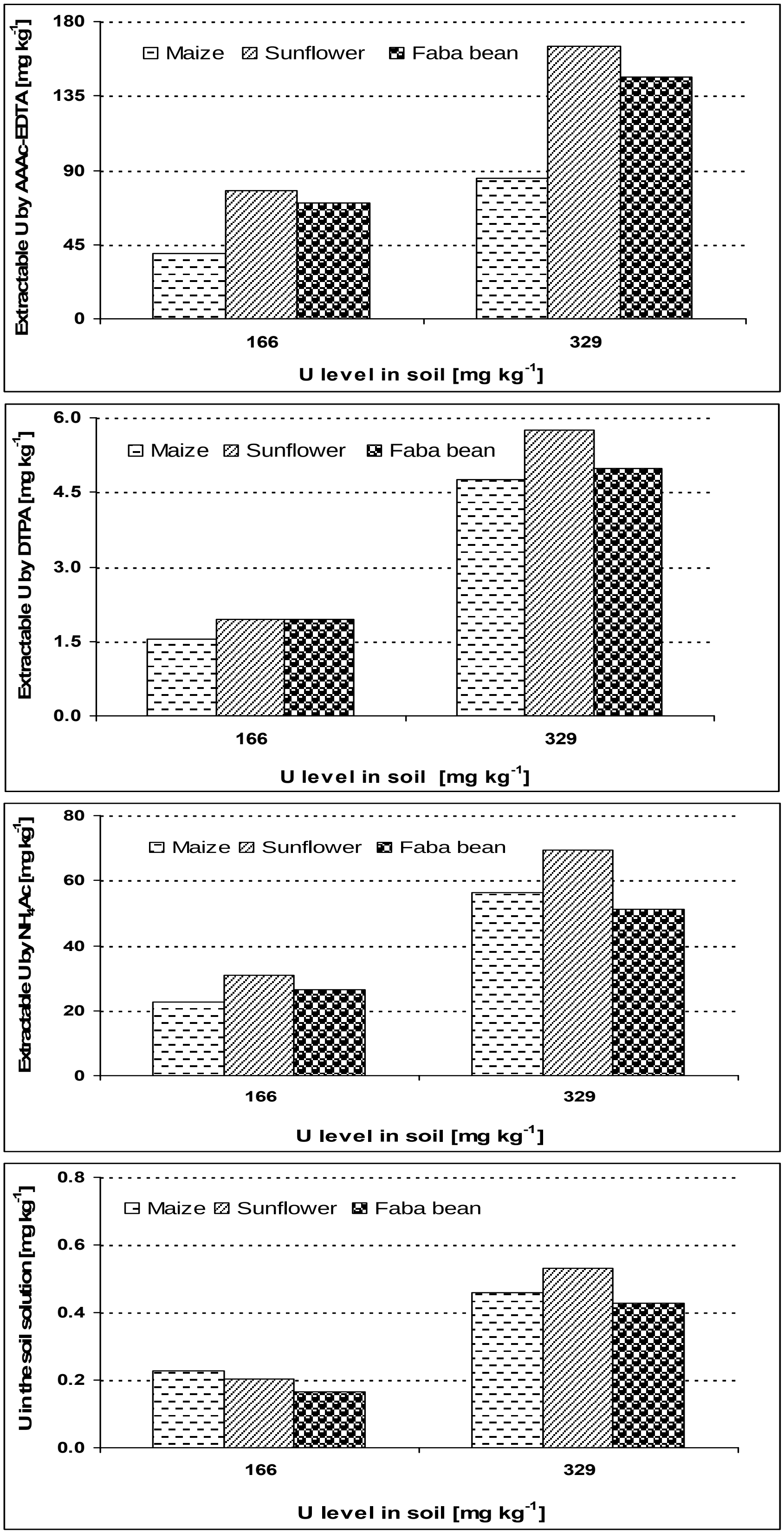

Figure 3.2: Relationship between extractable U (AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution) and the total soil U in relation to the three crops (maize, sunflower and faba bean).

The results in Figure 3.2 also imply that the different crops influenced vary in the mobility of U in soil after the harvest. The extractable U with any extractant from sunflower soil samples was higher than that of the other two crop soil samples regardless the U level in the soil in almost all cases followed by faba bean soil samples.

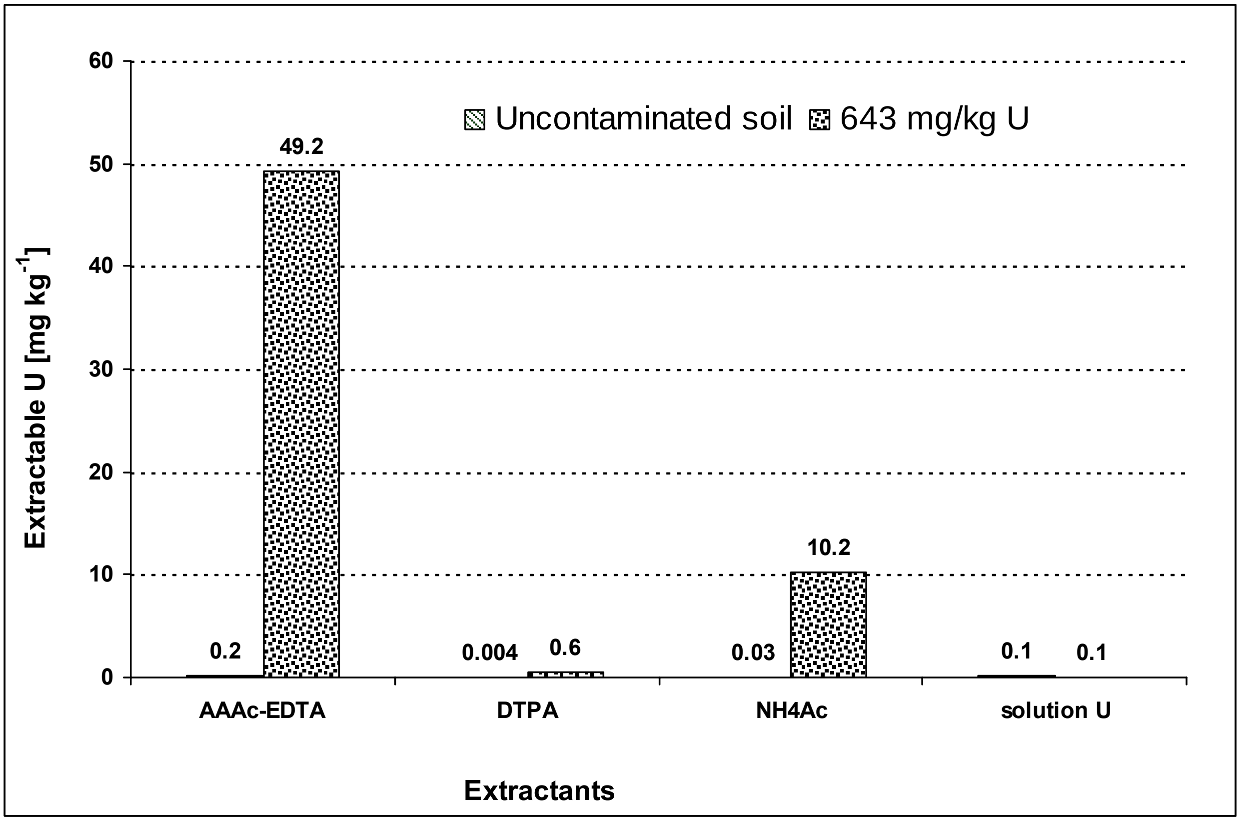

Figure 3.3: Comparison between extractable U (AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution) and the total U (un-contaminated soil and 643 mg $kg^{-1}U$) in soil from pot experiment with sunflower.

As expected, Figure 3.3 illuminates that the U extracted by any of the four extractants at the highest U level (643 mg kg^{-1}) in the soil samples of sunflower is higher than that extracted U from un-contaminated soil. Therefore, the higher U value in the soil the higher extracted U by any of the four extractants except the case of soil solution, where the extracted U was in the same level in both contaminated and un-contaminated soil.

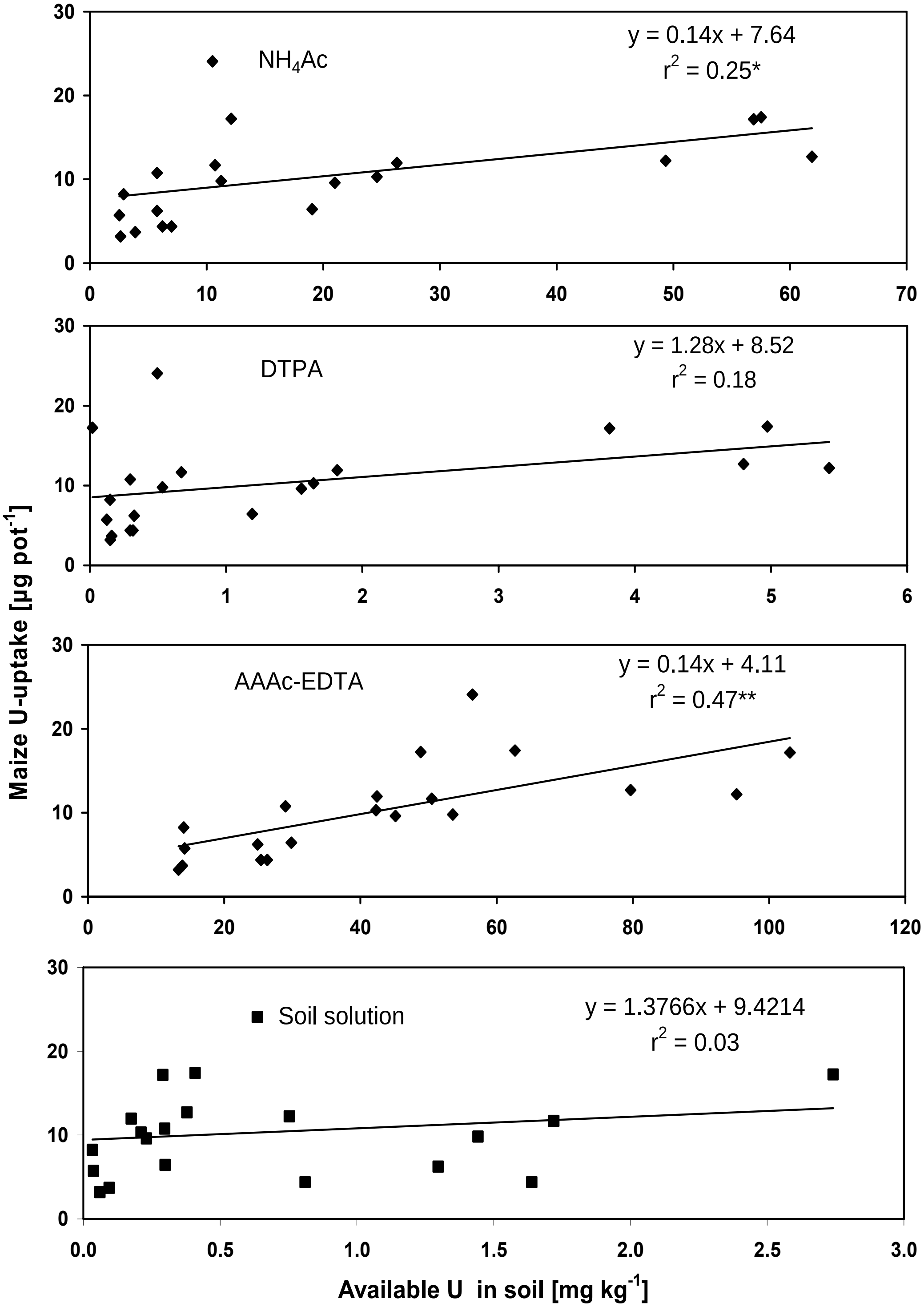

Figure 3.4: Relationship between extractable U (AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution) (data of the current study) and the U uptake by young maize shoots (data of Rivas study: Rivas, 2005).

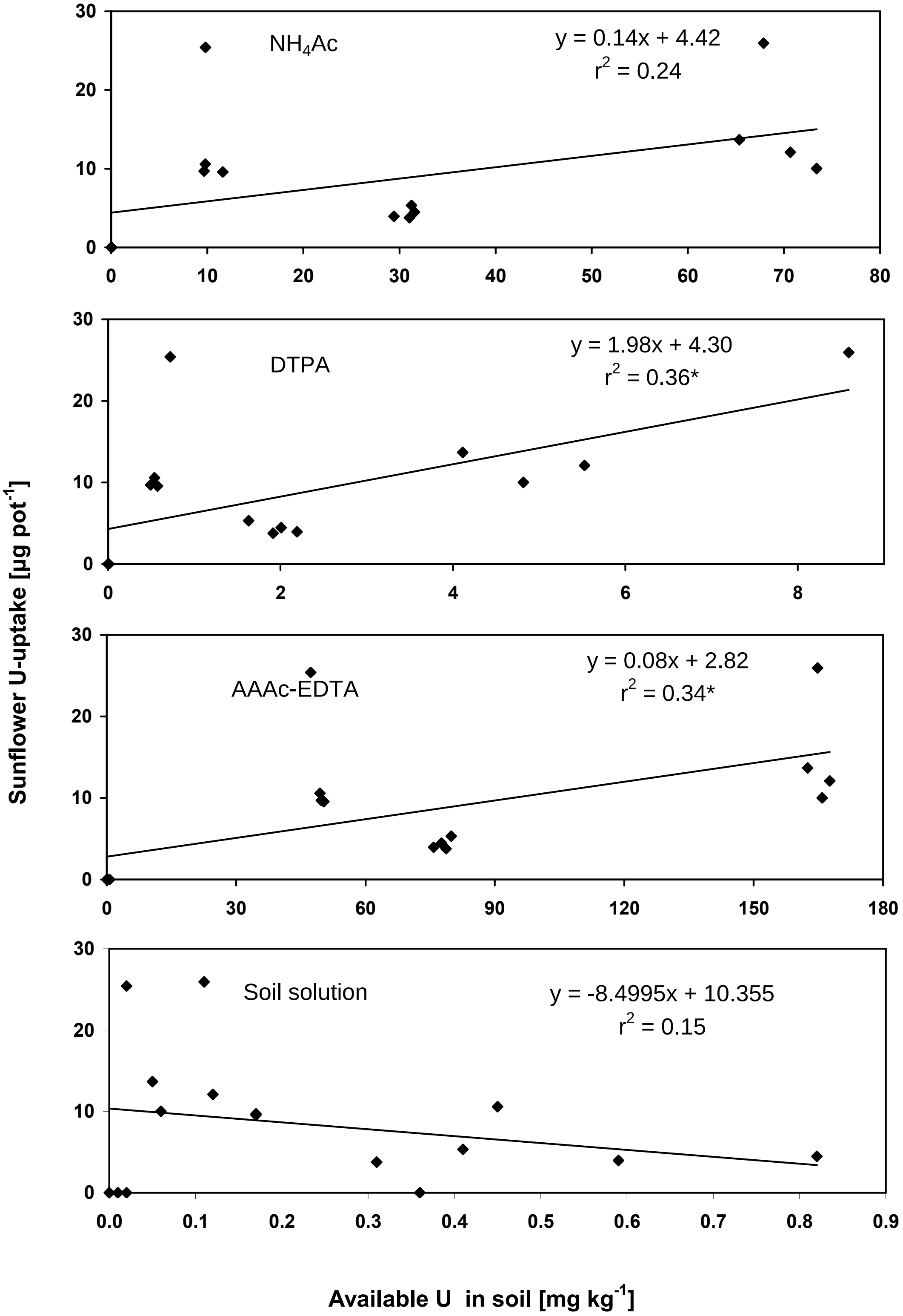

Figure 3.5: Relationship between extractable U (AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution) (data of the current study) and the U uptake by young sunflower shoots (data of Rivas study: Rivas, 2005).

Highly significant correlations were found for results from the three extractants (AAAc-EDTA, DTPA and NH_4Ac) with each other in maize soil samples, the correlation coefficients ranged from 0.82**-0.97** in this case, but not for results for soil solution U. In the case of sunflower soil samples, highly significant correlations were also found, not only between the three extractants, but also with solution U the correlation coefficients (r) values in this case ranged from 0.74**-0.92**. The same observation was found in the case of faba bean soil samples and ranged from 0.95**-0.98**, (Table 3.2). Despite the widespread use of these chemical extraction procedures, the chemical reactions and mechanisms by which available U is obtained are not completely understood.

3.1.3 Relationship between extracted U from soil and the plant U content

Uranium extracted by AAAc-EDTA showed a highly significant correlation with plant U-uptake by maize, whereas the relationship was less pronounced for U extracted by NH_4Ac (Fig. 3.4). The correlation coefficients (r) between maize uptake of U and AAAc-EDTA, NH_4Ac, DTPA and soil solution were 0.69**, 0.50*, 0.42, and 0.18, respectively (Table 3.2). It is therefore concluded that the AAAc-EDTA was the best predictor for maize U-uptake and soil U bioavailability followed by NH_4Ac, while both DTPA and soil solution were not able to predict well the U-uptake by maize.

In contrast to the maize plants, the correlation coefficients (r) between U extracted by DTPA, AAAc-EDTA, NH_4Ac and soil solution extractants and sunflower U-uptake were 0.60*, 0.58*, 0.49, and 0.39, respectively (Table 3.2). These results revealed that the DTPA extractant was equal best indicator for the U-uptake by sunflower plants with by AAAc-EDTA (Fig. 3.5), while the NH_4Ac and soil solution were not suitable for this purpose.

The statistical results summarized in Table 3.2 reveal that no relationship was found between U extracted by the three extractants and faba bean U-uptake, this means that none of the tested extractants was able to describe the available U for faba bean plants. The limited numbers of samples in the case of faba bean might have yielded this result so that further studies are required to fortify these findings.

In comparison, neither extractant fitted well with the U-concentration in plant shoots. The r values observed between the plant U-concentration and the extracted U with any of the four extractants used were rather low, this was true in all plants tested here (Table 3.2). Sunflower plants gave higher values than in the other two plants, but these values are still not significant, ranging from 0.13 in the soil solution to 0.48 in the AAAc-EDTA extractant.

3.1.4 Effect of total P in soil on the extractability of U

The presence of P compounds in soil had a distinctly diverse effect on mobility of U in soil. In the case of maize soil samples, the extracted U with AAAc-EDTA ranged from 29.8 to 103.1 mg kg^{-1} (18-31.3% of the total U in soil) when the P fertilizers were absent from the soil, in contrast the available U declined to the range of 13.3-56.5 mg kg^{-1} (6.5-8.8% of the total U) when the P fertilizers were added to the soil (Table 3.1). The (r) value between the P and the extracted U by AAAc-EDTA was -0.61**. This trend was more distinct in the case of NH_4Ac extractant, the extracted U values ranged from 19.0 to 61.9 mg kg^{-1} (11.5-18.8 % of the total U) in soil samples without P fertilizers, and fell to the range of 2.5-12.1 mg kg^{-1} (1.5-2.2% of the total U) in the presence of P fertilizers in soil. The (r) value in this case was -0.82** (Table 3.2). The U extracted with DTPA had the same behavior and ranged from 0.02-0.72 mg kg^{-1}and from 1.2-5.4 mg kg^{-1} in soil samples with and without P fertilizers, respectively (Table 3.1). The (r) value between the P and the extracted U by DTPA was -0.80** (Table 3.2). Soil solution U had weak positive relation with the P level in the soil. The soil solution U values ranged from 0.21 to 0.75 mg kg^{-1} (or 0.1-0.2 % of the total U) in soil samples without P fertilizers. These ranges changed to the range of 0.03-2.74 mg kg^{-1} (0.0-0.4% of the total U) in the presence of P fertilizers in soil. The positive (r) value in this case was 0.39 (Table 3.2).

The soil solution P from the maize soil samples also showed the same trend. The r values between the soluble P in soil solution and extracted U by different extractants were -0.34, -0.63**, -0.62**, and 0.67** for AAAc-EDTA, DTPA, NH_4Ac, and soil solution, respectively. The regression relationship between soil solution P and extractable U with different extractants in maize soil samples is illustrated in Figure 3.6.

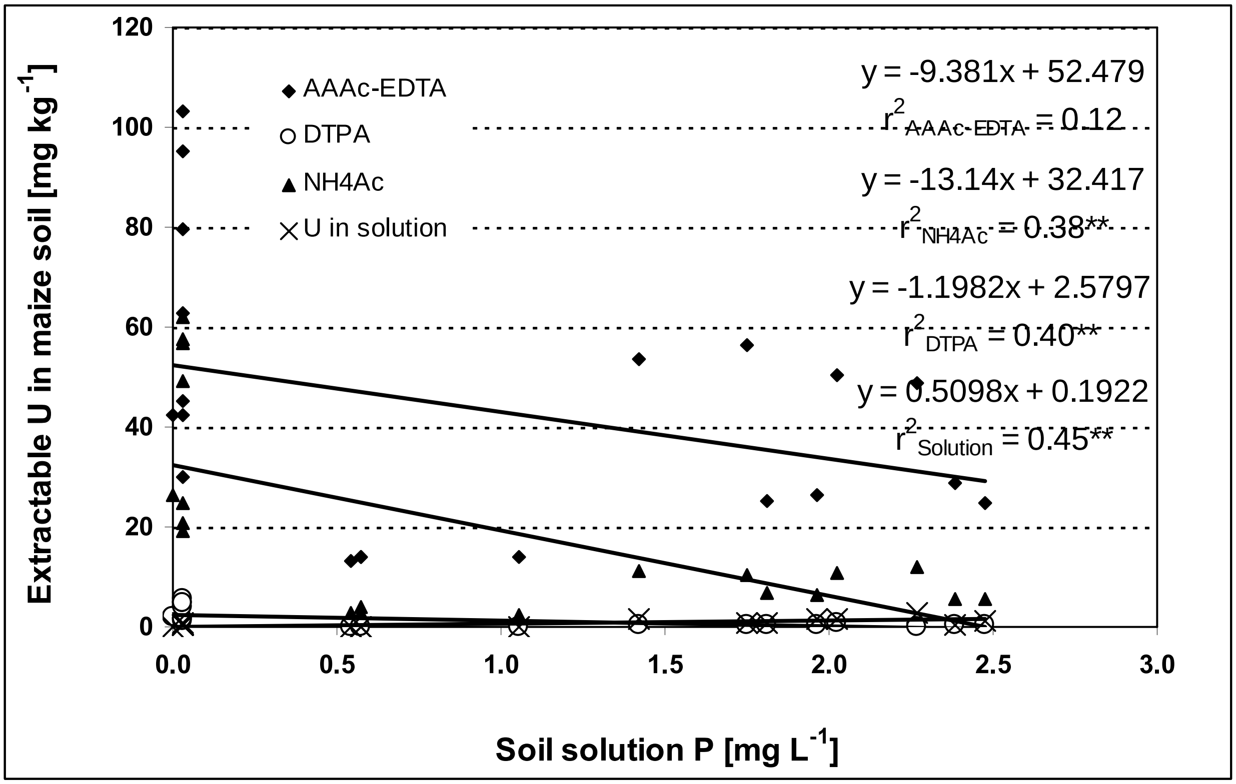

Figure 3.6: Influence of soil solution P on extractable U (AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution) in soil from pot experiment with maize.

For the second soil group's (sunflower) samples the same ranges of extracted U were still noticeable. The extracted U by AAAc-EDTA ranged from 75.8 to 167.7 mg kg^{-1} , from 29.4 to 73.4 mg kg^{-1} for NH_4Ac, from 1.6 to 8.6 mg kg^{-1} for DTPA and finally from 0.02 to 0.8 mg kg^{-1} in the soil solution. The percentage of the extracted U with AAAc-EDTA ranged from 45.7-51.0%, while these percentages were 17.7-22.3%, 1.0-2.6% and 0.1-0.3% of the total U for NH_4Ac, DTPA and soil solution, respectively in samples without P fertilizer. As expected, these ranges decreased to 7.4-8.8% of the total U for AAAc-EDTA, and ranged from 1.5-14%, 0.1-2.0% and 0.0-105% of the total U for NH_4Ac, DTPA and soil solution; respectively in the presence of P fertilizer (Table A.1). The negative (r) value between the P and the extracted U by AAAc-EDTA, NH_4Ac, DTPA and soil solution were -0.81**, -0.85**, -0.74**, and -0.59*, respectively (Table 3.2). These results suggested that the P compounds in the soil play an important role in extractability of U from the soil.

Table 3.2: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution and plant U concentration and uptake by the three crops (maize, sunflower and faba bean), soil pH, P, S and N levels in soil.

	DTPA	**NH_4Ac**	**Solution**	**Plant U-uptake**	**Plant U-concentration**	**P level**	**S level**	**Soil pH**	**U level with P**	**U level without P**	**N level**
Maize (n=20)											
AAAc-EDTA	.82**	.86**	.12	.69**	.27	-.61**	-.09	-.52*	.98**	.89**	-.07
DTPA	-	.97**	-.22	.42	-.01	-.80**	.02	-.72**	.63*	.96**	.01
NH_4Ac		-	-.18	.50*	.04	-.82**	-.05	-.77**	.98**	.98**	.03
Solution			-	.18	-.08	.39	.34	.45*	.77**	.67	-.06
Sunflower (n=16)											
AAAc-EDTA	.91**	.87**	.74**	.58*	.48	-.81**	-.01	-.64**	.99**	.99**	-.01
DTPA	-	.92**	.78**	.60*	.39	-.74**	.16	-.56*	.98**	.84**	.08
NH_4Ac		-	.77**	.49	.35	-.85**	-.01	-68**	.99**	.99**	-.03
Solution			-	.39	.13	-.59*	.15	-.35	-.06	.68	-.12
Faba bean (n=8)											
AAAc-EDTA	.96**	.98**	.97**	.14	.14	-.80*	.01	-.38	.99**	1.0**	
DTPA	-	.97**	.95**	-.06	-.06	-.82*	.04	-.33	1.0**	.97*	
NH_4Ac		-	.98**	-.00	-.01	-.87**	.05	-.50	.98*	.99*	
Solution			-	-.15	-.16	-.74	.33	-.35	.98	.94	

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

The same behavior was noticed in the faba bean soil samples but with less significance than the case of sunflower soil samples. The extracted U by AAAc-EDTA extractant ranged from 70.9 to 146.6 mg kg^{-1} (42.0-46.6% of the total U in soil) in soils without P fertilizers, the available U decreased to the range of 0.05-48.3 mg kg^{-1} (6.9-15.4% of the total U) when the P fertilizers were added to the soil. In NH_4Ac extractant the extracted U values ranged from 26.0 to 54.0 mg kg^{-1} (14.7-16.4 % of the total U) in soil samples without P fertilizers, and fell to the range of 0.04-11.3 mg kg^{-1} (1.3-11.5% of the total U) in the presence of P fertilizers in soil. The U extracted with DTPA had the same behavior and ranged from 0.01 to 0.53 mg kg^{-1} or about 0.1-1.6% and from 1.4 to 5.2 mg kg^{-1} or about 0.9-1.6% in soil samples with and without P fertilizers, respectively (Table A.2). The correlation between P in the soil and the extracted U by NH_4Ac was highly significant, the (r) value was -0.87**, the correlations were less pronounced in the two cases of AAAc-EDTA and DTPA, the (r) values for AAAc-EDTA and DTPA were -0.80*and -0.82*, respectively (Table 3.2). On the other hand the soluble U in the soil solution had a non significant negative correlation with the P level in the soil, the (r) value in this case was -0.74 (Table 3.2). The soluble U values ranged from 0.15 to 0.49 mg kg^{-1} (or 0.1% of the total U) in soil samples without P fertilizers. These ranges fall to the range of 0.0-0.09 mg kg^{-1} (0.0-1.1% of the total U) in the presence of P fertilizers in soil (Table A.2).

To assess the interaction between P fertilization and U in soil, the samples were separated into two groups; the first without P fertilizer and the second with P fertilizer. The statistical relationship between U level and extractable U was tested for both cases. The results presented in Table 3.2 reveal that highly significant correlation coefficients (r) were found between the U level in the maize soil samples without P fertilizer and extractable U with AAAc-EDTA, NH_4Ac and DTPA. The (r) values were 0.89**, 0.98**, and 0.96**, respectively. Soil solution U was not significantly correlated with P fertilizer (r=0.67). In the other case, with P fertilizer, highly significant correlation coefficients were found for AAAc-EDTA and NH_4Ac (r = 0.98** for both) and also for solution (r = 0.77**), while it was significant for DTPA (r=0.63*) (Table 3.2).

Table 3.2 also presents the relationships (r values) between U level in sunflower soil samples and extractable U with different extractants in relation to the presence of P fertilizers. The r values in the soil samples without P fertilization were highly significant for AAAc-EDTA, NH_4Ac and DTPA. The (r) values were 0.98**, 0.99**, and 0.84**, respectively, while it was non significant for solution (r=0.68), the same trend was found when the P fertilizer was present in the soil. These values were 0.99**, 0.99**, and 0.98** for AAAc-EDTA, NH_4Ac and DTPA respectively. No correlation was found between the U level in soil and the soluble U in the soil solution.

These correlations were less pronounced in the faba bean soil samples than the previous two cases. When the P fertilization was absent, the r values were highly significant only for AAAc-EDTA, while they were significant for both NH_4Ac and DTPA, The (r) values were 0.99**, 0.99*, and 0.97*, respectively. The r value was non significant for solution (r=0.94). A similar trend was also found in soil samples with P fertilizer. The r values in this case were 0.99**, 0.98*, 1.0** and 0.98 for AAAc-EDTA, NH_4Ac, DTPA and solution, respectively. The high values with low significance of r in the case of faba bean may be attributed to the low number of samples in this case.

3.1.5 Effect of soil pH on the extractability of U

Results presented in Table 3.2 show that the soil pH ($CaCl_2$) had both positive and negative effects on the extractability of U in soil. These effects were more pronounced for maize and sunflower soil samples. The r values between soil pH and extractable U with different extractants were -0.77**, -0.72**, and -0.52* for NH_4Ac, DTPA and AAAc-EDTA, respectively, the exception was 0.45* for solution in maize soil samples. A similar phenomenon was observed in the sunflower soil samples. The r values between soil pH and extractable U with different extractants were -0.68**, -0.56*, -0.64**, and -0.35 for NH_4Ac, DTPA, AAAc-EDTA, and solution, respectively. Lesser and no significant r values were observed in the third soil group’s (faba bean) samples. The r values ranged from -0.33 to -0.50.

In general, the results of the greenhouse experiment soil samples indicated that soil pH ($CaCl_2$) had a diverse effect on the extractability of U in soil. This effect was more pronounced in both cases of maize and sunflower soil samples, while it was not significant in the third soil group’s (faba bean) samples (Table 3.2). This meant that the effect of pH on the mobility of U in the soil is dependent on the plant cultivated in the soil. The r values between soil pH and extracted U with different extractants were -0.49**, -0.58**, -0.68**, and 0.27 for AAAc-EDTA, DTPA, NH_4Ac, and soil solution, respectively, in all greenhouse soil samples (Table A.15).

These results show that the lower pH values, more available U was extracted for the first three extractants, and less U was in soil solution. The regression relationship between soil pH and extractable U with different extractants in greenhouse soil samples are illustrated in Figure 3.7.

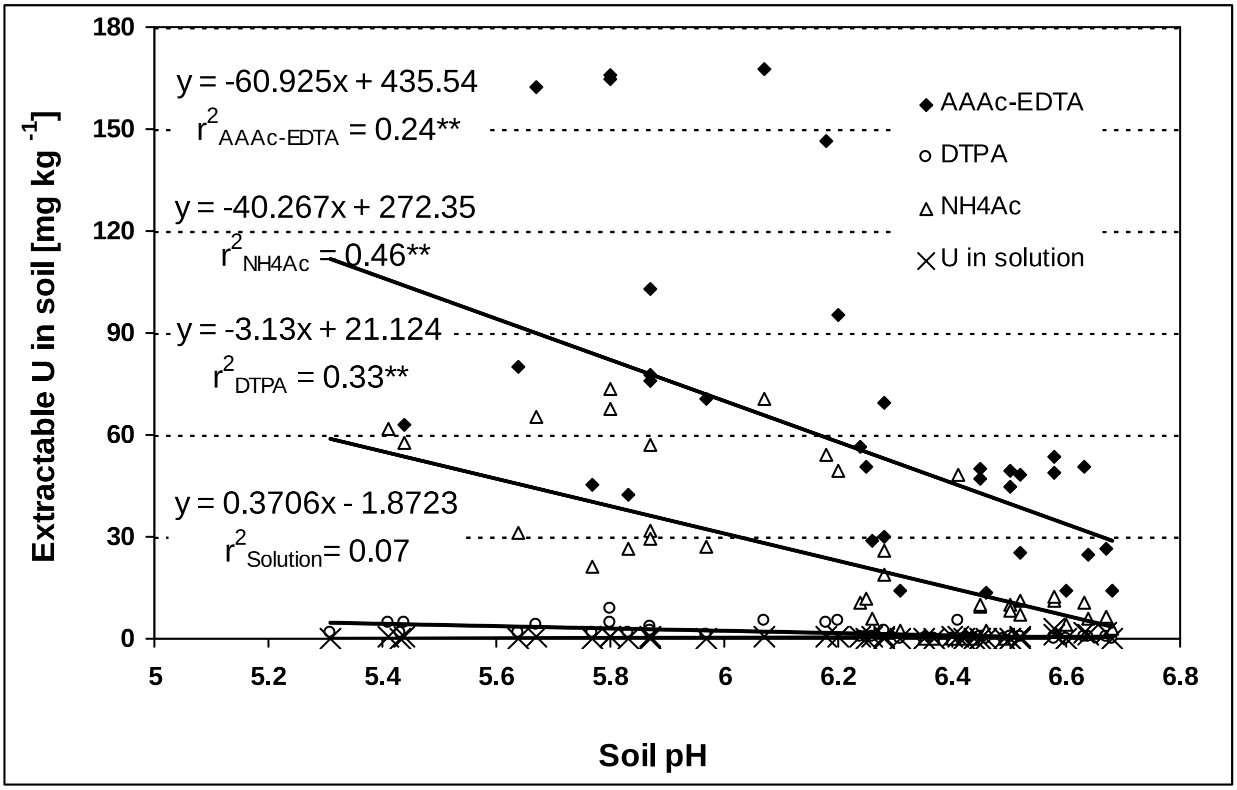

Figure 3.7: Influence of soil pH ($CaCl_2$) on extractable U (AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution) in soil from all pot experiment with the three crops (maize, sunflower and faba bean).

The solution pH (in all greenhouse soil samples) also had the same trend but with lower r values in the first three extractants, the r values between the soil solution pH and extracted U with different extractants were -0.38*, -0.39**, -0.43**, and 0.39** for AAAc-EDTA, DTPA, NH_4Ac, and soil solution, respectively (Table A.15). The r value between the soil solution-U and soil solution pH was more pronounced than that with soil pH.

3.1.6 Effect of the other factors on the extractability of U

No influences were observed for N fertilization rate and S fertilization rate on the extractable U from soil with the extractants in all three soil group's samples except for a weak correlation in the case of solution U with S fertilization in both maize and faba bean soil samples. The r values in both cases were 0.34 and 0.33, respectively (Table 3.2). The weak influences of both nutrients observed here could be related to their effect on the plant growth (indirect effect) not direct effect on the U extractability from soil.

3.1.7 Effect of storage time on the extractability of U

The results illustrated in Figure 3.8 document the comparison between the former extracted U (the former extracted U was performed by the year 2003, Rivas 2005) and the current extracted U (the current extracted U was performed in April 2007) in this study by AAAc-EDTA in same soil samples. This comparison reflected the effect of storage time on the availability of U in soil. For maize soil samples, results revealed that the former extracted U was higher than the current extracted in all five U levels in the soil. The differences between both current and former extraction were significant (different characters) at U level of 166, 329 and 643 mg kg^{-1}, while it weren't not significant (same characters) at U level of 173 and 385 mg kg^{-1} For instance at the U level of 329 mg kg^{-1} the average former extracted U was 120.1 mg kg^{-1}, while the current extracted U was 85.2 mg kg^{-1}. At the U level of 643 mg kg^{-1}, the former extracted U was 71.6 mg kg^{-1}, whereas the current extracted U was 52.3 mg kg^{-1} (Table A.6). This observation is consistent with the more recent application of U, the more of this U is bioavailable for maize plants. This observation was not clear for sunflower and faba bean soil samples. In the both cases, the current extracted U was significantly higher (different characters) than the former extracted U at the U levels of 166 and 329 mg kg^{-1}, in contrast the former extracted U was higher than the current one at the U level of 643 mg kg^{-1}. In the case of sunflower soil samples the current extracted U was 165.2 mg kg^{-1}, and the former extracted U was 115.7 mg kg^{-1} at the U level of 329 mg kg^{-1}. At the U level of 643 mg kg^{-1} the former extracted U was 64.2 mg kg^{-1}, while the current extracted U was 49.2 mg kg^{-1} (Table A.7).

In general, the more recent additions of U to the soil (the addition of U to the soil occurred only once in July 2000) were more available than the older additions; the above results also revealed that the effect of storage time on the U extractability is plant type dependent.

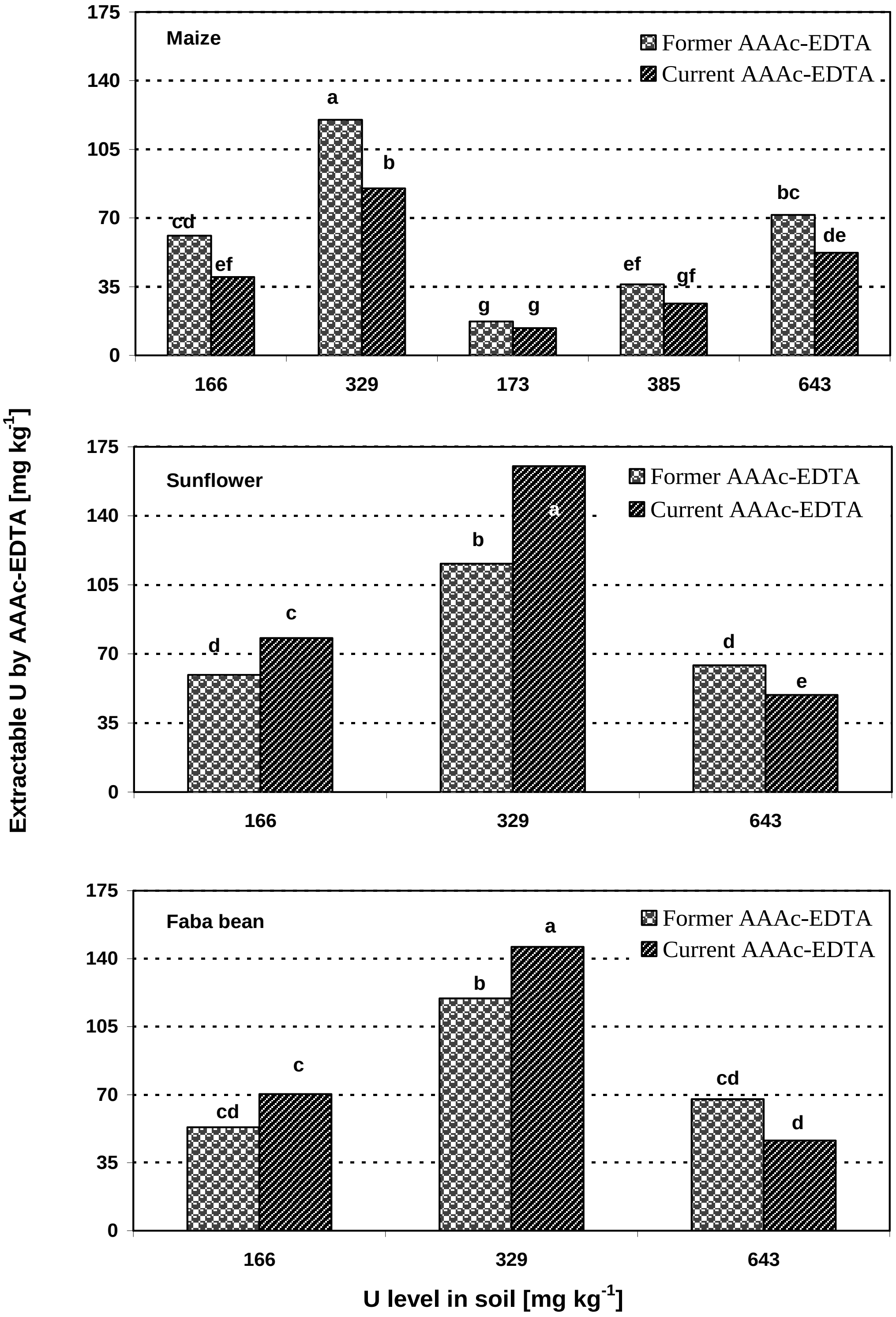

Figure 3.8: The effect of storage time: comparison between the former extracted U (Rivas 2005) by AAAc-EDTA and the current extracted U by AAAc-EDTA in this study in relation to the three crops (maize, sunflower and faba bean).

Values followed by the same letters are not significantly different by Tukey’s test at 0.05 levels.

The above results of greenhouse soil samples reveal that the AAAc-EDTA extractant was the most powerful extractant in most soil samples tested here, followed by NH_4Ac then DTPA and finally the soil solution. Sunflower plants had higher ability to release U into the soil in all U levels after plant growth period than that of faba bean and maize plants. The plant U-concentration was not useful for predicting by any of the extractants used here. AAAc-EDTA was the best predictor for maize U-uptake followed by NH_4Ac. While both DTPA and AAAc-EDTA extractants were the best indicators for the U-uptake by sunflower plants. For faba bean plants none of the tested extractants was able to predict the U-uptake.

For the factors studied in greenhouse soil samples the total U concentration in the soil had a positive effect on U extractability in soil. Both soil pH ($CaCl_2$) and total soil P concentration had a diverse effect on the extractability of U in all greenhouse soil samples. In the faba bean soil samples the effect of P was less pronounced, and the effect of soil pH was not significant, this may be attributed to the low number of samples. Soluble P in soil solution of maize soil samples had the same relation with (diverse effect) on extractability of U in soil, while the soluble P in the soil solution of sunflower and faba bean soil samples was lower than the detection limit. Results reported here implied that the more recent additions (former extracted U) of U to the soil were expected to be more available than the older additions (current extracted U). The results reported here also revealed that the effect of storage time on the U extractability depends on the plant cultivated the U contaminated soil. The indirect effect of both N fertilization rate and S fertilization rate was negligible on the extractability of U in all greenhouse soil samples. Therefore, the most important factors affecting the extractability of U in these soil samples were total soil U, P, pH and the effect of storage time.

3.2 Extractable U in incubation experiment soil samples

In this group of soils, two groups of soil samples were used, the first was the uncontaminated soil and the second was contaminated soil with U, each of them had the same treatments (non amended, amended with straw, amended with alfalfa). This combination provided the opportunity to study the effect of the addition of different organic materials on the extractability of U in soil.

3.2.1 Extracting forces of AAAc-EDTA, DTPA, NH_4Ac and soil solution for U from soil and the Effect of the addition of organic materials on the extractability of U

As in the case of the greenhouse experiment, the AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants significantly (different letters) extract different concentrations of U from the soil samples (Table 3.3). The extractable U with AAAc-EDTA was about 0.04 mg kg^{-1} in uncontaminated soil samples; the range here is very narrow while in the case of contaminated soil with 500 mg kg^{-1} this range became very wide (27.5 to 108 mg kg^{-1} , 5.5-21.6% of the total U in soil, Fig. 3.9, and Table A.16). Results indicate that the addition of different types of organic matter to the U contaminated soil had variable affect on the availability of U. The extractable U increased to the maximum (108 mg kg^{-1}) when the straw was added to the soil, but it declined to the minimum (27.5 mg kg^{-1}) when the alfalfa was added to the soil (Table 3.3).

The extractable U with DTPA ranged from 0.005 to 0.008 mg kg^{-1} in uncontaminated soil samples (Table 3.3), and ranged from 0.5 to 1.9 mg kg^{-1} in the contaminated soil samples. This equals 0.1-0.4% of the total U (Table A.16). The range was very narrow in the contaminated soil, and the percentage of extracted U was lower than that in the case of uncontaminated soil samples (Fig. 3.10). The extractable U with DTPA was significantly (different letters) different from the extractable U with AAAc-EDTA in both contaminated and uncontaminated soils.

U extracted by NH_4Ac ranged from 0.01 to 0.03 mg kg^{-1} in uncontaminated soil samples, and ranged from 14.3 to 25.7 mg kg^{-1} in the contaminated soil samples (Table 3.3). This ranged from about 2.7 to 6.2% of the total U in uncontaminated soil and ranged from 2.9 to 5.1% of the total U in the contaminated soil. The extractable U with NH_4Ac was significantly (different letters) different from the extractable U with AAAc-EDTA and DTPA in contaminated soil. Contrary to that of AAAc-EDTA, the highest percentage of extractable U was found in uncontaminated soil amended with alfalfa (Fig. 3.11).

Table 3.3: Available U in soil [mg kg^{-1}] extracted by AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution from incubation experiment soil samples.

Treatments		**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**	**Mean for U additive**
Additives	**U contamination**			**mg kg^{-1}**		
Without	Un-contaminated	0.04	0.006	0.02	0.003	**0.017 b**
Straw		0.04	0.005	0.01	0.003	**0.017 b**
Alfalfa		0.04	0.008	0.03	0.016	**0.026 a**
Mean for U extraction method		**0.044 a**	**0.007 c**	**0.022 b**	**0.008 c**	**LSD $_{0.05}$ 0.0076**
Without	contaminated with 500 mg kg^{-1}	92.47	0.514	25.71	0.020	**29.67 a**
Straw		107.96	1.387	14.30	0.212	**30.96 a**
Alfalfa		27.48	1.852	16.29	3.406	**12.25 b**
Mean for U extraction method		**75.76 a**	**1.25 c**	**18.77 b**	**1.21 c**	**LSD $_{0.05}$ 9.14**

The LSD $_{0.05}$ for additives: in uncontaminated soil =0.0065 and in contaminated soil =7.91
Mean values followed by the same letters in the same column or raw are not significantly different by Tukey's test at 0.05 levels.

Soluble U in the soil solution (obtained by centrifugation) ranged from 0.003 to 0.016 mg kg^{-1} (0.47-2.96% of the total U in soil) in the uncontaminated soil samples, and ranged from 0.02 to 3.4 mg kg^{-1} (0.004-0.63% of the total U) in the contaminated soil samples (Table 3.3). The Soluble U in the soil solution was significantly (different letters) different from the extractable U with AAAc-EDTA and NH_4Ac in contaminated soil. The alfalfa addition enhanced the extractability of U in both cases of contaminated and uncontaminated soil samples as compared to the addition of straw. This enhancement was higher in the case of uncontaminated soil samples (Fig. 3.12). Results showed that in both cases, DTPA and soil solution, the added U was less easily extracted than native U.

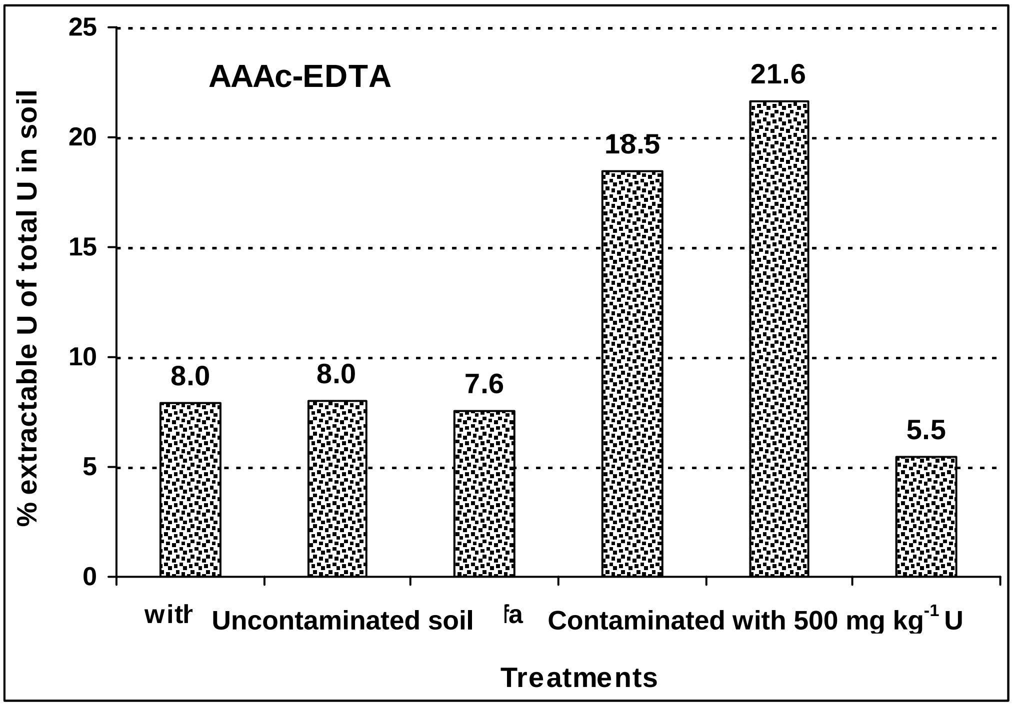

Figure 3.9: Extractable U with AAAc-EDTA expressed as a percentage of the total U in soil from the incubation experiment.

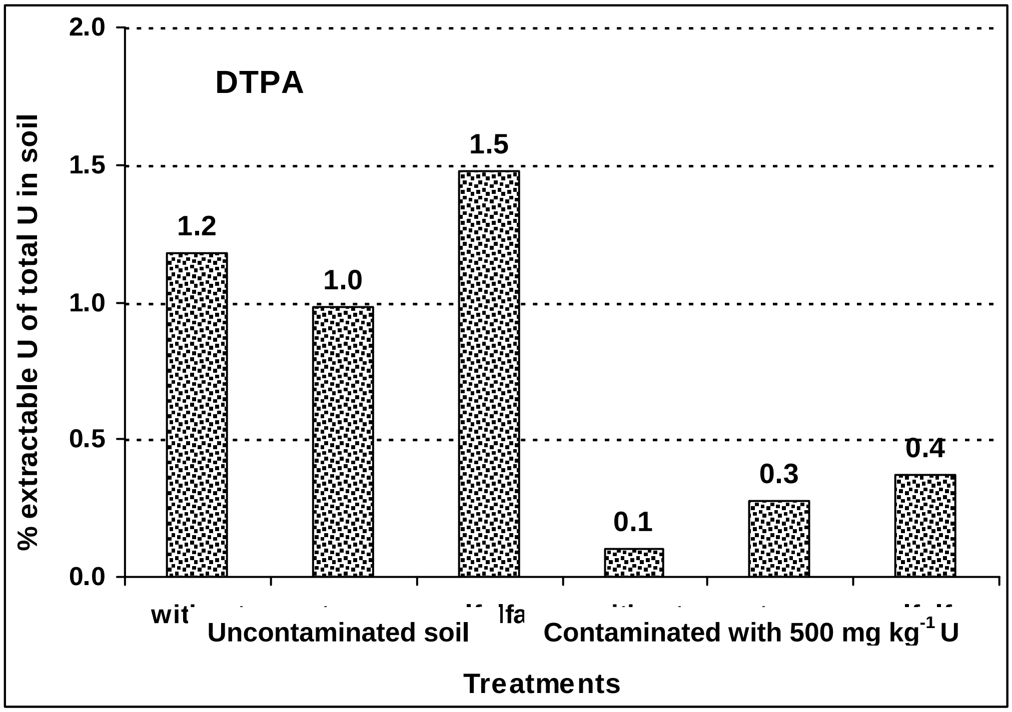

Figure 3.10: Extractable U with DTPA expressed as a percentage of the total U in soil from the incubation experiment.

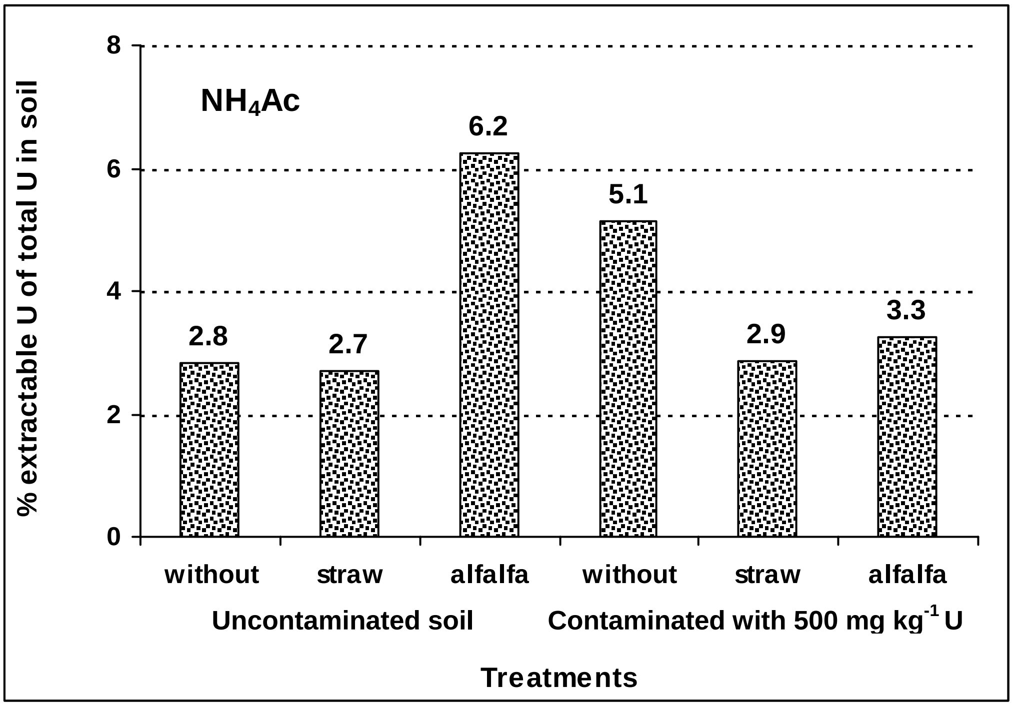

Figure 3.11: Extractable U with NH_4Ac expressed as a percentage of the total U in soil from the incubation experiment.

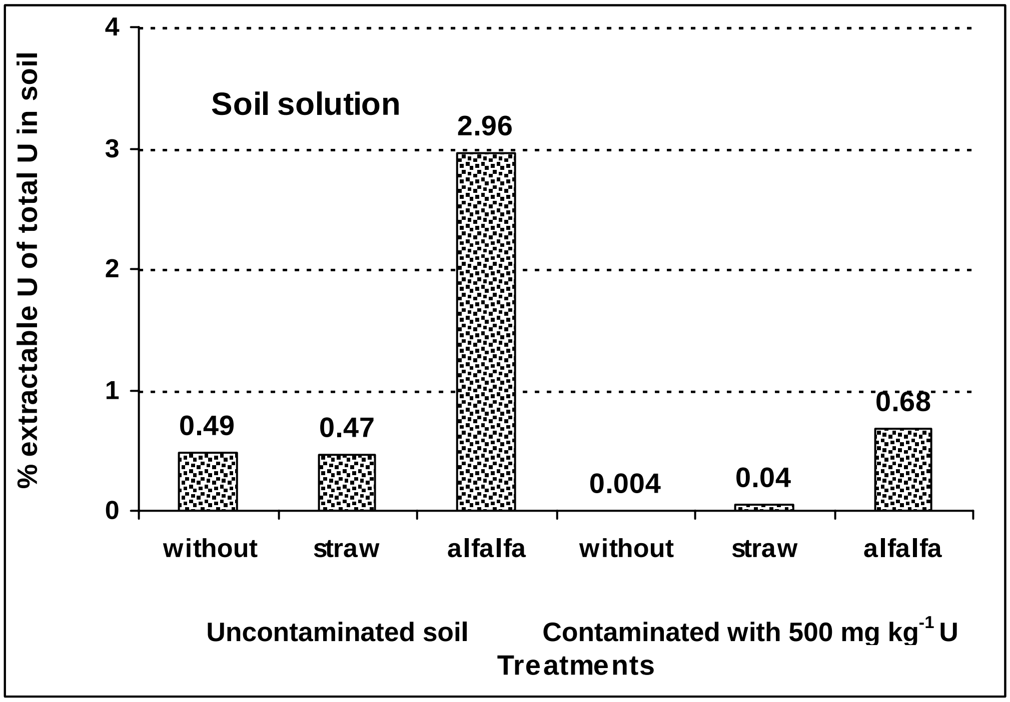

Figure 3.12: Soil solution U expressed as a percentage of the total U in soil from the incubation experiment.

Table 3.4: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution and total U in soil, soil solution pH and EC and soil pH ($CaCl_2$) in incubation experiment soil samples.

	AAAc-EDTA	**DTPA**	**NH_4Ac**	**Soil solution**	**Soil solution pH**	**Soil solution EC**	**Soil pH ($CaCl_2$)**
Total U	.83**	.78**	.84**	.45	-.12	-.17	-.13
AAAc-EDTA	-	.52	.78**	-.02	-.51	-.04	-.45
DTPA		-	.63*	.81**	.10	-.22	.22
NH_4Ac			-	.39	-.16	-.46	-.20
Soil solution				-	.52	-.38	.54
Solution pH					-	-.16	.75**

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

The correlations presented in Table 3.4 show that highly significant and significant correlations were found between NH_4Ac and both AAAC-EDTA and DTPA extractants, the correlation coefficients were 0.78** and 0.63*, respectively. Also highly significant correlation was found between the soil solution U and DTPA extractant. The r value was 0.81**.

3.2.2 Effect of soil pH on the extractability of U

The soil pH results were not consistent and didn't correlate well with any of the four extractants, but in the AAAc-EDTA case the correlation was higher and negative (r= -0.45), while in the case of soil solution the correlation was higher and positive (r=0.54), the other pH correlations were very low except with the solution pH (r=0.75**) (Table 3.4). The same behavior was found in the solution pH correlations, it had none significant correlations with both AAAc-EDTA and soil solution U, r values were -0.51 and 0.52, respectively (Table 3.4).

3.2.3 Effect of storage time on the extractability of U

Figures 3.13 and 3.14 illustrate the comparison between the former extracted U and the current extracted U in this study either by AAAc-EDTA or by DTPA from the same contaminated soil samples.

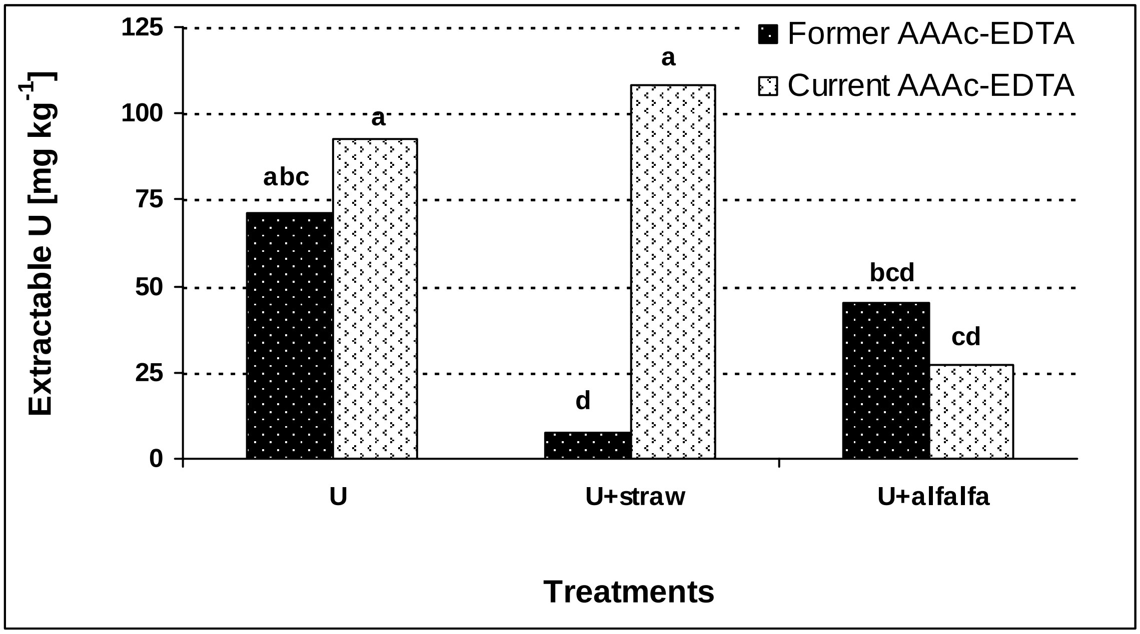

Figure 3.13: The effect of storage time: comparison between the former extracted U by AAAc-EDTA (Lamas et al., 2005) and the current extracted U in this study by AAAc-EDTA.

Values followed by the same letters are not significantly different by Tukey's test at 0.05 levels.

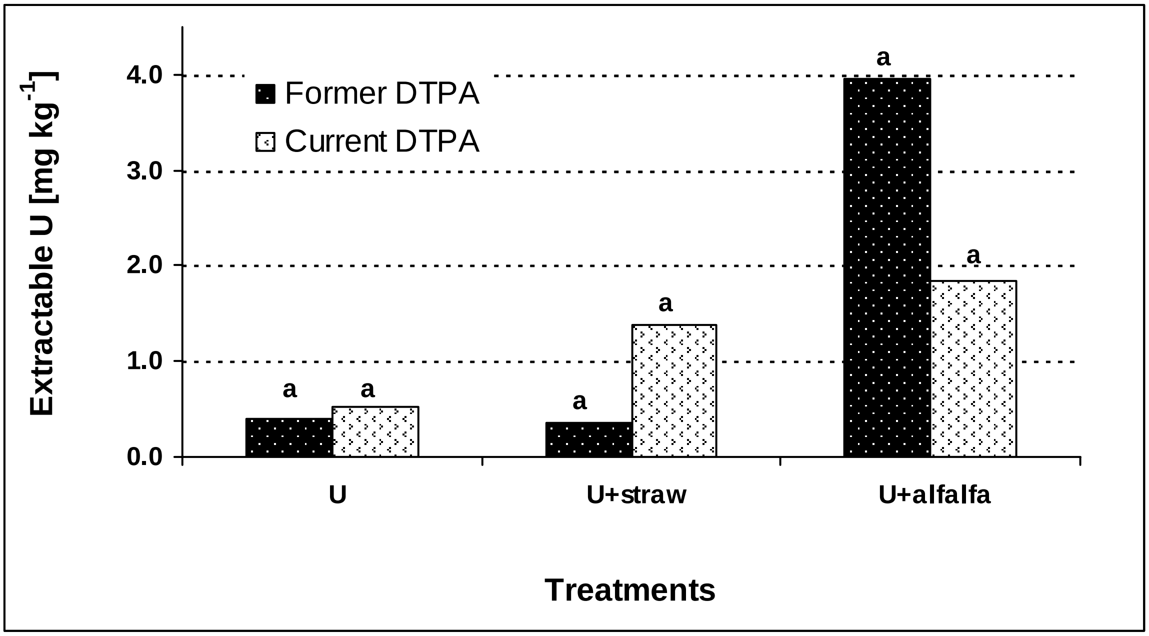

Figure 3.14: The effect of storage time: comparison between the former extracted U by DTPA (Lamas et al., 2005) and the current extracted U in this study by DTPA.

Values followed by the same letters are not significantly different by Tukey's test at 0.05 levels.

The results presented in Figure 3.13 show the comparison between the former extracted U (the former extracted U was performed by the year 2004, Lamas et al., 2005) and the current extracted U in this study (the current extracted U was performed in April 2007) by AAAc-EDTA from the same contaminated soil samples. This comparison reflected the effect of storage time on the availability of U in soil (the addition of U to the soil occurred one time only in July 2000). The results were not consistent. However, current extracted U was higher than the former extracted U in almost all soil treatments with one exception. The differences between both extractants changed depending on soil treatments. Only in U^+ straw treatment the difference was significant (different characters). The highest difference was found in straw-amended soil (differences between 108.3 - 5.7 and 107.6 - 9.5 mg kg^{-1}), while the lowest was observed in the case of non-amended soil.

Figure 3.14 shows the comparison between the former extracted U (Lamas et al., 2005) and the current extracted U in this study by DTPA from the same contaminated soil samples. Again, results were not consistent. Current extracted U was none significantly higher than the former extracted U in most soil treatments with two exceptions. As the same observation showed in the case of AAAc-EDTA, the differences between the both extractants changed depending on soil treatments. The highest difference was found in alfalfa-amended soil (difference between 2.6 - 0.14 mg kg^{-1}), while the lowest was observed in the case of non-amended soil too.

From the results of the incubation experiment soil samples, it could be concluded that the AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants extracted different amounts of U from soil. The results suggest that, for both cases of DTPA and soil solution, the lower concentration of total U in soil the higher the percentage of extractable U. The addition of cereal straw resulted in an increase of the percentage of extracted U by either AAAc-EDTA or NH_4Ac compared to non amended soil with organic materials or amended soil with milled alfalfa plants. Therefore, the addition of different types of organic materials to the U contaminated soil has variable and inconsistent affects on the availability of U. The total U in the soil was one of the factors affecting the extractability of U in soil. Soil pH was not one of the factors affecting the extractability of U from soil in incubation experiment soil samples. The effect of the storage time on the availability of U in this group of soil samples was displayed by the current extracted U being higher than the former extracted U by either AAAc-EDTA or DTPA. The results also revealed that the differences between both extractants (the former and the current one) changed depending on soil treatments. Results also revealed that more research is needed for better understanding of the effect of the storage time on U availability in soil.

3.3 Extractable U in Schneeberg (Saxony) soil samples

In this group of soils, the soil samples were collected from the Schneeberg mining area in the Saxony country. These samples covered a wide range of soil types and were contaminated with U, Cd, As and other toxic heavy metals. The wide range of U concentrations in these soil samples provided an opportunity to evaluate the efficiency of the extractants on the extractability of U in soils from another region of Germany.

Table 3.5: Extractable U with AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution [mg kg^{-1}] from Saxony soil samples.

Samples No.	**Total U in soil**	**Available U in soil extracted by**			
		AAAc-EDTA	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**
		mg kg^{-1}			
1	0.6	0.06	0.01	0.09	0.001
2	1.2	0.05	0.02	0.10	0.020
3	1.4	0.04	0.01	0.09	0.010
4	1.5	0.07	0.01	0.04	0.004
5	1.8	0.06	0.01	0.06	0.005
6	2.4	0.07	0.02	0.07	0.004
7	2.5	0.09	0.75	0.07	0.005
8	3.5	0.13	0.86	0.12	0.004
9	4.0	0.27	0.78	0.13	0.007
10	9.1	0.30	0.05	0.31	0.008
11	9.1	0.46	0.05	0.48	0.013
12	56.0	0.03	0.18	2.84	0.014
13	72.7	11.85	0.49	6.17	0.082
14	88.9	10.37	0.75	5.78	0.068

3.3.1 Extracting forces of AAAc-EDTA, DTPA, NH_4Ac and soil solution for U from soil

Table 3.5 shows that each of the AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants had different capabilities to extract U from the same soil samples. The AAAc-EDTA was usually the most powerful followed by NH_4Ac and DTPA. The extractable U with AAAc-EDTA ranged from 0.1 to 10.4 mg kg^{-1}. The extracted U by DTPA ranged from 0.01 to 0.86 mg kg^{-1}. A very large proportion of the total U was extracted by DTPA in three samples (Table 3.6), although these samples did not have the higher total U concentrations than the other soil samples. The results in the same table also revealed that the extractable U by NH_4Ac ranged from 0.04 to 6.17 mg kg^{-1}. As expected the soil solution had the lowest values, from 0.001 to 0.014 mg kg^{-1} only (Table 3.5). The comparison between the four extractants expressed as a percentage of total U in soil is presented in Table 3.6.

Table 3.6: Extractable U with AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution expressed as a percentage of total U from Saxony soil samples.

Samples No.	**Total U in soil**	**Available U in soil extracted by**			
		AAAc-EDTA	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**
		Relative to total U (%)			
1	0.6	10.3	2.4	14.2	0.15
2	1.2	4.5	1.8	7.8	1.62
3	1.4	3.1	0.7	6.5	0.73
4	1.5	4.8	0.5	2.7	0.29
5	1.8	3.4	0.5	3.2	0.29
6	2.4	3.0	0.6	3.1	0.16
7	2.5	3.5	29.4	2.8	0.19
8	3.5	3.7	24.4	3.5	0.12
9	4.0	6.9	19.6	3.3	0.17
10	9.1	3.3	0.6	3.4	0.08
11	9.1	5.1	0.6	5.3	0.14
12	56.0	0.05	0.3	5.1	0.03
13	72.7	16.3	0.7	8.5	0.11
14	88.9	11.7	0.8	6.5	0.08

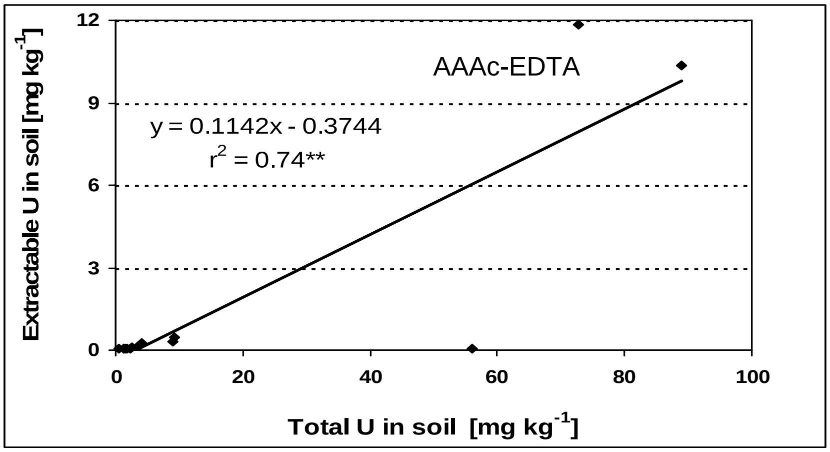

Figure 3.15: Relationship between total U and extractable U with AAAc-EDTA in Saxony soil samples.

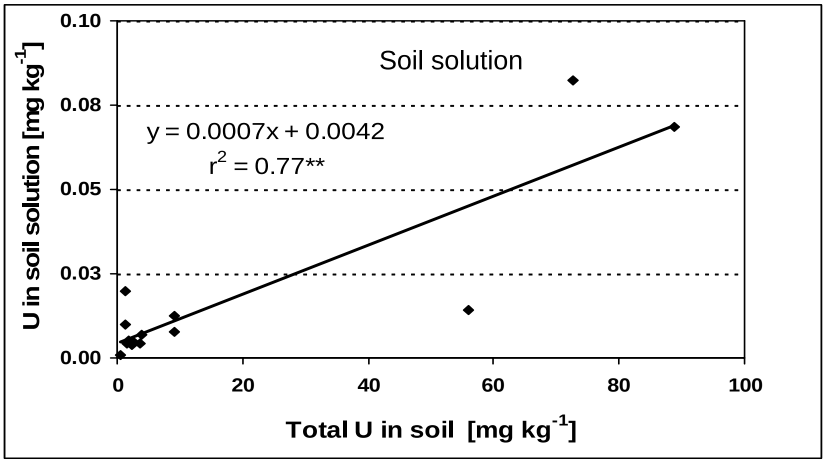

Figure 3.16: Relationship between total U and U in soil solution of Saxony soil samples.

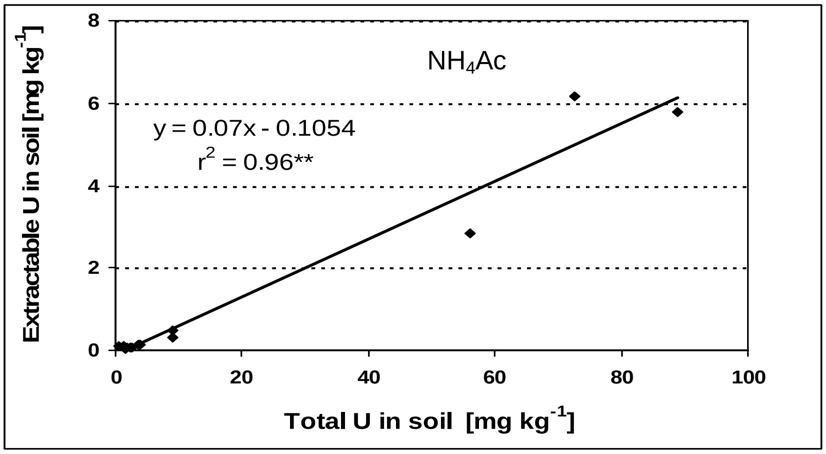

Figure 3.17: Relationship between total U and extractable U with NH_4Ac in Saxony soil samples.

3.3.2 Effect of total U in soil on the extractability of U

Figures from 3.15 to 3.17 show the relationships (only those with significant correlations) between total U in Saxony soil samples and extractable U with different extractants used in this study.

The correlations between the extractants and different soil parameters are presented in Table 3.7. Total U in the soil had highly significant correlations with the AAAc-EDTA, NH_4Ac and soil solution, r values were 0.86**, 0.98**, 0.88**, respectively, but only had a weak correlation with DTPA (Table 3.7).

Total U also had a highly significant correlation with soil Cd (r=0.96**) (Fig. 3.18), and at the same time the soil P had significant correlations with both total U (Fig. 3.19) and soil Cd (Fig. 3.20) with similar r values (r=0.55* and r=0.57*) (Table 3.7); this meant that both U and Cd in soil were related to soil P.

Table 3.7: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution and total U, soil solution pH and EC, soil pH ($CaCl_2$), P, Cd and As in Saxony soil samples**.**

	AAAc - EDTA	**DTPA**	**NH_4Ac**	**Soil solution**	**Solution pH**	**Soil Cd**	**Soil As**	**Solution EC**	**Soil pH ($CaCl_2$)**	**Soil P**
Total U	.86**	.35	.98**	.88**	.24	.96**	.14	-.15	.37	.55*
AAAc-EDTA	-	.39	.94**	.98**	.31	.70**	.09	.08	.26	.46
DTPA		-	.35	.33	.56*	.32	.78**	.29	.55*	.52
NH_4Ac			-	.95**	.25	.89**	.11	-.09	.33	.51
Soil solution				-	.17	.73**	.05	.03	.24	.43
Solution pH					-	.18	.49	.33	.48	.32
Soil Cd						-	.18	-.27	.40	.57*
Soil As							-	.20	.45	.33

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

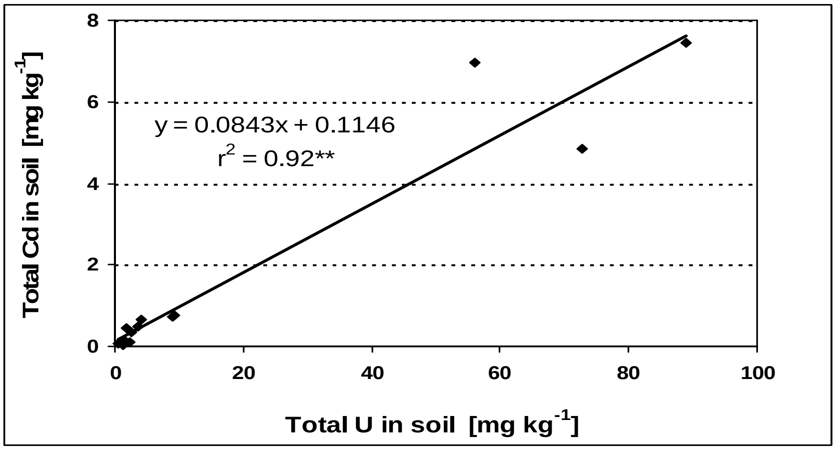

Figure 3.18: Relationship between total U and total Cd in Saxony soil samples.

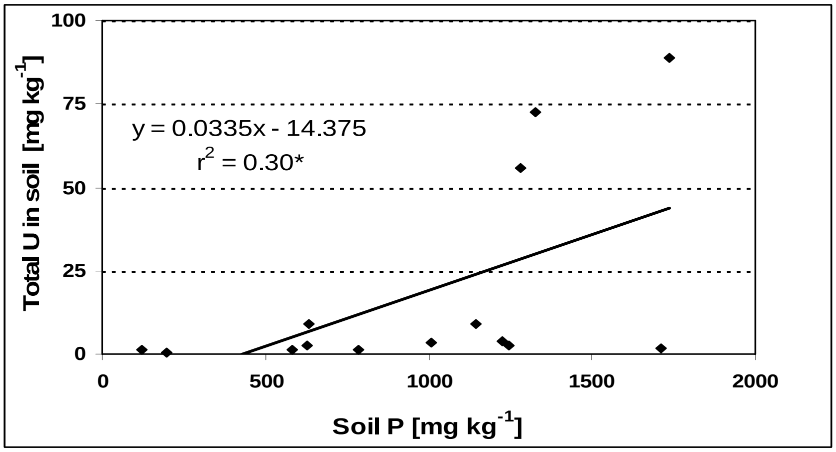

Figure 3.19: Relationship between soil P and total soil U in Saxony soil samples.

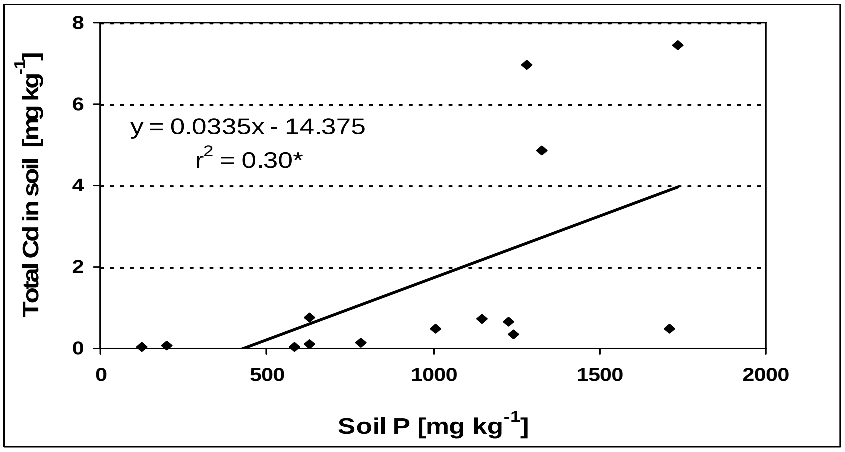

Figure 3.20: Relationship between soil P and soil Cd in Saxony soil samples.

3.3.3 Effect of total P in soil on the extractability of U

Just as surprising and contrary to that of the previous greenhouse experiment soil samples, the total soil P had non significant positive correlations with the four extractants used. The r values between soil P and AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants were 0.46, 0.51, 0.52 and 0.43, respectively.

3.3.4 Effect of soil pH on the extractability of U

The results in Table 3.7 also show that highly significant correlations were found between AAAc-EDTA and both NH_4Ac and soil solution, the correlation coefficients were 0.94** and 0.98**, respectively. Also highly significant correlation was found between the NH_4Ac and soil solution extractants, the r value in this case was 0.95**. The DTPA was the only extractant, which didn't correlate well with any of the other three extractants, but both solution pH and soil pH ($CaCl_2$) significantly correlated with DTPA only. Figure 3.21 illustrates the relationship between pH in Saxony soil samples and extractable U with DTPA.

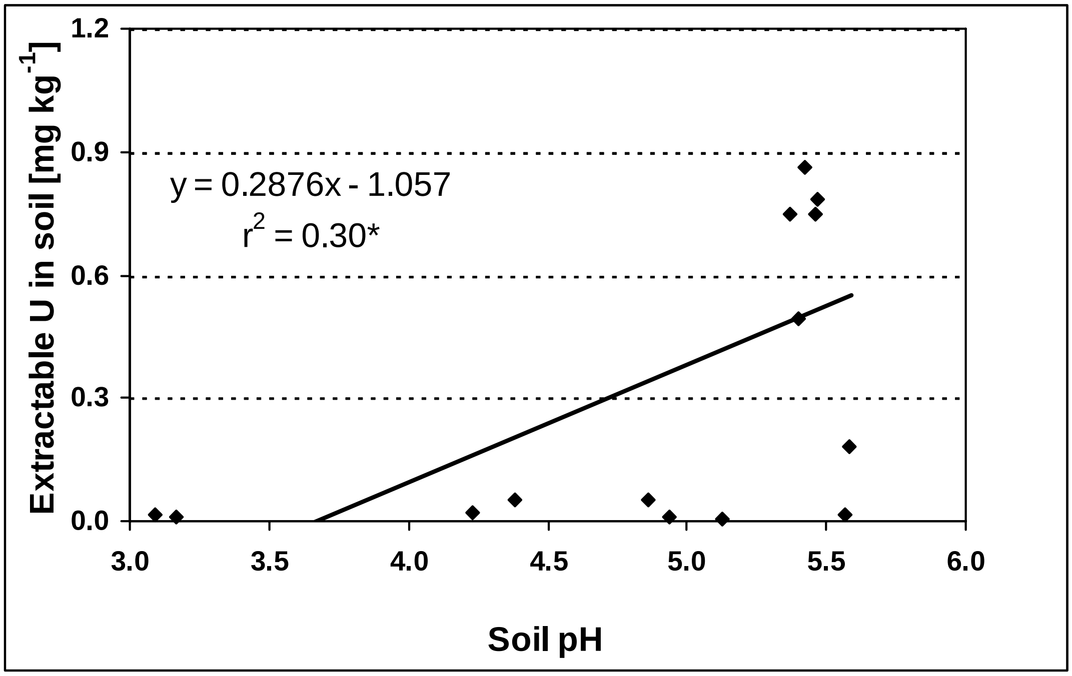

Figure 3.21: Relationship between pH ($CaCl_2$) and extractable U with DTPA in Saxony soil samples.

The results from statistical analysis also reveal that the As in the soil didn't correlate well with total U or total Cd or soil P or any of the other parameters in the soil. The r values between soil As and total U, soil P and pH were 0.14, 0.33 and 0.45, respectively (Table 3.7). This observation implied that the origin and behavior of As in the soil were different from that of U and Cd. It implied also that both soil pH and soil P had weak impact on As in the soil.

In this soil group the AAAc-EDTA extract the most U in most samples. While the NH_4Ac and DTPA extractants were more effective in the other samples. The results showed that the effect of the soil pH on the U availability (as assessed by the four extractants) was contrary to that of the previous observations of the last two soil groups (greenhouse and incubation experiments soil samples). Here the pH effect was positive in all extracting solutions.

As expected, the total soil U correlated with the U extracted by AAAc-EDTA, NH_4Ac, soil solution and DTPA. Total U also had a strong correlation with both soil Cd and P. These results mean that all of the U, Cd and P elements in the soil are geologically linked. The effect of total soil P was also positive but not significant on the extractability of U and contrary to that of the previous greenhouse experiment soil samples.

The results also showed that the As in the soil or in the soil solution didn't correlate well with total U or total Cd. This observation implied that the source and behavior of As in the soil were different from that of U and Cd in the soil. The total soil As didn't correlate with the soil P, while the soil solution As had a negative weak correlation with soil P (Table A.22). These observations may be attributed to that the soil P complexed with As in soil therefore reduced its solubility in the soil solution.

3.4 Extractable U in long-term trials soil samples

In this group of soils, the soil samples were collected from two long-term P fertilization experiments. The first one is located in Braunschweig and the second one is located in Freising. It could be possible to study the effect of long-term addition of P on soil U concentration in with the use of these samples. Also it was possible to study the effect of other soil constituents on the U availability.

3.4.1 Extracting forces of AAAc-EDTA, DTPA, NH_4Ac and soil solution for U from soil

The AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants had different abilities for U extraction from long-term P fertilization soil samples. Table 3.8 presents the extractable U with the four extractants expressed as a percentage of the total U in soil in Freising soil samples. The extracted U by AAAc-EDTA was higher than the extracted U by NH_4Ac in almost all Freising soil samples (Table 3.8). U extracted by AAAc-EDTA ranged from 0.04 to 0.06 mg kg^{-1} (3.4-5.2% of the total U in soil), and the extractable U with NH_4Ac ranged from 0.02 to 0.08 mg kg^{-1} or about 1.3-5.9% of the total U in Freising soil samples (Table 3.8 and Table A.23). The extractable U with DTPA was in the same range as Braunschweig samples. The range of soluble U in the soil solution of Freising soil samples was lower than that of Braunschweig samples.

Table 3.8: Available U extracted by AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution expressed as a percentage of the total U from Freising long-term fertilization trial soil samples.

Treatments	**Total U in soil**	**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**
	Relative to total U (%)				
NK	1.29	3.36	0.35	1.26	0.05
NK+FYM	1.20	3.50	2.40	1.37	-
NK+ straw	1.09	3.83	0.40	1.69	0.07
Super phosphate	1.40	3.66	0.27	5.90	0.04
Nova phosphate	1.19	5.06	1.47	0.00	0.06
Hyper phosphate	1.17	5.18	0.28	1.38	0.05

In contrast to the previous soil groups, the NH_4Ac was the most powerful extractant in Braunschweig soil samples. Results presented in Table 3.9 show the comparison between the NH_4Ac and AAAc-EDTA extractants. The results revealed that the U extracted by NH_4Ac was higher than that extracted by AAAc-EDTA in most Braunschweig soil samples. The extractable U with NH_4Ac ranged from 0.02 to 0.11 mg kg^{-1} (3.2-16.1% of the total U in soil), while U extracted by AAAc-EDTA ranged from 0.02 to 0.1 mg kg^{-1} (2.4-15.6% of the total U in soil) in Braunschweig samples (Table 3.9 and Table A.23). The extractable U with DTPA ranged from 0.004 to 0.01 mg kg^{-1} (0.62-1.4% of the total U in soil). The soil solution U in soil solution was very low and its percentage ranged from 0.09-0.4% of the total U in Braunschweig samples (Table A.23).

Table 3.9: Extractable U with AAAc-EDTA, DTPA, NH_4Ac and U in the soil solution expressed as a percentage of the total U in Braunschweig long-term fertilization trial soil samples.

Treatments	**Total U in soil**	**AAAc-EDTA**	**NH_4 Ac (pH 7)**
		Relative to total U (%)	
NK	0.65	15.64	8.78
NK	0.68	4.16	13.50
NK	0.65	2.36	11.45
NK	0.68	3.42	10.87
NK	0.65	2.74	16.11
NK	0.68	2.92	5.95
NK+FYM	0.69	5.58	3.24
NK+FYM	0.67	5.17	3.18
NK+FYM	0.69	2.67	3.51
NK+FYM	0.67	2.82	10.91
NK+FYM	0.69	2.52	15.66
NK+FYM	0.67	3.84	9.61
NPK+FYM	0.74	3.71	9.02
NPK+FYM	0.70	3.38	3.95
NPK+FYM	0.74	2.81	3.27
NPK+FYM	0.70	2.54	13.85
NPK+FYM	0.74	3.69	7.90
NPK+FYM	0.70	3.83	4.09

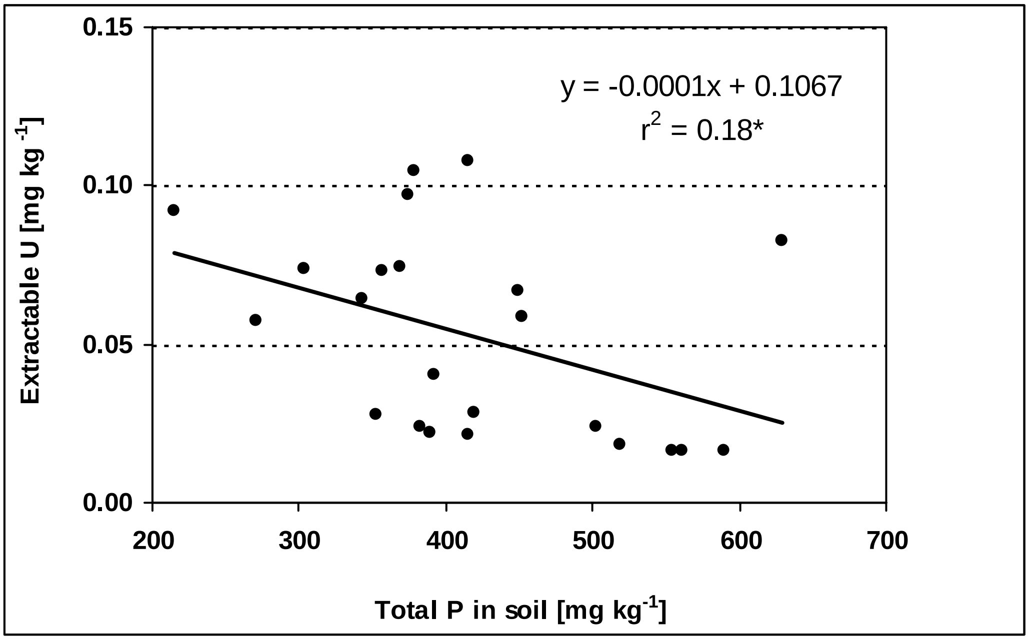

Figure 3.22: Relationship between total P and extracted U by NH_4Ac in soil samples from long-term trials (Braunschweig and Freising).

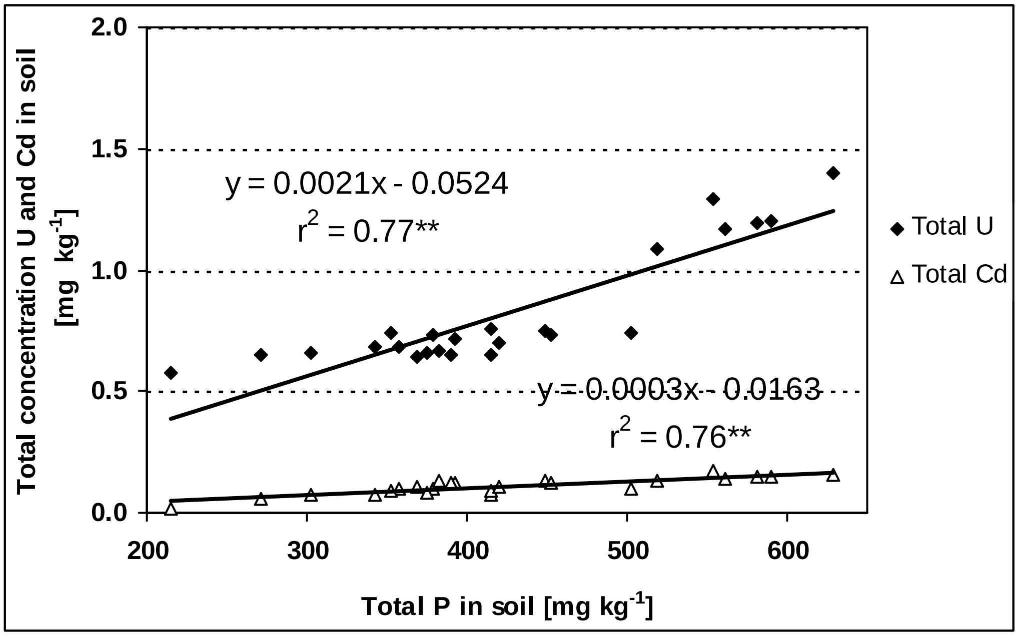

Figure 3.23: Relationship between total soil P and total soil U and Cd in soil samples from long-term trials (Braunschweig and Freising).

3.4.2 Effect of total U in soil on the extractability of U

The results presented in Table 3.10 show that weak correlations were found between different U extractants and total U in long-term trials soils except between total U and AAAc-EDTA, where significant correlation was found (r=0.44*).

3.4.3 Effect of total P in soil on the extractability of U

The total soil P only significantly affected on the U extracted by NH_4Ac. The r value between them was -0.43* (Fig. 3.22), while its effect on the other extractants was not significant. On the other hand the total soil P had highly significant effects on total U, Cd and Ni in soil. The r values in these cases were 0.88**, 0.87** and 0.82**, respectively (Table 3.10). This meant that U, Cd and Ni increased with the increase of the P in the soil. This phenomenon may be attributed to the fact that all of the four elements had the same origin in the soil (the addition of the P fertilizers for a very long time). The relationship between P and both U and Cd are presented in Figure 3.23.

The available P_{CAL} in soil is significantly negatively correlated only with AAAc-EDTA among the four extractants used for long-term trials soils, the r value in this case was -0.46* (Table 3.10 and Figure 3.24), while the relation between both of them turned to positively significantly correlation (r=0.82*) in the case of Freising long-term trials soils (Fig. 3.25). This means that the different fractions of soil P is one of the most important factors affecting the extractability of U in soil, beside its effect on the other heavy metals in the soil.

3.4.4 Effect of soil pH on the extractability of U

The soil solution pH was positively significantly correlated with AAAc-EDTA, while it was negatively significantly correlated with NH_4Ac among the four extractants used for long-term trials soils (Fig. 3.26). The r values in both cases were 0.45* and -0.43* for AAAc-EDTA and NH_4Ac, respectively (Table 3.10). The soil pH ($CaCl_2$) was negatively significantly correlated only with soil solution U (Fig. 3.27) among the four extractants used for long-term trials soils. The r value in this case was -0.42* (Table 3.10). This meant that the soil pH is one of the important factors affecting the extractability of U in soil. But its effect direction is depending upon the extractants used to extract U from soil.

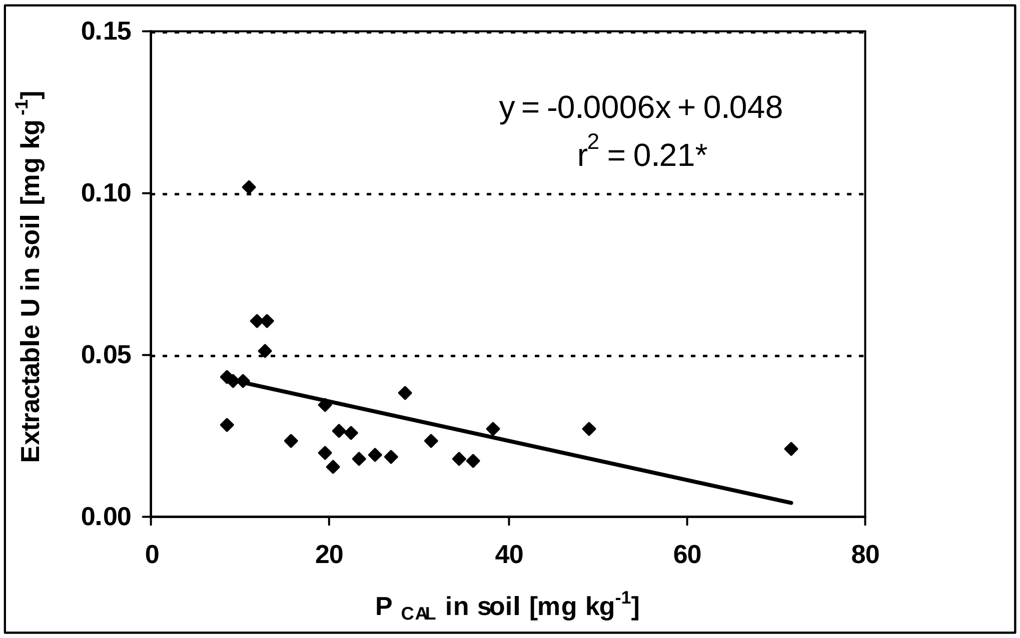

Figure 3.24: Relationship between soil available P $_{CAL}$ and extracted U by AAAc-EDTA in soil samples from long-term trials (Braunschweig and Freising).

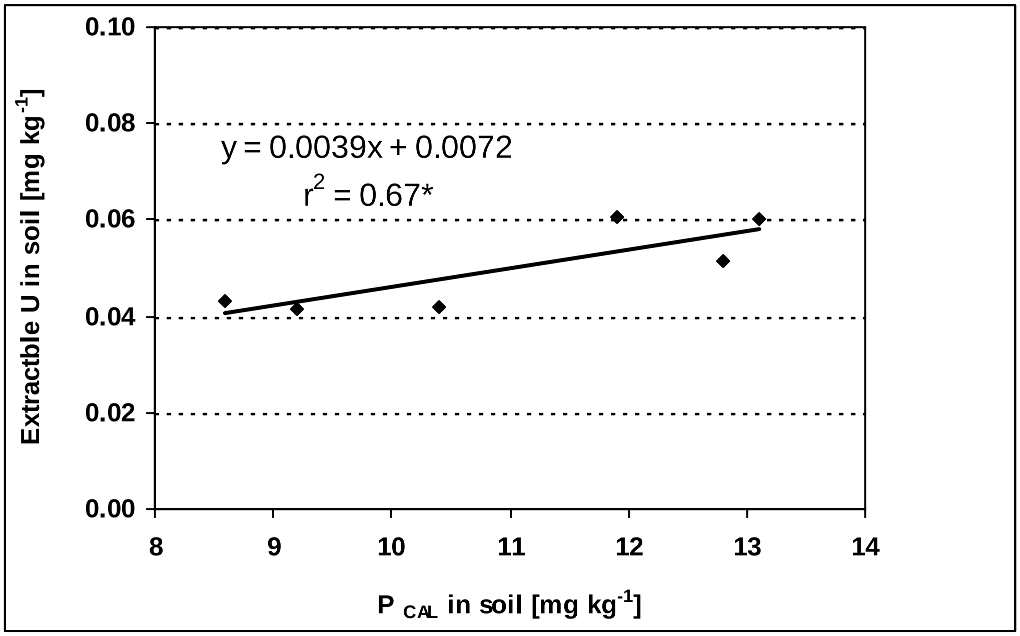

Figure 3.25: Relationship between soil available P $_{CAL}$ and extracted U by AAAc-EDTA in soil samples from Freising long-term trials.

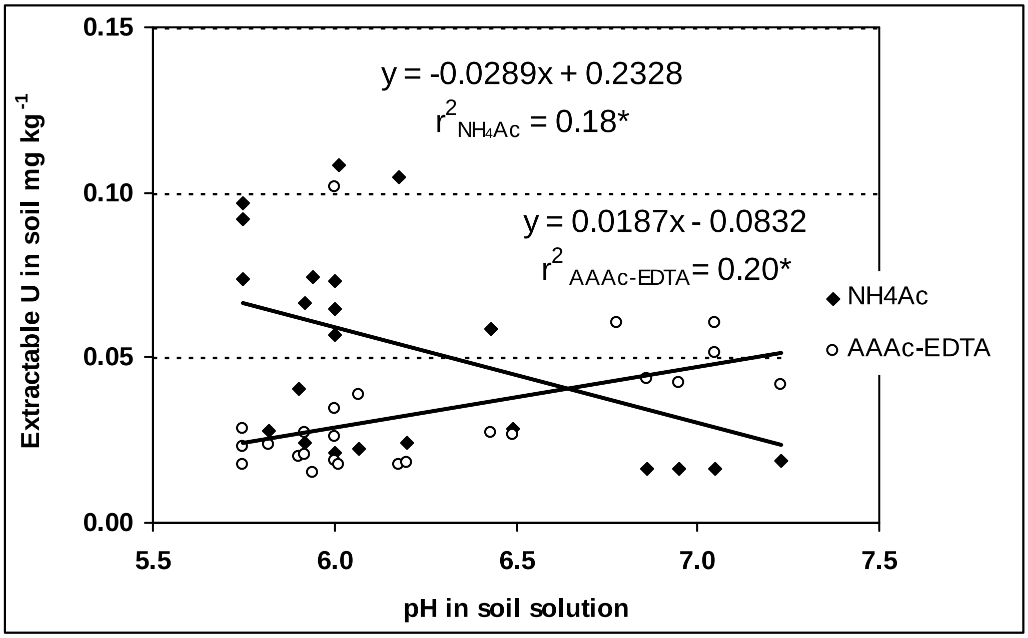

Figure 3.26: Relationship between soil solution pH and extracted U by AAAc-EDTA and NH_4Ac in soil samples from long-term trials (Braunschweig and Freising).

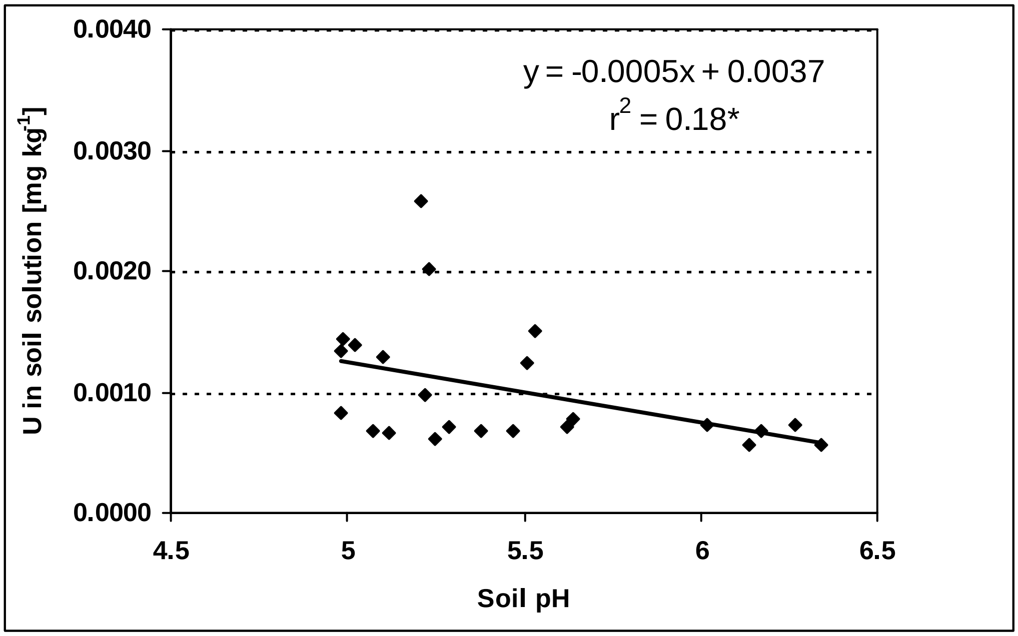

Figure 3.27: Relationship between soil pH ($CaCl_2$) and soil solution U in soil samples from long-term trials (Braunschweig and Freising).

Table 3.10: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and solution pH, soil U, P, pH, Cd, Ni, OC, S and available P_{CAL} in long-term fertilization trials soil samples (Braunschweig+Freising).

	AAAc-EDTA	**DTPA**	**NH_4Ac**	**Soil solution**	**Solution pH**	**Soil P**	**Soil pH**	**Soil Cd**	**Soil Ni**	**Soil Pb**	**P_{CAL}**	**Total OC**	**Soil S**
Total U	.44*	.29	-.31	-.37	.89*	.88**	.88**	.77**	.97**	.21	-.39	-.52**	.67**
AAAc-EDTA	-	.14	-.27	.31	.45*	.24	.37	.15	.47*	-.00	-.46*	-.40	.16
DTPA		-	-.08	.08	.23	.27	.28	.18	.33	.01	-.21	-.16	.28
NH_4Ac			-	.00	-.43*	-.42*	-.36	-.44*	-.40	-.12	.08	.34	-.22
Soil solution				-	-.25	-.37	-.42*	-.37	-.40	-.07	.16	.17	-.30
Solution pH					-	.83**	.91**	.75**	.90**	.33	-.45*	-.41*	.70**
Soil P						-	.84**	.87**	.82**	.36	-.03	-.30	.78**
Soil pH							-	.78**	.89**	.39	-.35	-.28	.82**
Soil Cd								-	.73**	.67**	-.08	-.07	.85**
Soil Ni									-	.16	-.52**	-.57**	.60**
Soil Pb										-	.05	.54**	.69**
P_{CAL}											-	.51*	.02
Total OC												-	.17

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

3.4.5 Effect of total S in soil on the extractability of U

Total S in soil was found to be one of the most important factors affecting the U in the soil, nevertheless it didn’t significantly correlate with any of the extractants, but it correlated well with total U, Cd, Pb, Ni in the soil. The r values in all of these cases were 0.67**, 0.85**, 0.60** and 0.69** for U, Cd, Pb, Ni in the soil, respectively (Table 3.10). This meant that all five elements had the same origin in the soil, and S in the soil affected their behavior. The relationships between the soil S and the four elements are presented in Figures 3.28 and 3.29.

The correlations amongst the four U extractants are presented in Table 3.10. No significant correlations were found between them. The r values were very low and sometimes were negative too. This meant that they had different behavior for extracting U from the soil.

3.4.6 Effect of total organic carbon (OC) in soil on the extractability of U

Total organic carbon (OC) was negatively correlated with AAAc-EDTA and DTPA, the r values for these relations were -0.46* and -0.21, for AAAc-EDTA and DTPA, respectively. It was positively correlated with NH_4Ac (Table 3.10). This phenomenon meant that the OC is possibly one of the factors affecting the U availability in soils. It also had positive significant correlation with available P (CAL) (Table 3.7) and this meant that this method extracted the organic P from the soil. The OC also positively correlated with Pb (r=0.54**) and negatively correlated with Ni in soil(r=-0.52**) (Table 3.10), this meant that the Pb complexed with organic matter while Ni was not complexed with organic matter in soils.

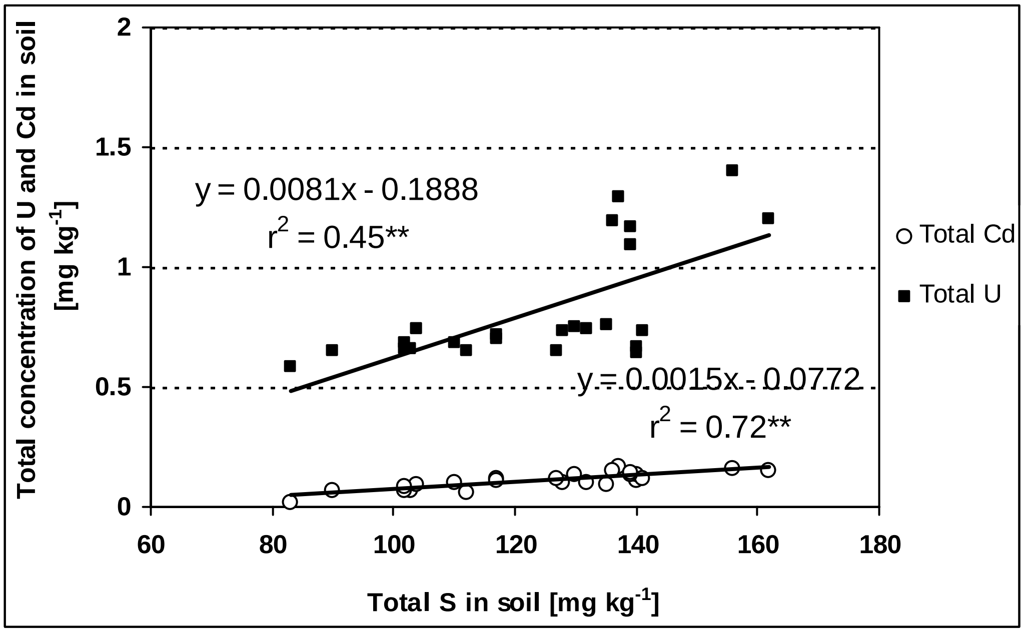

Figure 3.28: Relationship between total soil S and total U and Cd in soil samples from long-term trials (Braunschweig and Freising).

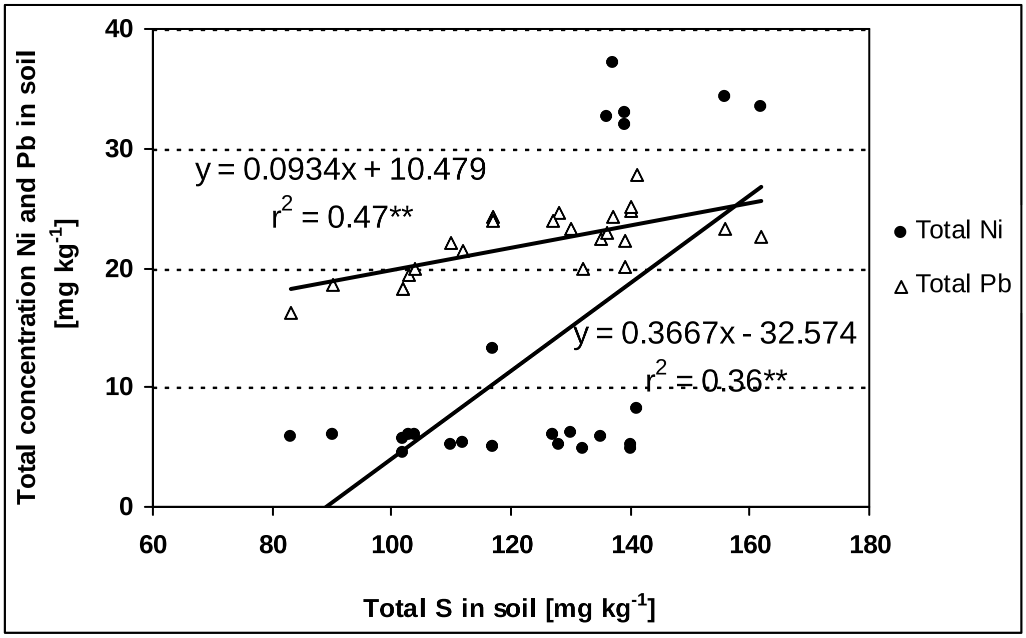

Figure 3.29: Relationship between total soil S and soil Ni and Pb in soil samples from long-term trials (Braunschweig and Freising).

The results of the long-term trials soil samples implied that the NH_4Ac was the most powerful extractant in Braunschweig samples, whereas the extracted U by AAAc-EDTA was higher than the extracted U by NH_4Ac in almost all Freising soil samples. The extracted U with DTPA was of the same range at both sites. The soluble U in the soil solution was very low and the values of the Freising soil samples were lower than that of Braunschweig soil samples.

Total organic carbon (OC) in the soil of long-term trials had weak correlations with AAAc-EDTA, DTPA and NH_4Ac. This phenomenon means that the OC is one of the factors affecting the U availability in soils, but its effect is weak. The OC also was positively correlated with Pb and negatively correlated with both total U and Ni in soil, while it didn't correlate with total soil Cd.

No significant correlations were found between the four extractants used. Weak relations were found between the total U and the different four U extractants. Soil total P didn't correlate with U extracted by the four extractants, with one exception in the case of NH_4Ac, which had a significant negative correlation with soil P. The soil pH also didn't correlate with U extracted by the four extractants used except for a significant negative correlation with soil solution. The pH of the soil solution correlated significantly with both AAAc-EDTA and NH_4Ac for long-term trials soils. On the other hand, the total soil P had highly significant effects on total U, Cd and Ni in soil. This means that the long term addition of P fertilizers significantly increased the total soil U, Cd and Ni in the soil. The available P_{CAL} in soil negatively significantly correlated only with AAAc-EDTA among the four extractants used for long-term trials soils. The total S in soil didn't significantly correlate with any of the extractants used. The total S correlated well only with total U, Cd, Pb, Ni in the soil, this may be means that all of the five elements are intrinsically present in the soil matrix in the soil, and the S may affect their behavior in the soil.

The above results of long-term trials samples indicated that the organic matter was the only factor affecting the extractability of U from soil, while total U, P, S and soil pH had no distinct impact on the U extractability. On the other hand the soil P, S and OC had a great effect on the heavy metals in soil.

4. Discussion

The main purpose of this research work were to evaluate some of the methods which could be used for extracting plant available U and assessing the bioavailability of U in different soils, and to investigate the main factors responsible for U mobility in a wide rang of U contaminated soils. The other purpose was to investigate the time effect on the U availability in soil. To achieve these aims a wide range of soils varying in U concentrations and with different characteristics were analyzed for this study.

The discussion of the results starts, therefore, with the discussion of the results of the greenhouse experiment soil samples (Chapter 4.1), followed by the discussion of the results of the incubation experiment soil samples (Chapter 4.2), then the discussion of the results of the Saxony soil samples (Chapter 4.3), and finally the discussion of the long-term- P fertilization soil samples is discussed (Chapter 4.4).

4.1 Extractable U in greenhouse experiment soil samples

The selected soil samples from the greenhouse experiment covered different U levels, S levels, P fertilization, N levels, and the influence of different crops. This combination aimed to investigate the effect of U level and different factors affecting the U mobility in soil, also to compare the extractability potential of the four extractants (AAAc-EDTA, DTPA, NH_4Ac and soil solution), and find out which of these extracting solutions or methods best predict plant U concentration and uptake. Furthermore, to study the time effect via comparing the effect of old (this study or current data) and more recent (Rivas data) applied U on the extractability of U from soil. The addition of U to the soil occurred only one time in July 2000. The former extracted U was performed by the year 2004 (Rivas 2005).

In the present soil samples group, it was observed that the U solubility was found to be a function of the extraction solution. The AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants had different capabilities to extract U from soil. The AAAc-EDTA extractant was usually the most powerful extractant. This could be attributed to the presence of chelating agent (EDTA) as a constituent of this extractant (Means et al., 1978; Cleveland and Reese, 1981) and also attributes to the lower pH value of this extractant, as these two characteristics released more U from the soil. Although the

DTPA extractant contains chelating sites, it had lower U concentration compared to both AAAc-EDTA and NH_4Ac, and this could be attributed to either the extraction ratio used in this case (DTPA: soil was 2:1) or neutral pH of this extractant. The same phenomenon was found by Lamas (2005). The results revealed that both DTPA and AAAc-EDTA extractants have different powers when extracting U from soils. Also, Sheppard and Evenden (1992) reported that the extraction efficiency of NH_4Ac for U in soil was weak, but reflected well the bioavailability of U. Their results also showed that, the extraction efficiency of NH_4Ac increased with higher concentration of U in soils, suggesting that the U became more extractable and therefore more bioavailable (Sheppard and Evenden, 1992).

On the other hand the soil solution had the lowest concentration of U for all soil groups (maize, sunflower and faba bean). This may be attributed to soil solution only captures the water soluble pool of the element.

More U was extracted by the four extractants used in this study, at the higher U level in soil, than was higher than that extracted from soil with a lower U level. This trend was observed in all crops soil samples, note that these soil samples have similar characteristics. The results presented in Table 3.2 revealed that highly significant and significant correlation coefficients were found between the U level in almost all soil samples and the extractable U with the four extractants used. This means that the U concentration in the soil influences the bioavailability of U assessed by the four extractants used in this study. Note that the effect of the presence of P in the samples interfered with the effect of U level in the soil because the P had a diverse effect on the extractable U in soil, while U level had positive effect on the extractable U in soil. For this reason the samples were divided into two groups, with and without P fertilizer, and compared the samples in each group together. These results are in good accordance with that of Rufyikiria et al. (2004). The results implied increasing total soil U from the background level (1.0 mg kg^{-1}) to about 88.0 mg kg^{-1} resulted in increasing of the extracted U by NH_4Ac from 0.02 to 16.8 mg kg^{-1} (2.2 to 19.8% of the total U). Increasing the total U also increased the soil solution U from 0.0005 to 0.043 mg kg^{-1} (0.05 to 0.12% of the total U).

There is much evidence in the literature to suggest that maize has a lower ability to release U into the soil after harvest than that of sunflower. Rivas (2005) reported that the average U uptake was highest in sunflower, lower in maize and the lowest in faba bean. This result was confirmed by the findings of Bargagli (1998). Also, sunflower was found to be very effective in recovering U from U-contaminated water (Entry et al., 1996). The U uptake was lower for cereal crops and higher for root crops than for most other crops (Sheppard and Evenden, 1988). The dicots roots (like sunflower) release more U in the soil than monocots (like maize) roots (Bargagli, 1998). Duquène et al. (2006a) reported that the soluble U in soil solution increased after plant growth as compared with that before plant growth, and the lowest increase was observed in soil after growth of maize.

For the present study, the results were in a good agreement with the above literature. The results implied that the extractable U with all extractants from sunflower soil samples was higher than that of the other two crops' soil samples in all U levels, in all U level in most cases followed by faba bean soil samples (Fig. 3.2). The literature gave an explanation for this phenomenon. Soil rhizospheres were found to have significantly different properties than the bulk soil (Gobran et al., 2001). Ions in the rhizosphere may either be depleted or accumulated, pH may change and trace elements may be complexed by root exudates (siderophores or organic acids) (Hernlem et al., 1999; Marschner, 2002). Although yet there are no specific studies about the direct effect of the rhizosphere on U bioavailability, it is generally accepted that rhizosphere processes play a significant role on U mobility. Plant uptake of U may be restricted to the root system and may adsorb on the outer root membrane rather than being incorporated into the interior of the root system (Sheppard et al., 1983). As a result the available U concentration increased in the root zone. Also, the U concentrations in soil solution after plant growth varied about 7-fold between the plant species studied, the root transfer factor was only 2-fold, but the shoot transfer factor was 42-fold (Duquène et al., 2006b).

One of the most important objectives of this study was to relate the U extracted by the different extractants to the measured plant U content (analyzed by Rivas 2005). The uptake of U by plants or animals is the mechanism by which U originating from soil or water enters the human food chain, so that the investigation of plant U uptake is the first step in the risk assessment of U for humans. The results of the present study conclude that the AAAc-EDTA was the best predictor for maize U-uptake followed by NH_4Ac, while both DTPA and soil solution were not able to correlate well with the U-uptake by maize. The r values between maize uptake of U and AAAc-EDTA, NH_4Ac, DTPA and soil solution were 0.69**, 0.50*, 0.42, and 0.18, respectively (Table 3.2). On the other hand, both DTPA and AAAc-EDTA extractants were the best indicator for the U-uptake by sunflower plants (Fig. 3.5), but the r values in these two cases were lower than that of U-uptake by maize. The NH_4Ac and soil solution were not suitable for this purpose. The r between U extracted by DTPA, AAAc-EDTA, NH_4Ac and soil solution extractants and sunflower U-uptake were 0.60*, 0.58*, 0.49, and 0.39, respectively (Table 3.2). The results of the present study also revealed that none of the tested extractants were able to predict the U-uptake by faba bean plants. The limited numbers of samples in the case of faba bean might have yielded this result so that further studies are required to fortify these findings.

As comparing with the results of the other researchers, Lamas (2005) used DTPA and AAAc-EDTA extractants to study the U bioavailability for uptake by *Lolium perenne*. The results reported that the U extracted by AAAc-EDTA showed better correlation with plant uptake than the U extracted by DTPA. The correlation coefficient between plant uptake and DTPA was 0.72^{***}, whereas it was 0.58^{***} for AAAc-EDTA in the fertilized soils. Good correlations were found by Sheppard and Evenden (1992) between the extracted U by NH_4Ac only, and U uptake of radish and beans from different contaminated soils compared to the U extracted by $NaHCO_3$. The soluble U in the soil solution was a better predictor for U uptake by ryegrass than for amounts of U extracted with either 0.11 M CH_3COOH or 0.4 M $MgCl_2$ (Vandenhove et al., 2007c). No correlations were found between the U soil-to-plant transfer factors (TF) (or U-uptake) and the U extracted with different extractants (NH_4Ac at pH 7, NH_4Ac at pH 5 and oxalate) by Laroche and Henner (2003) and Vandenhove et al. (2007a). The variations of the correlation between the plant uptake of U and the available U in soil among the different plants used in this study and the results of the literature review indicate that a number of factors govern the uptake of uranium by plants, involving many interacting soil and plant factors (Sheppard and Evenden, 1988; Saric et al., 1995; Zararsiz et al., 1997; Bunzl and Trautmannsheimer, 1999; McClellan et al., 2003).

The correlations between the plant U-concentration (analyzed by Rivas 2005) and the extracted U with the four extractants used were negligible and not significant. This was true in all plants tested, therefore these extractions were not able to predict the U-concentration in any of the three crops tested here. These results are in a good agreement with that of Sheppard and Evenden (1992). Their results implied that the plant-U concentration is not useful for prediction of the plant bioavailability, for the r values between U extracted by both $NaHCO_3$ and NH_4Ac, or the concentration ratio of radish plants of between 0.25 and 0.57. Similar results were also found by Morton et al. (2001). They reported that the U concentrations in stems or leaves of blueberry were not significantly correlated with the total U in soil. Also, Duquène et al. (2006b) reported that U in the soil solution was not able to explain the U in the plant.

Soil pH value is one of the most predominant factors influencing the U mobility in soils (Echevarria et al., 2001). The U is amphoteric, meaning that it can mobilize at either high or low pH (Grassi et al., 2005). Under acidic condition, the increasing solubility was attributed to the hypothesis of the presence of the UO_2^{2+} (Duff and Amrhein, 1996; Davis et al., 1998; Lamas, 2005). Tyler and Olsson (2001) studied the effect of raising soil pH using the addition of fine-grained calcium carbonate (pH range of 5.2-7.8) to an acid cambisol on the U soil-to-plant transfer factor (TF) of *Agrostis capillaries*. They observed increasing U solubility with increasing pH, and this increasing found to be linked with the formation of highly soluble negatively charged carbonate complexes. These results are in agreement with the observation of Vandenhove et al. (2007a), they found that only above pH = 6, log K_d (solid-liquid distribution coefficient for U) was linearly related with soil pH ($r^2 = 0.65$) and the high U concentration in soil solution was observed at alkaline pH. Also Duquène et al. (2006a) reported that the exchangeable U was higher eight folds in alkaline soil than in acid soil, while the soil solution U was higher five folds in alkaline soil than in acid soil.

The results of the greenhouse experiment soil samples revealed that soil pH had a diverse effect on the extractability of U in soil. This effect was more pronounced in both cases of maize and sunflower soil samples, while it was not significant in the third soil group's (faba bean) samples. This means that the effect of pH on the availability of U in soil is a plant-dependent effect. The solution pH (in all greenhouse soil samples) also had the same trend but with lower r values in the AAAc-EDTA, DTPA and NH_4Ac extractants. The r value between the soil solution-U and soil solution pH was more pronounced than that with soil pH.

Negative relationships were observed in different soils between both soil available P and soil solution P and soil U concentrations (Vandenhove et al., 2007a). The same observation was found by Lamas et al. (2005a). They demonstrated that the addition of $CaHPO_4$ reduced the available U in different soils near to the background level and also decreased the U-uptake by *Lolium perenne* grown in U-contaminated soil. These results are in agreement with those of Rivas (2005) and Schroetter et al. (2006). They found that the addition of P as $CaHPO_4$ to U-contaminated soil sharply reduced the U concentration and uptake by maize and sunflower plants, while it didn't decrease the plant-U concentration or uptake by faba bean plants. Similar observations were made by Straczek et al. (2006), they reported that the phosphate decreased the availability of U to roots of pea assessed by both EDTA and $CuSO_4$. Results of Seaman et al. (2001) are in accordance with the above results. These results revealed that hydroxyapatite (P compound) was highly effective at reducing U solubility and extractability (extracted with either 1 M NH_4Cl or 0.5 M $CaCl_2$) in both batch and column experiments.

In the present work, results revealed that the presence of P compounds in soil had an inconsistent effect on mobility of U in soil. The r values between soil P and the extracted U from maize soil samples by AAAc-EDTA, NH_4Ac, DTPA and soil solution were -0.61**, -0.82**, -0.80** and 0.39 respectively. For sunflower soil samples the r values between soil P and the extracted U by AAAc-EDTA, NH_4Ac, DTPA and soil solution were -0.81**, -0.85**, -0.74**, and -0.59*, respectively. While in the faba bean soil samples these values were -0.87**, -0.80*, -0.82*, and -0.74 for NH_4Ac, AAAc-EDTA and DTPA and soil solution, respectively (Table 3.2). The soluble P in soil solution of maize soil samples also had the same diverse effect on mobility of U in soil.

The decline of available U concentration in the soil solution in the presence of P compounds could attribute to the precipitation reactions of U-P compounds (Koch-Steindl and Pröhl, 2001), or to enhance U-sorption on the soil surfaces by formation of ternary surface complexes involving both UO_2^{2+} and PO_4 (Payne et al., 1996). Chen et al. (2005) reported that a moderate P level (20 mg P kg^{-1}) in the soil stimulated, but a higher P level (60 mg P kg^{-1}) impaired, increases in U accumulation in barley roots. These findings suggested that the U-P interaction should be concentration dependent. This means when high concentration of P was found, complexes between U and P could most likely to be formed in the soil.

Both N fertilization rate and S fertilization rate didn't affect the extractable U from soil with the extractants in any of the three soil group's samples, nevertheless weak correlations between soil solution U and S fertilization in both maize and faba bean soil samples existed. The weak influences of both N and S observed here could be related to their effect on the plant growth (indirect effect) not direct effect on the U bioavailability in soil. The present findings are well in accordance with the general understanding that the addition of N fertilizer in the form of NH_4Cl didn't promote the uptake of U by Chinese cabbage plants; this means that the addition of N fertilization didn't increase the availability of U in soil (Gramss et al., 2006).

In contrast, Schroetter et al. (2006) showed that the addition of sufficient N fertilization to maize and sunflower plants increased the U content in the both plants, while the S fertilization decreased the U content of maize, sunflower and faba bean. For this study, the addition of N fertilization didn't increase the availability of U in soil

The investigation of the effect of storage time on the availability of U in soil was carried out in the present study. A comparison between the former extracted U (performed in the year 2003, Rivas 2005) and the current extracted U (performed in April 2007) was made using AAAc-EDTA. However, results were not consistent. For the maize soil samples, results revealed that the former extracted U was higher than the current extracted in all five U levels in the soil, meaning that the more recent application of U the more bioavailable for plants. This observation was not seen in either case of sunflower and faba bean soil samples. In both cases the current extracted U was higher than the former extracted U at the U levels of 166 and 329 mg kg^{-1} in soil. In contrast, the former extractable U was higher than the current one at the U level of 643 mg kg^{-1} in soil. It is therefore concluded that the U applied more recently to the soil (the addition of U to the soil occurred one time only in July 2000) was more available than that applied earlier.

This observation is in a good agreement with that of Sheppard and Evenden (1988). They mentioned that the recent applied U had higher available U for plants than the old applied U in the field. The above results also revealed that the time effect on the U extractability is plant type dependent.

4.2 Extractable U in incubation experiment soil samples

The investigation of this group of soil samples aimed to study the effect of the addition of different types of organic materials on the extractability of U assessed by the four extractants. In addition the effect of the total U concentration in soil on the U extractability was investigated. Furthermore, the effect of storage time on the extractability of U were studied by comparing the former data with current data of the soil content of plant available U, of the same samples.

Organic matter in soil was found to be negatively correlated (r = -62) with extracted U by NH_4Ac. Sheppard and Evenden (1992) also found strong positive correlation (r = 75**) with background U concentration in soils. These results indicated that U could be sorbed, chelated or complexed with soil organic matter.

The presence of humic substances could also have enhanced the mobility of U(VI) as a result of its complex reactions with humic substances. For example, Crancon and Lee (2003) reported that a large fraction of U(VI) was associated with humic materials in various soils. Zhou and Gu (2005) found a strong linear relationship between U(VI) and total organic carbon released from the soil.

On the other hand, (Zielinski et al., 2006) extracted U with 0.1 M $NaHCO_3$ from different soils. The extractable U ranged from 5 to 42 % of the total U, and this correlated positively with organic matter content. They also reported that the fertilizer-derived U and natural U are efficiently sorbed onto soil organic matter and this results in very low concentrations (< 0.1 ppb) of dissolved U in runoff water.

Section on plant uptake and organic U. Morton et al. (2001) found that the U distribution in the plants and the uptake of U by blueberry plants were closely correlated to organically bound oxide fractions (extracted by sodium pyrophosphate) in soil.

In the present research work, as expected, the AAAc-EDTA, NH_4Ac, DTPA extractants and soil solution had different U concentrations from the same soil sample. The range of extracted U with AAAc-EDTA in uncontaminated soil was very narrow. The narrow range of extracted U in uncontaminated soil may be due to the low concentration of U in soil. In the contaminated soil, this range became much wider. The addition of different organic materials may be the reason for this very wide range. The addition of cereal straw resulted in an increase of extracted U compared to the non amended soil or soil amended with milled alfalfa plants. It may be that the addition of different types of organic materials to the U contaminated soil affects the extractability of U. The extracted U by NH_4Ac showed similar ranges in both cases of contaminated and uncontaminated soils.

The extractable U with DTPA was lower than that with AAAc-EDTA and NH_4Ac. The range of extracted U by DTPA was very narrow in the contaminated soil, and the percentage was lower than that in the case of uncontaminated soil samples. The presence of milled alfalfa plants resulted in an increase of extracted U compared to the amended soil with cereal straw. This means that the DTPA was more effective in the case of uncontaminated soil samples (lower concentration of U).

Soluble U in the soil solution showed a similar pattern and range to the U extracted by DTPA. These results implied that, in both the cases of DTPA and soil solution, the lower concentration of U in soil, the higher percentage of extractable U.

The results presented in Table 3.4 reflected highly significant correlations between the total U in the soil and the extractable U with NH_4Ac, AAAc-EDTA and DTPA extractants. This means that the total U concentration in the soil is one of the most important factors affecting the extractability of U in soil. Rufyikiria et al. (2004) found similar relations between the total U in the soil and the extractable U with NH_4Ac and soil solution U. But the results presented here showed no significant correlation ($r=0.45$) was found in this work between the soil solution U and the total U in the soil.

Both soil pH and soil solution pH didn’t correlate well with any of the four extractants used, except with both cases of AAAc-EDTA and soil solution the correlation was higher. This means that, in contrast to the samples of greenhouse experiment, if the effect of soil pH was weak on extractability of U in soil, it was also weaker than the effect of the total soil U concentration.

The study of the effect of storage time on the availability of U in soil in incubation soil samples revealed that the current extracted U (performed in April 2007) was higher than the former extracted U (performed by the year 2004, Lamas et al., 2005) by either AAAc-EDTA or DTPA. Note that the addition of U to the soil occurred only once in July 2000. The results also revealed that the differences between both extractants (the former and the current one) changed depending on soil treatments. This observation was contrary to that in the case of the greenhouse experiment and that of Sheppard and Evenden (1988). These results revealed that the effect of storage time on the availability of U in the soil for plants is not clear and more research is needed for better understanding of the time effect on the U availability in soil.

4.3 Extractable U in Schneeberg (Saxony) soil samples

The soil samples collected from the Schneeberg mining area at Saxony country covered a wide range of U concentrations in soils. This wide range of U concentrations in the samples gave the opportunity to evaluate the efficiency of different extractants on the extractability of U, also to study the effect of pH and P content on the availability of U from soil.

Like the last two soil groups (greenhouse and incubation experiment samples) the AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants extracted different amounts of U from soil. Again, the AAAc-EDTA usually extracted the most U, compared with NH_4Ac and DTPA, from soil samples, although these samples were not the higher U concentration. This may be due to the high pH and P values of these samples (the effect of soil pH and total soil P on the U availability of Saxony soil samples is positive).

The results summarized in Table 3.6 showed that the effect of the soil pH on the U availability (assessed by the four extractants) was contrary to that of the previous observations of the last two soil groups (greenhouse and incubation experiments soil samples). In these two groups, the effect of pH on the U availability in soil was negative in almost all extractants used, but here its effect was positive in all extracting solutions.

Zielinski et al. (1997) found that the U under alkaline conditions (high pH value) was more soluble and leachable, the relation here between soil pH and soil available U was positive. The mechanism controlling the increased solubility of U observed at high pH is the formation of highly soluble carbonate complexes with UO^{2+} ion (Duff et al., 1999; Elless and Lee, 1998; Tyler and Olsson, 2001). On the other hand, Morton et al. (2002) noticed that the soil pH was not correlated with U in podzolized soils.

As expected, the total soil U correlated with the extracted U by AAAc-EDTA, NH_4Ac, soil solution and DTPA. Total U also had a strong correlation with total soil Cd. Soil P had significant correlations with both total soil U and total soil Cd with nearly the same values (r^2= 0.55* and 0.57* respectively). The soil solution P was highly correlated with the soil solution Cd. These results mean that all of the U, Cd and P elements in the soil are geologically linked. Taylor (2007) noticed that the increase of total U concentrations in soils was associated with the use of P fertilizers. Zarcinas et al. (2004) found that the Cd in the soil was highly correlated with soil P.

The results of Saxony soil samples revealed that the As in the soil or in the soil solution didn’t correlate well with total U or total Cd. This observation implied that the origin and behavior of As in the soil were different from that of U and Cd in the soil. The soil As had a positive weak correlation with soil P, while soluble As in the soil solution had a negative weak correlation with soil P. These observations mean that the soil As could be associated with the soil P, and the soil P complexed with it in the soil therefore reduced its solubility in the soil solution.

The effect of total soil P was also positive on the extractability of U and contrary to that of the previous greenhouse experiment soil samples. This is also contrary to that found in the literature. It had non significant positive correlations with the four extractants used. And there are no enough references or knowledge to explain this effect.

4.4 Extractable U in long-term trials soil samples

It was possible to study the effect of long-term addition of P on U concentration in soil with the investigation of the soil samples collected from the two long-term P fertilization experiments (Braunschweig and Freising sites). Also it gave us important information about the effect of the other soil constituents and factors on the U availability.

As usual, the AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants extracted different amounts of U from soil. In addition, differences were seen in samples from the two sites (Braunschweig and Freising).The extracted U by AAAc-EDTA was higher than the extracted U by NH_4Ac in almost all Freising soil samples, while the extracted U by NH_4Ac was higher in Braunschweig samples. The extractable U with DTPA was in the same range in the both sites. The range of soluble U in the soil solution was very low and its values of Freising soil samples were lower than that of Braunschweig soil samples.

Unlike the other soil groups, weak relations were found between the total U and the different U extractants. Additionally, non significant correlations were found among the four extractants used.

U concentrations extracted by three extractants (AAAc-EDTA, DTPA and soil solution) were not significantly effected by soil total P. The exception was NH_4Ac, which had a significant negative correlation with soil P The soil pH also didn’t affect on the extracted U for three extractants used. This time the exception was a significant negative correlation with soil solution. The pH of the soil solution was positively significantly correlated with AAAc-EDTA, while in the same time it had negative significant correlation with NH_4Ac, for long-term trials soils. The low correlation between both soil pH and total soil P and the four extractants used was argued to indicate a large misunderstanding of the factors affecting the U availability in soils. So that further research is needed for better understanding of the factors affecting the U availability in soils.

On the other hand the total soil P had highly significant effects on total U, Cd and Ni in soil. This meant that all of the four elements may have the same origin in the soil, and the long term addition of P fertilizers significantly increased the total soil U, Cd and Ni in the soil. The available P_{CAL} in soil negatively significantly correlated only with

AAAc-EDTA among the four extractants used for long-term trials soils. This result is surprising. However, the relation between available P $_{CAL}$ and AAAc-EDTA was significantly positively correlation in the case of Freising long-term trials soils.

Total S in soil didn't significantly correlate with any of the extractants used. This observation was in a good agreement with that of the greenhouse experiment samples. Also, Zielinski et al. (1997) found a strong positive correlation between the dissolved U and soluble SO_4 in soil. Conversely, the total S in soil found to be one of the most important factors affecting the heavy metals concentration in the soil. It is important because total S correlated well with total U, Cd, Pb, Ni in the soil. This means either that all of the five elements are intrinsically present in the soil matrix in the soil, or that S in the soil affected on their behavior.

The importance of organic matter on the U in soil was also studied from the use of soil samples of long-term trials. Total organic carbon (OC) in the soil of long-term trials was not significantly correlated with AAAc-EDTA or DTPA or NH_4Ac (Table 3.7). This result indicates that the OC effect on U extractability is week. OC also had a significant positive correlation with available P $_{CAL}$, and this means that this method extracted the organic P from the soil. The OC also positively correlated with Pb and negatively correlated with both total U and Ni in soil, these mean that some Pb complexed with organic matter while Ni and U was largely not complexed with organic matter in soils. The OC in the soil also didn't correlate with total soil Cd indicating that Cd was largely not complexed with organic matter in the soil.

The regression relationship between the total soil organic carbon (OC) and the soil total U, Pb and Ni in long-term soil samples are illustrated in Figure 4.1.

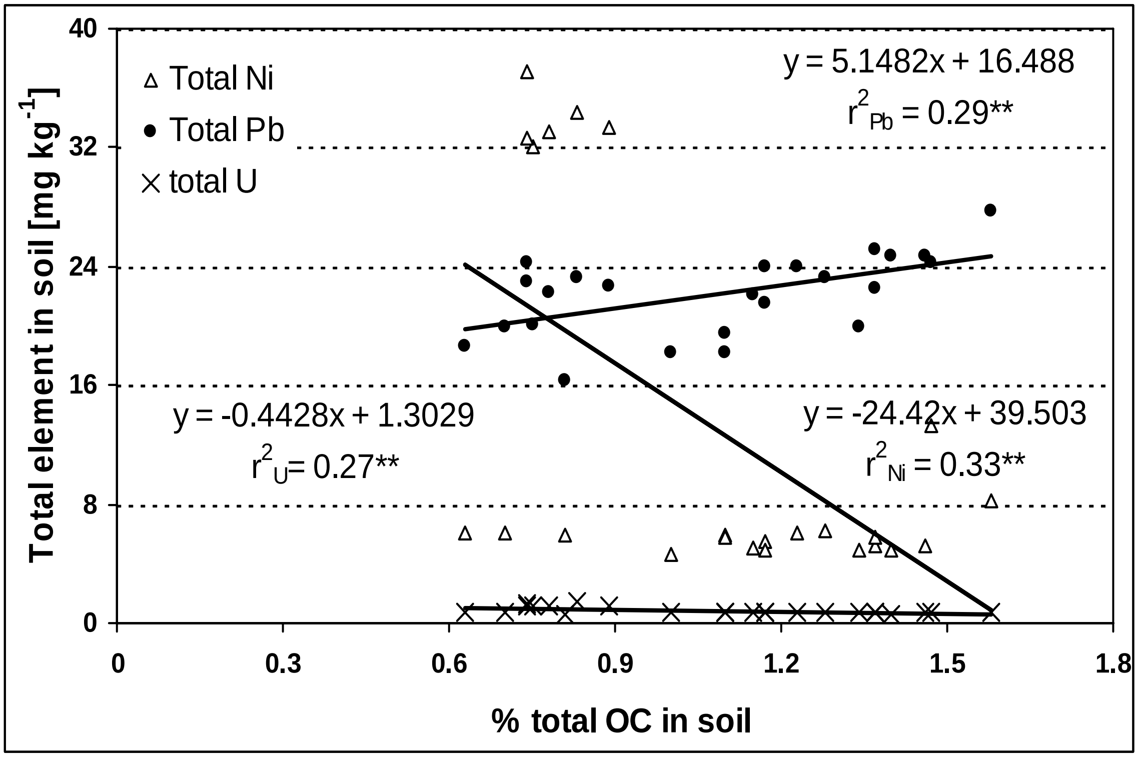

Figure 4.1: Relationship between total organic carbon (OC) and the total U, Pb and Ni in soil samples from long-term trials (Braunschweig and Freising).

These results for the OC were agreed with that of Davis, (1984). The results demonstrated that the Cd adsorption in soil was not significantly affected by the presence of organic matter such as complex formation with the organic ligands. On the other hand, these results are contrarily of that of Zarcinas et al., (2004), who found high correlation between total Cd and OC in the soil. Similar results were found by Blume and Brummer (1991), they reported that Cd and Pb were strongly bound by humus, and a soil which is rich in organic matter has a capacity to strongly immobilize Pb. Soil Ni on the other hand has a medium affinity to bind to organic matter.

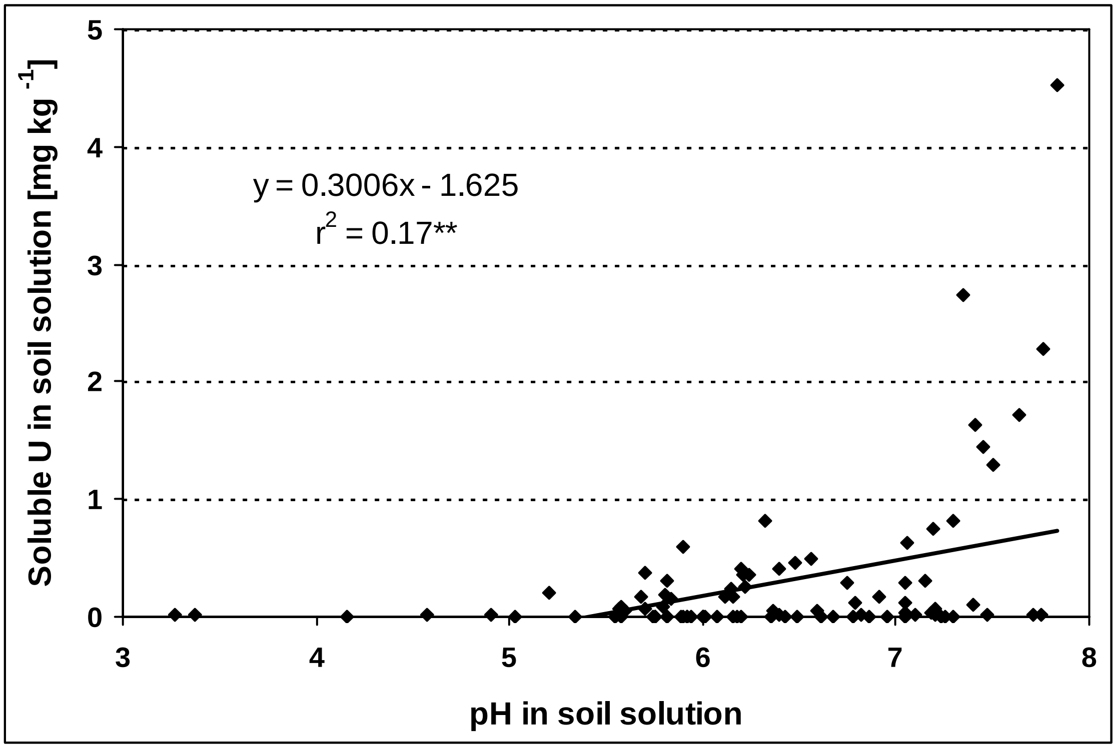

Figure 4.2: Relationship between soil solution pH and soil solution U of all soil samples used in this research work.

The separate results of the four soil groups discussed above didn’t show clear effect of the soil pH or the soil solution pH on the availability of U for plants in soil. The reason was that the soil pH had inconsistent effects (negative or positive) on extractable U in soil. The regression relationship between soil solution pH and the soluble U in the soil solution of all soil samples illustrated in Figure 4.2 clearly shows the overview relation between both of them. Highly significant positive correlation was observed, the r value between both of them was 0.41** (Table A. 29). This finding confirms the fact that the soil pH is one of the most important factors affecting the availability of U in soil.

5. Summary and Conclusions

Normally, U is present in most soils at very low concentrations. According to the United Nations, the normal concentration of U in soils is within the range of 0.3 - 11.7 mg kg^{-1}. The U behavior in soils is very complicated, this because U can be associated with numerous compounds and phases and many factors affect its behavior in soil. Few investigations have been published assessing the U bioavailability and the factors affecting the U bioavailability in soils. Better understanding of different factors governing the U behavior in soils is very useful because it leads to the best possible extraction procedures and the best remediation treatments in U-affected soils.

The main goals of the present work were to evaluate the extractability of U from soil samples assessed by common heavy metal extractants, and compare the differences in the extractability potential between them. Also to find out which of these extractants best predict the plant uptake and concentration of U. And finally to study some of the most important factors affecting the U bioavailability for plants in a wide range of U contaminated soils.

This research work was carried out at the Institute of Plant Nutrition and Soil Science (PB), Federal Agricultural Research Centre (FAL), Braunschweig, Germany. Four soil sample groups were collected covering a wide range of U concentration in soils. The first group of these samples was derived from a previously conducted greenhouse experiment by Rivas (2005). The second soil samples group was derived from a previously conducted incubation experiment under anaerobic conditions carried out by Lamas et al. (2005b). The third soil samples group was collected from the mining area of Schneeberg at the state of Saxony, Germany. The last soil samples group was collected from long term P fertilization experiments located at two sites in Braunschweig and Freising, Germany. Bioavailable U was determined using four extraction methods, which varied with respect to their extraction potential. Extractants used were: acid ammonium acetate-EDTA (AAAc-EDTA) at pH 4.65, 1N ammonium acetate (NH_4Ac) at pH 7.0, diethylene triamine pentaacetic acid (DTPA) at pH 7.3 and soil solution obtained by centrifugation (7,000 rpm for 20 min). Special emphasis was paid to the extraction of soil solution via centrifugation technique.

The most important findings of the research work presented here were:

1- The results of the present research work demonstrated that the U solubility was found to be a function of the extraction solution. The AAAc-EDTA, NH_4Ac, DTPA and soil solution extractants had different capabilities to extract U from soil. The AAAc-EDTA extractant was usually the most powerful extractant in most soil samples tested here with few exceptions, followed by NH_4Ac and then DTPA while the concentration of soluble U in the soil solution was very low. Generally, the AAAc-EDTA extractant was definitely superior to the other extractants; this may be attributed to the presence of chelating agent (EDTA) in this extractant.

2- The results revealed that the maize has a lower ability to release U into the soil in all U levels after the growth than sunflower and faba bean and this observation is well in accordance with the literature. This may be attributed to fact that dicot roots (like sunflower and faba bean) release more U in the soil from its compounds than monocot roots (like maize).

3- The results of the present study implied that the prediction of U bioavailability for plant via the extraction of U from soil is a plant dependent. The AAAc-EDTA was the best predictor for maize U-uptake followed by NH_4Ac. The DTPA and AAAc-EDTA extractants were the best indicators for the U-uptake by sunflower plants. None of the tested extractants was able to predict the U-uptake by faba bean plants. On the other hand, none of the four extractions were able to predict the plant U-concentration of any of the three crops tested here.

4- The total U concentration in the soil is one of the most important factors affecting the extractability of U assessed by the four extractants used in this study. Highly significant and significant correlation coefficients r were found between the total U in soil and the extractable U with the four extractants from soil. This phenomenon was true in most of the soil samples tested here with few exceptions.

5- Soil pH has various effects on the U extractability, a diverse effect of soil pH on the extractable U in soil was found in greenhouse experiment soil samples. The intensity of the effect of soil pH is dependent on the plant cultivated in the soil. In both soil samples of the incubation and long-term experiments, the effect of soil pH on the extractability of U in the soil was negligible. Positive correlations were found between soil pH and the U extracted by any of the extractants in all Saxony samples.

6- Like the effect of soil pH, the results revealed that the presence of P compounds in soil had an inconsistent effect on mobility of U in soil. The total P concentration in soil had a diverse effect on the extractability of U in greenhouse soil samples. The soluble P in soil solution of maize soil samples also had the same trend. Contrary to these findings, the effect of soil P on the extractability of U in Saxony soil samples was positive. The extractable U wasn't affected significantly by soil total P in most samples of long-term trails soil.

7- The results also gave important information about the effect of soil organic matter on the extractability of U in the soil. Total organic carbon (OC) in the soil of long-term trials correlated negatively, but none significantly with AAAc-EDTA and DTPA extractants. While it correlated positively, none correlated significantly with NH_4Ac extractant. This means that part of the U in the soil may complex with organic matter in soil, and NH_4Ac could extract some of U found in organic pool, while both AAAc-EDTA and DTPA couldn't extract this pool. The results also demonstrated that the addition of different types of organic materials (i.e., cereal straw and milled alfalfa plants) to the U contaminated soil affected vary on the availability of U.

8- The results reported here implied that the effect of storage time (time since the contamination with U) is one of the most important factors affecting the availability of U in soil. The former U extractant was the more available than the current U extractant in the greenhouse experiment samples. It could be concluded that the more recently applied U was more available than the older U applied in the greenhouse experiment samples. The results also revealed that the effect of storage time on the U extractability is plant type dependent. The investigation of the effect of storage time in the incubation experiment was the opposite of that of the greenhouse experiment, and changed depending on the soil treatments. Due to these results we concluded that the effect of storage time on the U extractability for plants in the soil is not clear and better understanding of this factor is needed on the U availability.

9- The other factors studied in this work had negligible effects on the extractable U. The N and S fertilization rates had weak correlations with the extractable U from soil with the four extractants in all greenhouse soil samples. Similar results were found in the long-term trial samples. The total concentration of S in soil didn't correlate with the extractability of U in all samples of long-term soil trials.

10- The presence of P compounds in the soil had an effect on the other heavy metals in the soil. The results of the long-term trials indicated that the total soil P had highly significant correlations with the total U, Cd and Ni in soil. This may be due to the addition of P fertilizers, which may be the source of these heavy metals in the soil. A similar phenomenon was found in Saxony soils, the results revealed that the U, Cd and P elements are highly correlated with each other in the soil.

11- The total content of S in the soil was found to be one of the important factors affecting the heavy metals concentration rather than U in the soil, because it correlated well with the total U, Cd, Pb, Ni in the soil. This means that all of the five elements are intrinsically present in the soil matrix.

12- Soil organic matter (expressed as OC in long-term samples) also impacted on the other heavy metals in the soil rather than U like Pb and Ni. The Pb was found to be complexed (positively correlated with OC) with organic matter, while Ni was not complexed (negatively correlated with OC) with organic matter in soils. On the other hand, the OC didn't correlate with total Cd in the soil.

Based on the results of the present work, it is therefore proposed that future investigations are needed for better comprehension of the behavior of U in soils with a wide range of U contamination and different soil characteristics. These investigations are also needed for better understanding of the factors affecting the extractability of U, which reflects the U bioavailability for plant in soils. A careful examination in the future of the detailed results of all investigations in the field of U should be useful in devising new soil extractants that may be of greater universal use than the extractants used in these investigations. With the limited results obtained from this research, it wasn’t possible to discover the ideal extractant for all soils with many different characteristics.

Zusammenfassung und Schlussfolgerung

Uran (U) ist unter natürlichen Bedingungen in Böden in sehr geringer Konzentration vorhanden. Nach den United Nations umfasst der Bereich der möglichen U-Bodenkonzentrationen 0,3 bis 11,7 mg kg^{-1}. Das Verhalten von U im Boden ist sehr komplex, da U in verschiedenen Verbindungen und Phasen vorkommt. Nur wenig Literatur ist veröffentlicht, die sich mit der U-Bioverfügbarkeit selbst und den Einflussfaktoren auf die Bioverfügbarkeit im Boden befasst. Ein besseres Verständnis dieser Prozesse ist Voraussetzung, um passende Extraktionsverfahren zu finden, die die Bioverfügbarkeit von U in kontaminierten Böden bestmöglich abbilden.

Das Hauptziel der vorliegenden Arbeit war es, U-Extraktionsverfahren aus herkömmlichen Schwermetallextraktionsverfahren zu evaluieren und diese hinsichtlich ihres Extraktionspotentials zu vergleichen. Im Ergebnis sollte das beste Verfahren für die Vorhersage der U-Pflanzenaufnahme aufgezeigt und die wichtigsten Parameter, die die Bioverfügbarkeit von U für Pflanzen in unterschiedlich U-kontaminierten Böden beeinflussen, bestimmt werden.

Die Arbeit wurde am Institut für Pflanzenernährung und Bodenkunde (PB) der Bundesforschungsanstalt für Landwirtschaft (FAL) in Braunschweig, Deutschland, durchgeführt. Vier Gruppen von Bodenproben wurden untersucht, die den weiten Bereich praktisch möglicher U-Konzentrationen abdecken.

Die erste Bodenprobengruppe wurde aus einem vorherigen Gefäßversuch von Rivas (2005) gewonnen; die zweite Probengruppe aus einem Inkubationsversuch unter anaeroben Verhältnissen (Lamas et al., 2005b), die dritte stammte aus einer Bergbauregion in Schneeberg (Sachsen, Deutschland) und die letzte Gruppe von Bodenproben entstammte Böden von zwei P-Dauerdüngungsversuchen (Freising und Braunschweig, Deutschland).

Die Bioverfügbarkeit von U wurde mittels vier verschiedener Extraktionsmethoden untersucht, die sich in ihrem Extraktionspotential unterschieden.

Für die Extraktion wurden AAAc-EDTA bei pH 4,65, 1N NH_4Ac bei pH 7,0, DTPA bei pH 7,3, sowie die durch Zentrifugation gewonnene Bodenlösung (20 min bei 7.000 U/min) eingesetzt.

Die Hauptergebnisse der Arbeit werden im Folgenden vorgestellt:

1. Die Arbeit zeigte, dass die U-Löslichkeit eine Funktion der Stärke der Extraktionslösung ist. Die Extraktionsergebnisse von AAAc-EDTA, NH_4Ac, DTPA und Bodenlösung variierten für U in Abhängigkeit von der Herkunft der Bodenproben. Die AAAc-EDTA-Lösung erzielte die besten Ergebnisse, gefolgt von NH_4Ac und DTPA, wenn die Konzentration von löslichem U im Boden sehr gering war. Generell war AAAc-EDTA allen anderen Extraktionsmitteln überlegen. Vermutlich liegt das an dem enthaltenen Cheliermittel (EDTA).

2. Die Versuche zeigten, dass Mais im Vergleich zu Sonnenblume und Ackerbohne ein geringeres Potential hat, aufgenommenes U über die Wurzel wieder in den Boden abzugeben. Das Wurzelsystem der dikotylen Sonnenblume und Ackerbohne kann mehr U in den Boden abgeben als die Wurzeln der monokotylen Pflanze Mais.

3. Es ist in der Studie aufgezeigt worden, dass die Vorhersage der U-Aufnahme pflanzenartenabhängig ist. Für die Vorhersage der U-Aufnahme von Mais aus U-kontaminierten Böden ist AAAc-EDTA das geeignetste Extraktionsmittel, gefolgt von NH_4Ac. Bei Sonnenblumen eignet sich DTPA, gefolgt von AAAc-EDTA am besten. Keines der geprüften Extraktionsmittel ermöglichte eine zutreffende Vorhersage für U-Aufnahme von Ackerbohnen. Mit keinem der vier Extraktionsmittel konnten Ergebnisse erzielt werden, die zuverlässig eine Beziehung zwischen dem aus dem Boden extrahierbaren U und der U-Konzentration im Blatt- und Stängelgewebe der drei Kulturpflanzen darstellen.

4. Die absolute U-Konzentration im Boden ist der Haupteinflussfaktor auf die Bioverfügbarkeit von U im Boden. Hochsignifikante Korrelationskoeffizienten

wurden bei dem Vergleich von U im Boden und der extrahierbaren U-Menge gefunden. Dies konnte in den meisten Bodenproben bewiesen werden.

5. Die U-Extrahierbarkeit variiert mit dem Boden-pH, wie anhand der Bodenproben aus einem Gefäßversuch gezeigt werden konnte. Bei dem Boden aus Sachsen bestand eine positive Korrelation zwischen Boden-pH und extrahierbarem U bei allen vier Extraktionsmitteln.

6. Die Phosphor (P)-Konzentration im Boden hatte abhängig von der Probenherkunft unterschiedliche Einflüsse auf die Bioverfügbarkeit von U. Vergleichbar war der Einfluss des Gehaltes an löslichem P im Boden.

7. Die Studie zeigte zudem den Einfluss von organischer Substanz auf die U-Bioverfügbarkeit. Der organisch gebundene Kohlenstoff im Boden des Langzeitversuches hat einen nicht-signifikanten negativen Effekt bei AAAc-EDTA- und DTPA-Extraktion. NH_4Ac verhält sich nicht-signifikant positiv. Das kann bedeuten, dass U an Humuskomplexen im Boden gebunden wird, die nur NH_4Ac lösen kann. Es zeigte sich, dass verschiedene Formen von organischem Material im U-kontaminierten Boden Einfluss auf die Bioverfügbarkeit von U haben.

8. Die Ergebnisse der Untersuchungen zeigen, dass die U-Verfügbarkeit im Boden zeit- und pflanzenartabhängig ist. Im Rahmen dieser Arbeit konnte jedoch kein sicherer Trend für den zeitlichen Effekt der U-Bioverfügbarkeit abgeleitet werden.

9. Bei N- und S-Düngung gab es keine Beziehung zur extrahierten U-Menge.

10. P-Verbindungen haben Einfluss auf Schwermetalle im Boden. Die Auswertung der Langzeitversuche zeigte, dass der Gesamt-P-Gehalt im Boden hoch signifikant mit U, Cd und Ni korreliert. Vermutlich liegt es an der vorhandenen Schwermetallkonzentration im P-Dünger. Dies wurde ebenfalls im Boden aus Sachsen gefunden und es zeigten sich enge Korrelationen zwischen U, Cd und P.

11. Zwischen dem Gesamt-S-Gehalt im Boden und den gemessenen Gesamt-U-, Cd-, Pb- und Ni- Konzentrationen wurde eine enge Beziehung nachgewiesen.

12. Organische Kohlenstoffgehalte im Boden haben einen größeren Einfluss auf Schwermetalle wie Pb und Ni als auf U. Pb ist im Gegensatz zu Ni an organisches Material gebunden (positive Korrelation bei Pb, negative bei Ni). Keinerlei Korrelationen bestanden mit Cd im Boden.

Die Ergebnisse legen nahe, dass zukünftige Arbeiten zu dieser Thematik größeres Augenmerk auf Beziehungen zwischen verschiedenen U-Gehalten im Boden und der U-Extrahierbarkeit unter Berücksichtigung unterschiedlicher Bodencharakteristika gelegt werden sollte. Keines der in dieser Arbeit untersuchten Extraktionsmittel erwies sich als bevorzugt geeignet, die U-Aufnahme durch Pflanzen aus kontaminierten Böden verlässlich vorauszusagen.

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7. Appendix

Table A.1: Extractable U with AAAc-EDTA, DTPA, NH_4Ac and soil solution [mg kg^{-1} and % of the total] in soil from pot experiment with sunflower in relation to the presence of P fertilizer

Presence of P	U level in soil	AAAc-EDTA	DTPA	NH_4 Ac (pH 7)	Soil solution	AAAc-EDTA	DTPA	NH_4 Ac (pH 7)	Soil solution
		mg kg^{-1}				Relative to total U (%)			
With P	0.34	0.65	0.004	0.05	0.02	190.4	1.2	14.0	6.82
		0.03	0.004	0.02	0.36	8.8	1.1	5.8	105.06
		0.03	0.007	0.03	0.01	8.4	2.0	8.6	3.18
		0.02	0.002	0.02	0.00	6.4	0.5	7.1	1.10
Without P	166	79.85	1.63	31.26	0.17	48.1	1.0	18.8	0.10
		78.70	1.91	31.04	0.17	47.4	1.2	18.7	0.10
		77.64	2.01	31.56	0.45	46.8	1.2	19.0	0.27
		75.82	2.19	29.44	0.02	45.7	1.3	17.7	0.01
Without P	329	165.86	4.82	73.40	0.41	50.4	1.5	22.3	0.12
		162.51	4.11	65.35	0.31	49.4	1.3	19.9	0.09
		167.67	5.53	70.66	0.82	51.0	1.7	21.5	0.25
		164.81	8.59	67.89	0.59	50.1	2.6	20.6	0.18
With P	643	49.75	0.49	9.67	0.06	7.7	0.1	1.5	0.01
		50.32	0.57	11.61	0.05	7.8	0.1	1.8	0.01
		49.42	0.54	9.78	0.12	7.7	0.1	1.5	0.02
		47.31	0.72	9.82	0.11	7.4	0.1	1.5	0.02

Table A.2: Extractable U with AAAc-EDTA, DTPA, NH_4Ac and soil solution [mg kg^{-1} and % of the total] in soil from pot experiment with faba bean in relation to the presence of P fertilizer.

Presence of P	**U level in soil**	**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**	**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**
		mg kg^{-1}				**Relative to total U (%)**			
With P	0.34	0.4	0.01	0.06	0.00	105.1	2.0	18.5	1.06
		0.1	0.01	0.04	-	15.4	1.6	11.5	-
Without P	166	70.9	1.44	27.15	0.15	42.7	0.9	16.4	0.09
		69.7	2.46	26.00	0.18	42.0	1.5	15.7	0.11
Without P	329	145.7	5.19	48.21	0.36	44.3	1.6	14.7	0.11
		146.6	4.78	54.03	0.49	44.6	1.5	16.4	0.15
With P	643	44.5	0.53	8.25	0.07	6.9	0.1	1.3	0.01
		48.3	0.51	11.29	0.09	7.5	0.1	1.8	0.01

Table A.3: Soil solution pH, EC and P and soil pH ($CaCl_2$) in maize soil samples.

Soil samples	**Solution pH**	**EC dS/m or mS/cm**	**Solution P (mg kg^{-1})**	**Soil pH ($CaCl_2$)**
166 mg kg^{-1} U	6.91	2.37	0.000	5.83
166 mg kg^{-1} U	5.2	4.23	0.030	5.43
166 mg kg^{-1} U	7.15	0.87	0.030	6.28
166 mg kg^{-1} U	6.15	1.71	0.030	5.77
329 mg kg^{-1} U	6.75	2.32	0.030	5.87
329 mg kg^{-1} U	5.7	4.45	0.030	5.41
329 mg kg^{-1} U	7.19	0.81	0.030	6.2
329 mg kg^{-1} U	6.2	2.37	0.030	5.44
173 mg kg^{-1} U	7.2	1.94	0.544	6.46
173 mg kg^{-1} U	7.05	3.13	1.058	6.31
173 mg kg^{-1} U	7.18	3.26	0.574	6.68
173 mg kg^{-1} U	7.4	0.92	0.574	6.6
385 mg kg^{-1} U	7.3	2.03	1.813	6.52
385 mg kg^{-1} U	7.05	3.37	2.387	6.26
385 mg kg^{-1} U	7.41	1.02	1.964	6.67
385 mg kg^{-1} U	7.5	0.82	2.478	6.64
643 mg kg^{-1} U	7.45	2.46	1.420	6.58
643 mg kg^{-1} U	7.06	4.29	1.753	6.24
643 mg kg^{-1} U	7.64	0.83	2.024	6.63
643 mg kg^{-1} U	7.35	0.77	2.266	6.58

Table A.4: Soil solution pH, EC and P and soil pH ($CaCl_2$) in sunflower soil samples.

Soil samples	**Solution pH**	**EC dS/m or mS/cm**	**Solution P (mg kg^{-1})**	**Soil pH ($CaCl_2$)**
without U	7.2	1.72	2.719	6.35
without U	6.24	2.47	0.030	6.4
without U	7.47	0.83	2.236	6.49
without U	7.3	1.28	2.417	6.37
166 mg kg^{-1} U	6.16	2.32	0.091	5.64
166 mg kg^{-1} U	5.68	3.58	0.030	5.31
166 mg kg^{-1} U	6.48	0.77	0.091	5.87
166 mg kg^{-1} U	6.82	3.38	2.447	5.87
329 mg kg^{-1} U	6.4	1.55	0.091	5.8
329 mg kg^{-1} U	5.82	3.65	0.030	5.67
329 mg kg^{-1} U	6.32	0.59	0.151	6.07
329 mg kg^{-1} U	5.9	1.32	0.030	5.8
643 mg kg^{-1} U	6.59	2.05	1.088	6.45
643 mg kg^{-1} U	6.36	3.77	1.813	6.25
643 mg kg^{-1} U	7.05	0.58	2.055	6.5
643 mg kg^{-1} U	6.79	0.77	2.599	6.45

Table A.5: soil solution pH, EC and P and soil pH ($CaCl_2$) in faba bean soil samples.

Soil samples	**Solution pH**	**EC dS/m or mS/cm**	**Solution P (mg kg^{-1})**	**Soil pH ($CaCl_2$)**
without U	5.82	1.8	3.324	6.42
without U	6.16	1.19	3.142	6.44
166 mg kg^{-1} U	5.84	1.88	0.091	5.97
166 mg kg^{-1} U	5.81	1.39	0.030	6.28
329 mg kg^{-1} U	6.21	1.33	0.060	6.41
329 mg kg^{-1} U	6.56	0.99	0.091	6.18
643 mg kg^{-1} U	5.57	1.93	1.783	6.5
643 mg kg^{-1} U	5.79	1.28	1.813	6.52

Table A.6: The effect of storage time: comparison between the former extracted U (Rivas 2005) by AAAc-EDTA and the current extracted U by AAAc-EDTA in this study from maize soil samples.

Soil samples	**Current AAAc-EDTA**	**Former AAAc-EDTA**
	mg kg^{-1}	
166 mg kg^{-1} U	42.4	64.32
166 mg kg^{-1} U	42.3	63.7
166 mg kg^{-1} U	29.8	56.0
166 mg kg^{-1} U	45.1	60.0
329 mg kg^{-1} U	103.1	118.2
329 mg kg^{-1} U	79.7	110.7
329 mg kg^{-1} U	95.2	124.5
329 mg kg^{-1} U	62.7	127.1
173 mg kg^{-1} U	13.3	15.9
173 mg kg^{-1} U	14.2	16.8
173 mg kg^{-1} U	14.0	17.5
173 mg kg^{-1} U	13.9	18.8
385 mg kg^{-1} U	25.4	48.4
385 mg kg^{-1} U	29.0	33.14
385 mg kg^{-1} U	26.3	32.5
385 mg kg^{-1} U	24.9	30.4
643 mg kg^{-1} U	53.6	84.9
643 mg kg^{-1} U	56.5	62.8
643 mg kg^{-1} U	50.5	70.7
643 mg kg^{-1} U	48.9	67.8

Table A.7: The effect of storage time: comparison between the former extracted U (Rivas 2005) by AAAc-EDTA and the current extracted U by AAAc-EDTA in this study from in sunflower soil samples.

Soil samples	**Current AAAc-EDTA**	**Former AAAc-EDTA**
	mg kg^{-1}	
166 mg kg^{-1} U	79.85	57.4
166 mg kg^{-1} U	78.70	60.1
166 mg kg^{-1} U	77.64	59.9
166 mg kg^{-1} U	75.82	60.1
329 mg kg^{-1} U	165.86	122.9
329 mg kg^{-1} U	162.51	108.6
329 mg kg^{-1} U	167.67	117.7
329 mg kg^{-1} U	164.81	113.7
643 mg kg^{-1} U	49.75	63.7
643 mg kg^{-1} U	50.32	64.7
643 mg kg^{-1} U	49.42	62.6
643 mg kg^{-1} U	47.31	65.9

Table A.8: The effect of storage time: comparison between the former extracted U (Rivas 2005) by AAAc-EDTA and the current extracted U by AAAc-EDTA in this study from faba bean soil samples.

Soil samples	**Current AAAc-EDTA**	**Former AAAc-EDTA**
	mg kg^{-1}	
166 mg kg^{-1} U	70.9	54.1
166 mg kg^{-1} U	69.7	52.5
329 mg kg^{-1} U	145.7	114.2
329 mg kg^{-1} U	146.6	124.8
643 mg kg^{-1} U	44.5	60.2
643 mg kg^{-1} U	48.3	75.2

Table A.9: ANOVA for the effect of total soil U on U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution, maize U concentration and uptake, soil pH, P, S and N levels in soil.

		Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
AAAc-EDTA	Between Groups	11991.81	4	2997.95	39.359	.000
	Within Groups	1142.55	15	76.17		
	Total	13134.36	19			
DTPA	Between Groups	59.85	4	14.96	121.257	.000
	Within Groups	1.85	15	.123		
	Total	61.70	19			
NH_4Ac	Between Groups	7570.34	4	1892.59	240.935	.000
	Within Groups	117.83	15	7.86		
	Total	7688.17	19			
Soil solution	Between Groups	6.65	4	1.66	7.303	.002
	Within Groups	3.41	15	.228		
	Total	10.06	19			
Plant concentration	Between Groups	18.34	4	4.59	1.118	.384
	Within Groups	61.50	15	4.10		
	Total	79.84	19			
Plant uptake	Between Groups	365.05	4	91.26	6.645	.003
	Within Groups	206.01	15	13.73		
	Total	571.06	19			
P level	Between Groups	7191245	4	1797811.20	.	.
	Within Groups	.000	15	.000		
	Total	7191245	19			
S level	Between Groups	.000	4	.000	.000	1.000
	Within Groups	12500.00	15	833.33		
	Total	12500.00	19			
N level	Between Groups	.000	4	.000	.000	1.000
	Within Groups	312500.0	15	20833.33		
	Total	312500.0	19			
P in soil Solution	Between Groups	16.318	4	4.08	68.567	.000
	Within Groups	.892	15	.059		
	Total	17.210	19			
Soil pH	Between Groups	2.62	4	0.65	9.13	.001
	Within Groups	1.07	15	.072		
	Total	3.69	19			

Table A.10: ANOVA for the effect of total soil U on U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution, sunflower U concentration and uptake, soil pH, P, S and N levels in soil.

		Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
AAAc-EDTA	Between Groups	57587.64	3	19195.88	8172.103	.000
	Within Groups	28.187	12	2.35		
	Total	57615.82	15			
DTPA	Between Groups	80.56	3	26.85	27.167	.000
	Within Groups	11.86	12	.99		
	Total	92.42	15			
NH_4Ac	Between Groups	11254.18	3	3751.39	1083.946	.000
	Within Groups	41.53	12	3.46		
	Total	11295.71	15			
Soil solution	Between Groups	.523	3	.17	6.105	.009
	Within Groups	.343	12	.029		
	Total	.866	15			
Plant concentration	Between Groups	40.96	3	13.65	12.336	.001
	Within Groups	13.28	12	1.11		
	Total	54.24	15			
Plant uptake	Between Groups	660.86	3	220.29	7.897	.004
	Within Groups	334.76	12	27.89		
	Total	995.62	15			
P level	Between Groups	5992704	3	1997568.00	.	.
	Within Groups	.000	12	.000		
	Total	5992704	15			
S level	Between Groups	.000	3	.000	.000	1.000
	Within Groups	10000.0	12	833.33		
	Total	10000.0	15			
N level	Between Groups	.000	3	.000	.000	1.000
	Within Groups	250000.0	12	20833.33		
	Total	250000.0	15			
Soil pH	Between Groups	1.76	3	0.59	20.51	.000
	Within Groups	0.34	12	.029		
	Total	2.11	15			

Table A.11: ANOVA for the effect of total soil U on U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution, faba bean U concentration and uptake, soil pH, P, and S levels in soil.

		Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
AAAc-EDTA	Between Groups	22299.07	3	7433.02	3543.75	.000
	Within Groups	8.39	4	2.097		
	Total	22307.45	7			
DTPA	Between Groups	29.98	3	9.99	66.14	.001
	Within Groups	.604	4	.151		
	Total	30.59	7			
NH_4Ac	Between Groups	3000.44	3	1000.15	180.06	.000
	Within Groups	22.218	4	5.56		
	Total	3022.66	7			
Soil solution	Between Groups	.172	3	.057	18.90	.019
	Within Groups	.009	3	.003		
	Total	.181	6			
Plant concentration	Between Groups	27.29	3	9.097	19.99	.007
	Within Groups	1.82	4	.455		
	Total	29.11	7			
Plant uptake	Between Groups	190.99	3	63.665	6.24	.055
	Within Groups	40.78	4	10.196		
	Total	231.78	7			
P level	Between Groups	2996352	3	998784.0	.	.
	Within Groups	.000	4	.00		
	Total	2996352	7			
S level	Between Groups	.000	3	.000	.000	1.000
	Within Groups	5000.0	4	1250.0		
	Total	5000.0	7			
Soil pH	Between Groups	.17	3	.057	3.035	.156
	Within Groups	0.075	4	0.019		
	Total	0.25	7			

Table A.12: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and plant U concentration and uptake by maize, soil pH, P, S and N levels in soil.

	DTPA	**NH_4Ac**	**Soil solution**	**Plant concentration**	**Plant uptake**	**U level**	**P level**	**S level**	**N level**	**Solution P**
AAAc-EDTA	.82**	.86**	.12	.27	.69**	.31	-.61**	-.09	-.07	-.34
DTPA	-	.97**	-.22	-.01	.42	-.13	-.80**	.02	.00	-.63**
NH_4Ac		-	-.18	.04	.50*	-.08	-.82**	-.05	.03	-.62**
Soil solution			-	-.08	.18	.79**	.39	.34	-.06	.67**
Plant concentration				-	.70**	.43	.08	-.52*	.27	.16
Plant uptake					-	.51*	-.28	-.12	.27	-.04
U level						-	.43	.00	.00	.68**
P level							-	.00	.00	.82**
S level								-	.00	.05
N level									-	.12

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

n = 20

Table A.13: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and plant U concentration and uptake by sunflower, soil pH, P, S and N levels in soil.

	DTPA	**NH_4Ac**	**Solution**	**Plant U concentration**	**Plant uptake**	**U level**	**P level**	**S level**	**N level**	**Soil pH ($CaCl_2$)**
AAAc-EDTA	.91**	.99**	.74**	.48	.58*	.28	-.81**	-.01	-.01	-.64**
DTPA	-	.92**	.78**	.39	.60*	.10	-.74**	.16	.08	-.56*
NH_4Ac		-	.77**	.35	.49	.12	-.85**	-.01	-.03	-.68**
Solution			-	.13	.39	.01	-.59*	.15	-.12	-.35
Plant concentration				-	.80**	.82**	-.05	-.18	.24	-.07
Plant uptake					-	.68**	-.19	.24	.24	-.08
U level						-	.16	.00	.00	.19
P level							-	.00	.00	.90**
S level								-	.00	.27
N Level									-	-.18

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).
n = 16

Table A.14: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and plant U concentration and uptake by faba bean, soil pH, P and S in soil.

	DTPA	**NH_4Ac**	**Soil solution**	**Plant U concentration**	**Plant Uptake**	**U Level**	**P level**	**S level**	**Soil pH ($CaCl_2$)**
AAAc-EDTA	.96**	.98**	.97**	.14	.14	.29	-.80*	.01	-.38
DTPA	-	.97**	.95**	-.06	-.06	.09	-.82*	.04	-.33
NH_4Ac		-	.98**	-.01	-.002	.14	-.87**	.05	-.50
Solution			-	-.16	-.15	.01	-.74	.33	-.35
Plant concentration				-	.98**	.96**	.24	-.15	.33
Plant Uptake					-	.90**	.21	-.24	.26
U Level						-	.16	.00	.35
P level							-	.00	.74*
S level								-	.10

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).
n = 8

Table A.15: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and plant U concentration and uptake by the three crops (maize, sunflower and faba bean), soil pH, P, S and N levels in soil.

	DTPA	**NH_4Ac**	**Soil solution**	**Plant concentration**	**Plant uptake**	**U level**	**P level**	**S level**	**N level**	**Soil pH ($CaCl_2$)**	**Solution pH**
AAAc-EDTA	.87**	.92**	.10	.32*	.42**	.23	-.70**	-.02	-.03	-.49**	-.38*
DTPA	-	.95**	.01	.15	.40**	.01	-.77**	.08	.04	-.58**	-.39**
NH_4Ac		-	.03	.17	.39**	.04	-.83**	-.02	.002	-.68**	-.43**
solution			-	-.07	.24	.43**	.15	.25	-.06	.27	.39**
Plant concentration				-	.73**	.67**	.059	-.34*	.26	-.10	-.24
Plant uptake					-	.66**	-.13	.02	.24	-.21	-.10
U level						-	.27	.00	.00	.26	.12
P level							-	.00	.00	.80**	.50**
S level								-	.00	.25	.28
N level									-	-.28	-.37*
Soil pH										-	.61**

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).
n = 44

Table A.16: Extractable U with AAAc-EDTA, DTPA, NH_4Ac and soil solution [mg kg^{-1} and % of the total] in soil from incubation experiment soil samples.

Treatments		**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**	**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**
Additives	**U contamination**	**Extracted U [mg kg^{-1}]**				**Relative to total U (%)**			
Without	Un-contaminated	0.05	0.010	0.02	0.005	9.4	1.8	3.1	0.83
Without		0.04	0.003	0.01	0.001	6.5	0.6	2.6	0.14
Straw		0.05	0.006	0.01	0.004	9.0	1.0	2.5	0.64
Straw		0.04	0.005	0.02	0.002	7.1	1.0	2.9	0.30
Alfalfa		0.05	0.007	0.03	0.013	8.3	1.3	5.3	2.33
Alfalfa		0.04	0.009	0.04	0.020	6.8	1.6	7.2	3.59
Without	contaminated with 500 mg kg^{-1}	85.02	0.525	17.64	0.015	17.0	0.1	3.5	0.003
Without		99.91	0.502	33.78	0.025	20.0	0.1	6.8	0.01
Straw		107.60	1.582	12.20	0.247	21.5	0.3	2.4	0.05
Straw		108.32	1.193	16.40	0.177	21.7	0.2	3.3	0.04
Alfalfa		38.05	2.561	25.12	4.527	7.6	0.5	5.0	0.91
Alfalfa		16.90	1.142	7.45	2.284	3.4	0.2	1.5	0.46

Table A.17: Soil solution pH, EC and P and soil pH ($CaCl_2$) in incubation experiment soil samples.

Soil samples	**Solution pH**	**EC dS/m or mS/cm**	**Solution P (mg kg^{-1})**	**soil pH ($CaCl_2$)**
Pure soil	7.25	3.17	0.060	6.3
Pure soil	6.67	2.75	0.091	6.7
Straw	6.35	8.23	0.030	6.27
Straw	6.61	4.84	0.060	6.55
Alfalfa	7.75	7.89	0.604	6.89
Alfalfa	7.71	8.14	0.906	7.02
U	7.10	2.53	0.030	6.3
U	6.4	2.67	0.030	6.25
U+straw	6.22	7.98	0.060	6.3
U+straw	6.12	8.33	0.060	6.54
U+alfalfa	7.83	-	-	7.0
U+alfalfa	7.76	7.79	-	6.9

Table A.18: The effect of storage time: comparison between the former extracted U (Lamas et al., 2005) by AAAc-EDTA or DTPA and the current extracted U by AAAc-EDTA or DTPA in this study from incubation experiment soil samples.

Soil samples	**Current AAAc-EDTA**	**Current DTPA**	**Former AAAc-EDTA**	**Former DTPA**
	mg kg^{-1}			
U	85.0	0.52	67.97	0.22
U	99.9	0.50	74.86	0.58
U+straw	107.6	1.58	5.67	0.55
U+straw	108.3	1.19	9.5	0.17
U+alfalfa	38.1	2.56	25.51	0.14
U+alfalfa	16.9	1.14	64.48	7.77

Table A.19: ANOVA for the effect of total soil U on U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and soil solution pH and EC and soil pH ($CaCl_2$) in incubation experiment soil samples**.**

		Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
AAAc-EDTA	Between Groups	17305.21	1	17305.21	22.70	.001
	Within Groups	7623.28	10	762.33		
	Total	24928.49	11			
DTPA	Between Groups	4.61	1	4.61	15.71	.003
	Within Groups	2.94	10	.294		
	Total	7.55	11			
NH_4Ac	Between Groups	1053.94	1	1053.94	23.75	.001
	Within Groups	443.82	10	44.382		
	Total	1497.76	11			
Soil solution	Between Groups	4.38	1	4.38	2.58	.139
	Within Groups	16.98	10	1.69		
	Total	21.36	11			
Solution pH	Between Groups	.069	1	.069	.15	.71
	Within Groups	4.76	10	.476		
	Total	4.83	11			
Solution EC	Between Groups	2.73	1	2.73	.28	.608
	Within Groups	97.08	10	9.71		
	Total	99.81	11			
Soil pH	Between Groups	.016	1	.016	.16	.698
	Within Groups	1.01	10	.10		
	Total	1.02	11			

Table A.20: Soil solution pH, EC and P in Saxony soil samples.

Soil samples	Solution pH	EC dS/m or mS/cm	Solution P (mg kg^{-1})
1	5.89	1.15	0.332
2	5.55	1.1	0.091
3	5.55	1.0	0.181
4	5.58	1.06	0.332
5	5.74	0.8	0.060
6	3.27	0.92	1.511
7	3.37	0.53	0.604
8	4.16	0.19	0.121
9	5.03	0.77	0.483
10	5.34	0.38	0.181
11	4.9	1.84	0.121
12	4.57	-	0.212
13	5.7	0.93	0.242
14	5.58	0.85	0.121

Table A.21: ANOVA for the effect of total soil U on U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and soil solution pH, EC, P, Cd, As and soil pH ($CaCl_2$), P, Cd and As in Saxony soil samples**.**

		Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
AAAc-EDTA	Between Groups	206.74	12	17.23	861.41	.027
	Within Groups	.02	1	.020		
	Total	206.76	13			
DTPA	Between Groups	1.62	12	.135	.	.
	Within Groups	.00	1	.000		
	Total	1.62	13			
NH_4Ac	Between Groups	60.83	12	5.07	350.83	.042
	Within Groups	.014	1	.014		
	Total	60.85	13			
Soil solution	Between Groups	.01	12	.001	54.17	.106
	Within Groups	.00	1	.00		
	Total	.01	13			
Solution pH	Between Groups	9.67	12	.81	8.33	.265
	Within Groups	.097	1	.097		
	Total	9.77	13			
Soil pH	Between Groups	9.20	12	.767	6.66	.295
	Within Groups	.12	1	.16		
	Total	9.32	13			
Soil P	Between Groups	3138288	12	261524.0	1.964	.511
	Within Groups	133128.0	1	133128.0		
	Total	3271416	13			
Solution EC	Between Groups	1.625	12	.135	.127	.984
	Within Groups	1.066	1	1.066		
	Total	2.69	13			
Soil Cd	Between Groups	91.32	12	7.61	16910.95	.006
	Within	.000	1	.000		

	Groups					
	Total	91.320	13			
Soil As	Between Groups	118633.9	12	9886.16	19.07	.177
	Within Groups	518.420	1	518.42		
	Total	119152.4	13			
Solution As	Between Groups	.028	12	.002	32.61	.136
	Within Groups	.00	1	.00		
	Total	.03	13			
Solution Cd	Between Groups	.001	11	.00	1.07	.645
	Within Groups	.00	1	.00		
	Total	.001	12			
Solution P	Between Groups	.074	11	.007	1.87	.520
	Within Groups	.004	1	.004		
	Total	.078	12			

Table A.22: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and total U in soil, soil solution pH and EC, soil pH($CaCl_2$), P, Cd and As and solution As, Cd and P in Saxony soil samples.

	AAAc-EDTA	**DTPA**	**NH_4Ac**	**Solution U**	**Solution pH**	**Soil pH ($CaCl_2$)**	**Soil P**	**Solution EC**	**Soil Cd**	**Soil As**	**Solution As**	**Solution Cd**	**Solution P**
Total U	.86**	.35	.80**	.88**	.24	.37	.55*	-.15	.96**	.14	-.03	.91**	.68*
AAAc-EDTA		.39	.94**	.80**	.31	.26	.46	.08	.70**	.09	.05	.83**	.29
DTPA		-	.35	.33	.56*	.55*	.52	.29	.32	.78**	-.08	.17	-.03
NH_4Ac			-	.95**	.25	.33	.51	-.09	.89**	.11	.01	.93**	.59*
Solution U				-	.17	.24	.43	.03	.73**	.05	.10	.88**	.36
Solution pH					-	.48	.32	.33	.18	.49	-.56*	.14	.01
Soil pH						-	.75**	-.08	.40	.45	-.50	.18	.30
Soil P							-	-.32	.57*	.33	-.43	.34	.34
Solution EC								-	-.27	.20	.14	.01	-.33
Cd									-	.18	-.09	.85**	.82**
As										-	-.16	.003	.03
Solution As											-	-.01	-.23
Solution Cd												-	.72**

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).
n = 14

Table A.23: Extractable U with AAAc-EDTA, DTPA, NH_4Ac and soil solution [mg kg^{-1} and % of the total] in soil from long term (Braunschweig + Freising) soil samples.

Treatments	**Total U in soil**	**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**	**AAAc-EDTA**	**DTPA**	**NH_4 Ac (pH 7)**	**Soil solution**
		[mg kg^{-1}]				**Relative to total U (%)**			
NK	0.65	0.10	0.007	0.06	0.0026	15.64	1.02	8.78	0.40
NK	0.68	0.03	0.008	0.09	0.0008	4.16	1.23	13.50	0.14
NK	0.65	0.02	0.006	0.07	0.0008	2.36	0.90	11.45	0.12
NK	0.68	0.02	0.006	0.07	0.0007	3.42	0.93	10.87	0.10
NK	0.65	0.02	0.006	0.10	0.0007	2.74	0.86	16.11	0.10
NK	0.68	0.02	0.007	0.04	0.0007	2.92	1.00	5.95	0.10
NK+FYM	0.69	0.04	0.005	0.02	0.0006	5.58	0.67	3.24	0.10
NK+FYM	0.67	0.03	0.005	0.02	0.0007	5.17	0.71	3.18	0.10
NK+FYM	0.69	0.02	0.005	0.02	0.0007	2.67	0.70	3.51	0.10
NK+FYM	0.67	0.02	0.007	0.07	0.0013	2.82	1.05	10.91	0.19
NK+FYM	0.69	0.02	0.006	0.11	0.0007	2.52	0.92	15.66	0.09
NK+FYM	0.67	0.03	0.008	0.06	0.0013	3.84	1.17	9.61	0.20
NPK+FYM	0.74	0.03	0.005	0.07	0.0010	3.71	0.73	9.02	0.13
NPK+FYM	0.70	0.02	0.006	0.03	0.0014	3.38	0.91	3.95	0.20
NPK+FYM	0.74	0.02	0.005	0.02	0.0012	2.81	0.63	3.27	0.17
NPK+FYM	0.70	0.02	0.008	0.10	0.0014	2.54	1.12	13.85	0.21
NPK+FYM	0.74	0.03	0.009	0.06	0.0015	3.69	1.20	7.90	0.21
NPK+FYM	0.70	0.03	0.004	0.03	0.0020	3.83	0.62	4.09	0.29
NK	1.29	0.04	0.005	0.02	0.0007	3.36	0.35	1.26	0.05
NK+FYM	1.20	0.04	0.029	0.02	-	3.50	2.40	1.37	-
NK+ straw	1.09	0.04	0.004	0.02	0.0007	3.83	0.40	1.69	0.07
Super phosphate	1.40	0.05	0.004	0.08	0.0006	3.66	0.27	5.90	0.04
Nova phosphate	1.19	0.06	0.018	-	0.0007	5.06	1.47	0.00	0.06
Hyper phosphate	1.17	0.06	0.003	0.02	0.0006	5.18	0.28	1.38	0.05

Table A.24: Total soil P, Cd, Ni, Pb, OC%, S and available P $_{CAL}$ in long-term fertilization trials soil samples (Braunschweig + Freising).

Samples	**Total P**	**Total Cd**	**Total Ni**	**Total Pb**	**P $_{CAL}$**	**OC%**	**Total S**
NK	271	0.06	5.43	21.5	11	1.17	112
NK	215	0.02	5.86	16.29	8.6	0.81	83
NK	369	0.11	4.92	24.75	20.4	1.4	140
NK	303	0.07	5.96	19.43	15.6	1.1	103
NK	379	0.1	5.18	24.65	23.4	1.46	128
NK	392	0.12	13.24	24.28	19.4	1.47	117
NK+FYM	390	0.12	6.04	24	28.5	1.23	127
NK+FYM	415	0.07	6.07	18.56	19.6	0.63	90
NK+FYM	382	0.13	5.18	25.11	26.8	1.37	140
NK+FYM	357	0.1	5.12	22.11	25.1	1.15	110
NK+FYM	415	0.09	5.78	22.5	36.1	1.37	135
NK+FYM	343	0.07	5.76	18.18	22.3	1.1	102
NPK+FYM	449	0.13	6.2	23.3	49.1	1.28	130
NPK+FYM	353	0.09	6.01	19.91	31.4	0.7	104
NPK+FYM	503	0.1	4.84	19.88	71.7	1.34	132
NPK+FYM	375	0.08	4.58	18.23	34.4	1	102
NPK+FYM	452	0.12	8.16	27.75	38.4	1.58	141
NPK+FYM	420	0.11	4.95	23.94	21.1	1.17	117
NK	554	0.17	37.1	24.3	8.60	0.74	137.0
NK+FYM	590	0.15	33.4	22.6	10.40	0.89	162.0
NK+ straw	519	0.13	32.0	20.1	9.20	0.75	139.0
Super phosphate	629	0.16	34.3	23.3	12.80	0.83	156.0
Nova phosphate	581	0.15	32.6	22.9	13.10	0.74	136.0
Hyper phosphate	561	0.14	33.0	22.3	11.90	0.78	139.0

Table A.25: Soil solution pH, EC and P and soil pH ($CaCl_2$) in long-term fertilization trials (Braunschweig + Freising) soil samples.

Samples	**Solution pH**	**EC dS/m or mS/cm**	**Solution P (mg kg^{-1})**	**soil pH ($CaCl_2$)**
NK	6.0	-	0.091	5.21
NK	5.75	0.23	0.030	4.98
NK	5.94	0.32	0.060	5.64
NK	5.75	0.19	0.030	5.12
NK	6.18	0.22	0.091	5.62
NK	5.9	0.16	0.030	5.29
NK+FYM	6.07	0.34	0.091	5.25
NK+FYM	6.0	0.23	0.030	5.07
NK+FYM	6.2	0.27	0.091	5.47
NK+FYM	6.0	0.2	0.091	5.1
NK+FYM	6.01	0.27	0.091	5.38
NK+FYM	6.0	0.24	0.091	4.98
NPK+FYM	5.92	0.5	0.030	5.22
NPK+FYM	5.82	0.41	0.091	4.99
NPK+FYM	5.92	0.32	0.091	5.51
NPK+FYM	5.75	0.29	0.091	5.02
NPK+FYM	6.43	0.29	0.091	5.53
NPK+FYM	6.49	0.28	0.121	5.23
NK	6.86	0.29	0.121	6.17
NK+FYM	6.95	0.28	0.121	6.28
NK+ straw	7.23	-	0.060	6.27
Super phosphate	7.05	0.26	0.151	6.14
Nova phosphate	6.78	0.28	0.151	6.02
Hyper phosphate	7.05	0.33	0.121	6.34

Table A.26: ANOVA for the effect of total soil U on U extracted by AAAc-EDTA, DTPA, NH$_4$Ac and soil solution and solution pH and EC, soil P, pH, Cd, Ni, OC, S and available P $_{CAL}$ in long-term fertilization trials soil samples (Braunschweig + Freising).

		Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
AAAc-EDTA	Between Groups	.006	17	.00	.73	.718
	Within Groups	.003	6	.00		
	Total	.009	23			
DTPA	Between Groups	.001	17	.00	21.99	.001
	Within Groups	.000	6	.00		
	Total	.001	23			
NH$_4$Ac	Between Groups	.020	16	.001	3.34	.072
	Within Groups	.002	6	.00		
	Total	.022	22			
Soil solution	Between Groups	.000	16	.000	.33	.964
	Within Groups	.000	6	.000		
	Total	.000	22			
Solution pH	Between Groups	5.15	17	.303	46.02	.000
	Within Groups	.040	6	.007		
	Total	5.19	23			
Solution EC	Between Groups	.118	16	.007	.61	.799
	Within Groups	.073	6	.012		
	Total	.190	22			
Soil P	Between Groups	227453.8	17	13379.64	2.82	.102
	Within Groups	28445.2	6	4740.86		
	Total	255899	23			
Soil pH	Between Groups	4.762	17	.280	9.93	.005
	Within Groups	.169	6	.028		
	Total	4.93	23			
Soil Cd	Between Groups	.026	17	.002	3.28	.074
	Within	.003	6	.000		

	Groups					
	Total	.029	23			
Soil Ni	Between Groups	3518.69	17	206.98	189.82	.000
	Within Groups	6.54	6	1.09		
	Total	3525.23	23			
Soil Pb	Between Groups	144.82	17	8.52	1.82	.236
	Within Groups	28.077	6	4.68		
	Total	172.89	23			
P $_{CAL}$	Between Groups	3764.55	17	221.44	1.06	.512
	Within Groups	1258.33	6	209.72		
	Total	5022.87	23			
OC	Between Groups	1.487	17	.087	1.202	.439
	Within Groups	.437	6	.073		
	Total	1.92	23			
Soil S	Between Groups	8158.83	17	479.93	2.396	.143
	Within Groups	1201.67	6	200.28		
	Total	9360.5	23			

Table A.27: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and solution pH, soil U, P, pH ($CaCl_2$), Cd, Ni, Pb, OC, S and available P_{CAL} in Freising long-term fertilization trials soil samples.

	AAAc-EDTA	DTPA	NH_4Ac	Soil solution	Solution pH	Solution EC	Soil Cd	Soil Ni	Soil Pb	Soil P	Soil pH ($CaCl_2$)	P_{CAL}	Total OC	Soil S
Total U	.04	-.18	.78	-.44	-.30	-.67	.83*	.65	.77	.79	.08	.29	.27	.40
AAAc-EDTA	-	-.15	.23	-.46	-.31	.41	-.10	-.30	.16	.28	.41	.82*	-.260	-.35
DTPA		-	-.27	.47	-.45	-.28	.01	-.23	.07	.27	-.88*	.11	.58	.51
NH_4Ac			-	-.56	.12	-.68	.33	.08	.25	.77	.23	.69	.28	.45
Soil solution				-	-.29	-.20	.00	.07	-.13	-.59	-.14	-.54	-.88*	-.67
Solution pH					-	.21	-.66	-.42	-.77	-.35	.15	-.25	.11	.12
Solution EC						-	-.56	-.15	-.39	-.76	.21	-.15	-.31	-.51
Soil Cd							-	.89*	.95**	.53	-.03	-.02	.07	.16
Soil Ni								-	.81	.16	.09	-.39	-.08	-.01
Soil Pb									-	.57	-.04	.15	.07	.10
Soil P										-	-.27	.68	.60	.66
Soil pH											-	-.12	-.82*	-.76
P_{CAL}													.16	.15
Total OC													-	.97**

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).
n = 6

Table A.28: Statistical correlations between U extracted by AAAc-EDTA, DTPA, NH_4Ac and soil solution and solution pH, soil U, P, pH ($CaCl_2$), Cd, Ni, Pb, OC, S and available P_{CAL} in Braunschweig long-term fertilization trials soil samples.

	AAAc-EDTA	**DTPA**	**NH_4Ac**	**Soil solution**	**Solution pH**	**Solution EC**	**Soil Cd**	**Soil Ni**	**Soil Pb**	**Soil P**	**Soil pH ($CaCl_2$)**	**P_{CAL}**	**Total OC**	**Soil S**
Total U	-.27	-.18	-.04	.04	.28	.39	.71**	.35	.57*	.23	.42	.65**	.44	.58*
AAAc-EDTA	-	.01	-.17	.64**	.04	-.55*	-.37	-.17	-.32	-.06	-.08	-.30	-.14	-.18
DTPA		-	.53*	.18	-.22	-.24	-.43	-.30	-.43	.26	-.21	-.23	-.03	-.30
NH_4Ac			-	-.13	-.27	-.14	-.34	.04	-.35	-.17	-.13	-.17	.16	-.06
Soil solution				-	.27	-.31	-.11	-.20	-.16	-.19	-.03	-.03	-.08	-.11
Solution pH					-	-.01	.43	.48*	.50*	-.01	.71**	.04	.47	.51*
Solution EC						-	.52*	.07	.46	-.17	.12	.60**	-.03	.30
Soil Cd							-	.49*	.73**	.09	.47	.80**	.43	.61**
Soil Ni								-	.58*	.03	.76**	.33	.82**	.87**
Soil Pb									-	.24	.83**	.46	.65**	.80**
Soil P										-	.28	-.12	.28	.03
Soil pH											-	.13	.80**	.84**
P_{CAL}												-	.30	.49*
Total OC													-	.86**

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

n = 18

Table A.29: Statistical correlations between the soil solution pH, EC and P in all soil samples used in this study.

	Soil solution EC	**Soil solution U**	**Soil solution P**
Solution pH	.25*	.41**	.30**
Soil solution EC	-	.03	.03
Soil solution U		-	.35**

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

n = 95

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- Scholarship, June1996 - Dec1997 in the Agricultural Microbiology Dept., NRC, Dokki, Giza, Egypt. The scholarship continued at the Soils and Water Use Dept., from Dec1997 - Sep1998.
- Assistant Research, Sep 1998 - Nov 2001, Plant Nutrition Dept., NRC, Dokki, Giza, Egypt.
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Attendance of congresses:

- “International symposium protecting water bodies from negative impacts of agriculture” Loads and fate of fertilizer derived uranium. June 4-5, 2007, Braunschweig, Germany. The poster was entitled “Evaluation of different methods used for the determination of uranium bioavailability in soils” Raafat Zewainy**,** Maria del Carmen Rivas, Jürgen Fleckenstein, and Ewald Schnug.
- 6th National congress on “Towards a strategy for soils and water”, October 29-30, 2002, ARC, Dokki, Giza, Egypt.
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Experiences and activities:

- Started from 16th March 2006: Two years fellowship financed by the Egyptian government at the Institute of Plant Nutrition and Soil Science (PB), Federal Agricultural Research Centre (FAL), Braunschweig, Germany.

- International TOEFL test “International Test of English as a Foreign Language” (Score 203).
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- Experience in Laboratory Instrumentation (Atomic Absorption, Spectrophotometer, Flame photometer, determination of nitrogen, total carbohydrate and organic matter, assessment of Eh in soil, and isolation of soil microbes.

Participation in national and semi-national projects:

- February 2004 - March 2006 - Role of plant in conservation of fertility of calcareous soils. Academy of Scientific Research and Technology & Plant Nutrition Dept, NRC, Cairo.
- June 2004 - March 2006: Evaluation of sugar cane filter mud on improving soil characteristics of calcareous soils. Plant Nutrition Dept, NRC, Cairo.

Publication

Articles ready to be submitted for publication:

-Raafat Zewainy, Maria del Carmen Rivas, Susanne Schroetter, Jürgen Fleckenstein and Ewald Schnug (2008) Evaluation of different methods used for determination of uranium extractability in soils.

-Raafat Zewainy, Susanne Schroetter, Jürgen Fleckenstein and Ewald Schnug (2008). Evaluation of factors and extraction methods for uranium in U-contaminated soils.

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