Non-critical uranium accumulation in soils of German and Danish long-term fertilizer experiments

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Highlights

- Soil U was measured in long-term sites receiving P from igneous rocks or basic slag
- Soils displayed 10 times lower U accumulation rates than those commonly reported
- U accumulation rates reflected the source of applied P fertilizers

Abstract

Phosphorus (P) fertilizers vary considerably in contents of uranium (U), thus raising concerns regarding U accumulation in agricultural soils. We examined U concentrations in soil from three long-term field experiments with different P fertilizer applications: Rengen (P fertilizer from basic slag, grassland, Germany), Thyrow (P fertilizer from igneous phosphate rocks, arable land, Germany) and Askov (P fertilizer from igneous phosphate rocks, arable land, Denmark). Accumulation rates were low for Rengen (1.3 µg U kg^{-1} yr^{-1}) and Thyrow (0.6 µg U kg^{-1} yr^{-1}) in P-treated plots compared with plots without P fertilization. These accumulation rates were 10 times lower than those previously reported (mean 17 µg U kg^{-1} yr^{-1}). Intriguingly, concentrations of acid-extractable U in the Askov topsoil increased from 1923 to 2016, regardless of whether P was added (5.1 µg kg^{-1} yr^{-1}) or not (4.7 µg kg^{-1} yr^{-1}). This suggests that at least part of the accumulated U originated from other sources than P fertilizers. Total U concentrations were significantly larger in the period 1985-2016 than in the period 1938-1976 in Askov soil treated with NPK but not in soils without P fertilization. Hence, long-term P fertilizer application did increase the soil U concentrations at Askov, although at a low level.

The low U accumulation rates in soils from these German and Danish long-term P fertilization experiments indicate that with current management, the soil U concentrations could remain at non-critical levels even on a centennial scale. This is attributed to the historic use of P fertilizers derived from sources with low U content (igneous phosphate rocks from Finland and Kola Peninsula for Askov and Thyrow, respectively; and basic slag for Rengen). Hence, U accumulation due to long-term P fertilization in agricultural soils may be alleviated by using phosphate rocks from low U sources in P fertilizer production.

Keywords

Long-term experiments; Phosphorus fertilizer; Phosphate rocks; Uranium accumulation rate; Agricultural soils

1. Introduction

Phosphate rocks contain total uranium (U) with an average concentration of 120 µg U g^{-1} (Altschuler, 1980). The majority (80−90%) of U in phosphate rocks is transferred to the final phosphorus (P) fertilizer products during their production (Kratz and Schnug, 2006). Many studies have shown that, repeated application of P fertilizers can lead to elevated U concentrations in agricultural soil (e.g. Rothbaum et al., 1979; McDowell, 2012; Bigalke et al., 2017).

Usually, U accumulates in the topsoil, where it is adsorbed to organic matter and poorly crystalline Fe/Al minerals (Taylor and Kim, 2008; Yamaguchi et al., 2009). Plants do not actively take up U from soil (Sheppard and Evenden, 1988; Schnug and Haneklaus, 2015), but U can be adsorbed on root surfaces and thus enter the food chain through root crops (Keith et al., 2013; Kratz et al., 2008). In addition, fertilizer-derived U can be leached into groundwater, thus posing a threat to human health (Zielinski et al., 2006; Liesch et al., 2015; Riedel and Kübeck, 2018). Food and water intake are the major pathways of human exposure to U. In the USA, critical soil contamination has been set at a total U concentration of 30 mg kg^{-1} (USNRC, 1992). Canada has implemented soil quality guidelines for the protection of human and environmental health by setting a threshold value of total U at 23 mg kg^{-1} for agricultural land use (CCME, 2007). At present, there is no regulation of U concentrations in fertilizer products, and the European Union did not include any related restrictions on U content in the recently revised fertilizer regulations (EP and Council of the EU, 2019). To permit a better risk assessment of U in European agricultural soils, we need a more comprehensive scrutiny of the extent of fertilizer-derived U accumulation in different regions and in soils receiving different sources of P fertilizers. Current estimates for annual total U accumulation vary regionally, ranging from 7 to 47 µg kg^{-1} yr^{-1} for grassland and from 1 to 18 µg kg^{-1} yr^{-1} for arable land (e.g., Takeda et al., 2006; Wetterlind et al., 2012;

Bigalke et al., 2017). Differences are related not only to the amounts of P fertilizers applied but also to the actual U concentration in P fertilizers, which in turn depends heavily on the source of raw phosphate rocks used in P fertilizer production (Sun et al., 2020). In this study, we analyzed U concentrations in soils from three long-term field experiments with P fertilizer treatments (Rengen and Thyrow in Germany; Askov in Denmark) to evaluate the accumulations of P fertilizer-derived U in soil and to link U accumulations in soil to sources of P fertilizers. This will raise awareness regarding the sustainability of P fertilizers that are able to maintain low concentration of U in agricultural soils.

2. Materials and methods

2.1 Description of study sites

The Rengen grassland experiment

The Rengen grassland experiment (RGE) was established in 1941 in the Eifel mountains (Germany, 50°13´N, 6°51´E) and treatments include continuous applications of basic slag (or Thomas slag) as the P fertilizer (Schellberg et al., 1999). Basic slag is a by-product of steel manufacture, where P in the iron ore is removed to ensure the production of high-quality steel. Basic slag contains significant amounts of P (12-20% is phosphorus pentoxide (P_2O_5)) but the U concentration is low. In addition to basic slag, mineral fertilizers of nitrogen (N) and potassium (K) were applied as ammonium nitrate (NH_4NO_3) and potassium chloride (KCl) or potassium sulfate (K_2SO_4), respectively. The soil is classified as Stagnic Cambisol (IUSS Working Group WRB, 2015). The study site has a mean annual precipitation of 811 mm and a mean annual temperature of 6.9 °C. The RGE is arranged in a completely randomized block design with five fertilized treatments (Ca (lime), Ca/N, Ca/N/P, Ca/N/P/KCl, Ca/N/P/K_2SO_4) and an untreated control, each with five field replications. Annual P fertilizer application has been 35 kg ha^{-1} since 1941 (Table 1; see Pätzold et al., 2013, for more details). The grassland in Rengen is strongly depleted in P, therefore excessive amounts of P have been applied in the long-term experiments (Pätzold et al., 2013). The permanent grassland vegetation is cut and removed from the fields twice a year in late June or early July and again in mid-October (no grazing since 1941). In the present study, 5 cores of topsoil (0-10 cm depth) were taken for each treatment in 2016 and analyzed for U and P concentrations.

The Thyrow long-term fertilization experiment

The Thyrow long-term "Nutrient Deficiency Experiment" (Thy D41) was established in 1937, at a site about 20 km south of Berlin, Germany (52°15´N, 13°14´E). The soil is Albic Cutanic Luvisol (IUSS Working Group WRB, 2015). The site is characterized by a mean annual precipitation of 510 mm and a mean annual temperature of 9.2 °C. A crop rotation of spring barley, potatoes and maize is applied at the site. The annual fertilizer applications for the respective treatments are 100 kg K ha^{-1} (as KCl or K_2SO_4) and 24 kg P ha^{-1} (as triple superphosphate), plus 60 kg N ha^{-1} (as NH_4NO_3 and $(NH_4)_2SO_4$) in years with spring barley and 90 kg N ha^{-1} with potatoes and maize. The limed treatments received calcific or dolomitic lime at about 200 kg CaO ha^{-1} yr^{-1}. Soil cores to a depth of 100 cm were taken from NK+ lime, NPK and NPK+ lime treatments, with four replications for each treatment. Three soil cores were taken at random locations in each plot and separated into five segments at a depth of 24 (soil horizon Ap1), 30 (Ap2), 50 (EBw1), 70 (EBw2) and 100 (E/Bt) cm, respectively. The Ap1 horizon corresponds to the actual soil tillage depth of 22 to 25 cm. The corresponding soil segments of the three cores taken in one plot were well mixed on site and sub-sampled for the present study (see Bauke et al., 2018 for sampling details).

The Askov long-term experiment

The Askov long-term experiment (initiated in 1894) is located at the Lermarken site, Askov Experimental Station, Denmark (55°28´N, 09°07´E). The soil is classified as Luvisol (IUSS Working Group WRB, 2015). The mean annual precipitation and temperature were 862 mm and 7.7 °C (1961-1990), respectively. The experiment tests crop response to different rates of N, P and K applied in animal manure (AM) or mineral fertilizers (NPK). Mean annual P application rates were 13, 17 and 20 kg P ha^{-1} yr^{-1} in the periods 1894-1922, 1923-1972 and 1973-2016, respectively. In the NPK treatments, P was added as single superphosphate. Mineral N was applied as Chilean nitrate ($NaNO_3$,1894-1939), calcium nitrate ($Ca(NO_3)_2$,1940-1972) and as calcium-ammonium nitrate ($Ca\text{-}NH_4NO_3$) since 1973. Mineral K was applied as KCl. Animal manure was derived from cattle. The experiment grows a four-course rotation of winter cereals, row crops, spring cereals and grass/legumes. Every 4-5 years, 3000-5000 kg ha^{-1} lime is applied to maintain soil pH between 5.5 and 6.5. Soil tillage involves ploughing to 20 cm and seedbed preparation. Since 1923, topsoil (0–20 cm) has been sampled every four years and archived as dried samples. In the present study, we analyzed soils sampled in the B2-field in 1923, 1938, 1945, 1953, 1964, 1976, 1985, 1996 and 2000 from plots with AM and NPK applications. Soil samples from unfertilized plots were included as references (here termed control treatment). Each soil sample was a pooled sample of the three field replicates. Soils sampled in 2010 and 2016 from each field replicate were analyzed separately. Christensen et al. (2019) provide further details on the Askov long-term experiments.

2.2 Sample preparation and element analysis

Each soil sample was air dried and passed through a 2 mm sieve before analysis. About 0.05 g soil was digested with 3 ml distilled ultrapure concentrated nitric acid

(HNO_3, 68 %) and 1 ml hydrogen peroxide (H_2O_2, 30 %) in a pressurized microwave-assisted digestion system (TurboWAVE, Milestone Srl, Italy). Three analytical replicates were processed by microwave-assisted digestion for each soil sample from all three study sites. This method extracts on average 60% of the total U (here termed acid-extractable U), but leaves behind a residual fraction of U in primary and secondary minerals (such as silicate phases) (Tessier et al., 1979; Xing and Yeneman, 1998). After microwave-assisted digestion, the soil-acid mixture was centrifuged at 5000 * *g* for 10 min. The supernatant was diluted with 2 % HNO_3 and its U and P concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900, Germany). Soil samples from Askov were additionally analyzed for total U concentration after digestion of 0.05 g soil with 0.25 g lithium meta/tetraborate at 1050 °C for 3 h (Delijska et al., 1988). The standard reference soil (NIST SRM 2709a) was included for quality control of the analytical procedures.

Statistical analyses were performed separately for each field experiment. Differences among the U concentrations in various treatments were analyzed by one-way ANOVA with a significance level $p < 0.05$ to detect significant differences among individual treatments for Rengen and Askov (soil sampled in 2010 and 2016). Due to incomplete randomization of the treatments in the Thyrow experiment, we considered the treatments within each block, as well as the five depth intervals within each soil profile, as paired samples. A paired-sample t-test was performed to reveal the significant differences in U concentrations among soils from the treatments NK+lime, NPK and NPK+lime. Differences in vertical soil U concentration among the soil horizons were analyzed by repeated ANOVA measures. The relationships between P and U concentrations were examined by linear regression models.

3. Results

3.1 Uranium concentrations in soil

Rengen (1941-2015)

The U concentration in soil without fertilization (control) at Rengen was 0.80 ±0.08 mg kg^{-1}. Soils receiving lime (Ca) or Ca/N contained similar concentrations of U (0.89 ±0.04 mg kg^{-1}), whereas mean U concentrations were significantly higher in soils fertilized with P in Ca/N/P, Ca/N/P/KCl and Ca/N/P/K_2SO_4, (0.96 ±0.08 mg kg^{-1}) than those from control plots (Fig. 1). Concentrations of U in soils receiving Ca/N/P, Ca/N/P/KCl, and Ca/N/P/K_2SO_4 did not differ significantly, indicating that the application of K fertilizers did not induce additional U accumulation.

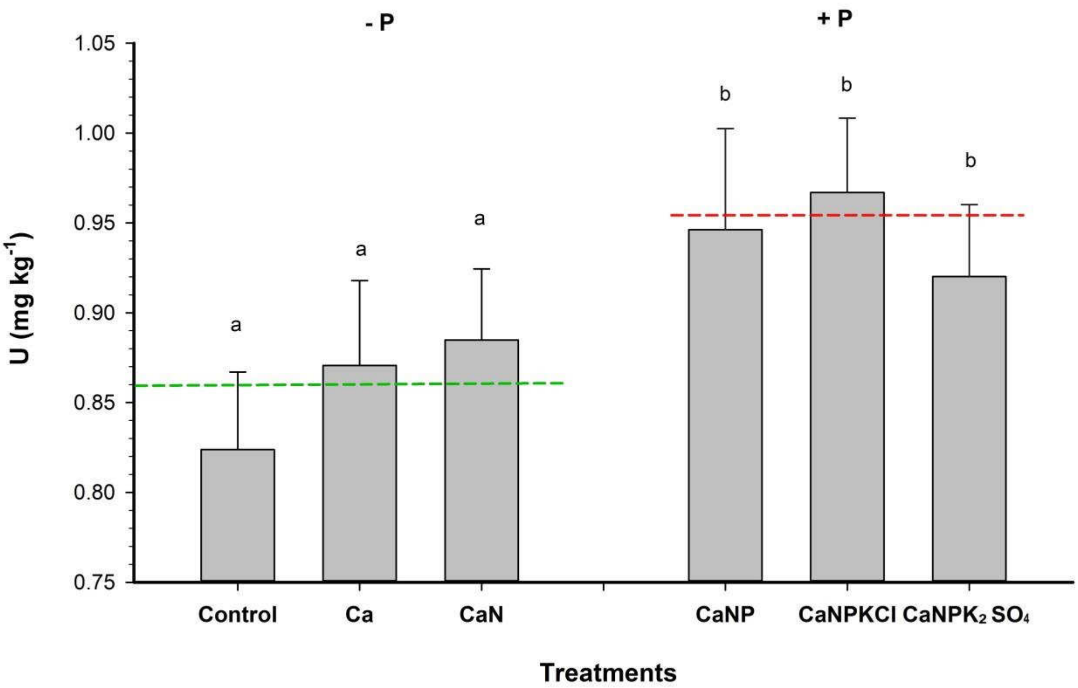

Figure 1. Uranium concentrations (acid-extractable) in topsoil of five fertilizer treatments in the Rengen Grassland Experiment**.** "Control" refers to the unfertilized treatments. Different letters indicate significant differences between treatments at $p< 0.05$ level. The dashed lines represent the average value for the three treatments with and without P fertilization.

Thyrow (1937-2016)

At the experimental site in Thyrow, soil cores down to 100 cm were collected in order to study the depth profile of U concentrations in soil. The vertical patterns of U concentration were similar for all three treatments (NK+lime, NPK+lime, NPK; Fig. 2), with higher U concentrations in the Ap1 horizon (0-24 cm) and in the E/Bt horizon (70-100 cm). Subsoil U concentrations generally increased with depth (30-100 cm). For each treatment, the mean U concentrations at different horizons were significantly different. In a comparison of different treatments for a given horizon, the U concentrations were significantly higher in the topsoil (Ap1) of the P-fertilized plots (NPK+lime, NPK, 0.37 mg kg^{-1}) than in the topsoil without P fertilization (NK+lime, 0.29 mg kg^{-1} ; Fig. 2). However, no significant differences in U concentration were observed between the fertilized and unfertilized plots in the deeper soil horizons.

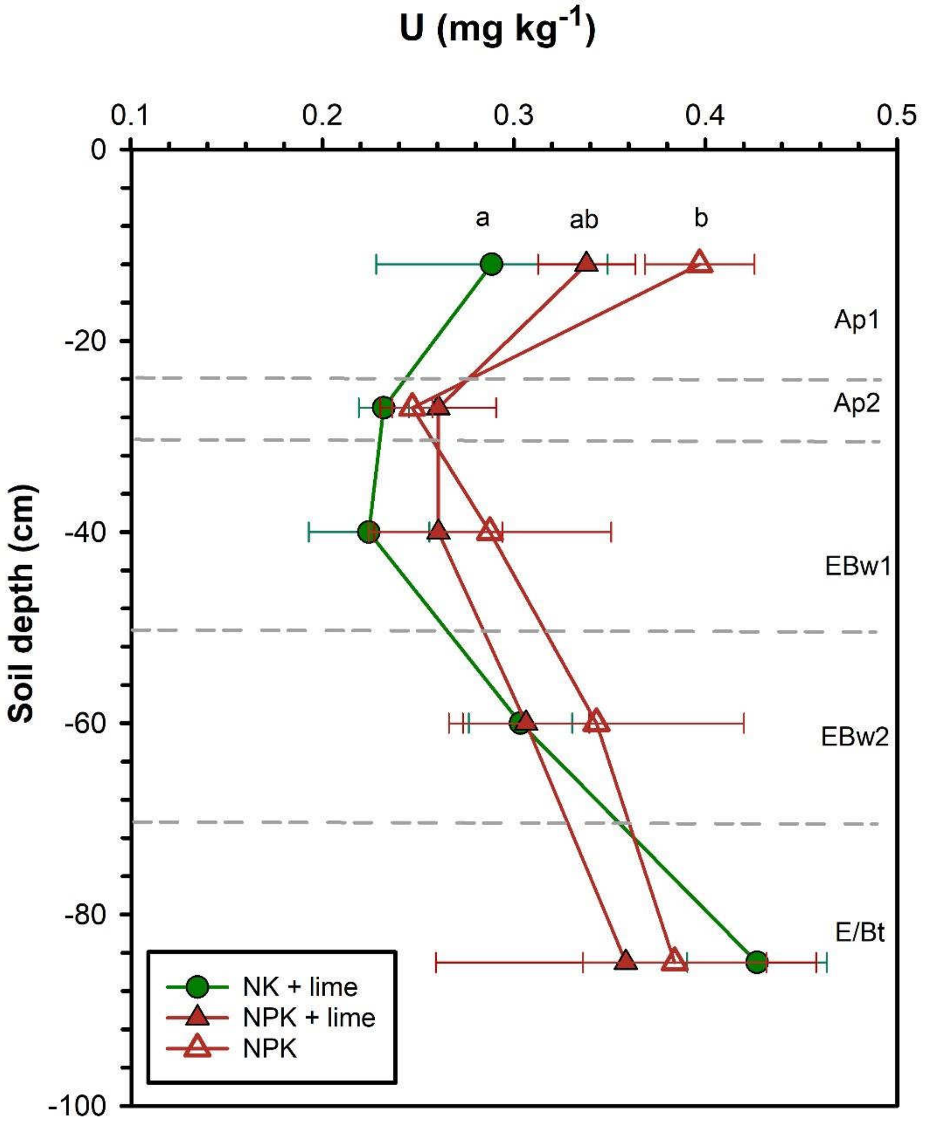

Figure 2. Depth profiles of U concentration (acid-extractable) in soils of the long-term experimental field at Thyrow. The error bars represent the standard deviations of the four field replicates.

Askov (1894-2016)

The concentration of acid-extractable soil U increased slightly from 1923 to 2016, i.e. from 0.66 to 0.96, 0.61 to 0.84 and 0.79 to 1.08 mg U kg^{-1}, for the control, AM and NPK treatments, respectively (Fig. 3). The increase in soil U concentration over time can be described by a significant linear regression ($p < 0.05$). The slopes of the linear regression represent the annual U accumulation in soils. The highest annual U accumulation was observed for NPK-treated soil (5.1 µg kg^{-1} yr^{-1}), followed by the control (4.7 µg kg^{-1} yr^{-1}) and the AM treatment (3.7 µg kg^{-1} yr^{-1}). Differences in soil U concentrations were not significant among the control, AM and NPK treatments in 2010 or in 2016. For the entire experimental period of 92 years, no significant differences in acid-extractable U were observed between the control soil and the soils receiving animal manure or mineral fertilizers.

To examine whether fertilizer-derived U in Askov had become un-extractable (by acid digestion) over time, the soils were analyzed for total U concentrations. Mean total soil U concentrations were significantly higher in the NPK treatment for the last 32 years (1985-2016) than for the first 38 years (1938-1976). This trend was not observed for the control and AM treatments (Fig. 3 – insert). This suggests that long-term mineral P fertilizer application did indeed result in U accumulation in the Askov soil although at a low level. In addition, a significant linear regression was observed for the total U concentrations over time in the Askov soils, but with a steeper slope compared with the acid-extractable U concentration (Fig. 3). However, we found no significant difference between the coefficients of regression. Apparently, fertilizer-derived U tends to remain in the acid-extractable fraction.

3.2 Relationship between P and U

At all three experimental sites, elevated concentrations of acid-extractable U in soil correlated with increased P (acid-extractable) concentrations in P fertilized treatments (Fig. 4; soil P concentrations are shown in Figs. S1-S3). However, the relation between the U and P concentrations differed for the Rengen, Thyrow and Askov sites. At Rengen, two obvious clusters of treatments were visible for plots with and without P fertilizer addition. The U concentrations were generally lower at Thyrow than at the other two sites, although the range of P concentrations was nearly the same in Askov and Thyrow. There was no significant correlation between the concentrations of U and P at Askov.

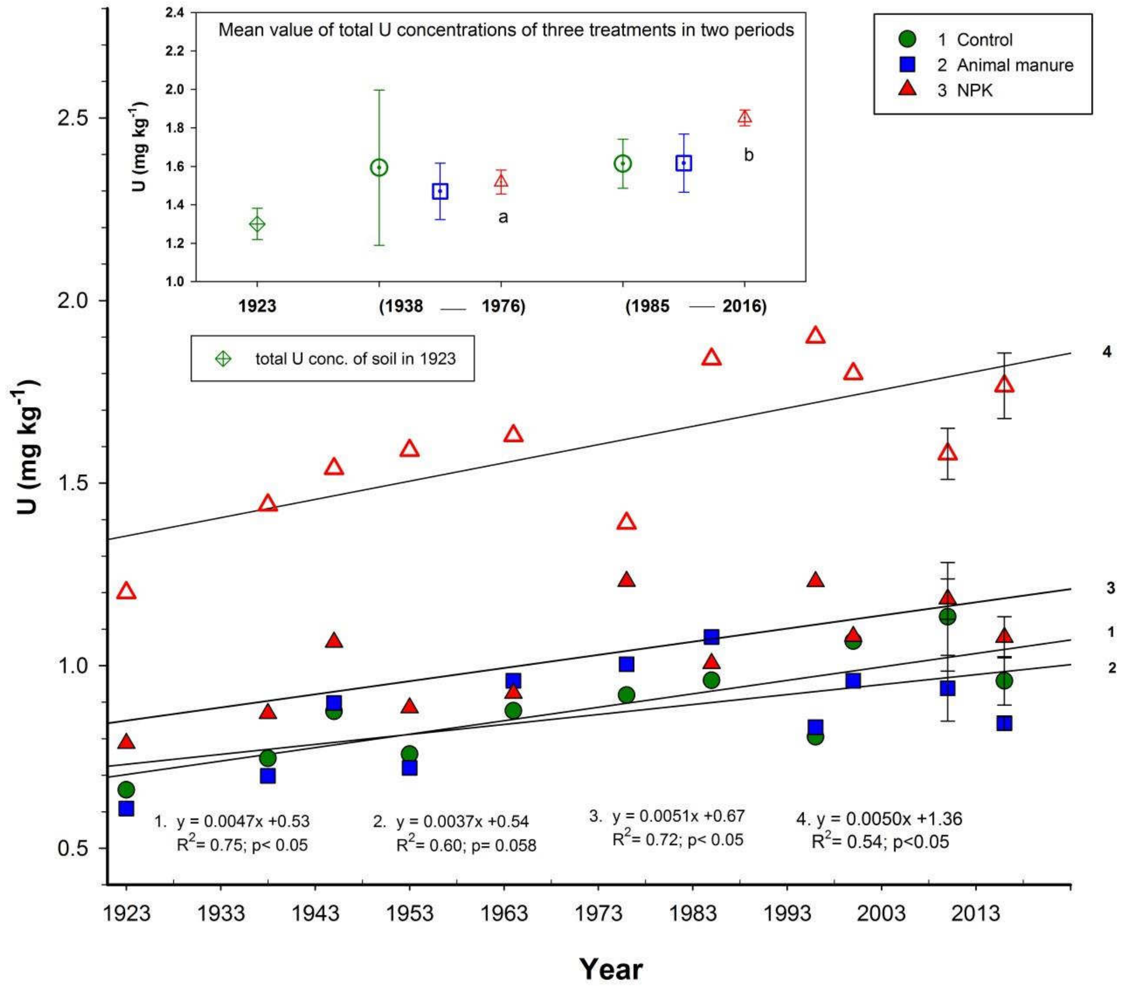

Figure 3. Changes of U concentrations (total and acid-extractable) over time in arable topsoil (0-20 cm) of the control, animal manure (AM) and NPK fertilizer treatments at Askov. Different shaped symbols denote samples from three treatments. The filled symbols signify acid-extractable U concentrations, whilst open symbols indicate total U concentrations. Different letters indicate significant differences between treatments at the p< 0.05 level.

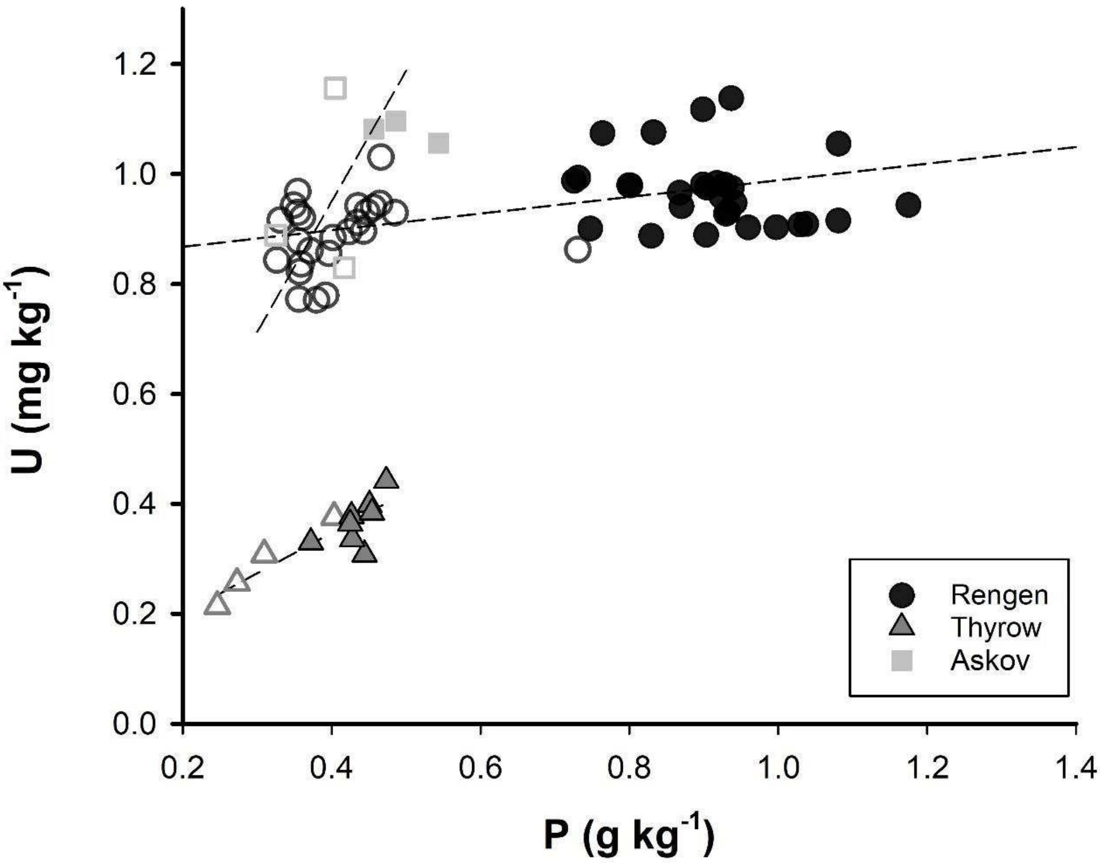

Figure 4. Relationships between concentrations of P (acid-extractable) and U (acid-extractable) in topsoil of Rengen (Control, Ca, Ca/N, Ca/N/P, Ca/N/P/KCl, Ca/N/P/K_2SO_4), Thyrow (NK+lime, NPK+lime, NPK) and Askov (Control and NPK treatments) long-term experiments. The different types of symbols represent different experimental sites. Empty symbols indicate treatments without P fertilizer application while filled symbols indicate treatments with P fertilizer application. Significant ($p <0.05$) linear correlations were found between P and U concentrations of topsoil at Thyrow and Askov.

4. Discussion

4.1 Extraction methods for soil uranium

Total U concentrations in soils reflect U derived from parent material and anthropogenic sources. To obtain total U concentrations, a complete digestion of the sample is mandatory and is typically achieved by combinations of highly oxidative acid (such as HNO_3) and hydrofluoric acid (HF), with the latter to release the element residing in the recalcitrant fractions (e.g. Bigalke et al., 2017). High-temperature fusion with lithium or sodium borates is also commonly used (e.g. Delijska et al., 1988). These methods, however, may introduce high amounts of matrix that complicate further analysis for some applications (e.g. in stable isotope studies). Other extraction methods attempt to partially dissolve the samples in order to access different phases of the element. These methods are usually used in a sequential extraction scheme to separate, e.g., for U in soil, an exchangeable fraction, a carbonate bound (weakly-absorbed) fraction, the Fe and Mn oxide bound (hydrous-oxide bound) fraction, the organically-bound or adsorbed fraction, and the fraction of U that resides in lattice material components (Tessier et al.,1979; Regenspurg et al., 2010). Such fractionations may provide more detailed information on the origin, biological and physicochemical availability and the mobility of the element (Zimmerman and Weidorf, 2010; Filgueiras et al., 2002). Uranium retained in the exchangeable fraction is considered to be bioavailable. However, changes in, e.g., pH, temperature, extraction time, and soil texture and mineralogy may lead to large variations of U concentrations in extracted fractions, resulting in incomparability of the data.

In the present study, we applied non-HF microwave-assisted digestion using concentrated HNO_3 following a protocol recommend by the United States Environmental Protection Agency (USEPA) (1994). This method has been widely applied to soil for elemental analyses (e.g. Sastre et al., 2002; Eskilsson and Björklund, 2000). The extracted U by this method is considered to be the potentially mobile, which may thus have the potential to enter the biosphere and the aqueous systems (Rao et al., 2008). In contrast, the un-extracted U is considered immobile and sequestered in structural silicate minerals. This “pseudo-total” concentration of U can provide information on the fate of anthropogenic U inputs, as these tend to reside in the first four fractions mentioned above, while the natural occurrence of U from the parent material is not extracted (Rapin et al., 1986). It has been shown that compared with unfertilized soil, the fertilizer-derived U tends to be adsorbed to organic matter or to poorly crystalline Fe/Al minerals (Yamaguchi et al., 2009; Takeda et al., 2006).

4.2 Uranium accumulation in agricultural soil by P fertilizer application

At Rengen and Thyrow, the accumulation of U is significantly related to the addition of P fertilizers (Figs. 1-2). Accumulation of U also occurred in the Askov arable soil with P fertilization, but intriguingly at a rate similar to the unfertilized control treatment (Fig. 3). This suggests that other sources may have contributed to U accumulation in soil (see Section 4.3), while P fertilization was only partially, if at all, responsible for increased U concentrations. The average annual U accumulation was 1.3 µg kg^{-1} yr^{-1} for Rengen grassland and 0.6 µg kg^{-1} yr^{-1} for Thyrow arable land in plots with P additions.

The accumulation rates for U in the present study were below 2 µg kg^{-1} yr^{-1} which is low compared with rates reported in previous studies from Germany, France and New Zealand with similar P fertilizer application rates which show annual U accumulation rates of up to 47 µg kg^{-1} yr^{-1} (Table 2, Fig. 5). The U accumulation rate in Rengen, almost ten times lower than the literature values, is attributed to the type of P fertilizer (basic slag / Thomas slag/ Thomas phosphate) applied during the first half of 20^{th} century. The basic slag is mainly produced in steel production in France, Germany and Luxembourg. Reports on U contents of basic slag used as P fertilizer are, however, scarce. According to data published by the former German Federal Agricultural Research Centre (FAL), U concentrations in basic slag (median 0.47 mg kg^{-1}) are far below those of other P sources (Kratz et al., 2004). The U concentration of basic slag applied in Rengen is around 1 mg kg^{-1} and is thus significantly lower than that in typical mineral P fertilizers (with a median value of 34 mg kg^{-1} for single superphosphate and 95 mg kg^{-1} for triple superphosphate; Taylor et al., 2014). Soils from other long-term experiments in Bonn and Freising applying basic slag show no measurable or very low U accumulation rates (2 µg kg^{-1} yr^{-1}; Rogasik et al., 2008).

The low U accumulation rates at Askov and Thyrow are also related to the types of P fertilizers applied. The two dominant sources of raw phosphate for P fertilizer production are sedimentary and igneous rocks. About 75% of the world's P sources originates from sedimentary phosphate rocks, which usually contain substantial U concentrations (27-245 mg U kg^{-1}; Sattouf, 2007) compared with igneous phosphate rocks (0.2-37 mg U kg^{-1}) (Van Kauwenbergh, 1997; Schnug et al., 1996; Sun et al., 2020). The P fertilizers applied in Askov and Thyrow are derived from igneous phosphate rocks mined in Finland and the Kola Peninsula of Russia, respectively. Soils from other long-term experimental sites in the former East Germany (Halle and Müncheberg) with P fertilizers of igneous origin most likely applied before 1990, showed small U enrichments (1 and 2 µg kg^{-1} yr^{-1}) similar to our sites (Rogasik et al., 2008). However, it is worth noting that since 1990 most of the P fertilizers used in German agriculture have been of sedimentary origin and inputs of U to soils may therefore have increased over the past 30 years in former East German regions (Rogasik et al., 2008). At Askov, the accumulation of U in soil with cattle manure was similar to that of the control, indicating that the applied manure was low in U concentrations. In general, organic fertilizers have lower U concentrations than mineral P fertilizers (Kratz et al., 2008). Taylor et al. (2014) reported a median U concentration for cattle manure of 0.17 mg kg^{-1}.

The large regional variations of annual U accumulation found in other studies (Fig. 5) are a consequence of the use of P fertilizers produced from different phosphate sources. The soil U accumulation rates reported for many European long-term experiments are relatively low (< 10 µg kg^{-1}), but higher U accumulation rates (> 10 µg kg^{-1}), have been observed for instance at Schuby, Germany, and Loir-et-Cher and Indre-et-Loire, France (Wetterlind et al., 2012). This most likely reflects the fact that phosphate rocks imported to Europe originate from various countries, such as Morocco (35% of total imported phosphate rocks), Russia (32%), Algeria, Israel and South Africa (Tulsidas et al., 2019). More dramatic U accumulation has been found in Japan and New Zealand with an average U increase of 40.5 and 27.5 µg kg^{-1} yr^{-1}, respectively (Fig. 5) (Takeda et al., 2006; Yamaguchi et al., 2009; Taylor and Kim, 2008; Schipper et al., 2011). For Japanese pastures, the annual U accumulation was reported to be more than 100 µg kg^{-1} and is partly attributed to the application of fertilizer with high U loads (Yamaguchi et al., 2009).

When related to the amounts of P fertilizer applied, U accumulation rates per kg P fertilizer were 0.26-0.77 µg U kg^{-1} (Table 2) in Japan, up to 0.84 µg U kg^{-1} in New Zealand and 0.18-0.74 µg U kg^{-1} for USA and France (Table 2). Imports of P fertilizers in Japan originate mainly from the USA (Webeck et al., 2015), whereas P fertilizers used in New Zealand originate from Western Sahara (WSRW, 2019). These supply chains are known to have phosphate rocks enriched in U compared with igneous rock sources (Sun et al., 2020).

The average background concentration of U in surface soil is currently about 2 mg kg^{-1} (NCRP, 1984). Considering the low U accumulation rates (< 2 µg kg^{-1} yr^{-1}) found in our study and a continuation of current fertilizer use, it would take approx. 10,000 to 50,000 years before P fertilizer-derived U accumulation exceeded the critical soil contamination criterion of 30 mg U kg^{-1} issued by the USNRC (1992).

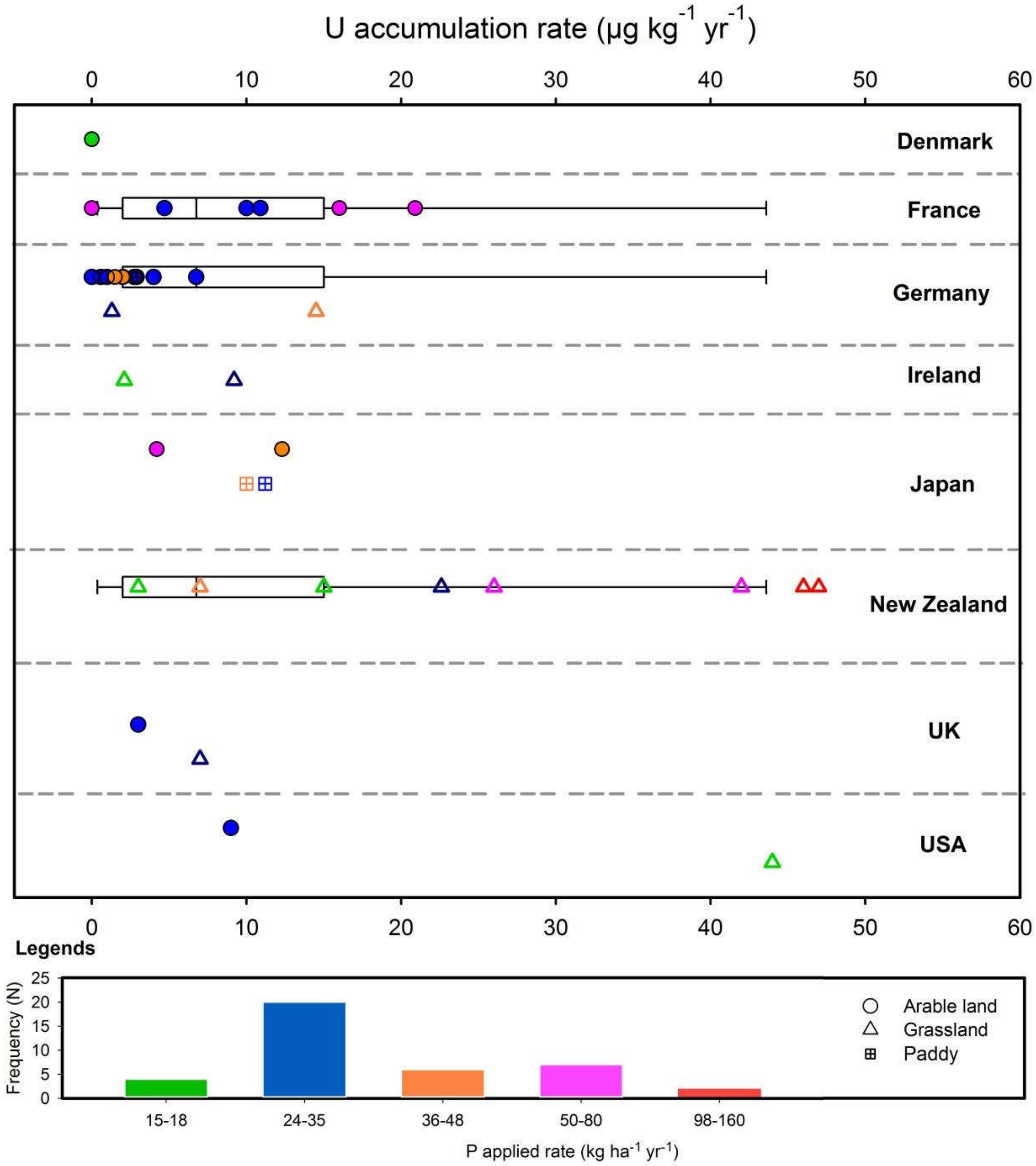

Figure 5. Summary of U accumulation rates in topsoil of various related studies. Different colors indicate P application rates in agricultural soils and different symbols indicate type of land use.

4.3 Other sources of uranium in agricultural soils

A gain in soil U without P fertilization was observed at Askov. This observation is in agreement with other studies (Rothbaum et al. 1979; Stojanovic et al., 2006). Soil U concentration increased by 0.11 mg kg^{-1} from 1870 to 1976 in unfertilized treatments of the Park Grass (UK) experiment in England (Rothbaum et al. 1979). A study in

Serbia found that U concentration increased by 0.66 mg kg^{-1} from 1989 to1995 without P fertilization (Stojanovic et al., 2006). Possible sources for the additional U in agricultural soils might be atmospheric deposition and/or long-term liming practices. Fly ash and other airborne emissions from coal-fired industry and power plants may historically be a source of U in soil. However, some studies suggested that U input by atmospheric deposition is negligible (Bigalke et al., 2017; Kratz et al., 2008).

Another potential source of U accumulation is application of lime. Jones (1992) suggested that liming leads to a long-term increase of soil U while other studies show that lime-derived U is insignificant (Taylor, 2007), or at least negligible when compared to the considerably higher amount of U applied with mineral P fertilizers. The reported U concentrations in lime are variable, ranging from < 1 to 50 mg kg^{-1} (Bell, 1963). And almost all limestones contains U concentrations of about 1 mg kg^{-1}, with an estimated average U concentration in lime of 0.6 mg U kg^{-1} (Taylor et al., 2014). With an annual application of 1000 kg ha^{-1} lime in the Askov experiment and a concentration in the lime of 0.6 mg U kg^{-1}, the estimated U accumulation induced by liming accounts for 0.3 µg kg^{-1} yr^{-1}. This corresponds to about 10% of the U increase in the control (4.7 µg kg^{-1} yr^{-1}) and AM (3.7 µg kg^{-1} yr^{-1}) treatments. Since the concentrations of U in lime applied at Askov remain unknown, we cannot assess the importance of lime-derived U at Askov in more detail. The assessment of lime-derived U at Askov is currently a speculation and requires further study. The concentration of U in lime varies widely and inputs of lime-derived U may be of quantitative significance for soils dressed with P fertilizers low in U concentrations.

At Thyrow, the vertical distribution of U concentrations was unaffected by P fertilization but was probably influenced by soil formation processes. The soil is an Albic Luvisol and illuviation processes have translocated clay, humus and particle-bound U from the eluvial horizon E into the illuvial Bt horizon (Baize and van Oort, 2014). Such processes may have depleted U in the upper soil horizons. Consequently, the increase in soil U concentration from the Ap2 to Bt horizon in Thyrow could be the mediated by pedogenic processes. Aubert et al. (2004) also found enrichment of U in deeper soil horizons resulting from illuviation. We surmise that the small, but significant U increase in the uppermost soil, the Ap horizon, results from P fertilizer application. In addition, the regression coefficient of the relation between P and U concentrations was statistically significant in the topsoil of Thyrow. However, this was also true for un-fertilized treatments. We attribute this observation to the parent material and local soil formation processes, which warrants further investigation.

Conclusions

Soils from P fertilized plots at the Rengen, Thyrow and Askov long-term agricultural field experiments showed very low U accumulation rates (< 2 µg kg^{-1} yr^{-1}), likely due to the use of P fertilizers derived from sources with low U concentrations (igneous phosphate rocks and basic slag). However, we also found a small but unexplained increase in soil U concentrations in unfertilized plots. We conclude that low and long-term sustainable concentrations of U can be maintained when agricultural soil receives P fertilizers produced from phosphate sources low in U.

Acknowledgments

The first author would like to thank for the Chinese Scholarship Council [CSC201506350148] for the support to her study in Germany. We appreciate the support of J. Schellberg and Th. Döring at Rengen experimental site. This work was supported by the German Federal Ministry of Education and Research (BMBF) in the framework of the funding initiative “Soil as a Sustainable Resource for the Bioeconomy – BonaRes”, project “BonaRes (Module A): Sustainable Subsoil Management - Soil^3

[grant numbers 031B0026A, and 031B0026C, 2015]. The Danish contribution was financially supported by funding from the Ministry for Environment, Food and Agriculture.

References

Altschuler, Z., 1980. The geochemistry of trace elements in marine phosphorites: Part I. Characteristics, abundances and enrichment. Society of Economic Paleontologists and Mineralogists Publication, 29, 19-30.

Aubert, D., Probst, A., Stille, P., 2004. Distribution and origin of major and trace elements (particularly REE, U and Th) into labile and residual phases in an acid soil profile (Vosges Mountains, France). Applied Geochemistry, 19(6), 899-916.

Baize, D., and van Oort, F., 2014. Potentially harmful elements in forest soils. In: Bini C. and Bech J. (Eds) PHEs, environment and human health. Springer, Dordrecht, pp. 151-198.

Bauke, S.L., von Sperber, C., Tamburini, F., Gocke, M., Honermeier, B., Schweitzer, K., Baumecker, M., Don, A., Sandhage-Hofmann, A., Amelung, W., 2018. Subsoil phosphorus is affected by fertilization regime in long-term agricultural experimental trials. European Journal of Soil Science, 69(1), 103-112.

Bell, K. G., 1963. Uranium in carbonate rocks. United States Geological Survey Professional Paper, 474A, AI-A29.

Bigalke, M., Ulrich, A., Rehmus, A., Keller, A., 2017. Accumulation of cadmium and uranium in arable soils in Switzerland. Environmental Pollution, 221, 85-93.

Canadian Council of Ministers of the Environment (CCME), 2007. Canadian soil quality guidelines for uranium: environmental and human health. Available online: https://

www.ccme.ca/files/Resources/supporting_scientific_documents/uranium_ssd_soil_1.2.pdf. Accessed 13 Dec. 2019.

Christensen, B.T., Thomsen, I.K., Eriksen, J., 2019. The Askov long-term experiments: 1894-2019 – A unique research platform turns 125 years. DCA Report No. 151, Aarhus University – Danish Centre for Food and Agriculture, Tjele, Denmark.

Delijska, A., Blazheva, T., Petkova, L., Dimov, L., 1988. Fusion with lithium borate as sample preparation for ICP and AAS analysis. Analytical and Bioanalytical Chemistry, 332, 362–365.

Eskilsson, C. S., Björklund, E., 2000. Analytical-scale microwave-assisted extraction. Journal of Chromatography A, 902(1), 227-250.

European Parliament (EP), Council of the European Union (EU), 2019. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019, laying down rules on the making available on the market of EU fertilizing products and amending regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing regulation (EC) No 2003/2003. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019R1009&from=EN. Accessed 13 Dec. 2019.

Filgueiras, A. V., Lavilla, I., Bendicho, C., 2002. Chemical sequential extraction for metal partitioning in environmental solid samples. Journal of Environmental Monitoring, 4(6), 823-857.

IUSS Working Group WRB, 2015. World Reference Base for Soil Resources 2014, update 2015, International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No.106. FAO, Rome.

Jones, R.L., 1992. Uranium and phosphorus contents in Morrow plot soils over 82 years. Communications in Soil Science and Plant Analysis, 23(1-2), 67-73.

Keith, S., Faroon, O., Roney, N., Scinicariello, F., Wilbur, S., Ingerman, L., Llados, F., Plewak, D., Wohlers, D., Diamond, G., 2013. Toxicological profile for uranium. Agency for Toxic Substances and Disease Registry (US), pp. 39-175.

Kratz, S. and Schnug, E., 2006. Rock phosphates and P fertilizers as sources of U contamination in agricultural soils, in: Merkel B.J., Hasche-Berger A. (Eds) Uranium in the Environment. Springer, Berlin, pp. 57-67.

Kratz, S., Fleckenstein, J., Schnug, E., 2004. Uran in P-haltigen Mineraldüngern (Uranium in mineral P fertilizers). Federal Agricultural Research Centre (FAL): Annual Report 2004, pp. 22-23. Available online: https://d-nb.info/1010831046/34. Accessed 19 June 2019.

Kratz, S., Knappe, F., Rogasik, J., Schnug, E., 2008. Uranium balances in agroecosystems, in de Kok. L. J. and Schnug, E. (Eds.), Loads and Fate of Fertilizer-derived Uranium. Backhuys Publishers, Leiden, pp. 179-190.

Liesch, T., Hinrichsen, S., Goldscheider, N., 2015. Uranium in groundwater—fertilizers versus geogenic sources. Science of the Total Environment, 536, 981-995.

McDowell, R., 2012. The rate of accumulation of cadmium and uranium in a long-term grazed pasture: implications for soil quality. New Zealand Journal of Agricultural Research, 55(2), 133-146.

National Council on Radiation Protection and Measurements (NCRP), 1984. Exposures from the uranium series with emphasis on radon and its daughter. Protection and Measurements. National Council on Radiation Protection and Measurements, Bethesda, MD. Report No. 77, 56-68.

Pätzold, S., Hejcman, M., Barej, J., Schellberg, J., 2013. Soil phosphorus fractions after seven decades of fertilizer application in the Rengen Grassland Experiment. Journal of Plant Nutrition and Soil Science, 176(6), 910-920.

Rao, C. R. M., Sahuquillo, A., Lopez Sanchez, J. F., 2008. A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. Water, Air, and Soil Pollution,189(1-4), 291-333.

Rapin, F., Tessler, A., Campbell, P. G. C., Carignan, R., 1986. Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure, Environmental Science and Technology, 20(8), 836–840.

Regenspurg, S., Margot-Roquier, C., Harfouche, M., Froidevaux, P., Steinmann, P., Junier, P., Bernier-Latmani, R., 2010. Speciation of naturally-accumulated uranium in an organic-rich soil of an alpine region (Switzerland). Geochimica et Cosmochimica Acta, 74(7), 2082-2098.

Riedel, T., Kübeck, C., 2018. Uranium in groundwater–a synopsis based on a large hydrogeochemical dataset. Water Research, 129, 29-38.

Rogasik, J., Kratz, S., Funder, U., Panten, K., Barkusky, D., Baumecker, M., Gutser, R., Lausen, P., Scherer, H., Schmidt, L., Schnug, E., 2008. Uranium in soils of German long-term fertilizer experiments, in: de Kok. L. J. and Schnug, E. (Eds.), Loads and Fate of Fertilizer-derived Uranium. Backhuys Publishers, Leiden, pp. 135-146.

Rothbaum, H., McGaveston, D., Wall, T., Johnston, A., Mattingly, G., 1979. Uranium accumulation in soils from long-continued applications of superphosphate. Journal of Soil Science, 30(1), 147-153.

Sastre, J., Sahuquillo, A., Vidal, M., Rauret, G., 2002. Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. Analytica Chimica Acta, 462(1), 59-72.

Sattouf, M., Kratz, S., Diemer, K., Rienitz, O., Fleckenstein, J., Schiel, D., Schnug, E., 2007. Identifying the origin of rock phosphates and phosphorus fertilizers through high precision measurement of the strontium isotopes ^{87}Sr and ^{86}Sr. Landbauforschung Völkenrode, 57, 01-11.

Schellberg, J., Möseler, B. M., Kühbauch, W., Rademacher, I. F., 1999. Long-term effects of fertilizer on soil nutrient concentration, yield, forage quality and floristic composition of a hay meadow in the Eifel mountains, Germany. Grass and Forage Science, 54(3), 195-207.

Schipper, L.A., Sparling, G.P., Fisk, L., Dodd, M., Power, I., Littler, R.A., 2011. Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer. Agriculture, Ecosystems & Environment, 144(1), 95-101.

Schnug, E., Haneklaus, N., 2015. Uranium in phosphate fertilizers–review and outlook, in: Merkel B., Arab A. (Eds.), Uranium - Past and Future Challenges. Springer, Cham, pp. 123-130.

Schnug, E., Haneklaus, S., Schnier, C., Scholten, L., 1996. Issues of natural radioactivity in phosphates. Communications in Soil Science and Plant Analysis, 27(3-4), 829-841.

Sheppard, S., Evenden, W., 1988. Critical compilation and review of plant/soil concentration ratios for uranium, thorium and lead. Journal of Environmental Radioactivity, 8(3), 255-285.

Stojanovic, M., Popic, J.M., Stevanovic, D., Martinovic, L., 2006. Phosphorus fertilizers as a source of uranium in Serbian soils. Agronomy for Sustainable Development, 26(3), 179-183.

Sun, Y., Amelung, W., Wu, B., Haneklaus, S., Maekawa, M., Lücke, A., Schnug, E., Bol, R., 2020. 'Co-evolution' of uranium concentration and oxygen stable isotope in phosphate rocks. Applied Geochemistry, 114, 104476.

Takeda, A., Tsukada, H., Takaku, Y., Hisamatsu, S.i., Nanzyo, M., 2006. Accumulation of uranium derived from long-term fertilizer applications in a cultivated Andisol. Science of the Total Environment, 367(2-3), 924-931.

Taylor, M. and Kim, N., 2008. The fate of uranium contaminants of phosphate fertilizer. in: de Kok. L. J. and Schnug, E. (Eds.), Loads and Fate of Fertilizer-derived Uranium. Backhuys Publishers, Leiden, pp.147-155.

Taylor, M., Kratz, S., schick, J., Schnug, E., Smidt, G., 2014. Comparing trace element concentrations in inorganic and organic fertilizers (Conference Paper). New Zealand Soil Science Society conference "Soil science for future generations", at Hamilton, New Zealand.

Taylor, M.D., 2007. Accumulation of uranium in soils from impurities in phosphate fertilizers. Landbauforschung Völkenrode, 57(2), 133.

Tessier, A., Campbell, P. G., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, 51(7), 844-851.

Tulsidas, H., Gabriel, S., Kiegiel, K., Haneklaus, N., 2019. Uranium resources in EU phosphate rock imports. Resources Policy, 61, 151-156.

Tunney, H., Stojanović, M., Mrdaković Popić, J., McGrath, D., Zhang, C., 2009. Relationship of soil phosphorus with uranium in grassland mineral soils in Ireland using soils from a long-term phosphorus experiment and a National Soil Database. Journal of Plant Nutrition and Soil Science, 172(3), 346-352.

United States Environmental Protection Agency (USEPA), 1994. method 3051, Microwave-Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, Washington DC.

United States Nuclear Regulatory Commission (USNRC), 1992. A Summary of NRC's Interim Radiological Cleanup Criteria and Current Dose Bases. U.S. Nuclear Regulatory Commission, Washington.

Van Kauwenbergh, S. J., 1997. Cadmium and other minor elements in world resources of phosphate rock. The International Fertilizer Society Proceedings 400. York, UK: The International Fertilizer Society.

Webeck, E., Matsubae, K., Nakajima, K., Nansai, K., Nagasaka, T., 2015. Phosphorus Flows in the Asian Region. Global Environmental Research, 15, 9-17.

Western Sahara Resource Watch (WSRW) Report, P for plunder, 2019. ISBN: 978-82-93425-27-4.

Wetterlind, J., Richer De Forges, A., Nicoullaud, B., Arrouays, D., 2012. Changes in uranium and thorium contents in topsoil after long-term phosphorus fertilizer application. Soil Use and Management, 28(1), 101-107.

Xing, B. and Yeneman, P., 1998. Microwave digestion for analysis of metals in soil. Communications in Soil Science and Plant Analysis, 29, 7-8.

Yamaguchi, N., Kawasaki, A., Iiyama, I., 2009. Distribution of uranium in soil components of agricultural fields after long-term application of phosphate fertilizers. Science of the Total Environment, 407(4), 1383-1390.

Zielinski, R.A., Orem, W.H., Simmons, K.R., Bohlen, P.J., 2006. Fertilizer-derived uranium and sulfur in Rangeland soil and runoff: A case study in central Florida. Water, Air, and Soil Pollution, 176(1), 163-183.

Table 1. Summary of the experimental field sites.

Site	Years	Land use type	Parent materials	Soil type	Clay %	Silt %	Sand %	Treatments	P fertilizer type	Mean P fertilizer application rate (kg ha^{-1} year^{-1})	Total carbon (g kg^{-1})	pH
Rengen, Germany	1941-2015	grassland (meadow)	Lower Devonian sandstones, siltstones, and clay slates	Stagnic Cambisol	23	54	23	Control	-	0	49.0	4.9
								Ca	-	0	41.9	6.5
								Ca N	-	0	43.8	6.5
								Ca N P	Basic slag	35	43.0	6.6
								Ca N P KCl	Basic slag	35	43.9	6.5
								Ca N P K_2SO_4	Basic slag	35	45.2	6.6
Thyrow, Germany	1937-2016	arable land	Periglacial sand overlying a loam and a calcareous glacial till	Cutanic Albic Luvisol	3	14	83	NK+lime	-	0	3.60	6.0
								NPK	Triple superphosphate	24	-	3.8
								NPK+lime	Triple superphosphate	24	3.80	6.0
Askov, Denmark	1894-2016	arable land	Morainic deposits from the Weichselian glaciation	Luvisol	12	13	75	No fertilizer	-	0	12.3	6.5
								Animal manure (AM)	Cattle manure	19	15.0	6.5
								Mineral fertilizer (NPK)	Superphosphate	19	13.7	6.5

Note: Total carbon data for Rengen are organic carbon contents from Pätzold et al., 2013.

Table 2. Literature review of fertilizer-derived U increase at different experiment sites

Country	Experiment sites	Years[a]	Land use type	Treatments	P fertilizer type	P fertilizer application rate (kg ha^{-1} yr^{-1})	Annual U increase (μg kg^{-1} yr^{-1})[b]	Annual U increase per kg fertilizer (μg kg^{-1} yr^{-1} kg^{-1} fertilizer)	Reference
Japan	Fujisaka Branch	1940-2001 (61)	arable land	NPK+compost+lime	superphosphate	65	16.9	0.26	Takeda et al., 2006
		1933-2000 (67)	paddy	NPK	fused phosphate fertilizer	26.2	11.2	0.43	Yamaguchi et al., 2009
		1968-2000 (32)	paddy	NPK	fused phosphate fertilizer	35.8	10	0.28	
		1976-1997 (21)	upland	NPK	fused phosphate fertilizer	48	12.3	0.26	
New Zealand	Mikimiki	43	grassland	NPK	superphosphate and triple superphosphate	59	26	0.44	Taylor and Kim, 2008
	Eltham	37	grassland	NPK		118	46	0.39	
	Taupo	37	grassland	NPK		19.7	15	0.76	
	Hinemaiai	36	grassland	NPK		98	47	0.48	
	Whatawhata	1983-2006 (23)	grassland	P_{30}	triple superphosphate	30	22.6	0.75	Schipper et al., 2011
				P_{50}	triple superphosphate	50	42	0.84	
	Winchmore	1952-1998 (36)	grassland	P_{18}	superphosphate	18	3	0.17	McDowell et al., 2012
				P_{36}	superphosphate	36	7	0.19	
UK	Rothamsted (Broadbalk)	1881-1976 (95)	arable land	P	superphosphate	33	3	0.09	Rothbaum et al.,1979
	Rothamsted (Park Grass)	1876-1976 (100)	grassland	P	superphosphate	33	7	0.21	
USA	Morrow plots	1904-1985 (81)	arable land	P	rock phosphate and superphosphate	32.7	9	0.28	Jones, 1992
	Florida	1967-1985 (18)	grassland	NPK	'P-containing fertilizer'	17.5	44	2.51	Zielinski et al., 2006
France	Loir-et-Cher	1976-1991 (15)	arable land	P_{26}	superphosphate	26	10	0.38	Wetterlind et al., 2012
				P_{52}		52	16	0.31	

	Indre-et-Loire	1976-1997 (21)	arable land	P_{26}	superphosphate	26	10.9	0.42	
				P_{52}		52	20.9	0.40	
	Vienne	1967-1997 (30)	arable land	P_{26}	superphosphate	26	4.7	0.18	
				P_{52}		52	0	0	
Ireland	Johnstown Castle	1968-2006 (38)	grassland	P_{15}	mineral P fertilizer	15	2.1	0.14	Tunney et al., 2009
				P_{30}	mineral P fertilizer	30	9.2	0.31	
Denmark	Askov	1923-2016 (93)	arable land	Mineral P fertilizer	superphosphate	18	0	0	this study
Germany	Rengen	1941-2015 (74)	grassland	Ca N P	Thomas slag	35	1.3	0.04	this study
	Thyrow	1937-2016 (79)	arable land	NPK	triple superphosphate	24	0.6	0.03	
	Schuby	1985-2005 (20)	grassland	P	superphosphate	41.2	14.5	0.35	
	Muncheberg*	1963-1998 (35)	arable land	NPK	superphosphate	38	2	0.05	
	Braunschweig	1980-2004 (24)	arable land	NPK	mineral P fertilizer	30.4	4	0.13	
	Halle	1949-2002 (53)	arable land	$NP_{high}K$	mineral P fertilizer	45	1.5	0.03	
	Bonn	1959-2005 (46)	arable land	Thomas phosphate	Thomas phosphate	26	0	0	Rogasik et al., 2008
				Hyperphosphate	hyperphosphate	26	1	0.04	
				Super phosphate	super phosphate	26	1	0.04	
	Freising	1935-1975 (40)	arable land	Thomas phosphate	Thomas phosphate	31	2	0.06	
				Hyperphosphate	Thomas slag in first 20 year	31	2.8	0.09	
				Super phosphate	super phosphate	31	6.8	0.22	

a: Years means the observed years at the experimental sites.

b: Individual U accumulation rate at each long-term experiment site was calculated using the following equation:

Annual U accumulation rate = $(U_{P\ fertilizer\ treatment} - U_{control}) / years_{P\ fertilizer\ applied}$,

Where $U_{P\ fertilizer\ treatment}$ was the U concentration in P fertilizers treatments soils, $U_{control}$ was the U concentration in no P fertilizer applied soils, and $years_{P\ fertilizer\ applied}$ was the years of P fertilizer applications. Therefore, the annual U accumulation rates shown in this study correspond to the average U accumulation rates.