Uranium in phosphate fertilizers – review and outlook

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Abstract. Uranium (U) can be found in concentrations of 2-200 mg/kg U in phosphate fertilizers if the rock phosphate is of sedimentary origin. About 14,000 tons of U were applied by mineral phosphate fertilizers in Germany from 1951 to 2013. This equals a cumulative load of 1 kg/ha U to agricultural soils. Actually, about 114 to 228 tons of U is distributed by fertilization.

Toxicity of uranium

U is carcinogenic and mutagenous. The chemical toxicity of U is estimated to be substantially higher than the radiological hazard (Drickhko et al. 2008, Bertell and Schmitz-Feuerhake 2008). The chemical toxicity of U ranges between that of Hg and Ni (Busby and Schnug 2008). Enhanced damages of the DNA by gamma radiation in the presence of U are reported (Smirnova et al. 2005). This suggests synergistic interactions between both modes of action. Such combination force has been attributed to the photoelectric effect: U bound to phosphate groups of the DNA absorbs ambient gamma radiation and the release of secondary electrons (beta radiation) multiplies the original alpha radiation by additional particle radiation. As a result the radiological toxicity of U increases stronger than an exclusively additive action of both radiological sources (Busby and Schnug 2008).

U concentrations of >10 µg/L (equaling the limit value for drinking water in Germany (Anonymous 2011)) induce reactions of oxidative stress in aquatic organisms and genotoxicity (Henner 2008; Beaugelin-Siller et al. 2011); leukemia may be caused (Winde 2011) and an estrogenic effect unfolded (for references see Schnug et al. 2008; Schnug and Lottermoser 2013). Important to note is that the toxicity of U is enhanced synergistically by Cd. An even significantly higher radiological and chemical toxicity of U decay products such as Po, Ra and Rn has not been considered (Thomas 2008). Moinester and Kronfeld (2014) suppose a special

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problem of Rn emanation from fertilizer-derived U in soils as farmlands all over the world are increasingly converted to housing. They allocate the problem not in the Rn emanation to the atmosphere where it is readily diluted, but in its leakage into buildings, driven by a pressure gradient for example through cracks in the foundation.

Uranium in fertilizers

All fertilizer products that contain mineral phosphates unfold U in varying concentrations of <1 to >200 mg/kg U (de Kok and Schnug 2008). In 1984 industry approved the augmented use of magmatic rock phosphates in order to reduce the Cd content as a measure of voluntary self-restriction, but there exists no proof for a trend towards lower Cd and coinciding U contamination of fertilizers. In contrast, fertilizers containing mineral phosphates, which were sampled from 1974 to 1984 showed by trend lower U concentrations than specimens collected from 1995 to 2005 (Sattouf et al. 2008).

The Institute for Crop and Soil Science of the Federal Research Institute for Cultivated Plants in Braunschweig, Germany maintains the worldwide largest database of elemental concentrations in phosphate fertilizers. In 303 fertilizer specimens with a P_2O_5 content of >5% and a mean P_2O_5 content of 23.1% the average U and Cd concentration was 57.9 mg/kg and 9.18 mg/kg, respectively. This equals 243 mg U/kg P_2O_5 and 35.2 mg Cd/kg P_2O_5. According to the German Fertilizer Ordinance (DümV 2012) an obligation to label the Cd content (>20 mg/kg P_2O_5) would have been necessary for 38.4% of all samples and 11.1% of the samples exceeded the limit value of 50 mg/kg P_2O_5 so that they would not be negotiable. The German Commission for Soil Protection (KBU 2012) suggested for U an obligation to label if concentrations are >20 mg U/kg P_2O_5 and a limit value of 50 mg U/kg P_2O_5. Following this approach more than 30% of the samples would not be negotiable and all other samples would require labeling of the U content.

A significant correlation between Cd and U content was determined, but the constant term of the regression is so high with values of 86 and 100 that theoretically a fertilizer product that is free of Cd will supposedly contain U in amounts, which exceed the proposed limit value by far (Schnug 2012). The results are congruent with other fertilizer surveys as that of Smidt et al. (2011a) in Brazil. Here, the mean P_2O_5, Cd and U content was 30.1%, 18.6 mg/kg (61.5 mg Cd per kg P_2O_5) and 70.6 mg/kg U (248 mg U per kg P_2O_5), respectively.

Accumulation of fertilizer-derived uranium in soils

The mean median value of U in German agricultural top soils varies between 0.5 and 3.2 mg/kg U (Utermann and Schnug 2013). Striking is the difference of 0.15 mg/kg U between median values of agricultural and forest soils (Utermann and Fuchs 2008). This value corresponds well with results determined by Salminen (2005), Huhle et al. (2008) and Takeda et al. (2006). The extractable U content of German agricultural soils is four times higher than that of forest soils (Huhle et al. 2008; Setzer et al. 2011). U is highly mobile under oxidizing conditions and in the presence of carbonate ions (Setzer et al. 2011; Baumann et al. 2008; Read et al. 2008) and thus differs from other heavy metals of environmental concern such as Cd and Zn.

The mean annual net input of U by fertilizers in Germany varies between 2.8 g/ha U if P is applied exclusively by organic fertilizers and according to the codes of Good Agricultural Practice (GAP) at a rate of 22 kg/ha P and 15 g/ha U if P is applied exclusively by mineral fertilizers (Kratz et al. 2008). Rogasik et al. (2008) analyzed soil samples from 7 long-term fertilizer experiments in Germany in order to determine the accumulation of U in soils. In all field trials the increase of the U content in the top soil correlated with the P rate. On average an accumulation rate of 3.7 µg/kg*yr U was determined with a minimum of 1 and a maximum of 15 µg/kg*yr U. The latter rate is in agreement with the values of 9.28 µg/kg*yr U from long-term studies in Japan (Takeda et al. 2006) and 14.5 µg/kg*yr U in Ireland (Tunney et al 2009). In comparison, accumulation rates of 19 to 37 µg/kg*yr U, which have been reported for New Zealand and Australia are distinctly higher (Imas and Lati 2005; Lottermoser 2009; Taylor and Kim 2008). The main reason is supposedly a slower leaching rate rather than higher phosphate fertilizer rates and a higher U content of fertilizer products.

U loads that have been calculated on basis of the official P balance yielded arithmetically an accumulation rate of 6 µg/kg*yr U equaling a mean increase of 0.32 mg/kg U in top soils within the last 60 years. This means that 5 to 15% of U in agricultural soils derives from previous fertilizations if the actual median values for the U content in top soils of Germany are used as basis (Kratz et al. 2011). This makes U the element which is accumulated in soils strongest when compared to the natural background value. Rogasik et al. (2008) determined a span of 0.13-0.20 mg/kg U which reflects the difference between calculated and actual accumulation rate of U in top soils of long-term P fertilizer experiments for the treatment where P rates equaled the off-take by harvest products. The authors identified the discharge of U by leachate as the main reason for the observed differences.

Transfer of uranium in the food chain

The mean transfer factor for U in soils to crop plants is 0.05 and thus comparable to that of As, Co, Hg and Pb (Schick et al. 2008). In general, the entry path soil/plant is evaluated as being not critical in the food chain. The U off-take by harvest products is distinctly lower than 0.5 g/ha U (Kratz et al. 2008; Gramss et al. 2011) and comparable to the annual atmospheric deposition (calculated from ATDSR (2013) and other sources). The low U uptake by plants and the fact that there exist no hyperaccumulator plants for U makes phytoremediation of contaminated soils infeasible (Haneklaus and Schnug 2008).

The by far greatest contribution to the daily intake of U by humans has U in liquids: German drinking water contributes with 65% to the daily U intake if standard consumer behavior is assumed (2000 calories per day (kcal/day), 2 liters liquids per day). An elevated intake of U was determined for 'carnivores', who prefer mineralized bottled water. Then drinking water contributes with up to 95% to the daily U intake (Hassoun and Schnug 2011). An investigation of German mineral and tap waters revealed that the relative distribution of U concentrations was similar: 1.9% and 2.3% of all samples showed an U content of > 2µg/L and 15.1% and 16.1% of > 10 µg/L, respectively (Knolle et al. 2011, Smidt et al. 2011b). The highest share of U contamination was found in tap water samples collected in Saxony-Anhalt and Thuringia, the lowest in Schleswig-Holstein (Smidt et al. 2011b).

Smidt et al. (2011b) determined not only the regional distribution of U in tap waters, but also the percentages of the population which has access to these waters. As a result up to 2 million inhabitants receive actually tap water that has a U content of >10µg/L U in Germany.

Uranium loads from agricultural soils to surface and groundwater

On a calculatory basis 420 g/ha U in German top soils that has been previously applied by fertilization cannot be traced. Higher redox potentials and higher pH values are typical for most agricultural soils and favor the mobility of U. Consequently, U is translocated into deeper soil layers and finally into surface and groundwater. Because of the distinctly higher solubility of fertilizer-derived U, this path of U contamination has to be assessed more critically than that of U from parent materials (Heshmati et al. 2008).

Conclusive evidence exists that fertilizer-derived U contaminates water bodies in Germany as it has been shown for other countries, too (Birke and Rauch 2008; Schnug et al. 2008, Garg 2012, Guttmann 1998). A close relationship between nitrate and U in shallow groundwater has been observed in intensively used agricul-

tural areas (Smidt et al. 2011b). There exist three hypotheses for the causal relationship between nitrate and U: Firstly, U from fertilizers is translocated in the form of uranyl-carbonate complexes by percolation water faster into deeper soil layers than other heavy metals; U resembles nitrate in its transport behavior through the soil matrix. Secondly, the nitrate content of groundwater and drinking water is a direct indicator for the fertilization intensity including that of P and thus for U loads in areas without intensive livestock production. The N and P input is linked as NP and NPK fertilizers are preferred by farmers. Thirdly, immobile U (IV) in soils is oxidized to U (VI) by nitrate and then translocated by percolation water (Wu et al. 2010).

Conservative model calculations showed that the "breakthrough" of fertilizer U into deeper soil layers can be expected after 50 years assuming a mean annual U load of 9 g/ha U under climatic and soil conditions of northern Belgium. The equilibrium concentration for this scenario is 22 µg/L U (Jacques et al. 2008).

Smidt et al. (2011b) calculated conservatively that up to a quarter (U > 0.5 µg/L) to three third (U >0.1 µg/L = worst case scenario) of all drinking water samples (n=369; 11% with > 2µg/L; 0.5% with > 10 µg/L; 0.3% with >20µg/L) in the northern plains of Germany could be contaminated with U from fertilization.

The percentage of U from previous fertilizer applications in groundwater depends on regionally differing geogenous background concentrations in soils. In regions with a low natural U background more than 90% of U in groundwater can be already fertilizer-derived. It is technically no problem to extract U from drinking water. The costs for extracting 1 mg U from 1 cubic meter water are about 0.25 € cent (Riegel 2009). Smidt et al. (2011b) calculated that 2.1 t U are extracted annually from German aquifers with drinking water.

Removal of uranium from rock phosphates and the energetic and economic significance of uranium in phosphate fertilizers

The U demand for nuclear use is rapidly increasing, the supply of U from decommissioning nuclear weapons decreasing (Ragheb 2010) so that stock market prices for U can be expected to be increasing (Hu et al. 2008). This implies that investments in technology for the extraction of U from rock phosphates will not yield higher fertilizer prices.

U in rock phosphates has a high commercial value (Schnug and Haneklaus 2012). The amount of U applied annually by mineral P fertilizers during the last 10 years would have been sufficient to satisfy the energy demand of 2.4 million households of medium size based on an energy supply of 50 MW by 1 kg natural U and an electricity demand of 3.55 MW/household. Alternatively, 5.6 million hectares of forest would have been required to provide the same amount of fuel

value by timber (assuming that 1 kg timber delivers 1 kW/h and a timber yield of 1.5 t/ha). Consequently, the use of mineral P fertilizers according to GAP on the basis of an U extraction process can be seen as a contribution to climate protection which adds up to 1.80 €/kg P when calculated on the figures of the CO_2 tax for cars. A monetary compensation of farmers in terms of a CO_2 (climate) bonus is expected to be motivating. Using the inherent energy in rock phosphates its natural U content may be a future option to produce higher quality phosphate fertilizers with reduced concentrations of contaminants (Haneklaus et al. 2014).

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