

Loads and Fate of Fertilizer-derived Uranium



editors: Luit J. De Kok & Ewald Schnug

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Cover: **“Uranyum“** hand sewn textile collage from velvet and silk (38 X 37 cm)
by Bettina Franckenberg, Bodrum, Turkey (2007)



The Rainbow Serpent is a monster etched into the cliff walls of the Upper Yule River in Australia long before European people ever set foot in the region - and discovered uranium there. It was originally painted by the Njama people of northeast Australia to guard over the elemental forces buried in the Earth. According to Njama legend, the Serpent sleeps within the Earth. Its job is to guard over the elemental forces that lie outside the realm of human control, but if the Serpent is disturbed, it will rise in vengeance in a deluge of destruction and death. The places where according to the tales the serpent sleeps were sacred to the Aborigines and were avoided. Frequently these places coincide with uranium deposits. The message of the Njama: “Leave the uranium in the earth”.



In her artwork “Uranyum” Bettina Franckenberg attempts a connection between the tales of the Australian Aborigines and the theme of the symposium “Fate and loads of fertilizer-derived uranium” (June 4 - 6, 2007 at FAL in Braunschweig, Germany). In the lower left quadrant the sleeping serpent represents the natural uranium in the soil with unspoiled environment and life in the world above it (upper left). But when the sleeping serpent is disturbed by man-made uranium contaminations (lower right) it may rise in vengeance with fatal consequences for life on earth (upper right).



About the artist: Bettina Franckenberg was born February 3, 1956 in Essen, Germany. Handcraft and artistic abilities were encouraged early in her parent's house. After graduating from college in 1975 she continued with her education in the field of occupational therapy, 1979 graduation and starting to specialize in psychiatry, supplementary qualification as psychodrama assistant - at the same time initiation to "patchwork". In 1982 she discovers the Mediterranean (living the first 2 years in Greece) as well as her "textile ambitions" - 1986 she opens her first exhibition in the Castle of St. Peter in Bodrum. She goes back to live in Berlin for some years - between 1989 and 1992 she works as an occupational therapist in psychiatry and organizes several "textile art" exhibitions in Germany, Switzerland, Latvia and Turkey. Since 1992 Bettina Franckenberg lives permanently in Bodrum, Turkey and between 1994 and 2005 she had her own ATELIER-Gallery in the holiday-village Sea-Garden in Yaliçiftlik. She continues working as a freelance textile artist living in Kizilagac near Bodrum.

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CONTENTS

Preface	ix
Radiological aspects of uranium contamination - <i>Inge Schmitz-Feuerhake and Rosalie Bertell</i>	1
Advanced biochemical and biophysical aspects of uranium contamination - <i>Chris Busby and Ewald Schnug</i>	11
Bioaccumulation of radionuclides and induced biological effects in situations of chronic exposure of ecosystems – an uranium case study <i>Pascale Henner</i>	23
Uranium in German soils - <i>Jens Utermann and Michael Fuchs</i>	33
Mobility of uranium from phosphate fertilizers in sandy soils - <i>Beate Huhle, Sascha Kummer, Susanne Stadler and Broder Merkel</i>	47
Modelling the fate of uranium from inorganic phosphorus fertilizer applications in agriculture - <i>Diederik Jacques, Dirk Mallants, Jirka Šimůnek and Martinus Th. van Genuchten</i>	57
The fate of uranium in phosphate-rich soils - <i>David Read, Stuart Black, Helen Beddow, Elaine Trueman, Thuro Arnold and Nils Baumann</i>	65
Uranium ammunition in soil - <i>Nils Baumann, Thuro Arnold and David Read</i>	73
Uranium in stream water of Germany - <i>Manfred Birke and Uwe Rauch</i>	79
Uranium in German mineral and tap waters - <i>Ewald Schnug, Manfred Birke, Nathalie Costa, Friedhart Knolle, Jürgen Fleckenstein, Kerstin Panten, Holger Lilienthal and Silvia Haneklaus</i>	91
A critical evaluation of phytoextraction on uranium contaminated agricultural soils - <i>Silvia Haneklaus and Ewald Schnug</i>	111
Combining energy and fertilizer production - vision for China's future - <i>Zhengyi Hu, Hongxun Zhang, Yanfen Wang, Silvia Haneklaus and Ewald Schnug</i>	127
Uranium in soils of German long-term fertilizer experiments - <i>Jutta Rogasik, Sylvia Kratz, Ute Funder, Kerstin Panten, Dietmar Barkusky, Michael Baumecker, Reinhold Gutser, Peter Lausen, Heinrich W. Scherer, Lothar Schmidt and Ewald Schnug</i>	135

The fate of uranium contaminants of phosphate fertilizer - <i>Matthew Taylor and Nick Kim</i>	147
Soil to plant interface of uranium - <i>Judith Schick, Susanne Schroetter, Maria Lamas, Maria Rivas, Sylvia Kratz and Ewald Schnug</i>	157
Food chain transfer of uranium series radionuclides - <i>Patricia A. Thomas</i>	169
Uranium balances in agroecosystems - <i>Sylvia Kratz, Florian Knappe, Jutta Rogasik and Ewald Schnug</i>	179
Significance of uranium and strontium isotope ratios for retracing the fate of uranium during the processing of phosphate fertilizers from rock phosphates - <i>Mamdoh Sattouf, Sylvia Kratz, Katrin Diemer, Jürgen Fleckenstein, Olaf Rienitz, Detlef Schiel and Ewald Schnug</i>	191
Setting normative rates of natural radionuclides in phosphorus fertilizers - <i>Vladimir Drichko, Alexandra Izosimova, Elvira Lisachenko, Stanislav Graschenko and Viktor Shamov</i>	203
Legal aspects of uranium in environmental compartments - <i>Felix Ekardt and Ewald Schnug</i>	209
Index of authors	219
Subject index	221



This book is dedicated to Dr. Jürgen Fleckenstein,
senior scientist at FAL (1974-2008), lately head chemist at the
Institute for Crop and Soil Science in Braunschweig.
He dedicated significant parts of his life to uranium chemistry and the environmental
impacts of fertilizer-derived uranium.

A quote from President John F. Kennedy's speech to the people of the United States on July 26, 1963:

” ...the number of children and grandchildren with cancer in their bones, with leukaemia in their blood, or with poison in their lungs [due to radioactive pollution] might seem statistically small to some, in comparison with natural health hazards. But this is not a natural health hazard -- and it is not a statistical issue. The loss of even one human life, or the malformation of even one baby -- who may be born long after we are gone -- should be of concern to us all. Our children and grandchildren are not merely statistics toward which we can be indifferent.....”

PREFACE

“Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. One important aspect of sustainable development in agriculture is the responsible management of natural resources of which soils and water bodies are the most endangered ones. A major threat for soils are loads with toxic heavy metals applied unintentionally with fertilizers and which accumulate and may pass through soils into ground and surface waters. Any agricultural system where the input of heavy metals exceeds the sum of removal by crops and unavoidable losses to the environment is in fact non-sustainable because it leaves a burden for further generations. One of the most dangerous heavy metals is uranium, because it is not only bio-chemically toxic but also radioactive. Uranium is dispersed in significant amounts for instance via phosphorus fertilizers. Although a lot of uranium research has been done under many viewpoints, the agricultural aspect and its environmental impact has not been paid much attention so far.

In this context the “Task Force Sustainable Agriculture (TFSA)” of the Agenda 21 for the Baltic Sea Region (BALTIC21) has organized a series of symposia entitled “Protecting Water Bodies from Negative Impacts of Agriculture”. Commissioned by the Federal Minister of Food, Agriculture and Consumer Protection and encouraged by her Scientific Advisory Board on Fertilizer Issues, the Federal Environment Agency Soil Protection Commission (KBU) and the Federal Institute for Risk Assessment (BFR), the former Institute of Plant Nutrition and Soil Science (PB) of the Federal Agricultural Research Centre (FAL) in Braunschweig (from 01.01.2008 on “Institute for Crop and Soil Science, Federal Research Centre for Cultivated Plants, Julius Kühn-Institut (JKI)”) and TFSA conducted under this general headline from June 4-6, 2007 the symposium “Loads and Fate of Fertilizer-derived Uranium”. The symposium brought together the world’s leading scientists on the subject. The papers of the symposium are compiled in this book and have been peer-reviewed. They present the most recent and comprehensive collection of data and references on agricultural matters related to uranium. It provides a solid base of scientific information for responsible decision-making in agricultural politics towards sustainable development in agriculture.

Luit J. De Kok
Ewald Schnug

MODELLING THE FATE OF URANIUM FROM INORGANIC PHOSPHORUS FERTILIZER APPLICATIONS IN AGRICULTURE

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Introduction

When inorganic P-fertilizers (e.g. monocalcium phosphate or triple superphosphate) are applied to agricultural fields, U is also added due to its natural occurrence in the raw material apatite. Compared to phosphate rock, mineral P-fertilizers are enriched in U since this element remains in the liquid phase during acidification of the phosphate rock (Barišić *et al.* 1992; Saueia and Mazzilli 2006). P-fertilizers hence often contain natural alpha-activity due to the presence of ²³⁸U, among other alpha emitters. Uranium concentrations (naturally occurring U contains 99% by weight ²³⁸U) in P-bearing fertilizers have been reported to be in the range of 300 to 3000 Bq kg⁻¹ of fertilizer (EC 1999), or 1700 to 9200 Bq kg⁻¹ of fertilizer for both ²³⁸U and ²³⁴U (Cogné 1993).

The environmental impact of P-fertilizers is in general relatively modest. Different studies have found different relative contributions of U from inorganic P-fertilizers to U concentrations in drainage and surface waters. For example, Rothbaum *et al.* (1979) and Zielinski *et al.* (1997) found that most U was retained in the soil profile, and that only very little U from P-fertilizers ended up in the drainage water. On the other hand, Spalding and Sackett (1972) attributed the increase in U in North American rivers to application of P-fertilizers on agricultural land. According to a study of Barišić *et al.* (1992), more than 20 percent of the annually deposited U by fertilizers is transported to drainage channels in the Kanovci area of Croatia. The mobility of agriculture-applied U (and P) depends strongly on soil conditions such as the pH, soil moisture, mineralogy and texture (Zielinski *et al.* 1997). Transient flow conditions in the soil (infiltration, evapotranspiration, moisture redistribution) furthermore can influence specific geochemical conditions in the soil (e.g., pH and solid phase reactivity), and thus also affect the mobility of aqueous elements (Jacques *et al.* 2007a).

Saueia and Mazzilli (2006) calculated internal doses due to the long-term application of phosphate fertilizers. Pathways for the internal doses were through the ingestion of milk, meat and terrestrial food via crops grown on fertilized fields. Radionuclide activities in these pathways were related to radionuclide activity concentrations in the

soil through transfer factors quantifying U uptake by food crops and livestock. However, lower activities in the root zone or soil due to leaching to deeper soil layers or groundwater were not considered. Still, the doses calculated by Saueia and Mazzilli (2006) were well below 1 mSv yr^{-1} in most cases. Another exposure pathway for U is via soil leaching and groundwater flow to surface water or drinking wells. Estimates of U-fluxes to groundwater are required as input for these types of pathway analyses. In this paper, we estimate such U-fluxes using the HP1 code of Jacques and Šimůnek (2007), which is a coupled reactive transport model that integrates a broad range of water flow, solute transport and geochemical processes in the vadose zone. The model allows one to account for specific U-soil-water interactions such as sorption on solid surfaces and aqueous complexation (Guzman *et al.* 2002). Groundwater concentrations for U will be calculated on the basis of a flux-concentration relationship determined separately (Gedeon and Mallants 2004). We further calculate the radiological impact associated with U intake via groundwater used by a small self-sustaining farming community. Concentrations and doses thus obtained will be compared with natural background values typical for Northern Belgium.

Predicted U-fluxes to groundwater

The HP1 simulator (Šimůnek *et al.* 2006; Jacques and Šimůnek 2007) was used to predict the leaching of Ca, P and U applied to an agricultural soil in the form of a mineral P-fertilizer (Jacques *et al.* 2007b). HP1 resulted from coupling the HYDRUS-1D one-dimensional water flow and solute transport model (Šimůnek *et al.* 2005) with the PHREEQC-2.13 geochemical speciation code (Parkhurst and Appelo 1999). As such, HP1 can account for a large number of geochemical processes, including aqueous complexation, cation exchange and surface complexation, during transient field situations (i.e. for time-variable precipitation, evapotranspiration, drainage, and soil-water contents). Jacques *et al.* (2006) previously showed that the invoked non-iterative operator splitting approach in HP1 is quite versatile for simulations involving transient flow if some care is taken in selecting the numerical time-stepping scheme.

Here we use the code to predict long-term U leaching from a soil profile in Northern Belgium that is assumed to be fertilized annually with a phosphate fertilizer naturally enriched in uranium. Complete details of the example are given by Jacques *et al.* (2007b). The soil at the site was a dry Spodosol consisting of seven soil horizons in the top 1 m. The moisture retention characteristics, the unsaturated hydraulic conductivity, the bulk density, soil organic matter and the Fe-oxide content of each horizon were measured by Seuntjes (2000). We assumed that cation exchange reactions took place only on organic matter, and surface complexation reactions only on the Fe-oxides.

The cation exchange capacity was related to the amount of organic matter by assuming that the amount of exchangeable protons on organic matter (OM) was 6 meq g^{-1} (Tipping 2002). To account for different functional groups on organic matter (and thus different dissociation constants for the protons), the total capacity was divided in six groups involving different OM functional groups, similar to the model of Appelo *et al.* (1998). The capacity of the surface sites was derived for the amount of Fe_2O_3 measured in the soil profile assuming 0.875 reactive sites per mole Fe (Waite *et al.* 1994).

Equilibrium constants were taken from Dzombak and Morel (1990). Elements exchanged on the exchange complex were H^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and UO_2 . Elements taking part in the surface complexation reactions were taken as H^+ , Ca^{2+} , Mg^{2+} , UO_2^{2+} , PO_4^{3-} , SO_4^{2-} and F^- . Meteorological data from the Brogel station (Belgium) for a 30-year period (1969-1999) were used to define daily precipitation and potential evaporation. The effects of vegetation (transpiration and U uptake) were neglected in the example. To obtain a 200-year time series for the modeling purposes, the 30-year period was simply repeated seven times. In addition to the transient flow simulation, a simulation with a steady-state water flux was done. The cumulative steady-state water flux after 200 years is equal to the long term net infiltration calculated during the transient flow simulation. Solute concentrations of the rain water were obtained from Stolk (2001) for station 231 located in Gilze-Rijen (The Netherlands), close to the site being modeled.

The fertilizer scenario assumed an annual application of Ca, P, and U. In Flanders (Northern Belgium), the amount of applied P that originates from mineral fertilizers decreased over the last decade from 13.9×10^6 kg P in 1990 to 2.38×10^6 kg P in 2003 (MIRA 2004). To simulate the long-term transport of P and U through the soil, the following assumptions were made: (1) P-fertilizers are applied each year on May 1 at a rate of 1 g P m^{-2} (or 6.35×10^6 kg P in all of Flanders) in the form of $Ca(H_2PO_4)_2$, and (2) 1 kg of $Ca(H_2PO_4)_2$ contains 10^{-3} mol U. Based on a specific activity of 2.96×10^6 Bq mol^{-1} U, 2960 Bq of alpha activity exclusively due to ^{238}U is present in 1 kg of $Ca(H_2PO_4)_2$. Thus, a fertilizer application of 1 g P m^{-2} corresponds to 1.61×10^{-2} mol of $Ca(H_2PO_4)_2$ containing 3.77×10^{-6} mol of U. The calculations assumed that the fertilizer was applied each year in the form of $Ca(H_2PO_4)_2$ in 1 cm of water and that it was completely dissolved in the irrigation water.

Preliminary calculations with HP1 showed a significant effect of pH and solution composition on U sorption. Consequently, an approach in which sorption is described with a linear distribution coefficient, K_d (the traditional linear equilibrium approach) may not be applicable. In fact, for relevant soil pH-conditions (between pH 3 and 6), the K_d would increase more than three orders of magnitude (in the absence of competing Ca and P elements from the fertilizer application) with increasing pH. We note that U is preferentially sorbed onto the cation exchange complex at the lower pH values, and on Fe-oxide surfaces at the higher pH's. The composition of the aqueous phase also influences K_d . The value of K_d decreased by almost three orders of magnitude when the concentrations of Ca, P, and U were at the levels of the dissolved fertilizer. Since transient flow conditions influence aqueous concentrations and the pH of the soil solution (e.g., Jacques *et al.* 2007a), K_d values will be very variable in both time and space. This is illustrated by the time series in Fig. 1 of the K_d of U at 5 and 25 cm soil depths for both transient and steady-state flow conditions. The transient flow simulation showed significant short-time variations in the K_d , which are clearly absent in the steady-state simulation results. We also found a long-time trend in K_d caused by long-time changes in the amounts of Ca, P, and U due to the annual fertilizer applications. Because U moves faster than P through the soil, there is still less competition for sorption on the Fe-oxide surface at a depth of 25 cm (P has not yet reached this depth), leading to an increase in U sorption over time. The amplitude of the short-time variations of K_d at the same time decreased with time. The adopted sorption isotherm is typically nonlinear, having a slope (the first derivative) that gradually decreases with

increasing aqueous concentration. The K_d , being the slope of the isotherm at a particular concentration, then also decreases with increasing aqueous concentration. In addition, variations in K_d with changing concentration (the second derivative of the isotherm) go to zero with increasing aqueous U concentration. In the long term, U concentrations increase due to the annual addition of the P-fertilizer, which may explain the decreasing fluctuations in calculated K_d values.

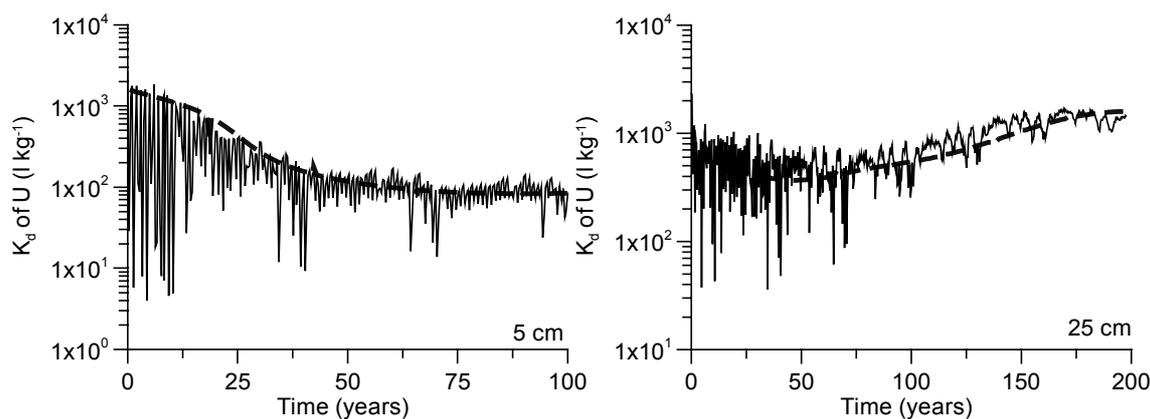


Fig. 1. Time series of the calculated K_d of U for transient (solid line) and steady-state (dashed line) flow simulations at depths of 5 cm (left) for the first 100 years and 25 cm (right) for the full 200 years of simulation (after Jacques et al. 2007b).

Fig. 2 shows the fluxes at three depths: the bottom of the A (7 cm), Bh2 (28 cm) and C2 (100 cm) horizons for both the transient and steady-state flow conditions. Steady-state fluxes were obtained after 40 and 100 years for the A and Bh2 horizon, respectively. While U reached the bottom of the soil profile after 80 years, a steady-state flux was not yet obtained within the 200-year simulation period. U fluxes increased earlier for the transient flow simulation, which reflects faster leaching due to interactions caused by short-time variations in water contents, water fluxes and geochemical conditions (Jacques et al. 2007b).

Dose calculations for groundwater use

The environmental impact of uranium leaching was assessed first by calculating the concentration of groundwater at a hypothetical well approximately 100 m downstream from a 5 ha field site which had received the long-term P-fertilizer applications. A flux-concentration relationship as determined by Gedeon and Mallants (2004) was used to derive groundwater concentrations for a sandy aquifer assuming no sorption onto the sandy sediments. For a unit radionuclide flux reaching groundwater over an area of 5 ha, the groundwater transport calculations by Gedeon and Mallants (2004) predicted a depth-averaged concentration of 4.7×10^{-5} Bq m^{-3} at the well (averaged between depths

of 3.8 and 5.9 m). Our steady-state leaching calculations produced a long-term maximum U-flux of 5.7×10^5 Bq yr⁻¹ over the 5 ha area, equivalent to a maximum concentration of 27 Bq m⁻³. By comparison, the transient leaching calculations suggest that the maximum flux could be approximately one order of magnitude higher if short-term variations in climate are accounted for. While these results are based on calculations for the shallower soil depths where steady-state had already been reached, we assumed that they would also hold for the fluxes at the bottom of the profile once the flux has reached its steady-state value. The latter should also be equal to the steady-state flux at shallower depth (i.e. 5.7×10^5 Bq yr⁻¹ over the 5 ha area) since the soil model assumed a fixed sorption capacity and uptake was neglected. In other words, the long-term maximum U concentration in groundwater under realistic climate conditions was estimated to be 270 Bq m⁻³. By comparison, local background U concentrations in the area were found to be in the order of 1000 Bq m⁻³ or less (Mallants et al. 2004).

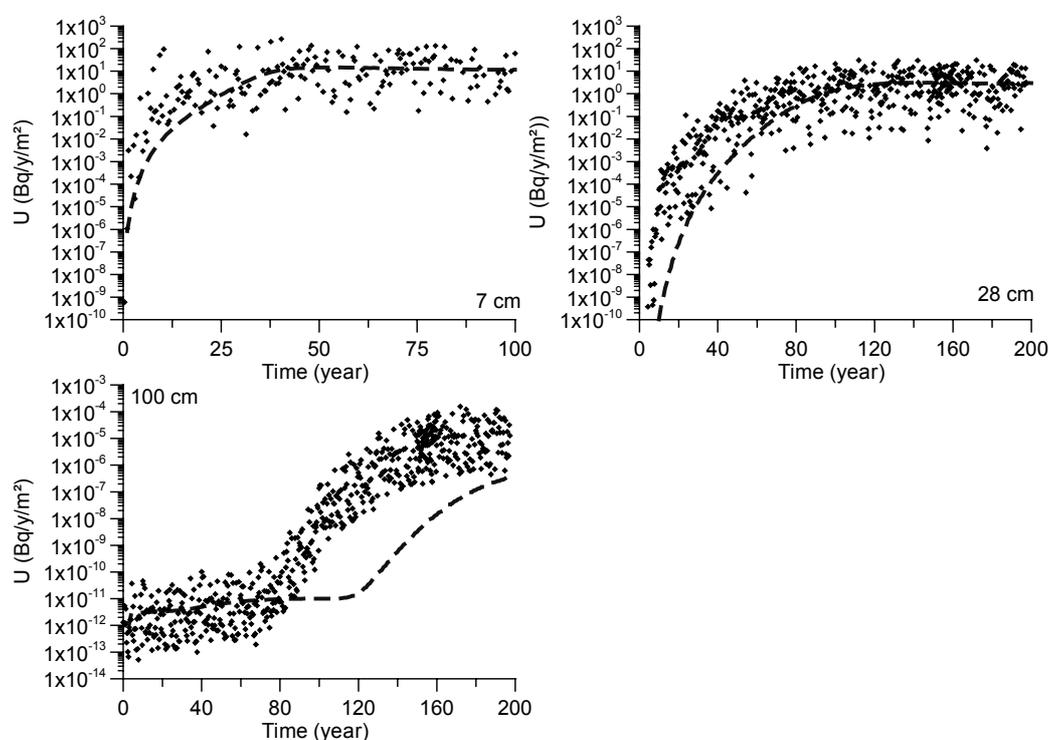


Fig. 2. Downward U fluxes (Bq/y/m²) at the bottom of the A (7 cm, 100 years), Bh2 (28 cm 200 years), and C2 (100 cm 200 years) horizons for the transient (dots) and steady-state (dashed line) flow simulations (after Jacques et al. 2007b).

The final step in our assessment was the estimation of the radiological impact owing to consumption of ²³⁸U-containing groundwater by a self-sustaining farming community. The biosphere model developed by Zeevaert and Sweeck (2000) was used for this purpose. We considered the effects of ²³⁸U on the dose calculations as well those of its short-lived daughter radionuclides that are in equilibrium with ²³⁸U, i.e. ²³⁴Th, ²³⁴Pa,

^{234m}Pa , by adding their dose factors to the dose factor of ^{238}U . When groundwater is used for irrigation of food crops and for drinking water by both residents and cattle, the total annual dose was $5.2 \times 10^{-7} \text{ Sv yr}^{-1}$, assuming a maximum groundwater concentration of 27 Bq m^{-3} . Approximately 90% of this total dose was due to ingestion of drinking water, while ingestion of food crops, milk and meat contributed far less to the total annual dose. Neglecting the contribution of drinking water, the upper bound to the annual total dose was only $5.2 \times 10^{-6} \text{ Sv yr}^{-1}$. The latter value is about three orders of magnitude below the natural background dose of about 2.5 mSv yr^{-1} in Belgium (FANC 2006). The long-term radiological impact for the conditions described in this paper seems therefore negligible. We note that our calculations neglected the effect of U-uptake by plants directly from the fertilizer application. However, based on results by Saueia and Mazzilli (2006), such doses are less than 1 mSv yr^{-1} .

Conclusions

We used the recently developed HP1 coupled geochemical transport code to calculate U-fluxes to groundwater originating from application of inorganic P-fertilizers to an agricultural field. The HP1 code was found to be a very convenient tool for studying interactions between water content and flow conditions, changes in pH, and retention of U. Results show that U will migrate considerable faster during transient flow conditions as compared to steady-state flow. A steady-state flow approach hence can only partially account for the various coupled physical and geochemical interactions in the vadose zone, whereas short-term variations involving considerable temporal variability require a transient model. Calculations of the radiological impact of U-containing groundwater demonstrate that the annual total dose owing to consumption of groundwater would not lead to values exceeding the natural background dose.

Our study was a first analysis that does not yet fully account for all physical and geochemical processes potentially relevant for predicting U leaching from fertilized agricultural soil profiles. Other important soil processes such as the carbon and nitrogen cycles (e.g. the effects of complexation with nitrate and carbonate) and vegetation-soil processes such as water uptake (and possibly U uptake), may well need to be incorporated in any future, more comprehensive modeling approach.

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