scaht

# Human and environmental impact of uranium derived from mineral phosphate fertilizers

## SCAHT report for BLW

**Nicolas Roth**

**Rex FitzGerald**

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# 1. Executive summary

SCAHT was requested by the Swiss Federal Office for Agriculture (BLW) to establish a risk profile of uranium (U) derived from P-fertilizers, with a focus on human health relevance, the impact on the food chain and the environment, and to review the scientific literature on the extent to which cadmium (Cd) and U content in P-fertilizers are correlated.

Uranium is a ubiquitous naturally occurring trace element, present mainly as U-238. It is a redox-sensitive element which can change oxidation state if conditions change, thus affecting its mobility in soil and aqueous media. The major relevant oxidation states are U(IV) and U(VI), the former being a low solubility form, and the latter a water-soluble mobile form.

Due to the low intrinsic specific radioactivity of U-238, chemical toxicity of U is of greater concern than radiotoxicity. U is poorly absorbed following oral exposure (ca. 2%). Most absorbed U is rapidly excreted in the urine.

The risks of U to human health and the environment are reasonably well characterized. The most sensitive adverse effect in humans is chemically-induced toxicity to the kidney; the tolerable daily intake (i.e. safe lifetime dose) is 0.6-1 µg U/kg body weight (EFSA 2009; WHO 2011). Uranium exposure in European consumers via food and water is well below this level (each about 0.1-0.2 µg/kg/day), but in regions in Europe with high levels of geogenic U, exposure via water may be up to about 0.5 µg/kg/day; infants consuming large amounts of formula diet made with water containing high levels of geogenic U may be at risk. In the environment, water organisms are most sensitive to the toxic effects with a PNEC of 5 µg U/L; uranium in water may exceed this level in geogenic "hotspots".

Studies have shown that P-fertilizer-derived U will increase soil U, but only marginally, and will thus not significantly increase U exposure in humans via food or in soil and sediment organisms. Both geogenic sources and P-fertilizers can contribute to U loads in water. The relative contribution of P-fertilizers to water U is likely to be undetectable except in regions with low geogenic levels of U, such as North Germany. Based on current data, there is no evidence that U contamination of soil or water from P-mineral fertilizers when used in accordance with Good Agricultural Practice (GAP) will increase risks to either human health or the environment.

There is very limited data reporting both Cd and U content of P-fertilizers, and there is inconclusive evidence of a correlation between U and Cd. Higher Cd levels generally imply higher U concentrations; however, it is not possible to reliably predict U concentrations based on measured Cd concentrations, and vice versa.

In conclusion, the impact of U on human health through the food chain is expected to be low, due to a limited transfer rate of U from soil to crops, medium to high mobility in agricultural soils and a poor human oral bioavailability.

SCAHT recommendations are as follows:

- Consider routine monitoring of U content in P-mineral fertilizers
- Consider routine U monitoring in soil, water bodies and sediments as part of the Swiss national surveillance programmes NABO, NAWA, and NAQUA
- Consider monitoring of drinking water U concentrations in suspected “hot spot” regions for which data are lacking (e.g. Berner Oberland, Nord-West Schweiz)
- Consider conducting an impact assessment on the introduction of a guideline value for U in P-fertilizers

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## 2. Abbreviations

| | |
|---|---|
| ATSDR | U.S. Agency for Toxic Substances and Disease Registry |
| BAFU | Bundesamt für Umwelt (Swiss Federal Office for the Environment) |
| BAG | Bundesamt für Gesundheit (Swiss Federal Office of Public Health) |
| BCF | Bioconcentration factor |
| BfR | Bundesinstitut für Risikobewertung (German Federal Institute for Risk Assessment) |
| BfS | Bundesinstitut für Strahlenschutz (German Federal Office for Radiation Protection) |
| BLW | Bundesamt für Landwirtschaft (Swiss Federal Office for Agriculture) |
| BMELV | Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz (German Federal Ministry of Food and Agriculture) |
| BUWAL | Bundesamt für Umwelt, Wald und Landschaft (merged 2006 with Bundesamt für Wasser und Geologie BWG to form the BAFU) |
| Bw | Body weight |
| CAS | Chemical Abstracts Service Registry Number |
| Cd | Cadmium |
| ChemRRV | Chemikalien-Risikoreduktions-Verordnung, SR 814.81 |
| DAP | Diammonium phosphate |
| DCP | Di-calcium phosphate |
| dw | Dry weight |
| EFSA | European Food Safety Authority |
| EINECS | European Inventory of Existing Commercial Chemical Substances |
| FIV | Fremd- und Inhaltsstoffverordnung, SR 817.021.23 |
| GAP | Good Agricultural Practice |
| GSchV | Gewässerschutzverordnung, SR 814.201 |
| Ha | Hectare |
| IAEA | International Atomic Energy Agency |
| INERIS | French National Institute for Industrial Environment and Risks |
| IRSN | French Institute of Radioprotection and Nuclear Safety |
| LOAEL | Lowest observed adverse effect level |
| LOD | Limit of detection |
| LOQ | Limit of quantification |
| MAP | Monoammonium phosphate |
| NABO | Nationales Bodenbeobachtungsnetz (Swiss Soil Monitoring Network) |
| NAQUA | Nationale Grundwasserbeobachtung (Swiss National Groundwater |

| | |
|---|---|
| | Monitoring program) |
| NAWA | Nationale Beobachtung Oberflächengewässerqualität (Swiss National Surface Water Monitoring program) |
| NEA | Nuclear Energy Agency of the OECD |
| NOAEL | No observed adverse effect level |
| NP | Nitrogen-phosphorus |
| NPK | Nitrogen-phosphorus-potassium |
| OECD | Organisation for Economic Co-operation and Development |
| P | Phosphor |
| $P_2O_5$ | Phosphorus (V) oxide (pentoxide) |
| PEC | Predicted environmental concentration |
| PNEC | Predicted no effect concentration |
| SCAHT | Swiss Centre for Applied Human Toxicology |
| SCHER | EU Scientific Committee on Health and Environmental Risks |
| SSP | Single superphosphate |
| TDI | Tolerable daily intake |
| TSP | Triple superphosphate |
| U | Uranium |
| UBA | Umweltbundesamt (German Federal Environment Agency) |
| UF | Uncertainty factor |
| $UO_2^{2+}$ | Uranyl (VI) cation |
| VBBo | Verordnung über Belastungen des Bodens, SR 814.81 |
| WHO | World Health Organization |

## 3. Introduction

Uranium (U) is a naturally occurring trace element which does not fulfil any known biological or physiological function, but which may exert toxic effects in living organism due to its radio- and chemical toxicity. Similarly to cadmium (Cd), U can be found at relatively high concentrations in phosphate rocks (P-rocks), depending on the geological deposit type, and thus occurs as a contaminant in commercial phosphate mineral fertilizers (P-fertilizers), since it is not removed during their manufacture. The application of P-fertilizers can therefore increase the input of U to agricultural soils and to water bodies, raising questions about its potential impact on human health through the food chain and water supplies and the environment.

U is not routinely monitored as part of the Swiss soil monitoring network (NABO) and water monitoring programmes (NAWA, NAQUA), and as a result available monitoring data for Swiss soils and waters are limited. Important knowledge gaps also exist regarding the U content of P-fertilizers on the Swiss market. Recent results from several Swiss Cantonal Laboratories (Bern, Basel, Zurich) showed that the U content of P-fertilizers (n=19) can vary to a great extent (0.02 – 1110.9 g U/ton P[1]), with a median value of 667.2 g U/ton P. However extremely limited, these preliminary results indicate that U can occur as an impurity in P-fertilizers in relative high concentrations. There is currently no limit value for U content in P-fertilizers in Swiss legislation (ChemRRV[2]).

This document is in response to a request from the Swiss Federal Office for Agriculture (BLW) to SCAHT to assess the relevance and contribution of U as an impurity in P-fertilizers to potential risks to human health and the environment, in the light of current scientific knowledge. In addition, because Cd and U typically occur as co-contaminants in P-fertilizers, SCAHT was requested by the BLW to review the literature on the extent to which Cd and U content of P-fertilizers are correlated.

The present report focuses on the chemical toxicity of U, following oral exposure through food and water. Because this is the major source of risk, other routes of exposure are not considered, nor is U potential radiotoxicity (by oral, dermal or inhalation exposure).

## 4. Data sources

All relevant regulatory data on physical-chemical properties, ecotoxicity, environmental fate and behaviour, and toxicity of U are accessible from the Organisation for Economic Co-operation and Development (OECD) eChemPortal (OECD, 2015) and from the "Portail Substances Chimiques" hosted by the French National Institute for Industrial Environment and Risks (INERIS, 2015). These data concern elemental U (CAS no. 7440-61-1; EINECS 231-170-6) but also U ions, compounds and salts.

Preference is given to public-access review documents from vetted sources such as regulatory agencies and other government bodies, which often benefit from an internal peer-review process by panels of experts, rather than primary data sources. For example, a useful summary of environmental chemistry, toxicity and fate of U is provided by the French Institute of Radioprotection and Nuclear Safety (IRSN, 2010); relevant toxicity data are

[1] Note: the concentrations of metals such as Cd or U in P-fertilizers are generally expressed at EU and international level in terms of phosphate pentoxide ($P_2O_5$), whereas in Swiss reports and legislation it is expressed in terms of elemental phosphorus (P). The conversion factor is $P_2O_5$ x 2.291 = P.

[2] Verordnung zur Reduktion von Risiken beim Umgang mit bestimmten besonders gefährlichen Stoffen, Zubereitungen und Gegenständen (Chemikalien-Risikoreduktions-Verordnung, ChemRRV) vom 18. Mai 2005, SR 814.81.

comprehensively detailed by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR, 2013) and are summarized in the U.S. ToxNet Hazardous Substances Databank (HSDB, 2015); the European Food Safety Authority (EFSA, 2009) and the World Health Organization (WHO, 2012b) summarise data relevant to human risk assessments; the EU Scientific Committee on Health and Environmental Risks (SCHER, 2010) give scientific opinion on the potential risks U pose to soil and water media; the International Atomic Energy Agency (IAEA) and the Nuclear Energy Agency (NEA) of the OECD issued in 2014 the 25$^{th}$ edition of the Uranium „Red Book“ (OECD, 2014), which is a recognised world reference providing background information on U trade, geographic resources, world supplies, etc.

# 5. Occurrence and physical-chemical properties

Uranium is a ubiquitous naturally occurring trace element in the earth's crust (average 2-3 ppm). It has three natural alpha-emitting radioisotopes, U-238, U-235 and U-234. Their relative abundance is >99%, 0.7%, and 0.005%, respectively. U-234 is more radioactive than the other isotopes and contributes approximately half of the total radioactivity from natural U. U-238 is the least radioactive isotope but because of its relative abundance it also contributes approximately half of the total radioactivity from natural U (IRSN, 2010).

Chemically, U is a redox-sensitive element and can change oxidation state if conditions change, which affects its mobility in soil and aqueous media. The geochemically relevant oxidation states are U(IV) and U(VI), the former being a low solubility form of U and the latter a water-soluble mobile form (Suksi, 2015). U(IV) is the primary oxidative state in minerals in association with hydroxides, phosphates and fluorides, arsenates and vanadates. In environmental oxidizing conditions, U(IV) is readily oxidised to U(VI) as uranyl ($UO_2^{2+}$) cation, which leaches out from the minerals to form soluble stable complexes in natural waters with carbonates, phosphates and sulphates (Murphy and Shock, 1999; Smedley et al, 2006, cited in Stalder et al, 2012). At higher pH, the uranyl cation hydrolyses extensively, forming monomers, dimers, and trimers (Bachmaf et al, 2008).

Uranium kinetics in the human body and the environment are determined by its chemical speciation; soluble U(VI) compounds (e.g. uranyl complexes) are more mobile than insoluble U(IV) compounds (e.g. U oxides). Besides U chemical speciation (and other intrinsic physico-chemical properties), the kinetics of U in all media will be determined by a number of simultaneously occurring factors such as pH, oxidizing or reducing conditions, as well as the properties, type and quality of any given environmental matrix.

These factors, among others, will contribute to determine the various transport processes and U mobility, i.e. its retention (sorption) or leaching from soil, water or sediment, and will affect U reactivity, bioavailability and toxicity in all environmental media (Poinssot and Geckeis, 2012; Zielinski et al, 1997).

# 6. Human health risk assessment

## 6.1 Hazard evaluation

### Chemical toxicity versus radiotoxicity

The chemical toxicity of natural U is generally considered to be of greater concern that its radiotoxicity (Kocher, 1989). This is primarily due to the low intrinsic specific radioactivity of U-238. For example, a joint opinion from the German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) and the Federal Office for Radiation Protection (Bundesamt für Strahlenschutz, BfS) concluded that the radiological risk for the German

consumer from dietary U intake (including drinking water and mineral water as well as foodstuffs) is very low; estimated exposure to radiation is well below guideline values. They concluded that, in the range of dietary exposure, the chemical toxicity of U poses a significantly greater risk to health than radiotoxicity (BfR, 2007). Similar conclusions have been expressed by the ATSDR (2013) and EFSA (2009).

**Critical target organ toxicity**

Experimental animal studies indicate that the kidney is the primary target for U chemical toxicity, following oral, inhalation and dermal exposure. The primary effect is damage to the renal proximal tubules, with possible involvement of the glomerulus at high exposures. The severity of effects after oral ingestion depends on the solubility of the U compound (ATSDR, 2013; EFSA, 2009). The mechanistic basis for U-induced renal toxicity is apparently the competition of the uranyl cation for $Mg^{2+}$ and $Ca^{2+}$ adenosine 5' triphosphate (ATP) binding sites and subsequent disruption of active transport in the cells of the renal proximal tubule and associated structures (HSDB, 2015).

Several epidemiological studies of populations exposed to U in drinking-water have shown a positive correlation with urinary markers of glomerular (e.g. albumin, glucose) or proximal tubule function (e.g. beta-2-microglobulin, calcium, phosphate) or markers of cytotoxicity (e.g. alkaline phosphatase) (Kurttio et al, 2002, 2006; Mao et al, 1995; Zamora et al, 1998) along with modest alterations in proximal tubular function (e.g. Zamora et al, 1998; Kurttio et al, 2002). However, values of exposed persons were often within the normal physiological range, and the findings are not consistent between studies. Other studies in exposed persons showed no evidence of alteration of renal proximal tubule function and no clear sign of nephrotoxicity (Kurttio et al, 2006; Seldén et al, 2009). Evidence for effects on the human kidney is equivocal even at relatively high exposure levels (95$^{th}$ percentile, 1094 µg U/day) (WHO, 2012b). WHO (op. cit.) concluded that no clear no-effect concentration can be derived from the human studies to date, given that most of the study populations are quite small (i.e. n=50-300), and that variations in the normal range of distribution of measured biological parameters (e.g. creatinine, glucose) are common in a population without necessarily having clinical significance. Overall, the epidemiological evidence does not provide a reliable dose response characterization, due to the large range of U levels in drinking water (i.e. between one and six orders of magnitude, depending on the study), as noted by the ATSDR (2013).

**Toxicokinetics**

U is poorly absorbed following inhalation, oral or dermal exposure and the amount absorbed is dependent on the solubility of the U compound. Studies in human volunteers indicate that only approximately about 2% (0.1-6%) of the U from drinking water and dietary sources is absorbed (EFSA, 2009; ATSDR, 2013; Chen et al, 2011). In body fluids, U(IV) is likely to oxidize to U(VI), followed by formation of the soluble uranyl cation. Circulating U is filtered through the kidney and excreted in the urine. The elimination half-time in the human kidney has been estimated to be 1-6 days for 99% of the total renal U, and 1500 days for the remainder (probably mainly in bone); thus, under conditions of normal daily intake, the terminal half-life of U in the whole human body has been estimated to range between 180 and 360 days. The normal adult total body burden has been reported to range from 40 to 90 µg, and to be distributed as follows: >50% in bone, 20% in muscle, 15% in fat, 4% in the blood,1-2 % in the lungs, liver and kidneys (EFSA, 2009). Higher estimates can be found in the literature for liver (16%) and kidneys (8%) (ATSDR, 2013).

**Health-based reference values (tolerable intake)**

A tolerable daily intake (TDI) of 0.6 µg U/kg body weight (bw) was established by WHO in the third edition of the Guidelines for Drinking-water Quality (WHO, 2004; see also WHO, 2012a, 2012b). This TDI was based on a study in rats (Gilman et al, 1998, cited in WHO, 2012b), in which U was administered in drinking-water for 91 day; the lowest observed adverse effect level (LOAEL) for degenerative lesions in the proximal convoluted tubule of the kidney in males was 0.96 mg uranyl nitrate hexahydrate/L, equivalent to a U dose of 0.06 mg U/kg/day. Application of an uncertainty factor (UF) of 100 for intraspecies and interspecies variation yields a TDI of 0.6 µg/kg bw. WHO did not add an additional UF to account for the use of a LOAEL instead of a no observed adverse effect level (NOAEL) because the lesions reported were of minimal severity, and neither did they add an additional UF for the length of the study (91 days, versus lifetime exposure in humans) because the estimated half-life of U in the kidney is 15 days, and there is no indication that the severity of the renal lesions would be exacerbated following continued exposure. Based on this TDI, WHO (2004) derived a provisional guideline value of 15 µg U/L for drinking water.

EFSA (2009) used the WHO (2004) TDI of 0.6 µg/kg in a risk assessment on dietary exposure to U in foodstuffs including mineral water. EFSA noted that no new data were identified that would require a revision of this TDI and endorsed it.

WHO (2012b) used human data to derive a revised (increased) TDI of 60 µg, i.e. 1 µg U/kg bw for a 60 kg person, for the fourth edition of the Guidelines for Drinking-water Quality (WHO, 2011). The TDI was based on data from a Finnish epidemiological study (Kurttio et al, 2006, cited in WHO, 2012b) which reported no evidence of renal damage from 10 renal toxicity indicators of both cytotoxicity and renal function at a median U concentration of 25 µg/L drinking water, with an interquartile range of 5-148 µg/L and a maximum concentration of 1500 µg/L. The NOAEL in this study was calculated to be 637 µg U/day, derived from the 95$^{th}$ percentile of the U exposure distribution (WHO, 2012b). Applying an UF of 10 for inter-individual differences to this NOAEL yielded the TDI of 60 µg.

Based on this TDI, WHO (2011) derived a provisional guideline value of 30 µg U/L drinking water. The same limit applies in the Swiss drinking water Ordinance (FIV, 2014[3]). In contrast, the German Trinkwasserverordnung sets a limit value of 10 µg U/L (BMG, 2011).

The WHO value was designated as provisional on the basis of scientific uncertainties surrounding U toxicity. Concerning these "uncertainties", Frisbie et al. (2013) noted that the "no-effect group" used by WHO (2011) to derive the TDI in fact had increased diastolic and systolic blood pressure, and increased urinary glucose excretion. Frisbie et al. (op. cit.) therefore expressed the opinion that the current derived WHO guideline value (30 µg U/L drinking water) may not protect children, people with predispositions to hypertension or osteoporosis, pre-existing chronic kidney disease, and anyone with long-term exposure. Since little information is available on the chronic health effects of exposure to environmental U in humans (WHO, 2011), it is not clear whether these endpoints are in fact related to U exposure; further research would be necessary to support the opinion of Frisbie et al. (2013).

**Conclusion**: there is a need to better address causality, increase study power with larger study populations and establish a clear dose-effect characterization in humans to better understand the long term effects on the kidney of low dose dietary exposure to U. More epidemiological research is needed to close these gaps. It should be noted that the key study in rats by Gilman et al. (1998) could not provide a clear dose response relationship; therefore, more chronic animal studies are needed to better establish the dose-response of U nephrotoxicity.

[3] Schweizerischen Fremd- und Inhaltsstoffverordnung (FIV, SR 817.021.23)

## 6.2 Exposure and risk evaluation from U in food and drinking water

Food and drinking water are the major human exposure pathways for the general, non-occupationally exposed population; additional exposure sources such as ambient air is considered to be extremely low (EFSA, 2009; WHO, 2011).

The following section focuses primarily on a dietary risk assessment of U in foodstuffs and water that was conducted by the EFSA CONTAM Panel (EFSA, 2009), but includes other relevant data as appropriate.

### Food

According to WHO (2011), the intake of U through food is between 1 and 4 µg U/day, while for ATSDR (2013), the estimated daily intake of U ranges from 0.9-1.5 µg U/day. According to Bosshard et al. (1992), the mean U intake in Switzerland from foodstuffs is assumed to be about 1.5 µg U/person/day.

In a dietary risk assessment, EFSA (2009) explored several U exposure scenarios via foodstuffs (and drinking water) for adults in Europe (see Table 1). It should be noted that occurrence data for U in food were based only on data from Germany.

For an average consumer and average occurrence values (scenario 1), taking upper-bound estimates, food contributed 47% of the total dietary exposure, 49% in scenario 2 and 32% in scenarios 3 and 4. Lower-bound estimates give values between 16-17%. General mean (scenario 1) and high consumption (scenario 2) exposure from food were 0.009-0040 µg U/kg bw/day and 0.016-0066 µg U/kg bw/day, respectively.

**Table 1: Dietary U exposure (µg/kg bw/day) in European consumers (EFSA, 2009)**

| | Scenario | | | |
|---|---|---|---|---|
| | 1<br>general mean consumption | 2<br>general high consumption | 3<br>local high contamination, mean consumption | 4<br>local high contamination, high consumption |
| Food | 0.009-0.040<br>(0.053) | 0.016-0.066<br>(0.094) | 0.036-0.087<br>(0.122) | 0.063-0.143<br>(0.222) |
| Water | 0.043-0.043<br>(0.064) | 0.082-0.082<br>(0.118) | 0.186-0.186<br>(0.278) | 0.355-0.355<br>(0.513) |
| Overall dietary | 0.052-0.085<br>(0.105) | 0.092-0.135<br>(0.171) | 0.222-0.275<br>(0.364) | 0.393-0.452<br>(0.622) |

Values are lower-bound and upper-bound values in µg U/kg bw/day (value in brackets = upper-bound country-specific maximum estimate). Lower-bound values = values below the LOD and values between the LOD and LOQ which were set to zero and to LOD, respectively. Upper-bound values: values below LOD and values between the LOD and LOQ which were set to LOD or LOQ value, respectively.
Scenario 1 = mean values for occurrence and consumption; scenario 2 = mean occurrence, lower and upper 95$^{th}$ percentile consumption; scenario 3 = 95$^{th}$ percentile occurrence, mean consumption; scenario 4 = 95$^{th}$ percentile occurrence and consumption (the most extreme and unlikely scenario).

**Drinking water**

EFSA (2009) collated data on U concentrations in European drinking water. Median U concentrations were ≤1.9 µg U/L, but the maximum values, 112.51 µg U/L in tap water and 152.70 in bottled water, exceeded the current WHO (2011) guidance limit of 30 µg/L (see Appendix B).

In a drinking water risk assessment, WHO (2011) concluded that intake through drinking-water is normally extremely low; however, in circumstances in which is present in a drinking-water source, the majority of intake can be through drinking-water. WHO (op.cit.) noted that levels in drinking-water are generally less than 1 µg U/L, although up to 700 µg U/L has been measured in private supplies, i.e. some levels substantially exceed the WHO provisional guideline value of 30 µg U/L. WHO (op.cit.) commented that precipitate action should be avoided (i.e. do not panic) if drinking water concentrations exceed the provisional guideline value; consideration should first be given to the availability of alternative safe sources, and reduction to 1 µg U/L should be achievable using conventional water treatment (e.g. coagulation or ion exchange).

From its dietary risk assessment, EFSA (2009) concluded that drinking water may contribute about 50% of total U exposure in the average exposure scenario for consumers (Table 1, Scenario 1); in more extreme scenarios, water may contribute more to total U exposure, i.e. between 60%-90%, based on lower bound and upper bound estimates (Table 1, Scenarios 2-4). In particular, EFSA considered the case of highly exposed sub-groups of the population at the 95$^{th}$ percentile, in some local communities with high U concentrations in their water supply, with a mean (Scenario 3) or high water consumption (Scenario 4). In the extreme case, when high local U concentrations occur together with high consumption (Scenario 4), the upper-bound exposure estimate is 0.36 µg U/kg bw/day as a median across the countries (country-specific maximum 0.51 µg U/kg bw/day).

Data on water consumption in Switzerland were available to EFSA (2009) from three Swiss surveys conducted in 2007 on a total of 83 subjects, comprising of both men and women. Mean and 95$^{th}$ percentile consumption values were, respectively, 740 and 1680 g/day for tap water, 270 and 860 g/day for bottled water, and 820 and 1740 g/day for the group “Tea, coffee, beer, soft drink”. Using these data, upper-bound U exposure estimates in water were equal to 0.062, 0.112, 0.259 and 0.467 µg U/kg bw/day according to the four exposure scenarios, respectively. Lower- and upper-bound estimates were virtually unchanged. Tap water and “Tea, coffee, beer and soft drinks” were the major contributors, accounting for 41 % and 44 % of total U exposure in scenario 1 and 3, respectively (EFSA, 2009).

These data show that Switzerland exposure estimates were at the upper end of the exposure range but still below the upper-bound country-specific maximum estimate as shown in Table 1.

Exposure in infants (3 month old, 6 kg) was also calculated by EFSA (2009) based on consumption of infant formula reconstituted with U containing water. The results are summarized in Table 2.

**Table 2: Uranium exposure to infants from water-based formula in Europe (EFSA, 2009)**

| | Scenario | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Tap water | 0.241-0.250 | 0.328-0.340 | 1.047-1.047 | 1.422-1.422 |
| Bottled water | 0.184-0.203 | 0.250-0.275 | 0.844-0.844 | 1.147 |

Values are lower- and upper-bound values in µg U/kg bw/day. Source: EFSA 2009

EFSA (2009) concluded that in specific areas where U concentrations in drinking water are high, the exposure estimates are close to, but still below the WHO (2004) TDI of 0.6 µg U/kg bw. However, for infants fed high quantities of infant formula made up with water containing high levels of U, exposure in relation to body weight may be up to three times higher than for adults, and recommended that such exposure should be avoided.

A similar conclusion for infants was reached by Stalder et al. (2012) based on reported U concentrations in Swiss water samples collected between 2002 and 2011[4]. Taking the infant scenario used by the EFSA (2009), Stalder et al. (2012) have calculated infant exposure to U for Switzerland (see Table 3). The WHO (2004) TDI of 0.6 µg U/kg bw adopted by EFSA (2009) is exceeded with mean consumption of formula at high U contamination levels (8.84 µg U/L water), and the WHO (2011) TDI of 1 µg U/kg bw is exceeded with high contamination and high consumption levels (917 mL).

Based on the Swiss regulatory limit of 30 µg U/L (FIV, 2014), Stalder et al. (2012) estimated that six communes (0.7% of the total population of Switzerland) considered as "hot spots" would have to implement measures to reduce U concentrations in parts of their water supply (see Appendix B). According to Bucheli et al. (2012), the Swiss competent authority (Federal Office of Public Health, BAG) considers that a limit value lower than 30 µg U/L is not justified. Since the revision of the FIV (2014), municipalities whose water supplies exceed the new drinking water guideline have a 5 years deadline to take the necessary cleaning measures (BAG, 2012).

**Table 3: Uranium exposure to infants (µg/kg bw/day) from water-based formula in Switzerland**

| | Assumed formula consumption | |
|---|---|---|
| **Level in water** | **675 mL/day (mean)** | **917 mL/day (95th percentile)** |
| 2.04 µg U/L (mean) | 0.23 | 0.31 |
| 0.77 µg U/L (median) | 0.09 | 0.12 |
| 8.84 µg U/L (95$^{th}$ percentile) | 0.98 | 1.33 |

Source: Stalder et al, 2012

**Note**: The water U concentration values used by Stalder et al. (2012) are comparable to those used by EFSA (2009) (Table 4).

**Table 4: Uranium levels (µg/L) in European drinking water (EFSA, 2009)**

| | U concentration (µg/L) | | |
|---|---|---|---|
| | **Median** | **95th percentile** | **Maximum** |
| Tap water (n=5475) | 0.66-0.77 | 9.46 | 112.51 |
| Bottled water (n=1565) | 0.36-0.50 | 7.63 | 152.70 |
| Soft drinks (n=57) | 0.00-0.50 | 3.20 | 5.60 |

The intervals indicate lower- and upper-bound values, while a single value indicates no difference between the two values.
Source: EFSA, 2009 (see Appendix B for individual country listings)

**Note**: The *German Trinkwasserverordnung* sets a limit value of 10 µg U/L (BMG, 2011).

[4] Median content by canton ranged from 0.18-2.28 µg U/L (Neuchatel and Uri, respectively). The highest value measured was 92.02 µg U/L in Martigny VS (Stalder et al, 2012).

Based on levels of U in German tap and mineral waters, Hassoun and Schnug (2011) (see also Hassoun, 2012) calculated that the contribution of drinking water to the daily dietary intake of U was 67-88%, with a much higher mean intake from highly mineralized bottled waters (15.1 µg U/person/day) than from tap water (2.9 µg U/person/day). These values correspond to an exposure of 0.25 µg U/kg bw/day and 0.048 µg U/kg bw/day for a 60 kg adult, respectively, and are in good agreement with the highest and lowest exposure scenario in EFSA (2009), respectively.

**Conclusion**: The EFSA (2009) dietary risk assessment showed that overall country-specific lower- and upper-bound U exposure estimates for adults varied between 0.05 and 0.45 µg U/kg bw/day considering different exposure scenarios, with water contributing between 50% up to 90% of the overall dietary exposure, based on lower- and upper-bound exposure estimates. For infants, the lower- and upper-bound U exposure estimates varied between 0.18 and 1.42 µg U/kg bw/day, for either bottled- or tap water - based infant formula.

These data show that human U exposure from food is below the WHO (2004) TDI of 0.6 µg U/kg bw and the WHO (2011) TDI of 1 µg U/kg bw, but that exposure via drinking water may in some cases exceed the TDI and therefore require risk management measures.

Uncertainties however exist in the EFSA (2009) dietary risk assessment. It concluded that its evaluation was more likely to have overestimated than underestimated the risk, because risk estimates in the high exposure scenarios (local average and high consumption of highly contaminated water) were rather conservative. However, it also noted that the lack of representative food results might have led to an underestimation in the average exposure scenario. More detailed data are needed on U concentrations in foodstuffs (from more than a single Member State) to improve the accuracy of the food exposure estimates and to better account for the contribution of food to the overall U dietary exposure across European populations. However, it is unlikely that this would shift the balance between food and water and it is anticipated that water would still remain the main contributor of U total body burden for the general, non-occupationally exposed population.

# 7. Environmental risk assessment

## 7.1 Hazard

Limited data on the ecotoxicity of U are available (SCHER, 2010). Some studies have recently compiled the available chemical toxicity data of U for non-human biota, in particular Hinck et al. (2010) and Sheppard et al. (2005); for more details, the reader is further referred to these works.

While there is no or very limited ecotoxicity data for species such as cynobacteria, aquatic vascular plants, amphibians or wild mammals, chemical toxicity of U has been reasonably well characterized in mammals (except wild species) and fishes; some data are also available for terrestrial and aquatic invertebrates (Hinck et al. 2010).

- Studies on mammals have shown that the kidney is also a sensitive target organ of U chemical toxicity, in a very similar manner to humans (cellular injury, tubular necrosis (ATSDR, 2013; Hinck et al, 2010).
- Studies on fishes show that U toxicity can vary widely, depending on water quality conditions, e.g. total hardness and alkalinity of the water, as shown by Sheppard et al. (2005).
- Studies on terrestrial (e.g. earthworm) or aquatic (e.g. bivalve) invertebrates usually show effects such as reduced mobility, increased mortality or decreased reproduction rate, but the range of U concentrations to which these organisms were exposed varied to a large extent, with hardly any information available on dose-response relationships (Hinck et al, 2010).

Sheppard et al. (2005) derived predicted no effect concentrations (PNECs) for chemical toxicity of U to non-human biota, including terrestrial and freshwater organisms, mammals and plants, for various environmental compartments, as summarized in Table 5.

**Table 5: Uranium PNECs**

| Type of biota | PNEC values |
|---|---|
| Terrestrial plants | 250 mg U/kg dry soil |
| Other soil biota | 100 mg U/kg dry soil |
| Freshwater plants | 5 µg U/L water |
| Freshwater invertebrates | 5 µg U/L water |
| Freshwater benthos | 100 mg U/kg dry sediment |
| Freshwater fish | 0.4 mg U/L water at <10 mg $CaCO_3$/L (very soft water)<br>2.8 mg U/L water at 10–100 mg $CaCO_3$/L (soft water)<br>23 mg U/L water at >100 mg $CaCO_3$/L (hard water)<br>or as a function of hardness (0.26 * mg $CaCO_3$/L) mg U/L |
| Mammals | 0.1 mg U/kg bw/day |

Source: Sheppard et al, 2005

The most sensitive organisms are freshwater plants and freshwater invertebrates, with a PNEC of 5 µg U/L water.

A detailed summary of these and other PNECs derived by various authors is given in IRSN (2010).

Sheppard et al. (2005) also estimated the corresponding radiological doses and concluded that the chemical toxicity of U is the greater concern for non-human biota in comparison with its radiotoxicity.

## 7.2 Exposure and risk

SCHER (2010) summarized the range of natural U concentrations in various environmental compartments (see Table 6).

**Table 6: Uranium concentrations in environmental compartments (SCHER 2010)**

| Matrix | Typical range of natural U | References |
|---|---|---|
| Soil | 0.3 – 11.7 mg/kg | (UNSCEAR 1993) |
| Surface water | 0.03 – 8.0 µg/L | (WHO 2001) |
| Groundwater | 0.003 – 2.0 µg/L | (Orloff et al 2004; WHO 2001) |
| River water | 0.2 – 0.6 µg/L | (Palmer & Edmond 1993) |

Source: SCHER, 2010

These values are in reasonably good agreement with those of Geochemical Atlas of Europe (De Vos et al, 2006, also cited in IRSN, 2010), which are summarized in Table 7.

**Table 7: Uranium concentrations in environmental compartments (De Vos et al, 2006)**

| | Unit | Min | Median | 90$^{th}$ %ile | Max |
|---|---|---|---|---|---|
| Subsoil | mg U/kg | <0.1 | 2.03 | 3.94 | 30.3 |
| Topsoil | mg U/kg | 0.21 | 2.00 | 3.76 | 53.2 |
| Water | µg U/l | <0.002 | 0.32 | 2.43 | 21.4 |
| Stream sediment | mg U/kg | <1.0 | 2.00 | 7.00 | 98.0 |
| Floodplain sediment | mg U/kg | <1.0 | 2.00 | 4.00 | 89.0 |

Source: De Vos et al, 2006

Median values for European soil (top- and subsoil) and sediments (stream and floodplain) are about 2 mg U/kg, while water contains about 0.3 µg U/L (De Vos et al, 2006).

These reported concentrations are substantially lower than PNECs for relevant organisms in soil and water, but maximum concentrations in sediments are close to the PNEC for freshwater benthos (100 mg U/kg dry sediment).

### Soil

In Europe, the median U concentration in soil is approximately 2 mg U/kg (De Vos et al, 2006; Table 7). Locally, specific geological conditions may lead to much higher concentrations of U (ca. 50 mg U/kg) (IRSN, 2009).

In German agricultural topsoils, median U concentrations are between 0.5 and 3.2 mg U/kg, depending on soil type (Utermann and Fuchs 2008, cited in UBA 2012; Utermann et al 2009).

Data for U levels in Swiss soils are scarce (Schmutz and Utinger, 2015; Surbeck, 2014). U is not routinely monitored as part of the Swiss soil monitoring network (NABO, Nationale Bodenbeobachtungsnetz). Limited data on U levels in Basel-Landschaft topsoils (n=64) have very recently been published by Schmutz and Utinger (2015), based on various cantonal monitoring campaigns[5], with a reported median of 1.2 mg U/kg dry weight (dw) (range: 0.5-3.6 mg U/kg dw). Schmutz and Utinger (2015) noted that the results were in good agreement with reported German values (UBA, 2012). Surbeck (2014) estimated that U levels in agricultural topsoils are ca. 3 mg U/kg (based on a study by Estier and Gurtner, 2013).

**Sediments**

Median values for European sediments (stream and floodplain) are about 2 mg U/kg according to De Vos et al. (2006), but U levels in sediments can peak as high as 89-98 mg U/kg, which is around 2-3 times higher than the maximum concentrations reported for soils (see Table 7).

In Germany, Schneider and Reincke (2006) found U concentrations of 76, 168.7 and 58 mg U/kg sediment (quarterly mean values, period 1992-2003) for three areas of the Zwickauer Mulde river basin catchment.

Small rivers sediments in Kanton Basel-Landschaft (n=11) showed values from 0.7-1.0 mg U/kg dw (Schmutz et al, 2013). We could find no data in the open literature for Swiss lake sediments.

**Surface water and groundwater**

In Europe, the average geochemical background of continental surface water is about 0.3 µg U/L (De Vos et al, 2006; see Table 7). Variation in U concentration in river water extends over four orders of magnitude (average content between 0.02 and 6 µg/L); it can attain 11 µg/L and on very rare occasions exceed 20 µg/L (IRSN, 2010). In France, the U background in river water is estimated to be 0.44 µg U/L in sedimentary rock areas and 0.15 µg U/L in the Hercynian shelf and Alpine areas; this inverse distribution from that found in soil is related to water chemistry, particularly its acidity (IRSN, 2010). Utermann et al. (2009) reported that U concentrations in leach water and superficial groundwater from loose rock areas in North Germany varied by three to four orders of magnitude; they were lower at forest than agricultural sites, and lower at sandy than loess soils. The dominant U species depended on pH; mainly mobile uranyl-carbonate species at agricultural sites, mainly less mobile uranyl cations at forest sites.

In regions with naturally occurring high concentrations of U ore deposits, natural background (geogenic) levels of U in water are up to 10 µg U/L (Canada, 2011). In Canada which has low geogenic U, surface water levels are much lower; it was shown that 75% of surface water samples had <1 µg U/L, and in many instances the levels were <0.05 µg U/L or below the detection limit (Canada, 2011).

The German UBA (2012) reported that the regional distribution of U concentrations in groundwater largely agrees with the geological setting. 90$^{th}$ percentile concentrations ranged from 0.57-14.9 µg U/L, maxima from 11.8-1134 µg U/L.

Similarly, high levels of U in Swiss waters are associated with geogenic sources (Bucheli et al, 2012). In a national monitoring survey by the Swiss Federal Office of Public Health (BAG), Stalder et al. (2012) assessed 5548 Swiss water samples (2002-2011, 92% groundwater, see Appendix B). U content varied considerably (<0.05-92.02 µg U/L); the samples with

[5] Data („Archivproben“) have been collected from 64 sites out of which 4 were NABO sites

higher U concentrations generally originated from regions with known higher geogenic U content (Fribourg, Wallis, Graubünden, Tessin). In these cantons, 92% of the samples had <10 µg U/L, and 63% had <2 µg U/L.

Currently, U is not routinely monitored as part of the Swiss national surveillance programmes of surface waters (NAWA, Nationalen Beobachtung der Oberflächengewässerqualität) and groundwater (NAQUA, Nationale Grundwasserbeobachtung). The Swiss Federal Office for the Environment (BAFU) reported the results of a pilot study conducted by the University of Neuchatel and BAG in 2005 and which investigated 50 surface water samples for the sum of U-234 and U-238 (BAFU, 2009); the median value was 23 mBq/L (corresponding to 1.9 µg U/L[6]), and the range was 10-266 mBq/L (corresponding to 0.8-21.5 µg U/L). Some additional data are available and were reviewed by Surbeck (2014).

**Potential for bioaccumulation and biomagnification of U in the terrestrial and aquatic foodchains**

The bioavailability of U in terrestrial, aquatic and sediment ecosystems is controlled by U chemical speciation, the physico-chemical properties of the environmental matrix under consideration, and kinetics. Chapter 8 details U behaviour in soil, water and sediments.

U enters the terrestrial or aquatic foodchains via adsorption by plants or consumption of prey. Terrestrial plants poorly accumulate U, and bioaccumulation is also low in foraging grazers. No data are available for wild mammals or birds. Bioconcentration factors (BCFs) for U vary across aquatic species; they are rather high for algae, low for aquatic vascular plants, intermediate for fish and highly variable for aquatic invertebrates.

Planktivorous and bottom-feeding (benthic) species have been shown to accumulate higher U concentrations than piscivorous fish, due to the potential ingestion of sediments (Driver, 1994, cited in Hinck et al, 2010). Early studies observed that organisms feeding on or near stream and lake sediments receiving drainage from U mill tailings contained higher concentrations of U than pelagic or predatory species (Hanson, 1985, cited in Hinck et al, 2010.

Driver (1994) postulated that BCFs would decrease about one order of magnitude at each step in an aquatic food chain and further concluded that:

- biomagnification of U does not occur through food-chain transfers, with low transfer coefficients from plants to foraging grazers in terrestrial environments (Driver 1994, cited in Hinck et al, 2010).
- biomagnification of U would not occur in aquatic or semi-aquatic food chains with species such as amphibians, fish-eating birds and mammals such as otters;

Despite many knowledge gaps, we did not find any evidence from our review of the literature that contradict the above conclusions.

**Conclusion**: The upper estimates of U levels in soil in the range of ca. 3-3.6 mg U/kg soil (Schmutz and Utinger, 2015; Surbeck, 2014; Utermann et al, 2009) are still well below the estimated PNECs for terrestrial organisms, mammals and plants as well as benthic organisms in sediments. Although many of the water samples reported by Stalder et al. (2012) have U concentrations below the $PNEC_{water}$ for freshwater plants and invertebrates of

[6] For reference purposes, 1 µg U/L equals 12.4 mBq $^{238}U$/L

5 µg U/L, which are the most sensitive organisms (Sheppard et al, 2005), there may be some risk (i.e. water concentration > PNEC) to water organisms in geogenic "hotspots".

Many knowledge gaps still exist in the ecotoxicity database of U, but more insight has been gained over the last few years. Still little is known about the contribution of sediments to U exposure for some type of biota such as aquatic vertebrates, and water-sediment systems need to be better characterized, taking into account biotic and abiotic factors. The extent to which sediments can act as a reservoir sink for U, as shown for many other metals (e.g. Hinck et al, 2010; Korfali et al, 2006; NRC, 2003; Schneider and Reincke, 2006; Wu et al, 2014), remains to be determined.

Data on U concentrations in Swiss soils and sediments are scarce; more data are available for Swiss waters, but data for lakes in particular are needed.

# 8. P-fertilizer derived U contribution to environmental/human risk

Some authors consider that P-fertilizers are the primary (if not the sole) source of U entry into agricultural soils (Rogasik et al, 2008; Kratz and Schnug, 2006; Kratz et al, 2011). Other sources, in addition to geogenic sources, include natural (e.g. erosion) and anthropogenic combustion processes and construction activities in the alpine environment (Utermann et al, 2009).

A continuous input of U through fertilization may lead to an increase of U in soils. In turn, this may threaten the integrity of agricultural soils and the sustainability of agriculture, and contaminate the food chain and drinking water supplies.

Rafsanjani et al. (2008) argued that because of the distinctly higher solubility of P-fertilizer-derived U, this path of U contamination has to be assessed more critically than that of geogenic U. It has been suggested that anthropogenic sources may redistribute much faster U in the environment that through the natural processes (Deutscher Bundestag, 2011), and that P-mineral fertilizers use may increase the mobility of soil U (UBA, 2012).

Yet U derived from the application of P-fertilizers and U from natural (geogenic) origin are virtually the same. As noted by Poinssot and Geckeis (2012), establishing the origin of U in the water compartment is a complex task, because the biosphere and the geosphere are interconnected via groundwater movement, and U residence time in surface water and groundwater can span months and years, respectively. It has been suggested that sediments may act as a reservoir sink for U, similarly to observations for other metals (Alam and Cheng, 2014; Hinck et al, 2010; Schneider and Reincke, 2006).

## 8.1 U kinetics in soil

The retention and mobilization capacity of U in soils control its fate. Degryse et al. (2009) concluded that soil pH is the most important soil property determining the retention of free metal ion and thus leaching rate, based on a detailed technical review on the role of pH in solid–liquid partitioning of metals in soil. Uranium partition coefficients (Kd) for soils are very variable; Vandenhove et al. (2007) suggested that pH was the best predictor of soils partition coefficients (Kd) for soils with a pH ≥ 6, but that organic matter content or amorphous iron oxides were better predictors at more acidic pH values (Hooda, 2010).

The mobility of U in soil will also be strongly influenced by the soil characteristics such as the soil type (e.g. clay, lime, sand) and texture, moisture, mineralogy (e.g. presence of strongly binding iron oxides) and the presence or absence of certain specific ligands (e.g. carbonate,

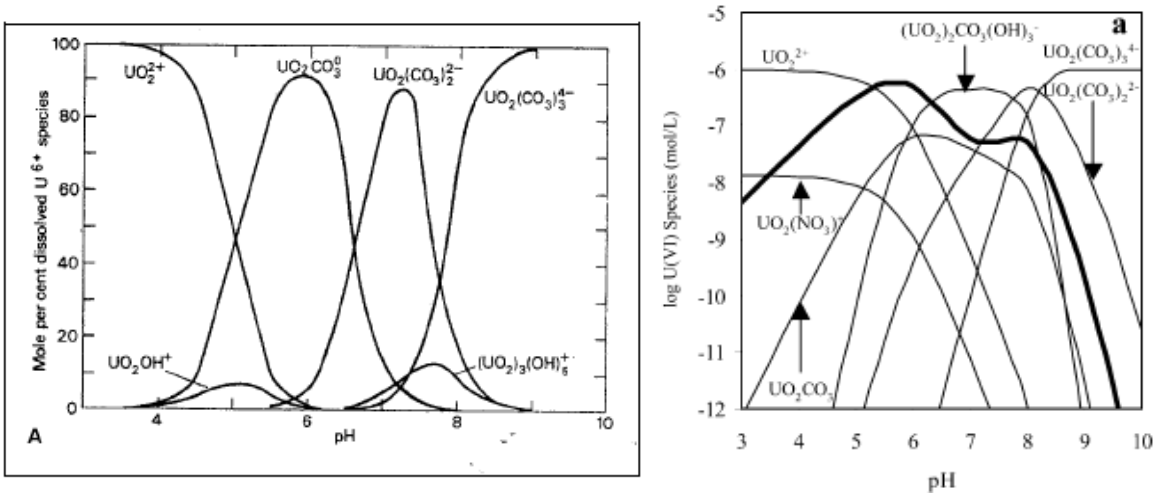
phosphate, sulfate), which will affect U sorption to soil particles and other transport processes (Poinssot and Geckeis, 2012; Zielinski et al, 1997).

Organic matter, in particular humic acids, also plays an important role in the retention/mobilization of U in soils. Uranium mobility can be reduced by complexation to humic acids (Dall'Aglio, 1971) and increased when humic acids are mobilized (Karlsson et al., 2015).

Inorganic ligands such as carbonate and phosphate ions influence largely U(VI) sorption and transport in soil as dissolved uranyl cation in the aqueous fraction (see Figure 1):

- Phosphate may interact with various metal oxides and either decrease or increase U adsorption to soil particles. For example, P competition with U for surface sites on soil iron oxides will decrease U adsorption, whereas formation of ternary complexes U-P complexes will enhance the adsorption of both U and P. Precipitation of U(VI)-phosphate solids can also decrease aqueous uranyl concentration by removing it from solution. Therefore P plays an important role in governing U mobility (Bachmaf et al, 2008).
- Carbonate content in soil strongly affects U(VI) sorption and is a key driver of U mobility in soils, in particular at pH close to neutral (Zheng et al, 2003). Several studies have reported increased U solubility with increasing carbonate content, due to the formation of negatively charged U-carbonate-complexes with a lower affinity to sorption-active soil components (Echevarria et al, 2001; Vandenhove et al, 2007; Yamaguchi et al, 2009; Setzer et al, 2011; Zheng et al, 2003). It was shown that increasing soil calcium carbonate content led to a pronounced suppression of the pH-dependent sorption curve in the neutral pH range due to the formation of a very stable neutral complex of calcium uranyl carbonate in solution (Zheng et al, 2003) (see Figure 1).
- Uranyl phosphate and uranyl carbonate complexes were found to be the U species preferentially taken up by the roots and transferred to the shoots (Vandenhove et al, 2007).

**Figure 1: Distribution and influence of carbonate on U sorption to soils**




(LEFT) Various existing uranyl species in the aqueous carbonate fraction (from Ivanovich 1992, cited in Laukenmann, 2002). (RIGHT) Distribution of U(VI) speciation in a 0.01 mol/L $NaNO_3$ solution with a total dissolved U(VI) of 1.0_10-6 mol/L in equilibrium with atmospheric $pCO_2$ (10-3.5 bar) as a function of the solution pH; the thick curve represent the total concentration of U(VI) hydroxy complexes (from Zheng et al, 2003).

It is generally considered that U is relatively mobile in soils under oxidizing and acidic conditions [note SCAHT: typically pH 5-6.5], where cationic uranyl-hydroxo species (e.g. $UO_2OH^+$) predominate; this can be explained by a weak sorption of U and ion exchange on negative binding sites (Hooda, 2010).

Some authors argued that higher redox potentials and higher pH values [note SCAHT: typically 6.5-7.5] found in most agricultural soils favour the mobility of U through mobilization of highly mobile uranyl-carbonate species (Utermann et al, 2009; Schnug and Haneklaus, 2015). As the pH increases, negatively charged binding sites increase, but the dominant solution species become the anionic carbonate complexes, and so sorption decreases. This effect of carbonate complexation producing anionic species is considered to be the most important factor influencing U mobility in soils (Echevarria et al, 2001; Vandenhove et al, 2007 in Hooda, 2010).

Setzer et al. (2011) investigated agricultural topsoils and subsoils from different agricultural sites in Germany. Soil pH values varied from 4.1 to 7.9, with an average of 6.5; topsoils had calcium carbonate contents with an average of 1.2% and a maximum of 5.1%, while subsoils had values higher than 10%. Utermann et al. (2009) compared U content in topsoil and subsoil of ca. 1000 locations in Germany. Mean U concentration was 0.15 mg/kg higher in agricultural compared to forestry topsoils. U concentrations in leach water and superficial groundwater from loose rock areas in North Germany varied by 3-4 orders of magnitude; they were lower at forest than agricultural sites, and lower at sandy than loess soils. The dominant U species depended on pH: mainly mobile uranyl-carbonate species at agricultural sites, mainly less mobile uranyl cations at forest sites.

Once solubilized as uranyl in the aqueous fraction, U will be translocated into deeper soil layers and eventually leaches out from the soil or through surface run-offs, and thus contaminate surface-, ground- and drinking water supplies (Knolle et al, 2011; Smidt, 2011). According to Utermann et al. (2009), U concentrations in European soil leachates are in the range < 0.1 µg U/L (sand) to > 1 µg U/L. Surbeck (2014) has estimated the leaching from agricultural soils to be 1.5 µg U/L (range: <0.1 to 3 µg U/L).

**Conclusion:** U (as uranyl cation) appears to be fairly mobile in agricultural soils, in the range of pH values normally encountered in most of them (i.e. 5-7.0). More research is needed to clarify the environmental fate of U in soils, in particular:

- Leachability studies to better inform on the mobility and residence time of U in soils;
- Sorption studies to better understand the behaviour of U in topsoils, subsoils and sediments;
- Modelling studies to understand seasonal variation and predict future trends of U concentrations in soil.

## 8.2 Effects of P-fertilizer on soil U

The amount of U introduced via P-fertilization into agricultural soils obviously depends on the U content of the fertilizer and the amount applied. As summarized by Smidt, Landes et al (2011), the annual U load from P-fertilizer when used at Good Agricultural Practice (,) application rates is estimated to be 15 g U/ha/year.

A number of studies have investigated potential soil accumulation of U-derived from long-term P-fertilizers application (e.g. Rothbaum et al, 1979; Takeda et al, 2006; Taylor 2007; De Kok and Schnug, 2008; Yamaguchi et al, 2009; Utermann et al, 2009; Schipper et al, 2011). Rogasik et al. (2008) studied the influence of long-term P-fertilization on the accumulation of U in soils at 7 sites in Germany. In all experiments P rates correlated with the increase of the U content in topsoils. Their results are summarized together with those of previous studies in Table 8.

**Table 8: Mean changes in soil U after long-term P-fertilizer application (Rogasik et al, 2008)**

| Country/ Site | | Time (years) | U accumulation rate (mg $kg^{-1}yr^{-1}$) | Reference |
|---|---|---|---|---|
| Germany | Schuby* | 20 | 0.015 | see Table 2 |
| | Thyrow | 68 | 0.001 | see Table 3 |
| | Müncheberg | 35 | 0.002 | see Table 4 |
| | Braunschweig | 24 | 0.002 | see Table 5 |
| | Halle | 53 | 0.001 | see Table 6 |
| | Bonn | 46 | 0.001 | see Fig. 3 |
| | Freising | 40 | 0.004 | see Fig. 3 |
| Greece | Kalohori | 38 | 0.018 | Papastefanou *et al.* (2006) |
| Japan | Fujisaka Branch | 61 | 0.001 | Takeda *et al.* (2005) |
| New Zealand | Mikimiki* | 43 | 0.026 | Taylor and Kim (2008) |
| | Eltham* | 37 | 0.046 | Taylor and Kim (2008) |
| | Taupo* | 37 | 0.015 | Taylor and Kim (2008) |
| | Hinemaiai* | 36 | 0.047 | Taylor and Kim (2008) |
| UK | Rothamsted (BK) | 95 | 0.003 | Rothbaum *et al.* (1979) |
| | Rothamsted (BN) | 106 | 0.003 | Rothbaum *et al.* (1979) |
| | Rothamsted (PG)* | 100 | 0.007 | Rothbaum *et al.* (1979) |
| USA | Morrow plots | 81 | 0.012 | Jones (1992) |
| | Florida* | 30 | 0.020 | Zielinski *et al.* (2006) |

*grassland

Source: Rogasik et al, 2008, Table 9

The mean accumulation rate in the Rogasik study (Germany) was 3.7 µg U/kg/year (range 1-15). According to Schnug and Haneklaus (2015), the maximum value is in close agreement with the accumulation rate of 9 and 14.5 µg U/kg/year calculated for long-term field experiments in Japan and Ireland, respectively. In contrast, accumulation rates reported for New Zealand and Australia are distinctly higher with 19-37 µg U/kg/year. The reason for this appears to be lower U leaching rates in New Zealand and Australia (Schnug and Haneklaus, 2015).

Smidt, Landes et al. (2011) concluded that due to the high U content in of German P-fertilizers, the calculated loads of U on arable soils indicate a significant contamination risk in agroecosystems. However, it must be noted that these increases are minimal. For example, in the longest-running substudy in Halle, the two plots with the highest input of P-fertilizer (plots 3 and 6, total 2385 kg P/ha over 53 years = 45 kg P/ha/year, substantially higher than the current GAP application rate of 22 kg P/ha/year) had soil U of 0.95 and 0.97 mg U/kg, respectively, versus 0.89 and 0.91 mg U/kg in the untreated plots 1 and 4 (Rogasik et al, 2008, Table 6); this represents an increase in soil U of about 7% (0.96 vs 0.90) in 53 years.

Based on the average European soil content of about 2 mg U/kg dw (De Vos et al, 2006), the addition of 3.7 µg U/kg soil/year from P-fertilizers calculated by Rogasik et al. (2008) represents about 0.2% of the background concentration.

For Switzerland, Surbeck (2014) has estimated that the P input through P-fertilization is around 15 ± 5 kg P/ha or 35 ± 12 kg $P_2O_5$/ha per year, which according to Surbeck was a possible overestimation.

## 8.3 Impact of P-fertilizer-derived soil U on environmental and human health

Concerning additional environmental risks of U from P-fertilizers, the German Federal Ministry of Food and Agriculture (BMELV) expressed the opinion that the use of mineral P-fertilizers has undoubtedly led to accumulation of U in the soil, but they do not see any danger of unacceptable risks to soil and sediment organisms from this accumulation (BMELV, 2013).

Minimal increases of soil U as discussed in the previous section will not affect human risk estimates, because U transfers very poorly into the food chain, is not readily transferred from soil to crops, and has also a low transfer factor from grass to animals, although U concentrations of U can reach up to 15 mg/kg in farmland soil due to use of P-fertilizers (EFSA, 2009).

To assess the potential impact on human health of U from soil derived from the application of P-fertilizer, one has to consider:

- The behaviour and fate of U in agricultural soils, in particular its potential for accumulation in soils land its leachability (discussed in section 8.1)
- The U transfer rate from soil to plants/crop and its potential for accumulation in plants/crops to assess the possible contribution of vegetables, cereals and cereal-based products to the total U dietary exposure
- The U transfer rate from grass to animal and its potential for accumulation in animal tissues to assess the possible contribution of dairy products, meat and meat-based products to the total U dietary exposure

Under oxidizing environmental conditions, U has a relatively medium to high mobility in soils, depending on the acidity or alkalinity, and it is expected that it will leach out from the soil and therefore will not accumulate in agricultural soils.

Uranium concentrations in plants are generally several orders of magnitude lower than in soil (Mitchell et al, 2013). It is considered that the transfer rate from soil to crops is generally low, depending on the type of soil, the plant/crop type and the chemical speciation of U (EFSA, 2009; Shahandeh et al, 2002)[7]. Vandenhove et al. (2007) reported that $UO_2^{2+}$, uranyl carbonate complexes and $UO_2PO_4^-$ are preferentially taken up by the roots and transferred to the shoots, but did not find any association between soil solution U concentration and plant uptake. The mean transfer factor for U in soils to crop plants is 0.05 (Schick et al, 2008 in Schnug and Haneklaus, 2015). It has been estimated that the U off-take from soils by crops is lower than 0.5 g/ha (Kratz et al, 2008; Gramss et al, 2011, in Schnug and Haneklaus, 2015).

ATSDR (2013) noted that U has a tendency to adsorb onto the surface of plants roots and is not easily transferred from the roots to the plant, so that little or no U will finally enter the

[7] N.B: an extensive aompilation of concentration ratios for U in various plants/crops and soil types can be found in IAEA, 2010.

plant. Shahandeh et al. (2002) have investigated 34 plants for their U accumulation potential and found a maximum concentrations ratio between shoots and roots of 1:60 (102 vs 6200 mg U/kg). Plants grown in soils with high carbonate-U fractions accumulated the most U levels in shoots and roots, while the lowest plant U levels occurred in clay acid soils with high iron, manganese and organic U-fractions. Anke et al. (2009) found that wild and cultivated plants from the immediate vicinity of U waste dumps stored eight-fold more U than the control plants. Leafy plant species accumulated much U, whereas tubers, thick parts of stalks, fruits and grains stored less U.

According to EFSA (2009), available food data (from Germany only) indicated that the U content may vary depending on the type of foodstuffs considered and U levels in soil and water. Foodstuffs rich in sugar, starch, and fat (fruits, seeds, flour) proved to contain less U compared to leafy vegetables, tea and herbs. In particular, asparagus were found to contain substantial amount of U (> 50 µg U/kg dw) (EFSA, 2009).

Also, U has a low transfer factor from grass to animals, and it has been shown that terrestrial animals accumulate less U than fish, crustaceans or algae (EFSA, 2009). Limited data exist on bioconcentration factors in fish, but ATSDR (2013) concluded overall that there will be no biomagnification through the food chain.

The results of the EFSA (2009) dietary assessment indicate that exposure through foodstuffs in general is low. Estimated medians of country specific U exposure (expressed as lower- and upper-bound values) for the main food contributors to the total dietary exposure were: 0.001-0.019 µg U/kg bw/day for starchy roots and potatoes; 0.001-0.021 µg U/kg bw/day for cereal and cereals products; 0.001-0.021 µg U/kg bw/day for meat and meat products; 0.001-0.041 µg U/kg bw/day for dairy products; and 0.004-0.043 µg U/kg bw/day for vegetables.

EFSA (2009) concluded that according to the state of current scientific knowledge, U uptake by plants is not considered to be an issue, and there is no unacceptable risk via dietary exposure from food. This conclusion was also supported by the German Umweltbundesamt (UBA, 2012).

**Conclusion:** it appears that U transfers very poorly into the food chain and will not biomagnify, is not readily transferred from soil to crops, and has also a low transfer factor from grass to animals. This is reflected in the low human exposure through foodstuffs in general in a dietary assessment by EFSA (2009). The poor human oral bioavailability of U (ca. 2%) will reduced human internal exposure further.

Therefore it can be concluded that the risk for human health from P-fertilizer U via the food chain is minimal.

## 8.4 U kinetics in water

The chemical speciation of U in water bodies is very complex, and the specific forms and concentrations of the various U species is strongly determined by water characteristics such as pH, temperature, and hardness. Modelling results show that conditions which favour the formation of the soluble uranyl ion include low pH and low concentrations of natural organic matter, and probably low alkalinity (Canada, 2011).

The mobility of U in groundwater depends on the local mineralogical and geological structure of the bedrock (e.g. molasse/sandstone, schist, gneiss, granite), the chemistry of the water and the physical conditions (including erosion, diffusion, mass flow, dissolved U or bound to

suspended particles). Leaching studies have shown that U can be readily transferred from uraninite ($UO_2$) in pegmatites (Dall'Aglio, 1971) and pitchblende ($U_3O_8$) in granites (Labhart and Rybach, 1974) to the water through mineral dissolution and/or U desorption from mineral surface, and that the oxidation potential and the partial pressure of carbon dioxide are key determinants of the U concentration in natural waters (as reviewed by Stalder et al, 2012). In reducing conditions (absence of air) U precipitates, forming concentrated secondary deposits (Nuccetelli et al, 2012; Stalder et al, 2012). Leaching studies by Alam and Cheng (2014) with natural sediment have shown that low redox potential decreases aqueous U concentration due to reductive precipitation.

In Switzerland, it is well known that higher U concentrations in drinking water supplies originate from regions (e.g. Fribourg, Graubünden, Tessin, Wallis) known for their higher U content in groundwater due to the local geology of the bedrock, such as the Verrucano, Silvretta and Leventina nappes in alpine regions (Deflorin, 2004; Stalder et al, 2012) or Mont Vully (FR) (Schott and Wiegand, 2003).

It is often difficult to specify a direct relationship between U concentrations in groundwater and the underlying geology of the region owing to the fact that the water flows underground and so does not necessarily originate in the same rock as the source of U. Soluble uranyl ($UO_2^{2+}$) can be transported for long distances from its source of origin. This is evidenced by the fact that U can occur in groundwater at much higher concentrations than is expected from the underlying aquifer rock (Dall'Aglio, 1971). Uranium transport from deep groundwater reservoirs to shallow groundwater reservoirs or surface water has also to be considered; the residence time in surface water and groundwater can span months and years, respectively (Poinssot and Geckeis, 2012).

Interestingly, Schnug & Haneklaus (2015) noted that a close relationship has been observed between U and nitrate in shallow groundwater in intensively used agricultural areas. They suggested three possible reasons for this:

- 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 NP and NPK fertilization intensity and thus for U loads in areas without intensive livestock production.
- Thirdly, immobile U(IV) in soils is oxidized to soluble U(VI) by nitrate and then translocated by percolation water.

## 8.5 U kinetics in sediments

Uranium (VI, as uranyl) tends to adsorb in sediment systems to mineral surfaces such as iron and manganese (oxy)hydroxides and silicates (Chappaz et al, 2010; Alam and Cheng, 2014), and its interactions depend on the physicochemical properties of these solid matrices. Under reducing conditions and sulfate environments, U may precipitate as sulfides. Sorption experiments show that U adsorption by lake sediment is strongly pH dependent, being high in the pH range 5-6.5 and maximal near neutral pH, but decreasing at lower and higher pH values (Koroleva, 2005).

The dissolution of U containing solids and the desorption of U(VI) surface complexes in the contaminated sediments are slow (PNNL, 2005). Dissolution/desorption extent was found to decrease with decreasing water content and at 21% water saturation was only 1 to 3% of total U. Increasing aqueous bicarbonate concentration decreased the extent of U adsorption.

Both precipitated and adsorbed U exists in the sediments. Adsorbed U(VI) predominates in sediments with total U <25 mg/kg (PNNL, 2005).

It has been suggested that sediments, in particular those with high organic content, act as a sink for U because the concentrations measured are typically higher than the water at the sediment-water interface (Laukenmann, 2002; Hinck et al, 2010).

## 8.6 Effects of P-fertilizer on water U

Leaching of U into water is pH-dependent. Once solubilized as uranyl in the aqueous fraction, U will be translocated into deeper soil layers and leaches out from the soil or through surface run-offs, and finally contaminates surface-, ground- and drinking water supplies (Knolle et al, 2011; Smidt, 2011). According to Utermann et al. (2009), U concentrations in European soil leachates are in the range < 0.1 µg U/L (sand) to > 1 µg U/L. Surbeck (2014) has estimated the leaching from agricultural soils to be 1.5 µg U/L (range: <0.1 to 3 µg U/L). Utermann et al. (2009) reported that U concentrations in leach water and superficial groundwater from loose rock areas in North Germany varied by 3-4 orders of magnitude; they were higher at agricultural than forest sites (attributable to pH-dependent formation of mobile uranyl-carbonate species).

BfR (2009) stated that the risk of contamination of the groundwater from P-fertilizer-derived U cannot be ruled out; that the mid to long-term risk in groundwater is yet to be assessed to ensure the quality and safety of drinking water, and that it remains to be clarified if fertilizer-derived U is more mobile (because more readily soluble) than geogenic U (BfR, 2009; Deutscher Bundestag, 2011).

Smidt, Hassoun et al. (2011) presented evidence for a diffuse anthropogenic U contamination of water in areas of intense agricultural crop production, especially in shallow groundwater. Using tap water data from a geogenically U-poor area in the northern German lowland, they estimated that 67% of tap waters might be potentially contaminated above 0.1 µg/L (the current German drinking water limit is 10 µg U/L), and 25% above 0.5 µg/L. (For comparison, the WHO (2011) and Swiss (FIV) drinking water limit is 30 µg U/L).

Hassoun and Schnug (2011) argued that because agriculture is the only significant source of U input to the environment (apparently referring to the geogenically U-poor area in the northern German lowland; see Smidt, Hassoun et al, 2011) and because recent research indicates leaching of U from arable soils and presence of fertilizer-derived U in ground and drinking water, there should be a legal limit set on U levels in P-fertilizers.

A book chapter review by Schnug and Haneklaus (2015) concluded that there is "conclusive evidence" that fertilizer-derived U contaminates water bodies; the percentage of U from previous fertilizer applications in groundwater depends on regionally differing geogenic background concentrations in soils, but in regions with a low natural (geogenic) U background, more than 90% of U in groundwater may be fertilizer-derived.

This conclusion differs from that of the BMELV which concluded that due to substantial local and regional differences in geogenic levels of U in soil and water, it is not possible to unequivocally establish a P-fertilizer-derived increase in U concentration in waters (BMELV, 2013)[8]. A similar conclusion was reached by the German Frauenhofer Institut für Umwelt-, Sicherheits- und Energietechnik (UMSICHT, 2012) which stated that there are currently no

[8] BMELV 2013 original (German): "*Die bisherigen Ergebnisse erlauben wegen der erheblichen groß- und kleinräumigen geogen bedingten unterschiedlichen Urangehalte in Böden und Gewässern nicht, eine eindeutig P-düngungsbedingte Zunahme der Uran-Konzentration in Gewässern zu* erfassen."

concrete data to support a direct link between P-fertilization and the U burden in soils and water bodies.

For Swiss groundwater, Surbeck (2014) concluded that there is very limited information available on the current U environmental burden derived from fertilization versus geogenic sources. Surbeck estimated the contribution of U from P-fertilizers to U in groundwater in Switzerland as follows, assuming:

- Precipitation rate 600 ± 200 mm/year = 6 ± 2 *10E6 L/ha/year;
- P-mineral fertilizer use = 35 ± 12 kg $P_2O_5$/ha/year (= 15 ± 5 kg P/ha/year);
- U concentration in P-mineral fertilizer= 250 ± 100 mg U/kg $P_2O_5$;
- Leaching of soil U = 100%.

(Note: Surbeck cited publications which suggested that P-fertilizers use may increase the mobility of soil U[9]. This was addressed by the conservative assumed leaching rate of 100%.)

Predicted mean U concentration in leachate from P-mineral fertilizers is therefore 35*250/60 = 1.5 µg U/L. Accounting for uncertainty, the range is <0.1 to 3 µg U/L.

Surbeck (2014) noted that 50-80% of measured groundwater U concentrations in Switzerland are within this concentration range, but that this does not mean that these measured U concentrations in groundwater are due to P-mineral fertilizer input alone; rather, geogenic and anthropogenic inputs could be in the same range.

**Conclusion**: Overall, it is clear that soil U will leach to surface and groundwater, but high uncertainties exist about the relative contribution of geogenic and P-fertilizer U. Given that geogenic sources are known to be important on a local and regional scale due to the movement of U in groundwater, it appears misleading to conclude that there is "conclusive evidence" that P-fertilizer-derived U is responsible for the contamination of water bodies.

Many knowledge gaps exist, which preclude a more robust evaluation and risk assessment of the contribution of P-fertilization to the total U burden of soil and water bodies, in particular:

- A lack of information of the amount of U applied to soils via P-fertilization;
- A lack of information of U concentrations in soils, water bodies and sediments;
- Limited data on U leachates from soil, which is a parameter associated with highest uncertainty.
- A lack of information about temporal trends and the impact of seasonal variability on retention/leaching processes in agricultural soils

More research is needed to close these gaps. More leachability studies and controlled field experiments with different soils pH, soil type and quality would help to better understand the fate of P-fertilizer derived U in agricultural soils. The role of sediments remains to be assessed, as they have been shown to be a reservoir sink for many metals.

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[9] In fact, 2 of the 3 publications cited by Surbeck (Dienemann and Utermann, 2012 [=UBA, 2012]; Kiefer and Fischer, 2013) do not suggest that P-fertilizer use may increase the mobility of soil U. Instead they state that agricultural soil provides the biochemical environment leading to increased U mobility and thus transfer into groundwater. The third citation by Surbeck (Hinrichsen, 2013) is an unpublished Master thesis.

## 9. Uranium content of P-fertilizers in Switzerland

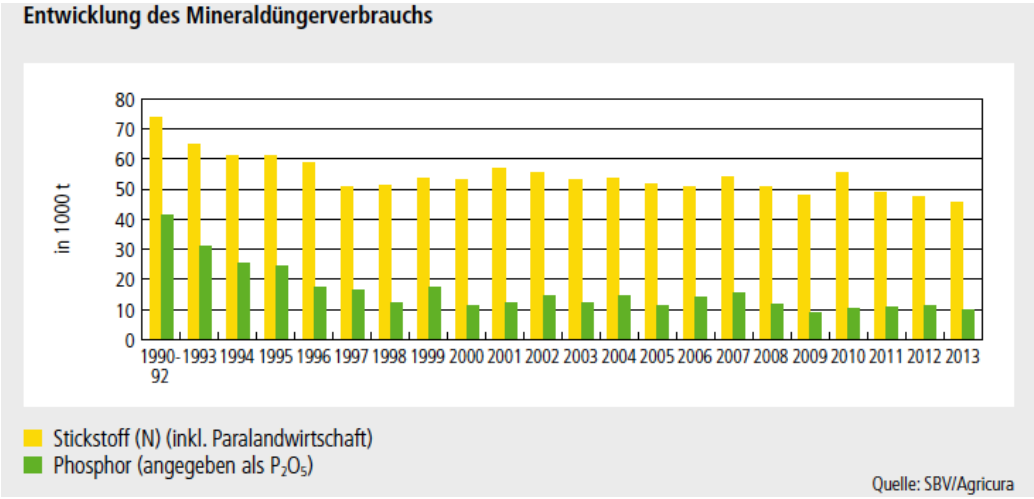
Agricultural production widely relies on the use of P-fertilizers, because phosphorus is an essential nutrient for plant growth that cannot be replaced by any other substance.

P-fertilizers are primarily derived from phosphate (P) rock (mined as naturally occurring ores) which also contain heavy metals including U and Cd. U can occur in substantial amount in P-rocks (see Appendix A, Table A1). Significant deposits are found in Morocco and the Western Sahara, Russia (Kola), South Africa, the USA, Jordan, and China. The average U levels in P-rocks of sedimentary origin are usually around 120 mg/kg (range 50-220 mg U/kg), whereas P-rocks of igneous origin typically contain levels below 10 mg U/kg (Kratz and Schnug, 2006).

Production of P-fertilizers (e.g. triple superphosphate TSP; single superphosphate SSP; monoammonium phosphate MAP; diammonium phosphate DAP; nitrogen-phosphorus-potassium NPK; di-calcium phosphate DCP) involves digestion of P-rock by phosphoric acid, which will also solubilize U (IAEA, 2003; Saueia et al, 2005). The U content in various P-fertilizers is positively correlated with that of phosphate (e.g. Bouwer et al, 1978; Spalding and Sackett, 1972; Sattouf, 2007). The $U/P_2O_5$ ratio will determine how much U is loaded onto a soil at a given P rate; this ratio varies between different type of fertilizers and fertilizer produced by different manufacturers (Sattouf, 2007). Mean U concentrations in P-fertilizers of different origins can vary enormously: between 2-325 mg U/kg for SSP, 50-362 mg U/kg for TSP, 2.9-188 mg U/kg for NP fertilizers, 43-205 mg U/kg for raw phosphates, 82-99 mg U/kg for PK fertilizers and 0.5-66 mg U/kg for NPK fertilizers (Kratz et al, 2007 in Hooda, 2010).

The Swiss and EU market is dominated by P-rocks from sedimentary origin (e.g. North Africa, Israel), while P-rocks with lower U content, such as from the deposit ores in Finland or Russia (Kola) are restricted for these countries own use or may only find their way in very limited amounts. Improved and more efficient agricultural practice has contributed to massively reduce the application of P-fertilizers in Europe since the 1990's. In Switzerland, use of P-fertilizers has been lowered by two-third during the period 1990-2002 (Spiess, 2005); import was below 5000 ton P for the year 2010-2012 (BLW, 2014) (see Figure 2). However, concern has been expressed that over time low-grade P-rock quality with higher content of U and other potentially toxic trace elements will dominate the market (Sattouf, 2007).

**Figure 2: P-fertilizers consumption in CH, period 1990-2012 (BLW, 2014)**




Source: BLW, 2014. Agrarbericht, p. 90

It has been suggested that U recovery as a by-product from phosphoric acid may be an advantageous economic and sustainable approach to ensure food and environmental safety, by reducing levels of U in P-fertilizers, thus preventing the continuous release of low concentrations of U through P-fertilization into the environment, while offering altogether interesting prospects in term of energy and national security (Ulrich et al, 2014).

In German P-mineral fertilizers, Smidt, Landes et al. (2011) reported mean U content of 61.3 mg U/kg fertilizer dry weight.

Available data for U content in P-fertilizers at international level have been recently summarized by UBA (2012) (refer to Appendix A, Table A2). Reported mean values for Germany (period 2003-2007, based on Kratz et al, 2008) were: 91 mg U/kg dw for SSP; 106 mg U/kg dw for TSP; 65 mg U/kg dw for raw-phosphate; 27 mg U/kg dw for NP-fertilizers; 82 mg U/kg dw for PK-fertilizers; and 9.9 mg U/kg dw for NPK-fertilizers (origin of the P-rocks was not reported).

In Switzerland, non-systematic monitoring of U content in P-fertilizers marketed in the 1980s showed U content of about 100 mg U/kg (BUWAL, 1991, p.12). Monitoring data of the Basel City Cantonal Laboratory in 2011-2012 (personal communication A. Gisler, BLW) showed that the U content of P-fertilizers can vary greatly (0.002–271 mg U/kg dw), with a median of 49 mg U/kg, which is equivalent to 667.2 mg U/kg P = 291 mg U/kg $P_2O_5$ (see Table 9).

**Table 9: Uranium content in 19 P-mineral fertilizers, CH, period 2011-2012**

| | mg U /kg dw | mg U /kg $P_2O_5$ | mg U /kg P |
|---|---|---|---|
| Median | 49.0 | 291.2 | 667.1 |
| Min | 0.002 | 0.010 | 0.023 |
| Max | 271.0 | 484.9 | 1110.9 |

Source: Personal communication A. Gisler, BLW (Basel City Cantonal Laboratory monitoring 2011-12)

Currently there is no regulatory limit value for U in P-fertilizers in the Swiss ChemRRV, nor in any country worldwide (Ekardt and Schnug, 2011), but the German Federal Environment Agency has proposed a limit value of 50 mg U/kg $P_2O_5$ (UBA, 2012). UBA based its decision on the assumptions that: i) P-fertilization of agricultural soils is the only significant source of input into the environment; ii) recent research indicates leaching of U from arable soils; and iii) fertilizer-derived U has been measured in ground and drinking water (Smidt et al, 2011).

**Conclusion**: Swiss data for U content in P-fertilizers are extremely scarce. Available results, though very limited (n=19 samples), indicate that there is a very large variability in U content in P-fertilizers on the Swiss market. High values were found compared to those reviewed for Germany in this report, which warrants further research. This situation calls for more sampling to better monitor the occurrence of U in P-fertilizers; this is a prerequisite to any further action. In addition, information on P-fertilization application rate is needed.

The concentration of U in any given P-fertilizers depends on the concentration of the P-component in the fertilizer itself, the origin of the P-rocks it was derived from, and the manufacturing (P extraction) process. Some uncertainties and shortcomings exist in the literature regarding the U content in P-fertilizers:

- Data are heterogeneous and the comparability between studies is generally poor;

- U content in P-rock varies greatly according to its geological origin; U will occur to a greater or lesser extent in the final P-fertilizer product, depending on the manufacturing process;
- The P component (in % of P or $P_2O_5$) and the P/U ratio in the P-fertilizer are not reported in many studies;
- The type of P-fertilizers is often not known;
- Data are sometimes not reported on a weight basis (mg/kg) but as a partial activity of the radionuclide (mBq). Conversion rules exist (1 Bq of U-238 corresponding to 0.08 mg of natural U), but they are for purposes of information and comparison only; in practice, due to possible imbalances between U isotopes in the sampled compartments, only measurement is valid (IRSN, 2010).

## 10. Correlation Cd-U in P-fertilizers

The content of both Cd and U content of P-rocks can vary considerably (<1 to >500 mg/kg $P_2O_5$) depending on the natural geographical and geological properties of the P-rock they originate from, even in the same mineral deposit (IFDC, 2010; Sattouf, 2007); this accounts for the large concentration differences reported in the literature (see Appendix A). A summary of data from studies reporting levels of both Cd and U in rocks used for P-fertilizer production is given in Appendix A (Table A1). The reported U/Cd ratios ranged between 0.35 (Tunisia) and >42 (Burkina Faso). Most were however greater than one, indicating that the content of U in these P-rocks is higher than the content of Cd.

Few studies have simultaneously analysed the content of both U and Cd in P-fertilizers.

Smidt, Landes et al. (2011) reported Cd and U content of P-fertilizers used in Germany (n=75) and Brazil (n=39) (Table 10 and 11), but without specifying which type of P-fertilizer has been investigated; high mean concentrations of Cd (12.0 and 18.6 mg Cd/kg, respectively) and U (61.3 and 70.16 mg U/kg, respectively) were observed, while maximum concentrations of 56 mg Cd/kg and up to 200 mg U/kg were found. They found a significant correlation between Cd and U content per kg $P_2O_5$, but the constant term of the regression is high, so that in principle a Cd-free product could have a high U content or vice versa[10].

[10] "*Zwischen den Cadmium- und Uran-Gehalten je kg $P_2O_5$ besteht zwar eine signifikante Korrelation, jedoch ist das konstante Glied der Regression mit Werten zwischen 86 und 106 so hoch, dass selbst bei einem theoretisch Cadmium-freien Düngemittel $P_2O_5$-bezogene Uran-Gehalte zu erwarten sind, die weit über den weiter unten vorgeschlagenen Grenzwerten liegen.[...] Einschließlich 2 Extremwerten mit $U/P_2O_5$ > 1000: $4{,}25 \cdot P_2O_5 + 109$; r2=17%; ohne Extremwerte: $3{,}93 \cdot P_2O_5 + 86$; r2=17%; (Extreme: 2 PK-Dünger mit S: 12% $P_2O_5$, $U/P_2O_5$ 1568 und 1713)*" (Source: Schnug, 2012).

**Table 10: Cd and U concentrations in German P-fertilizers (Smidt, Landes et al, 2011)**

**Table 1** $P_2O_5$, Cd and U concentration in fertilizers with a $P_2O_5$-content of >5% which have been traded in Germany in 2007 ($n=78$) and weighted mean values provided by Dittrich und Klose (2008)

| | $P_2O_5$ (%) | Cd (mg/kg) | U (mg/kg) | mg Cd/kg $P_2O_5$ | mg U/kg $P_2O_5$ |
|---|---|---|---|---|---|
| Mean[a] | 22.8 | 12.0 | 61.3 | 47.0 | 283 |
| Median | 17.0 | 7.40 | 39.8 | 50.0 | 264 |
| Minimum | 5.00 | 0.11 | 0.73 | 0.24 | 6.39 |
| Maximum | 38.0 | 34.8 | 206 | 107 | 1713 |
| Percentile 25 | 10.8 | 2.89 | 11.7 | 18.0 | 79.8 |
| Percentile 50 | 17.0 | 7.40 | 39.8 | 49.9 | 264 |
| Percentile 75 | 40.0 | 20.2 | 87.4 | 67.1 | 402 |
| Weighted mean values from Dittrich and Klose (2008) ($n=193$)[b] | 25.8 | 9.40 | 63.3 | 37.0 | 245 |

[a] Note: Out of 78 samples 29% had a Cd content above the obligation to label and 48% exceeded the limit value.
[b] Note: Out of 193 samples 41% had a Cd content above the obligation to label and 17% exceeded the limit value.

Source: Smidt, Landes et al, 2011

**Table 11: Cd and U concentrations in Brazilian P-fertilizers (Smidt, Landes et al, 2011)**

**Table 2** $P_2O_5$, Cd and U concentration in fertilizers with a $P_2O_5$-content of >5% which have been traded in Brazil in 2007 and 2008 ($n=39$) and weighted mean values taken from da Conceicao et al. (2006)

| | $P_2O_5$ (%) | Cd (mg/kg) | U (mg/kg) | mg Cd/kg $P_2O_5$ | mg U/kg $P_2O_5$ |
|---|---|---|---|---|---|
| Mean[a, b] | 30.1 | 18.6 | 70.6 | 61.5 | 248 |
| Median | 21.5 | 10.8 | 59.9 | 52.0 | 283 |
| Minimum | 14.2 | 1.30 | 0.30 | 2.80 | 1.40 |
| Maximum | 52.5 | 56.8 | 200 | 189 | 498 |
| Percentile 25 | 17.8 | 7.4 | 25.2 | 40.0 | 113 |
| Percentile 50 | 21.7 | 10.8 | 59.9 | 52.0 | 283.1 |
| Percentile 75 | 46.0 | 28.3 | 98.2 | 76.4 | 257 |
| Weighted mean values from da Conceicao (2006) ($n=6$) | 42.7 | 2.17 | 65.2 | 6.64 | 190 |

[a] Note: Out of 39 samples, 4 had a Cd content above the Brazilian limit value for P-containing fertilizers of 4 mg Cd per percent of $P_2O_5$.
[b] Note: Out of 39 samples 23% had a Cd content above the obligation to label and 44% exceeded the limit value.

Source: Smidt, Landes et al, 2011

Dittrich and Klose (2008) investigated U and Cd content of P-fertilizers including NP, PK and NPK-fertilizers from Sachsen, Germany (period 2005-2006). Results showed that medians for Cd were rather consistent for 3 types of P-fertilizers but that U varied to a certain extent, in particular when the $P_2O_5$ content is lower (Table 12): 64 and 65.7 mg Cd/kg $P_2O_5$ vs 177 and 22.5 mg U/kg (ca. 70.5 and 4 mg U/kg $P_2O_5$ for raw phosphates "*Teilaufgeschlossenes Rohphosphat*" and *"Rohphosphat mit kohlensaurem Kalk aus Meeresalgen",* respectively;

62.1 mg Cd/kg $P_2O_5$ vs 104 mg U/kg (ca. 47.3 mg U/kg $P_2O_5$) for TSP. (Results for NP, PK and NPK-fertilizers are shown in Appendix C, Table C1).

These results indicate also that in raw phosphate 2 and TSP, medians for U are lower than for Cd. This is in contrast with Smidt, Landes et al. (2011) who reported higher median values for U, that is a U/Cd ratio >1. There is no apparent chemical correlation between Cd and U. More variability is observed in U concentrations compared to Cd, in particular when the $P_2O_5$ content varies.

**Table 12: Cd and U concentrations in German P-fertilizers (Dittrich and Klose, 2008)**

| **P-fertilizer** | **$P_2O_5$ (%)** | **Cd (mg/kg $P_2O_5$ dw)** | **U (mg/kg dw)** |
|---|---|---|---|
| Raw phosphate 1 *[Teilaufgeschlossenes Rohphosphat]* (n=21) | | | |
| Median | 39.8 | 64.0 | 177 |
| Min-max | 39.3 – 41.0 | 26.6 – 79.2 | 131 – 200 |
| TSP (n=11) | | | |
| Median | 45.5 | 62.1 | 104 |
| Min-max | 45.3 – 46.3 | 36.7 – 73.1 | 42.7 – 173 |
| Raw phosphate 2 *[Rohphosphat mit kohlensaurem Kalk aus Meeresalgen, mit Mg] (n=5)* | | | |
| Median | 17.8 | 65.7 | 22.5 |
| Min-max | 17.7 – 18.2 | 53.6 – 71.7 | 19.1 – 31.3 |

Source: Dittrich and Klose 2008

Sattouf (2007) investigated two sets of P-fertilizers of different origin for their Cd and U content:

- the first set was collected between 1975-1985 and included 4 straight P-fertilizers, 1 PK-fertilizer and 8 NPK-fertilizers;
- the second set was collected after 1995 and included 4 straight P-fertilizers, 8 PK-fertilizers and 16 NPK-fertilizers. U content was 13.6-70.2% higher than the first set.

The concentration of U in different types of P-fertilizers decreased in the following order: sedimentary P-rocks > P-fertilizers made of sedimentary P-rocks > P-fertilizers > organomineral fertilizers > organic manures > igneous P-rocks. The U content in sedimentary P-rocks was 27-245 mg U/kg, while the U content in igneous P-rocks from the Russian Kola Peninsula ranged from 3.0-3.35 mg U/kg.

Sattouf (2007) investigated the suitability of the metal pattern to identify the origin of P-rocks and P-fertilizers. Results showed that the range of metals in P-rocks was very wide and that no single element could be used to discriminate the origins of P-rocks; heavy metal patterns could only be used to distinguish between igneous P-rocks and sedimentary P-rocks.

Sattouf found that Cd and U are largely retained in P-fertilizers produced from the raw phosphates, but that the ratio of their concentrations in P-fertilizers vs raw material could vary (see Appendix C, Table C2); a negative, poorly non-significant correlation (<0.5;-0.42) was found between Cd and U in the analysed P-rocks.

Sattouf (op. cit.) noted that Cd and U concentrations were positively correlated with the P content of the fertilizer (see Table 13), but that it was not possible to trace back the origin of P-fertilizers made of sedimentary P-rocks based on heavy metal patterns, because elemental

composition of a P-rock and derived P-fertilizers might differ considerably depending on the manufacturing process.

Similarly to Smidt, Landes et al. (2011), Sattouf did not specify which type of P-fertilizers were used for the analyses.

**Table 13: Cd and U content (%) in various P-fertilizers (Sattouf, 2007)**

| P-fertilizer | P (%) | Cd (%) | U (%) |
|---|---|---|---|
| Syria | 18.7 | 0.0008 | 0.0085 |
| Morocco (no.2) | 14.2 | 0.0016 | 0.0095 |
| Israel | 10.6 | 0.0022 | 0.0100 |
| USA | 8.6 | 0.0006 | 0.0066 |
| Morocco (no.1) | 7.03 | 0.0007 | 0.0064 |

Source: Sattouf, 2007 (extracted from Appendix C, Table C2)

**Conclusion:** SCAHT has located only three studies in the literature that have investigated both Cd and U simultaneously in P-fertilizers. Overall, U content in P-fertilizers usually tend be higher than Cd content, but it is not possible to predict one from the other. Based on this very limited (and partly contradictory) information, it is difficult to conclude anything with certainty about a possible correlation between Cd and U. Increased monitoring of both elements for each type of P-fertilizer is needed to establish if Cd/U content are correlated. However, consideration should be given to the following sources of uncertainty, which are likely to endure:

- there is an inherent variability in Cd/U concentrations ratio between a P-rock and its final P-fertilizer product, due to the P-rock origin and the production process, even for a given P-fertilizer marketed by the same producer;
- there is an even greater variability for heavy metals content in NP-, PK-, and NPK-fertilizers which are derived from many other sources than P-rocks (organic manure, limestone, potassium, nitrogen and sulphur salts, etc); it is a complex task to determine the amount of Cd and U in all these different sources, and it is not possible to determine the amount of Cd and U in the P component alone (Sattouf, 2007).

# 11. Conclusions

The risks of U to human health and the environment are reasonably well characterized. The most sensitive adverse effect in humans is chemically-induced toxicity to the kidney; the tolerable daily intake (i.e. safe lifetime dose) is 0.6-1 µg U/kg bw (EFSA, 2009; WHO, 2011). Uranium exposure via food is well below this level, but exposure via water may be much closer, particularly for high consumption by infants of formula diet made with water from "hot spots" with high levels of geogenic U. In the environment, water organisms are most sensitive to the toxic effects with a PNEC of 5 µg U/L. Uranium in water may exceed this level in geogenic "hotspots".

We conclude that P-fertilizer-derived U will increase soil U only marginally and will thus not significantly increase U exposure in humans via food or in soil and sediment organisms.

Although there are many knowledge gaps and uncertainties, it appears that U will normally not accumulate in agricultural soils but leaches out to the water compartment. Transfer from soil to crops and from grass to animal is low, and given its toxicokinetic profile, U is not expected to bioconcentrate in animal tissues (or only to a minor extent) and biomagnify though the terrestrial and aquatic food chains. When considering internal exposure, the poor oral U bioavailability further reduces the human health risk.

Both geogenic sources and P-fertilizers can contribute to U loads in water; the relative contribution of P-fertilizers is likely to be undetectable except in regions with low geogenic levels of U, such as North Germany. Based on current data, there is no evidence that U contamination derived from P-mineral fertilisers will increase risks to either human health or the environment, when they are used at GAP application rates. Based on a "worst case" P-fertilization rate of 45 kg P/ha/year calculated for Germany (which is substantially higher than the current GAP rate of 22 kg P/ha/year and than the upper estimate of 20 kg P/ha/year calculated by Surbeck for Switzerland) with a 7% increase of soil U over 53 years, it could be speculated that increase of U in Swiss soils would be lower. However, given the many data gaps regarding the amount of U introduced in agricultural Swiss soils annually via P-fertilization, this prediction is associated with a high degree of uncertainty.

It is currently very difficult to assess if Cd and U are correlated in P-fertilizers, given the paucity and contradictory nature of the available data; the correlation, if any, does not appear to be strong. The U content of P-mineral fertilizers may in some cases be higher than Cd content, but it is not possible to predict one from the other.

## 12. Recommendations

SCAHT recommends the following actions:

- Consider routine monitoring of U content in P-mineral fertilizers

  In order to quantify the contribution of contaminated batches to Swiss soil U input, it would be helpful if Swiss monitoring campaigns for U in P-fertilizers could include information on import volumes and application rates, in addition to levels of U contamination.

- Uranium should be monitored on a routine basis in soil, water bodies (incl. lakes) and sediments as part of the Swiss national surveillance programmes (NABO, NAWA, NAQUA)

- Consider monitoring of drinking water U concentrations in suspected “hot spot” regions for which data are lacking (e.g. Berner Oberland, Nord-West Schweiz)

  Evaluation of possible risk reduction/risk mitigation measures, e.g. Stalder et al (2012): “*A reduction of U concentration in drinking water can be achieved in several ways. The simplest, most practical solution would be via dilution, simply mixing water from a source with higher concentration with that of a lower. This has the advantage that there is no residue requiring disposal. If this is either not possible or does not result in a low enough concentration then it may be possible to remove U from the water. Several methods have been postulated, such as coagulation with ferric or aluminium sulphate at an optimal pH (80–95% removal), filtration, lime softening, anion exchange or reverse osmosis (99% removal) although not all methods have been tested on an industrial scale and disposal of the residue must also be considered*”

- Consider evaluating the impact of introducing a guidance value for U in P-fertilizers similarly to Germany, as a precautionary principle.

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# Appendix A: Cd/U content in phosphate rocks

**Table A1: Cd and U content in phosphate rocks**

| Region/ Country | Deposits/ Type of rocks (Igneous*, Sedimentary°) | $P_2O_5$ or P (%) | Trace element content (Cd mg/ kg $P_2O_5$); U (mg/kg) | | U/Cd ratio (approx.) |
|---|---|---|---|---|---|
| | | | Cd | U | |
| Europe | | | | | |
| Finland [a] | n.a* | n.a. | < 1 | | |
| Africa | | | | | |
| Algeria | Djebel Onk° [b] | 29.3 | 13 | 25 | 2 |
| | n.a.° [g] | n.a. | | 47.5 | |
| | n.a.° [h] | n.a. | | 44.2 | |
| Burkina Faso [b] | Kodjari° | 25.4 | < 2 | 84 | >42 |
| Egypt [f] | Quseir° [f] | 12.7 | 8 | | |
| Mali [b] | Tilemsi° | 28.8 | 8 | 123 | 15 |
| Morocco | Khouribga° [b] | 33.4 | 3 | 82 | 27 |
| | Khouribga° [c] | n.a | 55 | | |
| | Khouribga° [f] | 13.8 | 15 | | |
| | Boucraa° [c] | n.a | 97 | | |
| | Boucraa° [f] | 15.7 | 38 | | |
| | Youssoufia [c] | n.a | 120 | | |
| | Youssoufia [f] | 14.2 | 40 | | |
| | Qued Zem | 24.4 | 507 | | |
| | n.a.° [a] | n.a. | > 60 | | |
| | n.a.° [g] | n.a. | | 135.4 | |
| | n.a° [h] | n.a. | | 143 | |
| Niger [b] | Parc W° | 33.5 | < 2 | 65 | >32 |
| Senegal | Taiba° [b] | 36.9 | 87 | 64 | 25 |
| | Taiba° [c] | n.a. | 221 | | |
| | Taiba° [f] | 15.9 | 75 | | |
| | n.a.° [h] | n.a. | | 109 | |
| South Africa | n.a.* [a] | n.a. | < 1 | | |
| | Pharlaborwa* [c] | n.a. | 0.38 | | |
| | Pharlaborwa* [f] | 17.2 | 4 | | |
| Syria | Khneifiss° [b] | 31.9 | 3 | 75 | 25 |
| | n.a. ° [c] | n.a. | 22 | | |
| | n.a.° [g] | n.a. | | 130.2 | |
| | n.a.° [h] | n.a. | | 58.6 | |
| Tanzania [b] | Minjingu° | 28.6 | 11 | 390 | 35 |
| Togo [b] | Hahotoe° | 36.5 | 48 | 77 | 1.6 |
| | n.a. [c] | n.a. | 147 | | |
| | n.a.° [h] | n.a. | | 116 | |
| Tunisia | Gafsa° [b] | 29.2 | 34 | 12 | 0.35 |
| | Gafsa° [c] | n.a | 173 | | |
| | Gafsa° [f] | 13.4 | 38 | | |
| | n.a.° [a] | n.a. | > 60 | | |

| Region/ Country | Deposits/ Type of rocks (Igneous*, Sedimentary°) | $P_2O_5$ or P (%) | Trace element content (Cd mg/ kg $P_2O_5$); U (mg/kg) | | U/Cd ratio (approx.) |
|---|---|---|---|---|---|
| | | | Cd | U | |
| | n.a.° [g]<br>n.a.° [h] | n.a.<br>n.a. | | 28.3<br>36.1 | |
| Asia | | | | | |
| China [b] | Kaiyang° | 35.9 | < 2 | 31 | >6 |
| Japan | Okinawa [d] | 33.6 | 29.5 | | |
| Middle East | | | | | |
| Former Soviet Union [a] | n.a.* | n.a. | < 1 | | |
| India [b] | Mussoorie° | 25.0 | 8 | 26 | 3 |
| Israel [c] | Nahal Zin<br>n.a.° [h] | n.a.<br>n.a. | 61 | <br>140 | |
| Jordan | El-Hassa° [b]<br>n.a.° [a] | 31.7<br>n.a. | 4<br>> 20 | 54 | 13 |
| Russia | Kola* [c]<br>Kola* [f]<br>Kola* [g]<br>Kola* [h]<br>Slyudanka* [d] | n.a.<br>17.2<br>n.a.<br>n.a.<br>37.7 | 0.25<br>0.2<br><br><br>0.15 | <br><br>5<br>3.15<br> | |
| Syria [a] | n.a.° | n.a. | > 20 | 75 | <3.75 |
| Turkey [e] | Mazidag° | 18.5 | 8 | | |
| North and South America | | | | | |
| Peru [b] | Sechura° | 29.3 | 11 | 47 | 4.3 |
| USA | Central Florida° [b]<br>Florida° [c]<br>Florida° [d]<br>North Florida° [f]<br>Idaho [d]<br>North Carolina° [b]<br>North Carolina° [c]<br>North Carolina° [f]<br>Wyoming [d]<br>n.a.° [h] | 31.0<br>n.a<br>32.7<br>13.3<br>6.12<br>29.9<br>n.a.<br>13<br>28.4<br>n.a. | 6<br>24<br>3.31<br>3<br>199<br>33<br>120<br>41<br>1.45<br> | 59<br>41<br><br><br><br><br><br><br><br>113 | 9.8<br>1.2<br><br><br><br><br><br><br><br> |
| Venezuela [b] | Riecito° | 27.9 | 4 | 51 | 12.75 |

**Sources:**

a = Table 27 in FAO 2004 (Use of phosphate rocks for sustainable agriculture. Fertilizer and Plant Nutrition Bulletin 13, 2004. ftp://ftp.fao.org/agl/agll/docs/fpnb13.pdf); b = Geologues nr 162 d'après Van Kauwenbergh 1997; c = Ossterhuis F. H., Brouwer F.M., Wijnants H.J. (2000). A possible EU wide charge on cadmium in phosphate fertilizers: Economic and environmental implications. Final Report to the European Commission;
d = Swe Swe Mar, Masanori Okazaki, Microchemical Journal 104 (2012) 17–21; e = Aydin et al. Microchemical Journal 96 (2010) 247–251; f = Ware G. (Ed.) Reviews of Environmental Contamination and Toxicology Vol. 192, 2008; g = A. Fourati, G. Faludi, Changes in radioactivity of phosphate rocks during the process of production (of), Radioanalytical and Nuclear Chemistry 125/2 (1988) 287–293; h = Sattouf M, 2007.
*igneous: formed deep within the earth; ° sedimentary: formed on the sea bed by the decay of organic matter
Level of concern: < 1 = no ; 20-60 = acceptable; > 60 = high;
N.B: highlighted values are P (conversion factor P = P2O5/ 2.2915)

**Table A2: Uranium content in various P-fertilizers**

| Düngertyp / Ursprung | n | Min. | Max. | Mittelwert | Quelle |
|---|---|---|---|---|---|
| **Superphosphat** | | | | | |
| USA | 3 | 60.5 | 172 | **104** | *6, 9* |
| Mexiko | 5 | 90.2 | 90.6 | **90.5** | *4, 5* |
| Brasilien | 11 | 21.4 | 93.7 | **65.2** | *2, 13* |
| Tansania | 1 | | | **325** | *8* |
| Ungarn (RP Kola) | 6 | 1.8 | 2.0 | **2.0** | *1* |
| Deutschland (RP unbekannt) | 1 | | | **91** | *1* |
| **Triple Superphosphat** | | | | | |
| USA | 4 | 143 | 208 | **178** | *6, 9, 11* |
| Mexiko | 4 | 196 | 197 | **197** | *4, 5* |
| Brazilien | 11 | 14.7 | 69.7 | **50.2** | *2, 13* |
| Tansania | 1 | | | **362** | *8* |
| Deutschland(RP unbekannt) | 2 | 52.3 | 160 | **106** | *1* |
| **Weicherdiges/gemahlenes Roh-phosphat** | | | | | |
| USA | 4 | 8.7 | 144 | **42.9** | *6* |
| Nord-Afrika | 32 | 10 | 1117 | **205** | *7, 12* |
| Deutschland (RP unbekannt) | 2 | 56.6 | 72.9 | **64.8** | *1* |
| **NP Dünger** | | | | | |
| USA | 16 | 161 | 165 | **163** | *11* |
| Mexiko | 1 | | | **188** | |
| Brazilien | 2 | 49.6 | 93.8 | **71.7** | *2* |
| Marokko | 1 | | | **133** | *3* |
| Rumänien (RP unbekannt) | 4 | 3.5 | 149 | **59.4** | *10* |
| Ungarn (RP Kola) | 2 | 2.8 | 3.0 | **2.9** | *1* |
| Deutschland (RP unbekannt) | 3 | 0.62 | 61 | **27** | *1* |
| **PK Dünger** | | | | | |
| USA | 3 | 69.9 | 109 | **89.4** | *9* |
| Belgien (RP unbekannt) | 1 | | | **98.6** | *3* |
| Deutschalnd (RP unbekannt) | 3 | 31.2 | 163 | **82.1** | *1* |
| **NPK Dünger** | | | | | |
| USA | 5 | 39.7 | 113 | **65.5** | *9* |
| Brazilien | 12 | 5.2 | 54.3 | **27.1** | *14* |
| Rumänien (RP unbekannt) | 3 | 24 | 62 | **42.7** | *10* |
| Ungarn (RP Kola) | 8 | 0.04 | 1.9 | **0.5** | *1* |
| Belgien (RP unbekannt) | 1 | | | **46** | *3* |
| Deutschland (RP unbekannt) | 20 | <0.05 | 33.3 | **9.9** | *1* |

1 FAL sample collection, 2003-2007; 2 Conceicao & Bonotto, 2006; 3 El Ghawi et al., 1999; 4 Godinez et al., 1997; 5 Guzman et al., 1995; 6 Hamamo et al., 1995; 7 Heiland, 1986; 8 Makweba & Holm, 1993; 9 McBride & Spears, 2001; 10 Pantelica et al., 1997; 11 Robarge et al., 2004; 12 Sam et al., 1999; 13 Saueia & Mazilli, 2006; 14 Yamazaki & Geraldo, 2003;
RP = Rohphosphat

Values are mg/kg dw

Source: UBA, 2012 p.14 (summarizing data from Kratz et al 2008)

# Appendix B: Occurrence of U in water

### *EFSA (2009)*

EFSA collated literature data on the occurrence of U in drinking water. In Europe, North America and Asia, measured U concentrations in water ranged between 0.003 and 87.05 µg/L. (Northern Spain and India, respectively); the highest measured concentration in Europe was 44.2 µg/L (Germany, mineral water).

efsa European Food Safety Authority

**Table 3.** Occurrence of uranium in water.

| Country/Area | Type of sample | n | Uranium concentration, µg/L | |
|---|---|---|---|---|
| | | | Average | Range (min – max) |
| Canada/Ontario | Treated drinking water | 3,700 | 0.40 | 0.05-4.21 |
| USA, New York City | Drinking water | 978 | 2.55 | |
| Germany | Mineral water | 1,456 | 2.64 | < 0.2-44.2 |
| Northern Germany | Wells water | 48 | 0.87 | 0.015-8.95 |
| | Tap water | 39 | 0.18 | 0.015-1.44 |
| | Favourite bottled water | 17 | 1.84 | 0.015-10.6 |
| Northern Greece | Wells water | 42 | | 0.061-10.02 |
| Austria | Mineral water | 9 | | 0.012-5.4 |
| Germany | Tap water | 152 | 1.3 | 0.05-8.6 |
| | Mineral and medicinal | 252 | | < 0.015-24.5 |
| Iran | Drinking water | 200 | | 1-10.9 |
| India, Upper Silwaliks | Drinking water | 34 | | 1.08-19.68 |
| Western Uzbekistan | Drinking water | 11 | | 0.01-27.63 |
| | River and canal water | 22 | | 1.54-11.31 |
| Poland | Bottled mineral water | 28 | | < 0.04-0.62 [(a)] (< 0.5-7.7 mBq/L) |
| Italy | Bottled water | 8 brands | | 0.15-8 |
| Italy | Mineral water | 17 | | 0.017 - 8.3[(a)] (0.21-103 mBq/L) |
| Northern Spain | Treated water | 4 water treatment plants | 0.064[(a)] | 0.003 - 0.23[(a)] (0.039-2.90 mBq/L) |
| India, Punjab [(b)] | Drinking water | 24 | 30 | 2.23-87.05 |
| Southern Finland [(b)] | Wells water | 325 | 131 | 0.001-1920 |

(a): Conversion of the $^{238}U$ activity concentration using the conversion factor of 1 Becquerel/L (Bq/L) equivalent to 80.37 µg/L
(b): Regions with high natural uranium concentration in soil and water (hot spots)

EFSA (2009) collated data on uranium concentrations in European drinking water. Median U concentrations were ≤1.9 µg/L, but the maximum values, 112.51 µg/L in tap water and 152.70 in bottled water, exceeded the current WHO (2011) guidance limit of 30 µg/L.

efsa European Food Safety Authority

**Uranium in Food**

**Table 8a.** Descriptive statistics of uranium concentration in tap water (µg/L). The intervals indicate values in the lower- and upper-bound scenarios, respectively. A single value indicates no difference between lower- and upper-bound results.

| Country | n | P5 | Mean | Median | P95 | Maximum |
|---|---|---|---|---|---|---|
| France | 642 | 0.00-0.27 | 3.12-3.33 | 0.43-0.71 | 11.45 | 112.51 |
| Germany | 97 | 0.50 | 0.82-0.83 | 0.50 | 1.80 | 10.50 |
| Hungary | 25 | 1.01 | 2.06 | 1.90 | 4.18 | 4.20 |
| Italy | - | - | - | - | - | - |
| Portugal | - | - | - | - | - | - |
| Sweden | 255 | 0.00-1.20 | 1.79-2.75 | 0.00-1.20 | 13.60 | 40.80 |
| Switzerland | 4,423 | 0.06 | 2.12 | 0.73 | 9.41 | 92.02 |
| UK | 33 | 0.00-0.78 | 0.12-0.83 | 0.00-0.80 | 0.80 | 1.69 |

**Table 8b.** Descriptive statistics of uranium concentration in bottled waters (µg/L). The intervals indicate values in the lower- and upper-bound scenarios, respectively. A single value indicates no difference between lower- and upper-bound results.

| Country | n | P5 | Mean | Median | P95 | Maximum |
|---|---|---|---|---|---|---|
| France | 94 | 0.24 | 8.74 | 1.89 | 41.79 | 152.70 |
| Germany | 1,224 | 0.00-0.04 | 1.08-1.29 | 0.15-0.50 | 5.30 | 35.00 |
| Hungary | -- | - | - | - | - | - |
| Italy | 51 | 0.04 | 0.72 | 0.33 | 2.89 | 7.15 |
| Portugal | 77 | 0.00 | 1.03 | 0.26 | 6.99 | 13.90 |
| Sweden | - | - | - | - | - | - |
| Switzerland | 66 | 0.01 | 2.54 | 1.02 | 7.71 | 30.35 |
| UK | 51 | 0.00-0.16 | 3.31-3.32 | 1.69 | 10.76 | 14.86 |

### *Swiss waters survey (Stalder et al, 2012)*

In Switzerland, measured U concentrations in water ranged between 0.025 and 92.02 µg/L.

**Table 2**
Statistical summary of uranium data for water samples from this study and literature; $n$ = number of samples, $N$ = total number of samples.

| | Cantons of GR, TI, VS [U] (µg L$^{-1}$) | | All cantons excluding GR, TI, VS [U] (µg L$^{-1}$) | | All cantons [U] (µg L$^{-1}$) | |
|---|---|---|---|---|---|---|
| N | 2539 | | 3009 | | 5548 | |
| Minimum | 0.025 | | 0.025 | | 0.025 | |
| Maximum | 92.02 | | 27.90 | | 92.02 | |
| Median | 1.12 | | 0.69 | | 0.77 | |
| Arithmetic mean | 3.27 | | 1.00 | | 2.04 | |
| Geometric mean | 0.96 | | 0.66 | | 0.78 | |
| Standard deviation | 5.72 | | 1.36 | | 4.16 | |
| 95th percentile | 13.7 | | 2.70 | | 8.84 | |
| [U] (µg L$^{-1}$) | $n$ | % | $n$ | % | $n$ | % |
| <1 | 1199 | 47 | 2097 | 70 | 3296 | 59 |
| <2 | 1607 | 63 | 2735 | 91 | 4342 | 78 |
| <10 | 2325 | 92 | 2997 | 99.6 | 5322 | 96 |
| >15 | 107 | 4.2 | 3 | 0.10 | 110 | 2.0 |
| >20 | 59 | 2.3 | 2 | 0.07 | 61 | 1.1 |
| >30 | 18 | 0.7 | 0 | 0 | 18 | 0.3 |

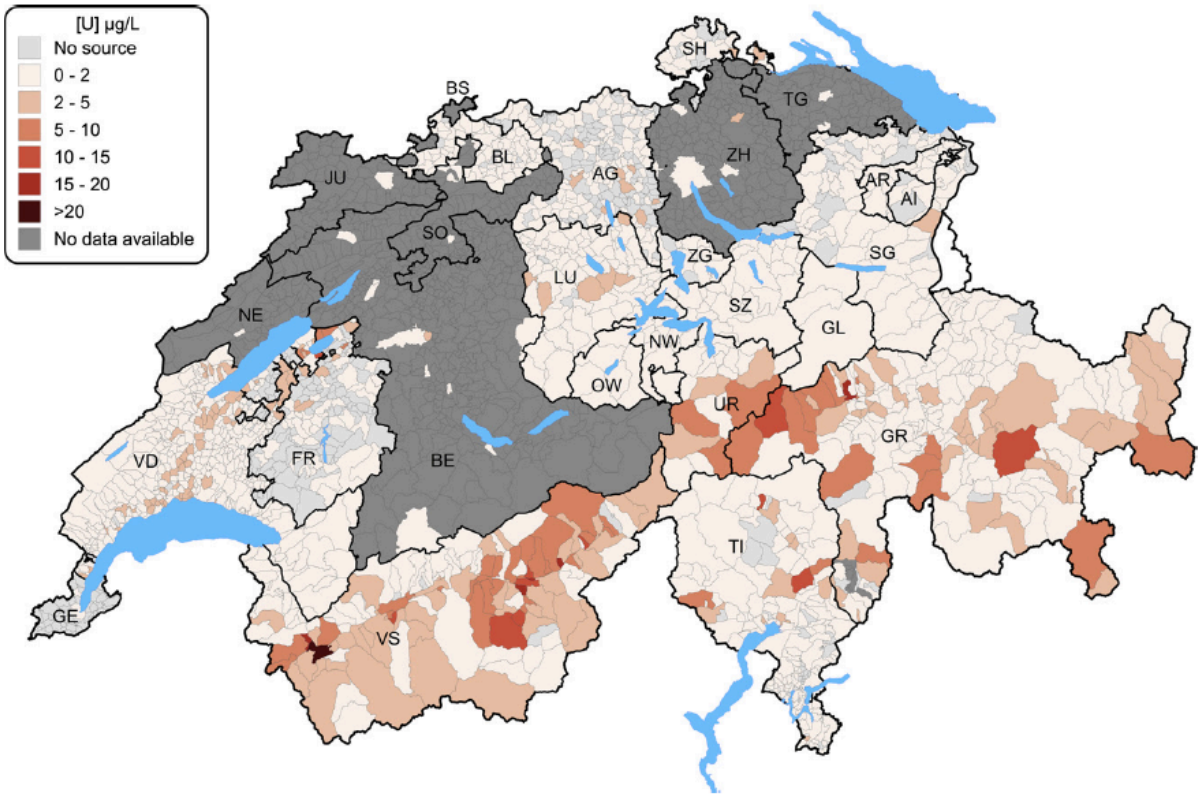


**Fig. 2.** Overview of uranium concentration in Swiss water. Majority of data for Graubünden taken from literature (Deflorin, 2004).

Source: Stalder et al, 2012

# Appendix C: Cd and U content in various P-fertilizers

## Table C1: Cd and U content in NP, PK and NPK-fertilizers (Dittrich and Klose, 2008)

**Tabelle 12: Schwermetallgehalte in NP-Düngern**

| NP-Dünger | | $P_2O_5$ | As | Pb | Cd | Cr | Ni | Hg | Tl | Cu | Zn | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % | mg/kg TM | | | | | mg Cd /kg $P_2O_5$ TM | | | | |
| NP-Dünger (insgesamt) | | | | | | | | | | | | |
| n = 69 | MW | 34,6 | 6,04 | 3,69 | 26,7 | 144 | 19,5 | 0,03 | 0,18 | 23,8 | 191 | 76,7 |
| | Min | 9,54 | 0,15 | 0,01 | 0,05 | 2,42 | 0,01 | 0,01 | 0,01 | 1,64 | 4,52 | 0,03 |
| | Max | 52,4 | 15,2 | 61,2 | 54,2 | 343 | 51,9 | 0,1 | 0,54 | 407 | 894 | 224 |
| NP-Dünger 18-46 (DAP) | | | | | | | | | | | | |
| n = 32 | MW | 46,2 | 7,97 | 0,87 | 43,1 | 272 | 35,1 | 0,01 | 0,31 | 26,5 | 330 | 121 |
| | Min | 45,1 | 4,19 | 0,01 | 31,7 | 227 | 21,4 | 0,01 | 0,17 | 10,5 | 224 | 74,7 |
| | Max | 47,0 | 10,9 | 2,22 | 49,7 | 343 | 46,0 | 0,04 | 0,43 | 33,8 | 410 | 224 |
| NP-Dünger 20-20 | | | | | | | | | | | | |
| n = 12 | MW | 20,7 | 4,27 | 3,73 | 8,04 | 6,66 | 0,01 | 0,01 | 0,05 | 11,3 | 70,3 | 28,8 |
| | Min | 20,1 | 0,15 | 0,01 | 0,05 | 5,25 | 0,01 | 0,01 | 0,01 | 10 | 57,5 | 0,03 |
| | Max | 21,2 | 15,2 | 5,68 | 47,6 | 9,28 | 0,01 | 0,02 | 0,25 | 12,5 | 85,2 | 166 |

**Tabelle 13: Schwermetallgehalte in PK-Dünger**

| PK-Dünger | | $P_2O_5$ | As | Pb | Cd | Cr | Ni | Hg | Tl | Cu | Zn | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % | mg/kg TM | | | | | mg Cd /kg $P_2O_5$ TM | | | | |
| ThomasKali | | | | | | | | | | | | |
| n = 10 | MW | 7,66 | 1,76 | 4,7 | 39,7 | 160 | 4,41 | 0,70 | 0,29 | 5,68 | 134 | 28,5 |
| | Min | 6,8 | 0,99 | 1,54 | 34,0 | 130 | 2,63 | 0,01 | 0,11 | 2,89 | 104 | 20,6 |
| | Max | 10,9 | 2,21 | 10,7 | 46,9 | 201 | 7,53 | 2,04 | 0,62 | 8,88 | 155 | 40 |
| PK-Dünger | | | | | | | | | | | | |
| n = 11 | MW | 19,8 | 4,06 | 0,38 | 55,6 | 77,6 | 17,9 | 0,03 | 0,29 | 20,1 | 202 | 64,3 |
| | Min | 11 | 2,49 | 0,01 | 42,5 | 6,94 | 10,4 | 0,01 | 0,20 | 5,84 | 129 | 35,2 |
| | Max | 25,1 | 6,09 | 1,04 | 65,66 | 222 | 25,7 | 0,05 | 0,45 | 64,4 | 287 | 84,6 |
| PK-Dünger mit Mg (Thomasphosphat Kali) | | | | | | | | | | | | |
| n = 5 | MW | 8,1 | 2,13 | 3,32 | 46,9 | 228 | 6,32 | 0,04 | 0,06 | 7,88 | 7,11 | 54,2 |
| | Min | 7,8 | 1,89 | 0,01 | 43,8 | 213 | 2,36 | 0,02 | 0,02 | 4,44 | 2,69 | 53,8 |
| | Max | 8,82 | 2,22 | 4,03 | 52,07 | 241 | 8,43 | 0,05 | 0,09 | 13,8 | 11,2 | 65,9 |

**Tabelle 14: Schwermetallgehalte in NPK-Düngern**

| NPK-Dünger | | $P_2O_5$ | As | Pb | Cd | Cr | Ni | Hg | Tl | Cu | Zn | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % | mg/kg TM | | | | | mg Cd /kg $P_2O_5$ TM | | | | |
| **NPK-Dünger (insgesamt)** | | | | | | | | | | | | |
| n = 61 | MW | 13,6 | 2,9 | 2,18 | 15,8 | 43,4 | 23,1 | 0,02 | 0,05 | 26,7 | 82,8 | 11,2 |
| | Min | 6,5 | 0,01 | 0,01 | 0,06 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 |
| | Max | 20,5 | 9,6 | 20,7 | 76,6 | 200 | 198 | 0,23 | 0,16 | 321 | 296 | 50,9 |
| NPK-Dünger 15-15-15 | | | | | | | | | | | | |
| n = 14 | MW | 15,5 | 1,3 | 2,55 | 4,7 | 13,2 | 0,97 | 0,01 | 0,05 | 7,21 | 69,4 | 5,58 |
| | Min | 14,5 | 0,2 | 0,02 | 0,06 | 3,14 | 0,01 | 0,01 | 0,01 | 4,08 | 48,4 | 0,01 |
| | Max | 16 | 3,7 | 5,21 | 41,3 | 86 | 8,69 | 0,03 | 0,16 | 9,93 | 150 | 36,5 |
| NPK-Dünger 16-16-16 | | | | | | | | | | | | |
| n = 8 | MW | 16,4 | 3,3 | 2,4 | 0,17 | 8,05 | 1,28 | 0,01 | 0,01 | 21,7 | 38,4 | 4,98 |
| | Min | 15,9 | 1,26 | 0,01 | 0,11 | 6,74 | 0,01 | 0,01 | 0,01 | 15,5 | 34,9 | 0,02 |
| | Max | 16,9 | 5,5 | 5,48 | 0,25 | 9,27 | 2,5 | 0,01 | 0,01 | 24,2 | 40,3 | 36,8 |

Source: Dittrich and Klose, 2008