Rock phosphates and P fertilizers as sources of U contamination in agricultural soils

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Abstract. U concentrations were analyzed in a set of mineral fertilizers with and without P and compared to U concentrations in various organic fertilizers. Mean concentrations between 6 and 149 mg/kg U were found in P containing mineral fertilizers, while mean concentrations in mineral fertilizers without P were below 1.3 mg/kg U. Mean U concentrations in farmyard manures did not exceed 2.6 mg/kg U. As a consequence, an average P dressing of 22 kg/ha P would charge the soil with up to 17-61 g/ha U when added as mineral fertilizer but less than 10 g/ha when given as farmyard manure or slurry. Expected U uptake by crops is less than 1 g/ha U.

Introduction

Phosphate fertilizers are used in agriculture worldwide to supply crops with adequate amounts of P for growth and development. In 2002/2003, 1.46 million tons of P were used for agriculture in the European OECD countries, 142746 t of which in Germany (Statistisches Bundesamt 2004). P fertilizers may contain considerable amounts of U, data on U concentrations from the international literature range from less than 10 to more than 360 mg/kg (Hamamo et al. 1995; Makweba and Holm 1993). Little data exists on U accumulation in soils and U plant uptake from P fertilization. According to Mortvedt and Beaton (1995), no increase in soil and plant U was detected in a long term experiment with triple superphosphate fertilization. Similar results were published by Hamamo et al. (1995). However, as these authors stated, considering the mobilility of U^{6+} (uranyl ion), it is hardly surprising that no soil accumulation was found, rather, these results imply that the U applied with the P fertilizer had leached into the groundwater that drained from the experimental fields. Increased U concentrations in surface and ground water and water from drainage channels after long term mineral P fertilization have been reported for the Kanovci Area, Croatia (Barisic et al. 1992), as well as for wetlands in the Florida Everglades (Zielinski et al. 2000) and for the river waters of the Corumbatai River Basin, Brazil by Conceicao and Bonotto (2000, 2003). Considerable research efforts on U extraction from phosphoric acid, which is the basic component of P fertilizer production, were already made in the 1960s (Romero Guzman et al. 1995a), however, the problem of U in mineral fertilizers has not been addressed in Germany until very recently.

In this paper, results from a screening of U concentrations in a set of various mineral and organic fertilizers are presented and compared to data from the international literature. U loads from P fertilization with various types of fertilizers are calculated and options for the reduction of uranium inputs into agricultural soils with fertilization are discussed.

Uranium in rock phosphates

The basic raw material for the production of P containing mineral fertilizers are rock phosphates. About 87% of the rock phosphates used for fertilizer production are of marine-sedimentary origin (Van Kauwenbergh 1997). During deposition and diagenesis, U and other heavy metals or trace elements from the seawater are enriched in marine-sedimentary phosphates (Aly and Mohammed 1999; Karhunen and Vermeulen 2000), therefore they are often characterized by high concentrations of these elements (El-Arabi and Khalifa 2002; Makweba and Holm 1993). In the apatite structure, U may occur mainly in two forms (El-Arabi and Khalifa 2002):

- as U^{4+} , it substitutes for Ca^{2+} in the apatite crystal
- as U^{6+} , or more precisely, as uranyl ion $(UO_2)^{2+}$, it is either adsorbed to a phosphate mineral, or fixed to the phosphate ion to form a secondary phosphate mineral.

Table 1 shows how U concentrations vary depending on the origin of the rock phosphate for the 10 largest producers worldwide.

Production processes of P fertilizers

There are two common types of production for P containing fertilizers, which differ in the type of acid used to dissolve the rock phosphate and the type of fertilizer resulting from the process.

Wet process phosphoric acid

Wet process phosphoric acid is produced by attacking the rock phosphate with concentrated sulphuric acid (H_2SO_4) (Fig. 1). In this process, phosphogypsum is formed as a by-product. After filtration and decantation, the phosphoric acid is concentrated in an evaporation process and can then be granulated into superphosphate. By adding more rock phosphate to the H_3PO_4, triple-superphosphate can be manufactured, while the addition of ammonia (NH_3) allows for the production of ammonium phosphate (Pantelica et al. 1997; Erdem et al. 1996; Romero Guzman et al. 1995b).

Table 1. Uranium concentrations in rock phosphates of different origin, sorted by amount of production (mine production data from Jasinski 2003; uranium data from Hayumbu et al. 1995; Pantelica et al. 1997; Raven and Loeppert 1997; Romero Guzman et al. 1995a; Van Kauwenbergh 1997).

Origin (s = sedimentary, i = igneous)	Mine Production in 2002 (gross weight, in 1000 t)	U concentrations, range (in mg/kg)
United States (s)	35800	65 - 141
Morocco + Western Sahara (s)	24000	75 - 130
China (s)	21000	23 - 31
Russia (i)	10500	27 - 85
Tunisia (s)	7500	32 - 48
Jordan (s)	7000	46 - 129
Brazil (i)	4700	182 - 220
Israel (s)	3500	99 - 150
South Africa (i)	2800	23
Syria (s)	2400	75 - 106

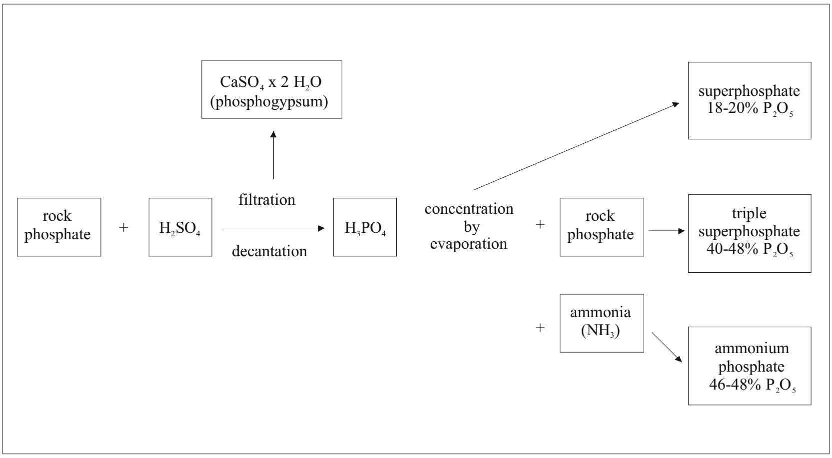

Fig. 1. Flow chart for phosphate fertilizer production by sulphuric acid attack (modified after Romero Guzman et al. 1995b; Pantelica et al. 1997).

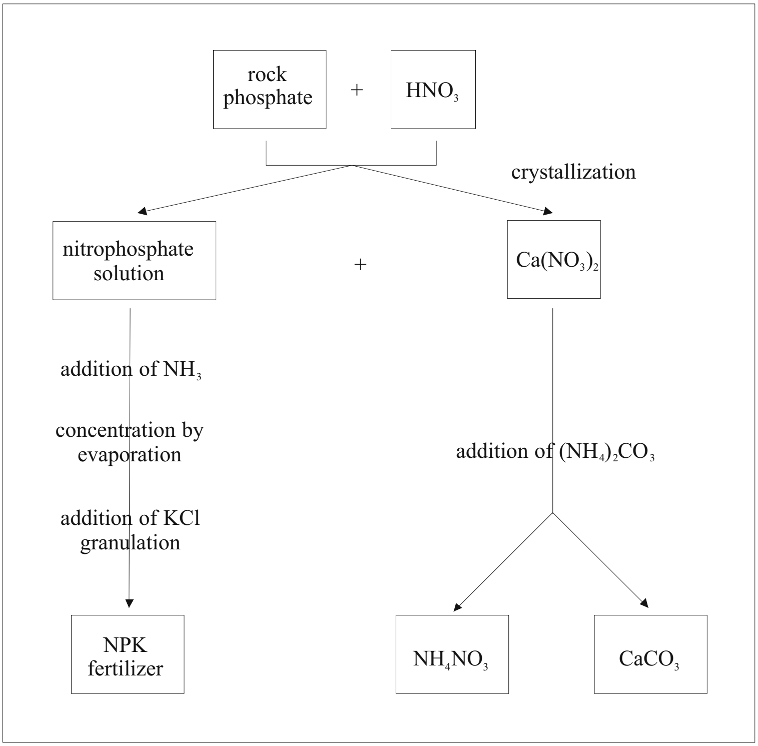

Fig. 2. Flow chart for phosphate fertilizer production by nitric acid attack (modified after Pantelica et al. 1997; Gupta and Singh 2003).

Nitrophosphate process

By attacking rock phosphate with nitric acid (HNO_3), fertilizers of the nitrophosphate type (NP, NPK) are obtained (Fig. 2). In the first step, a nitrophosphate solution is produced. This solution is further enriched with N by adding NH_3, and is then concentrated by evaporation. Now, an NP fertilizer can be manufactured, while the addition of KCl results in an NPK fertilizer.

As is shown in Figs. 1 and 2, in both processes a P containing acid solution is produced from the rock phosphate, which is then concentrated by evaporation. Due to this evaporation step, U is enriched in the final product compared to the raw material (Erdem et al. 1996; Uyanik et al. 1999).

U concentrations and loads in fertilizers

A literature review was made to collect information on U concentrations in mineral and organic fertilizers in a database on unwanted substances in fertilizers (FAL database). In addition to this, a set of 65 mineral and organo-mineral fertilizers as well as a collection of 500 manures and slurries from organic farms were analyzed for their U concentration. The results are presented in Tables 2-4.

Table 2. Uranium concentrations (mg/kg) in mineral fertilizers without and with P, from different sources (DB-NE = FAL database, non-european sources, DB-E = FAL database, European sources, FAL = FAL sample collection)

Fertilizer type	Data source	n	min	max	mean	s
Mineral fertilizers without P						
N fertilizer	DB-NE	1			0.26	
N fertilizer	FAL	7	0.02	1.39	0.35	0.48
K fertilizer	DB-NE	2	0.23	0.49	0.36	0.18
K fertilizer	FAL	3	0.03	0.62	0.23	0.34
Lime	DB-NE	1			1.31	
Secondary nutrient fertilizer	FAL	4	0.04	2.24	0.99	0.95
Mineral fertilizer with P						
P fertilizer	DB-NE	18	8.7	362	149	101
P fertilizer	FAL	12	1.8	160	35	47
NP fertilizer	DB-NE	4	2.9	198	131	90
NP fertilizer	DB-E	4	3.5	149	59	70
NP fertilizer	FAL	5	0.62	61	17	25
PK fertilizer	DB-NE	1			99	
PK fertilizer	FAL	3	31	163	82	71
NPK fertilizer	DB-NE	1			46	
NPK fertilizer	DB-E	3	24	62	43	19
NPK fertilizer	FAL	22	0.04	28	6.3	8.1
organo-mineral NPK	FAL	5	7.4	28	19	8.1

Table 3. Uranium concentrations (mg/kg) in different types of P fertilizers, from different sources (DB-NE = FAL database, non-european sources, FAL = FAL sample collection).

Fertilizer type	Data source	n	min	max	mean	s
Superphosphate	DB-NE	7	80	325	134	90
Superphosphate	FAL	6	1.8	2.0	1.9	0.09
Triple superphosphate	DB-NE	7	186	362	225	62
Triple superphosphate	FAL	2	52	160	106	76
Soft rock phosphate	DB-NE	4	8.7	144	43	67
Soft rock phosphate	FAL	2	57	73	65	11

U concentrations in mineral fertilizers

As is shown in Table2, mean U concentrations in mineral fertilizers without P are below 1.4 mg/kg, while mean U concentrations in P containing mineral fertilizers range from 6 to 149 mg/kg. In the literature, maximum concentrations up to more than 362 mg/kg are found. The highest concentrations are found in pure P and in NP fertilizers, which also have the highest P concentrations.

Looking at different types of P fertilizers, it can be seen that even within a particular type, large variations of U concentrations may occur (Table 3). This is probably due to the different origins of the rock phosphates used for production, as they vary strongly in their U concentrations, too (see Table 1). For example, the 6 superphosphates analyzed by FAL were all produced from Kola phosphates, which are very low in U concentration. The highest U concentrations are found in triple superphosphate, which is also the P fertilizer with the highest P concentration.

U concentrations in organic fertilizers

Organic fertilizers like manures and slurries are generally low in U concentrations, no matter whether they come from organic or conventional farms. Mean U concentrations do not exceed 2.6 mg/kg dry weight, while maximum concentrations may reach up to 11.6 mg/kg dry weight in individual cases (Table 4). For sewage sludge, only one reference was found, which reports a mean U concentration of 8 mg/kg dry weight for unstabilized wet sludge, and 31 mg/kg dry weight for sludge stabilized with lime.

Table 4. Uranium concentrations (mg/kg dry weight) in different types of organic fertilizer, from different sources (DB-NE = FAL database, non-european sources, DB-E = FAL database, European sources, FAL = FAL sample collection).

Type of fertilizer	Data source	n	min	max	mean	s
Manure and slurry from organic farming						
Organic cattle manure	FAL	197	0.05	3.7	0.75	1.2
Organic pig manure	FAL	57	0.03	1.4	0.24	0.24
Organic poultry manure	FAL	43	0.05	4.6	1.1	1.2
Organic sheep manure	FAL	22	0.07	11.6	2.6	2.6
Organic goat manure	FAL	3	0.05	1.14	0.28	0.27
Organic cattle slurry	FAL	46	0.09	0.37	0.23	0.13
Organic pig slurry	FAL	1	0.05	0.05	0.05	.
Manure and slurry from conventional farming						
Conventional broiler manure	FAL	10	0.33	5	0.97	1.42
Conventional cattle slurry	DB-NE	20	0.1	3.5	1.4	
Sewage sludge						
Germany	DB-E	204			3.5	
Lower Saxony, Germany	DB-E	10			0.91	

U loads with P fertilization

Under good agricultural practice, P fertilization is usually done according to the P demand of the crop. Therefore it is interesting to know which U loads are put onto agricultural soils with typical rates of P fertilization. In Table 5, U loads are calculated for a number of different mineral and organic P fertilizers when a P rate of 22 kg/ha P is applied. For comparison, expected U uptake of plants is also shown. With only very few exemptions at the lower end of the given ranges, U uptake by plants, which can be expected to be less than 1 g/ha*a, will be exceeded no matter which type of fertilizer is used, however, the “excess supply” is much higher for mineral fertilizers than for farmyard manures or slurries. U loads applied with sewage sludge, are also comparatively low.

Strategies for reduction of U inputs into agricultural soils from fertilization

Looking at the potential U loads to be expected from P fertilization it is clear that some measures should be taken to prevent the accumulation of U in agricultural soils and its discharge into the environment by leaching in the long term. In theory, there are two ways to tackle this problem: One is for the fertilizer industry to

Table 5. U loads for different types of P fertilization and expected U uptake by plants (based on data on U concentrations from Mortvedt and Beaton 1995; data on DM yield after Hydro Agri Dülmen 1993).

Type of fertilizer	P concentration (% P)	U load (g/ha*a) at a P rate of 22 kg/ha P (=50 kg/ha P_2O_5)
Triple superphosphate[1]	18.5	6.2 - 19
NP[1]	5.3 - 21.6	0.13 - 17
PK[1]	5.8 - 8.4	11 - 61
NPK[1]	1.5 - 13.2	<0.01 - 20
Organic cattle slurry[1]	0.14 - 2.5	0.31 - 5
Conventional cattle slurry[2]	0.8	3.8
Organic pig manure[1]	0.23 - 2	0.1 - 9.4
Conventional broiler manure[1]	1.2 - 1.5	0.57 - 9
Sewage sludge[2]	2.1 - 2.2	0.9 - 3.3
Type of crop	DM yield (dt/ha)	U uptake by plants (g/ha*a)
Corn grain and leaves	75+75	0.15
Wheat grain and straw	70+70	0.28
Timothy forage	130	0.78

[1] data from FAL samples,

[2] data from literature; note: ranges are given where raw data sets were available, otherwise, a mean value is given)

produce U free mineral fertilizers, the other is for farmers to select fertilizers which are low in U concentration for P fertilization.

Options for the fertilizer industry: U extraction from phosphoric acid

Several methods have been developed to extract U from phosphoric acid. The scope of this paper only allows a short description, for more technical details on this topic the reader is referred to Gupta and Singh (2003).

1. Precipitation of U from phosphoric acid, using an organic reagent (e.g. acetone) as dispersant and ammonium fluoride (NH_4F) as precipitant. Reduction of U^{6+} to U^{4+} by addition of Fe powder. In order to produce "yellow cake", U needs to be recovered from the precipitate by dissolution in diluted H_2SO_4 or HNO_3 and subsequent purification by ion exchange or solvent extraction.
2. Ion exchange separation with a chelating resin (with subsequent elution and precipitation of U in order to produce yellow cake).
3. Membrane separation of U, using liquid membranes with a strong affinity for U (as yet still in experimental development stage).
4. Froth flotation: complexing U with a surface active agent of hydrophobic nature (froth needs to be purified to produce high grade yellow cake).
5. Solvent extraction of U, using various synergistic mixtures of organic solvents such as DNPPA (di nonyl phenyl phosphoric acid) + TOPO (tri n octyl

phosphine oxide) (Singh et al. 2001), followed by purification and precipitation. In this process, U extraction rates of >90% can be realized.

Of the methods listed here, solvent extraction appears to be the most successful one, which is well capable to be practiced by the uranium industry on a large commercial scale (Gupta and Singh 2003). However, according to WISE (2002), operating costs for the uranium recovery plants which had been built in the United States, Canada, Spain, Belgium, Israel and Taiwan from the 1970s onwards were by far higher than the current uranium market price, which is why most of them have been closed again by now. Therefore, as yet U extraction from phosphoric acid remains more of scientific than of commercial interest (Romero Guzman et al. 1995b).

Options for farmers: Selection of adequate fertilizers

As long as no U free fertilizers are produced, the only option for farmers to reduce the U input into soils and the environment by fertilization is to select fertilizers which are low in U concentrations. The use of rock phosphates from deposits which are low in U concentration still allows to produce such mineral fertilizers. Prerequisite for an informed choice by farmers is that U concentrations in commercial fertilizers are openly declared. As the above calculations imply, farmyard manures and slurries appear to hold quite some attraction, since they – when applied according to the rules of good agricultural practice - allow to supply the crops with the required amount of P by keeping uranium loads at a relatively low level.

Conclusion

According to WISE (2002), the potential uranium concentration of known phosphate rock world reserves is in the range of 5 to 15 million t U. Thus, at the current global rate of consumption, phosphatic uranium could meet the global demand for about 440 years, while known uranium resources will only last for about 86 years (OECD 1999, cited in Singh et al. 2001).

In the context of the ongoing discussion on sustainable farming, the conservation of resources and the precaution principle, we suggest that more emphasis should be placed on further development of economically feasible methods for the extraction of uranium from phosphoric acid. In addition to this, the efficient use of farmyard manures as a P source which is very low in uranium should be given increased consideration.

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