

Solubility of uranium in fertilizers

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Abstract

Several extractants listed by the European fertilizer ordinance for assessing P solubility were tested in this study for their suitability to assess U solubility in P containing fertilizers, including aqua regia (AR), 2 % formic acid (FA), 2 % citric acid (CA), neutral ammonium citrate (NAC), alkaline ammonium citrate (AAC), and water. The sample set consisted of 35 samples, including straight P fertilizers, compound fertilizers, organo-mineral fertilizers, and phosphate rocks. A significant correlation was found for each two extractants for uranium solubility, except for aqua regia with water and alkaline ammonium citrate (at the 0.01 level). The highest mean solubility of uranium, (both total and relative), after aqua regia, was found in 2 % citric acid, except for straight P fertilizers, where AAC was the strongest extractant. The lowest soluble uranium fraction in all groups was also in water, its mean varying from 2.6 % of total uranium in phosphate rocks to 16.8 % in straight P fertilizers. The relative solubilities (i.e. referred to AR) in CA, AR, and water were significantly different from each other as well as from relative solubility in NAC, FA, and AAC (at the 0.05 level). However, there were no significant differences between the relative solubilities in NAC, FA, and AAC. The results of this study showed that uranium solubility in P containing fertilizers changes according to kind of extractant and type of P containing fertilizer. It was concluded that the tested extractants may be suitable to assess the maximum potential amount of U that will be released from the various fertilizers. In order to evaluate the suitability of the various extraction methods for estimating the amount of potentially plant available uranium, future studies should investigate the relationship between the solubility of fertilizer derived U in a chemical extractant and its plant uptake (bio response).

Keywords: Fertilizer, phosphate, solubility, uranium

Zusammenfassung

Löslichkeit von Uran aus Düngemitteln

In der EU-Düngemittelverordnung zur Beschreibung der P-Löslichkeit gelistete chemische Extraktionsmethoden wurden auf ihre Brauchbarkeit zur Einschätzung der Löslichkeit von Uran aus P-haltigen Düngemitteln untersucht, darunter Mineralsäure (Königswasser, AR), 2 %ige Ameisensäure (FA), 2 %ige Zitronensäure (CA), neutrales (NAC) und alkalisches (AAC) Ammoniumcitrat sowie Wasser. Analysiert wurden 35 verschiedene Düngemitteltypen (Rohphosphate, reine P-, Mehrnährstoff- und organisch-mineralische Dünger). Zwischen den mit unterschiedlichen Extraktionsmitteln löslichen Uranfraktionen bestanden signifikante paarweise Korrelationen ($p < 0.01$), eine Ausnahme bildeten lediglich die Paare AR / Wasser und AR / AAC. Im Mittel fand sich die höchste (relative und absolute) Uranlöslichkeit in 2 %iger CA (nach AR), nur bei reinen P-Düngern erwies sich AAC als stärkstes Extraktionsmittel. Wasser extrahierte in allen Düngern den niedrigsten Urananteil, mit mittleren relativen Löslichkeiten von 2.6 % (Rohphosphate) bis zu 16.8 % (reine P-Dünger). Die relativen Löslichkeiten (Bezug: AR) in CA, AR und Wasser unterschieden sich sowohl voneinander als auch von denen in NAC und AAC sowie in FA signifikant ($p < 0.05$). Zwischen den 3 letztgenannten Extraktionsmitteln bestanden keine signifikanten Unterschiede. Die Ergebnisse zeigen, dass die Löslichkeit von Uran aus P-haltigen Düngern in Abhängigkeit von Düngemitteltyp und Extraktionsmittel variiert. Die getesteten Extraktionsmittel sind offenbar geeignet, den löslichen Urananteil aus verschiedenen P-haltigen Düngern einzuschätzen. Um darüber hinaus auch Schlüsse auf den potentiell pflanzenverfügbaren Urangehalt ziehen zu können, sollten künftige Untersuchungen sich auf die Beziehung zwischen chemischer Löslichkeit düngemittelbürtigen Urans und dessen tatsächlicher Aufnahme durch die Pflanze ("bio response") konzentrieren.

Schlüsselwörter: Düngemittel, Extraktionsmittel, Löslichkeit, Phosphat, Uran

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Introduction

Uranium is the heaviest naturally occurring radionuclide in the environment, which is known for both its radio-toxicity and chemical toxicity. For most radionuclides of the U-series, radiological dose is more important than chemical dose for human health, but for uranium itself, chemical toxicity supersedes radiological dose (Sheppard *et al.*, 2005). Knowledge about distribution and transfer of uranium in the soil-water-plant system, especially in agricultural and plant production, is necessary to decrease its effect on public health (Takeda *et al.*, 2006).

Uranium can be loaded onto agricultural soils by applying phosphorous sources. Phosphate fertilizers or phosphate rocks are used in all types of farming fields to supply phosphorus for the growing plants. Phosphate rocks, as a direct application or original source for producing the phosphate fertilizers, may contain considerable amounts of uranium (Romero Guzman *et al.*, 1995; Kratz and Schnug, 2006; Rothbaum *et al.*, 1979; Makweba and Holm, 1993; Takeda *et al.*, 2006). Uranium contents vary according to geographical origin from less than 10 up to more than 200 mg kg⁻¹ (Kratz *et al.*, 2008). In general, the U content in sedimentary phosphate rocks is higher than in igneous phosphate rocks. The uranium content in mineral phosphate fertilizers is also considerable, and it is related to phosphate content and origin of phosphate rock as initial P source. The uranium contents of the Minjingu ground phosphate rock, triple super phosphate, and simple super phosphate are as high as 377, 571, and 315 mg/kg respectively (Makweba and Holm, 1993). Based on a world wide literature survey, Kratz and Schnug (2006) reported mean uranium concentrations of 6 to 146 mg kg⁻¹ in different types of phosphate containing mineral fertilizers and less than 2.2 mg kg⁻¹ in mineral fertilizers without phosphorus.

An increase of uranium concentration in topsoil of fields with long applied fertilizers has been reported by several authors (Takeda *et al.*, 2006; Makweba and Holm, 1993), while others found no changes in uranium concentration in the field soil over 82 years with applied rock phosphate and P fertilizers (Jones, 1992). It may be assumed that the fertilizer-derived uranium was either leached from the soil or taken up by plants. It has been repeatedly reported that uranium uptake is positively affected by uranium concentration in contaminated soils or nutrient solution (Lamas, 2005; Rivas, 2005; Vandenhove, 2002; Environment Canada, 2002; Meyer *et al.*, 2004; Gulati *et al.*, 1980; Eapen *et al.*, 2003). Laroche *et al.* (2005) also reported a linear relationship between total uranium concentration in the hydroponics solution and total uranium in the roots of *Phaseolus vulgaris*. Uranium concentrations in harvested products are usually found to be very low or non detectable. However,

any increase in soil uranium content may cause higher uranium content in crops and then enter the human food chain in the long run. On the other hand, plant uptake of uranium depends on several factors, including factors related to the plants themselves as well as those related to the solubility and plant availability of uranium in the soil and in the fertilizers put onto the soil. In order to investigate the latter, a study was undertaken to find a chemical extraction method which is suited to describe the solubility of fertilizer-derived uranium.

Material and methods

Different types of phosphorus containing fertilizers including straight P fertilizers (SPF), compound fertilizers (CF), organo-mineral fertilizers (OMF) and phosphate rocks (PR) were selected and extracted with commonly used extractants to assess P solubility of fertilizers according to the German and European Fertilizer Ordinances: 2 % formic acid (2 % FA), 2 % citric acid (2 % CA), neutral ammonium citrate (NAC), alkaline ammonium citrate (AAC), and the water (in equilibrium with air CO₂, and at ambient temperature). Samples were oven-dried 24 h at 40°C for 24 h, and then ground with a vibrating disc mill (Retsch RS100) with a zirconia grinding set. In all extraction and dilution steps, twofold deionized water was used. Inductively Coupled Plasma-Quadrupole Mass Spectroscopy (ICP-QMS) was used for the uranium determination in all extractions (VG Elemental PlasmaQuad 3, Thermo Elemental, United Kingdom). Phosphorus was measured with a spectrophotometer at 882 nm (John, 1970). Statistical analysis of data was performed using SPSS. Correlations between uranium soluble in various extractants were calculated and differences between means of extractable uranium were tested by Duncan's test following a one-way ANOVA.

Results and discussion

The solubility of U and P differed strongly between extractants, with the solubility of U in water being significantly lower than that of P in water in all types of fertilizers analyzed. For all fertilizer types, the solubility of U and P in 2 % CA was quite similar, however, there were also differences when looking at each group of fertilizers separately. While U showed a somewhat lower solubility in NAC than P, it was more soluble in AAC than P (Table 1). Soluble U fractions extracted by different methods had significant correlation coefficients from 0.54 between water and 2 % CA to 0.86 between 2 % FA and 2 % CA at the 0.01 level (Table 2). The highest mean solubility of uranium, after aqua regia, was found in 2 % citric acid and the lowest in water (in both expressions as concentration and percentage). The relative solubility (i.e. referred to AR) of

U, calculated over all types of fertilizers analyzed here, in 2 % CA, AR, and water were significantly different from each other as well as from relative solubility in NAC, 2 % FA, and AAC (Table 3). However, there were no significant differences between the relative solubility in NAC, 2 % FA, and AAC. Also, average percentages of soluble uranium in these extractants were approximately equal (about 42 %), while average soluble uranium fractions in water and 2 % citric acid were 10 % and 61 % of total uranium, respectively (Table 3).

Table 1:
Soluble uranium and phosphorus in different fertilizers

Extractant	Type of fertilizer	N	Mean concentration		Mean relative solubility (% of aqua regia content)	
			U (mg kg ⁻¹)	P (g kg ⁻¹)	U %	P %
Aqua regia	SPF	3	81.3	191.9	100	100
	CF	12	37.2	47.5	100	100
	OMF	5	18.7	26.2	100	100
	PR	15	136.8	143.5	100	100
Formic acid (2 %)	SPF	3	26.1	215.1	30	112
	CF	12	22.9	41.8	72	91
	OMF	5	8.59	21.3	50	83
	PR	15	22.2	53.0	17	39
Citric acid (2 %)	SPF	3	58.6	215.8	62	112
	CF	12	31.8	42.1	107	93
	OMF	5	9.59	17.2	55	68
	PR	15	27.7	34.3	25	25
Neutral ammonium citrate	SPF	3	55.8	205.6	71	107
	CF	12	13.7	36.3	64	84
	OMF	5	4.94	11.7	34	49
	PR	15	23.7	8.7	20	7
Alkaline ammonium citrate	SPF	3	71.2	208.8	84	109
	CF	12	28.0	24.9	79	55
	OMF	5	3.78	8.4	22	32
	PR	15	11.3	1.4	10	1
Water	SPF	3	13.8	186.9	17	97
	CF	12	3.92	28.4	17	71
	OMF	5	2.23	9.6	14	40
	PR	15	2.71	7.8	3	5

Different types of P containing fertilizers showed significant differences in their U solubility in various extractants (Table 4). In CF, OMF, and PR types, the highest U solubility was found in 2 % citric acid, while for straight P fertilizers, the strongest extractant was AAC. The lowest U solubility

was found in water varying from 2.6 % in PRs to 16.8 % in SPFs (related to total U content measured in aqua regia digests; Table 4).

Table 2:
Correlation coefficients between soluble uranium percentage (related to U in AR) in different extractants (Pearson correlation, $n = 35$)

Extractant	2 % Formic acid	2 % Citric acid	Neutral ammonium citrate	Alkaline ammonium citrate
2 % Citric acid	0.862**	1		
Neutral ammonium citrate	0.685**	0.661**	1	
Alkaline ammonium citrate	0.806**	0.848**	0.701**	1
Water	0.551**	0.541**	0.560**	0.559**

** Correlation is significant at 0.01 level (2-tailed).

Table 3:
Differences between extractants with regard to mean U concentration and relative U solubility, calculated over all types of fertilizers analyzed by one-way ANOVA. Different letters show significant differences at $P < 0.05$

Extractant	N	Mean U concentration (mg kg ⁻¹)	Mean relative U solubility (% of U _{AR})
Water	35	4.0a	10.2a
Neutral ammonium citrate	35	20.4ab	41.3b
2 % formic acid	35	20.8ab	41.3b
Alkaline ammonium citrate	35	21.1ab	41.7b
2 % citric acid	35	29.2b	60.6c
Aqua regia	35	81.0c	100d

There was no significant difference between the U solubility in water between the 4 types of P-containing fertilizers (Table 5). However, for the U solubility in 2 % FA, 2 % CA, NAC, and AAC some significant differences were found between the groups. PRs and OMFs were similar with regard to their U solubility in NAC, AAC, and 2 % CA. Also, there were no significant differences between U solubility of CFs and SPFs in NAC and AAC. The strongest extracting power of water, NAC, and AAC was observed in straight P fertilizers, while the strongest extracting power of 2 % FA and 2 % CA was found in compound fertilizers. The lowest extracting power of all 5 extractants tested was found for phosphate rocks (Table 5).

Table 4:

Differences between relative U solubility in different extractants, calculated separately for each group of P containing fertilizers and analyzed by one-way ANOVA. Different letters show significant differences at $P < 0.05$

Extractants	Mean relative U solubility (in % of U_{AR})			
	Straight P fertilizers	Compound fertilizers	Organo- mineral fertilizers	Phosphate rocks
	(n = 3)	(n = 12)	(n = 5)	(n = 15)
Water	16.8a	16.6a	13.8a	2.6a
2 % Formic acid	29.5a	71.5b	49.6ab	16.8bc
Neutral ammonium citrate	71.1b	64.1b	33.8ab	19.6cd
Alkaline ammonium citrate	83.5bc	79.4bc	22.2ab	9.5ab
2 % Citric acid	61.5b	107.3cd	54.9b	24.9d
Aqua regia	100c	100cd	100c	100e

Table 5:

Differences between U solubility of various types of P containing fertilizers, tested for 5 different extractants and analyzed by one-way ANOVA. Different letters show significant differences at $P < 0.05$

Type of fertilizers	U solubility (% of U_{AR})				
	Water	2 % FA	NAC	AAC	2 % CA
Phosphate rocks (n = 15)	2.6a	16.8a	19.6a	9.5a	24.9a
Organo-mineral fertilizers (n = 5)	13.8a	49.6bc	33.8ab	22.2a	54.9a
Compound fertilizers (n = 12)	16.6a	71.5c	64.1bc	79.4b	107.3b
Straight P fertilizers (n = 3)	16.8a	29.5ab	71.1c	83.5b	61.5a

Conclusions

It is evident that the uranium solubility in P containing fertilizers is dependent both on the extractant and on type of P containing fertilizer. The solubility of U differed from that of P in the tested extractants. However, in order to draw further conclusions about the suitability of the various extraction methods for estimating the amount of potentially plant available uranium, future studies should investigate the relationship between the solubility of fertilizer derived U in a chemical extractant and uranium plant uptake (bio response).

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