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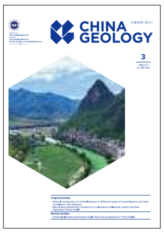

Risks and governance of heavy metals in European soil applied phosphate fertilizers

Lian-kai Zhang[a,*], Xiang Liu[a], Ya-jie Sun[b], Bernd G. Lottermoser[c], Roland Bol[d], Heike Windmann[e], Silvia H. Haneklaus[e], Ewald Schnug[e, f]

[a] *Kunming General Survey Center for Natural Resources, China Geological Survey/Technology Innovation Center for Natural Ecosystem Carbon Sink, Ministry of Natural Resources/Yunnan Technology Innovation Center of Natural Resources Carbon Sink Investigation and Carbon Asset Assessment, Kunming* 650111, *China*
[b] *College of Resources and Environment, Shandong Agricultural University, Tai'an* 271018, *China*
[c] *Institute of Mineral Resources Engineering, RWTH Aachen University, Aachen D-*52062, *Germany*
[d] *Forschungszentrum Jülich, Jülich D-*53428 , *Germany*
[e] *Institute for Crop and Soil Science, Julius Kühn-Institut, Federal Research Centre for Cultivated Plants, Braunschweig D-*38116, *Germany*
[f] *Institute for Applied Ecology, Chinese Academy of Sciences, Shenyang* 110016, *China*

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ABSTRACT

Phosphorus (P) poses a global challenge to the environment and human health due to its natural association with heavy metals. Sustainable use of P is crucial to ensure food security for future generations. An analysis of the 150 phosphate fertilizers stored at the Institute for Crop and Soil Science in Germany has been conducted, supplemented by previously published data. The elements Cd, Bi, U, Cr, Zn, Tl, As, B, Sb, Ni, and Se are found in higher concentrations in sedimentary derived phosphates compared to igneous derived phosphates. Mineral fertilizers contain more than ten times the amount of U, Cd, B, and As compared to farmyard manure. Principal component analyses (PCA) indicate that U, Cd, Be, and Cr are primarily present in sedimentary derived phosphates and their concentrations are 2 to 10 times higher than those in igneous derived phosphates. Regarding heavy metal contamination, over 1000 potential combinations were identified; 36% of these were significant but weak (> 0.1). It is estimated that approximately 707 t of uranium enter farmland annually through the application of mineral phosphate fertilizers in European countries. This contribution addresses environmental issues related to the utilization of rock phosphate as well as alternative production methods for cleaner and safer phosphate fertilizers while presenting a roadmap with measures for mitigation.

1. Introduction

Phosphorus (P) is essential for life, and phosphorus fertilizer is also a boon to food security (Follain S et al., 2009; Guedes P et al., 2017). Mineral fertilizers based on phosphate rock have been the most important source of P in plant production for a century (Cardoso EJBN et al., 2013). However, improvements in crop quality and yield often come at the cost of human health and the environment (Bai ZH et al., 2013). One of the side effects of P fertilizer used in agriculture is soil pollution due to its significant concentrations of potentially toxic elements (Haneklaus N et al., 2017). Less attention has been paid to the fact that these toxicant-contained fertilizers are a significant source for soil contamination. Heavy metal pollution from phosphate fertilizer has become a concern in some countries (Loganathan P et al., 2003; Kratz S et al., 2016; Azzi V et al., 2017).

The content of heavy metals in phosphate fertilizer is related to phosphate ore as raw material (Husson F et al., 2011). Conventional inorganic phosphate fertilizers (diammonium phosphate, calcium superphosphate, etc.) may add heavy metals as impurities to fields (Gichangi E et al., 2009). Phosphates originate primarily from the formation process of sedimentary rocks and participate in the biological cycle as dissolved orthophosphates (Guedes P et al., 2017), so they bind to almost all heavy metals present in the surrounding soil and water over time. After phosphorus fertilizer applying into the soil, the heavy metals in it will

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* Corresponding author: *E-mail address*: zhang_liankai@126.com (Lian-kai Zhang).

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pollute the soil and water, and then be absorbed by plants and posing a health threat to the human body (Taylor M et al., 2016; Schnug E and Lottermoser BG, 2013). Excessive levels of heavy metals in foodstuff can have detrimental effects on human health, market access and trade, and the ability to change from one land use to another (Ulrich AE, 2019). Therefore, developing strategies and measures to close the agricultural phosphorus cycle is crucial for sustainable crop production (Schnug E et al., 2023).

Agricultural production strategies combine the economic, social, and environmental expectations of various stakeholder groups (Bigalke M et al., 2017). The so-called 4R Nutrient Stewardship provides a framework for farmers to achieve increased production and profitability, to enhance environmental protection and to improve sustainability (Schnug E and De Kok LJ, 2016). The concept addresses the right fertilizer source, the right fertilizer rate, the right fertilization time, and the right fertilizer placement.

In this paper, the undesired inorganic elements in P fertilizers were analyzed in phosphate rock and fertilizer samples, and the possibility to trace the origin of phosphate rocks and P fertilizers by employing tracer techniques were evaluated. In this contribution, innovative ideas are presented for the cycling of phosphate rock by extracting undesired and precious metals such as Cd, U and rare earth elements (REE), and processing of wastes from P fertilizer production were outlined. Next the recovery of additional resources during phosphate fertilizer production is reviewed, insights into valorization paths of fertilizer production provided and the major challenge of achieving valorization of fertilizer production critically described. Last, but not least, the current state of regulatory measures to reduce the dispersion of hazardous elements in agro-ecosystems will be discussed on the issues of mitigation of heavy metal contamination. Generally, this paper summarizes the relationship between phosphorus fertilizer use and heavy metal pollution in European countries with a large number of data systems, and puts forward its own technology and policy measures to reduce heavy metal pollution, so as to provide referable measures for phosphorus use in China.

2. Materials and methods

The Institute of Crop and Soil Science (JKI-PB) in Braunschweig, Germany, has a large collection of fertilizers, with the oldest mineral fertilizer specimens dating back to the 1970s. The sample suite includes commercial samples obtained directly from European fertilizer companies and traders, or professionally sampled by the official fertilizer market watchdog. There were 150 mineral fertilizers, in which, 22 were derived from igneous rocks and 128 originated from sedimentary rocks. According to Bloem E et al. (2016) and Chouchene K et al. (2022) for element analysis, 200 g of dried sample for each soil sample was suspended in a NaCl solution. The mixture was stirred and then filtered through paper filter. The filter was finally determined by ICP-OES and ICP-MS for element content.

The coefficient variation (cv) was determined to assess the variability of the analyzed elements in phosphate rock samples. The geometric mean indicates the central tendency or typical value of a set of data as it is based on the product of the measured values in contrast to the arithmetic mean which uses their sums. The geometric mean is defined as the n^{th} root of the product of n entries. The impact of outliers is greatly reduced when the geometric mean is calculated.

PCA is a multivariate statistical procedure, which reduces the variability observed in a larger number of parameters, for example different element concentrations in mineral P fertilizers to a smaller straightforward number of so-called nameless principal components (PC) or factors (Benadela L et al. 2022). The smaller number of PC carries the information about the variability of a much larger set of variables. This makes an interpretation easier as cluster of variables emerge clearer (Husson F et al., 2011). A PCA can be graphically displayed for up to three PC.

A PCA comprises the following three general steps: Standardization of the initial data matrix so that $\overline{x} = 0$ and $s^2 = 1$, calculation of the correlation matrix, and extraction of principal components. PC is linear combinations of all variables in a data matrix with the general formula (Formula 1):

$$F_A = W_{1A}x_1 + W_{2A}x_2 + \cdots W_{nA}x_m \tag{1}$$

where W_{nA} is the weight of variable x_m in principal component A.

The correlation between a PC and a variable is called the loading of a variable on a PC. PCA is an algorithm where the weights for a PC are chosen to maximize its explained variability for the entire set of variables. The sum of the squared loadings on a PC is called its eigenvalue. The number of PC extractable from a dataset equals the number of variables in the dataset, but the number of PC extracted from a dataset is usually limited to those with an eigenvalue > 1. A PC with an eigenvalue < 1 explains less variability than a single variable and thus is pointless.

3. Results

3.1. Heavy metals in phosphate feedstocks and phosphate fertilizers

The element P was discovered in 1669 by chemist Hennig Brand (Krafft F, 1969). The annual global consumption of P now is 156×10^6 t (Ulrich AE, 2019). From a purely statistical point of view, the geogenic P-stocks would be consumed in 115 years (Schnug E and De Kok LJ, 2016). Commercial mineral fertilizers are one of the main contributing factors to heavy metal accumulation in agricultural soils (Kratz S et al., 2011). The phosphates take part in the biological cycle as dissolved orthophosphate and then enter the geo-biochemical cycle in form of sedimentary apatite deposits (Filippelli GM, 2002).

Phosphate rocks of sedimentary origin contain more than 10 times higher concentrations of Bi, Cd, and Ca, 5–10 times higher concentrations of U and Cr and 2–5 times more S, Tl, Zn, Sb, and B than igneous phosphates. Two-fold higher concentrations occur for As, Se, and Ni. In comparison, the samples of igneous origin contain >400 times more Fe, Mg, Al, and Na, 5–10 times more Co, Mn, Nd, Sm, Ce, Pr, and >2 times higher concentrations of Ti, K, Sr, Cu, and the REEs of Eu, Gd, Tb, La, Dy, Ho, and Er (Table 1).

The highest cv values (>200) in sedimentary rock

Table 1. Chemical composition of mineral fertilisers (n: 150), grouped according to their origin (sedimentary or igneous) and listed with their geometric mean and coefficient of variation (cv).

Element	Igneous phosphate fertiliser		Sedimentary phosphate fertiliser		Significance[2]
	mean /(mg/kg)	cv /%	mean /(mg/kg)	cv /%	
Al	2726	91	2642	113	ns
As	3.33	102	5.59	106	ns
B	400	138	398	65	***
Be	0.488	65	1.21	41	***
Bi	< LLD[3]	109	0.090	159	ns
Ca	201817	48	2162246	317	*
Cd	0.397	285	7.96	108	***
Co	12.0	145	1.20	248	***
Cr	14.7	157	87.3	68	***
Cu	34.5	83	13.7	179	**
Fe	7160	206	2466	269	*
K	11393	131	3189	304	**
Li	8.30	90	6.65	105	**
Mg	6630	12	4499	127	*
Mn	377	86	43.9	597	ns
Mo	5.04	163	3.80	91	***
Na	841	105	1902	86	ns
Ni	14.6	305	19.8	62	ns
P	141801	29	114373	265	**
Pb	6.25	97	5.78	239	ns
S	3251	256	14146	125	*
Sb	0.446	232	1.16	67	**
Se	1.60	243	2.48	171	ns
Sn	0.387	282	0.219	480	ns
Sr	2609	132	878	70	***
Ti	350	67	94.9	109	***
Tl	0.100	139	0.329	126	**
V	34.9	54	53.8	90	*
Zn	58.7	24	163.9	71	***
REE					
Ce	198	141	40.3	145	**
Dy	19.7	87	6.41	76	***
Er	10.0	75	4.31	78	**
Eu	7.23	119	1.62	114	***
Gd	31.9	120	7.39	97	***
Ho	3.63	77	1.41	129	***
La	122	155	36.3	94	**
Lu	0.690	69	0.513	86	ns
Nd	151	132	30.1	127	***
Pr	34.1	134	7.03	126	***
Sm	30.4	128	6.12	120	***
Tb	4.16	108	1.11	82	***
Tm	0.96	65	0.546	81	ns
Yb	5.47	67	3.36	84	ns
Actinides					
Th	5.08	219	2.75	92	**
U	7.56	119	59.6	69	***

[1] a cv can be calculated, even if the geometric mean is zero because the standard deviation is divided by the arithmetic mean; [2] Significance levels (F-test) : ns=p > 0.05, * =p<0.05, ** =p<0.01, *** =p<0.001; [3] LLD - Lower Limit of Detection

phosphates, sorted in decreasing order, were determined for Mn, Sn, Ca, K, Fe, P, Co, and Pb, and the lowest (<100) for Gd, La, Na, Lu, Yb, Tb, Tm, Er, Dy, Zn, Sr, U, Cr, Sb, B, Ni, and Be. In contrast, the highest cv values (>200) were found for Ni, Cd, Sn, S, Sb, Th, Fe and the lowest (<100) for Pb, Al, Li, Dy, Mn, Cu, Ho, Er, Lu, Ti, Yb, Tm, Be, Zn, and Mg in igneous rock phosphates (Table 1).

Table 2 shows the element concentrations in manufactured (mineral (n=419) and organo-mineral (n=65)) fertilizers according to the definition of the German Fertilizer

Table 2. Geometric mean, coefficients variation (cv[1]) of the mineral content in mineral and organo-mineral fertilizers, and farmyard manures.

Element	Mineral P fertilizers		Farmyard manures		Organo-mineral fertilizers		Significance[2]
	mean /(mg/kg)	Cv /%	mean /(mg/kg)	cv /%	mean /(mg/kg)	cv /%	
Al	2159	133	466	97	1680	153	***
As	4.67	726	0.345	134	1.68	148	ns
B	297	129	31.6	49	59.4	214	***
Be	0.495	85	0.096	40	< LLD	140	***
Bi	< LLD	62	0.116	67	0.180	160	***
Ca	56116	82	13663	71	60065	73	***
Cd	2.87	136	0.195	50	0.379	113	***
Co	1.32	438	1.67	312	0.918	142	ns
Cr	46.3	211	8.22	205	8.45	93	***
Cu	18.9	333	48.7	71	26.0	166	ns
Fe	2809	244	1223	98	3311	157	***
K	12416	125	25640	63	16559	105	***
Li	2.06	141	0.880	31	2.12	91	***
Mg	5434	136	4806	60	8372	11	***
Mn	92.0	496	288	55	93.4	199	ns
Mo	3.65	600	2.91	57	1.64	455	ns
Na	1720	88	1306	80	2109	100	ns
Ni	14.5	194	6.07	165	6.94	109	***
P	89151	533	9854	55	19199	75	***
Pb	2.79	335	1.49	95	3.44	155	*
S	< LLD	98	3530	58	< LLD	121	***
Sb	0.722	165	0.367	67	0.308	230	**
Se	< LLD	300	1.07	57	1.09	207	ns
Sn	0.273	358	0.770	45	0.802	168	**
Sr	398	196	31.9	66	129	86	***
Ti	118	110	18.2	67	79.8	771	***
Tl	0.171	173	0.075	67	0.064	59	***
V	56.2	102	1.62	65	5.21	110	***
Zn	121	234	231	60	130	117	ns
REE							
Ce	29.3	233	–	–	3.44	91	*
Dy	3.72	142	–	–	< LLD	83	**
Er	2.65	110	–	–	< LLD	86	***
Eu	1.05	208	–	–	< LLD	67	*
Gd	4.57	202	–	–	< LLD	122	*
Ho	0.862	120	–	–	< LLD	57	***
La	24.6	222	–	–	2.10	93	*
Lu	< LLD	91	–	–	< LLD	44	***
Nd	18.3	231	–	–	1.63	82	*
Pr	4.39	228	–	–	0.556	80	*
Sm	3.56	236	–	–	< LLD	79	*
Tb	< LLD	177	–	–	< LLD	51	**
Tm	< LLD	91	–	–	< LLD	44	***
Yb	2.29	92	–	–	< LLD	91	***
Actinides							
Th	2.46	270	–	–	0.158	120	ns
U	23.8	106	0.429	62	1.00	170	***

[1]a cv can be calculated, even if the geometric mean is zero because the standard deviation is divided by the arithmetic mean; [2]Significance levels (F-test): ns=p>0.05, *=p<0.05, **=p<0.01, ***=p<0.001; [3]LLD - Lower Limit of Detection; - no data

Ordinance, and farmyard manures (*n*=126). The reason for including organic P sources, and animal manures in Table 2 is that the rational use of organic wastes on farms is in the limelight of discussions and heavy metal loads discharged by fertilizer practices a centerpiece in the discussion of sustainable agricultural management.

In terms of heavy metal loads, manufactured mineral fertilizers are clearly disadvantaged to farmyard manures as they contain > 10 times more U, Cd, and As. Elements found in distinctly higher concentrations in farmyard manures than in manufactured fertilizers are S and Mn (Table 2). As a mixture of organic and mineral materials, organo-mineral fertilizers reveal intermediate element concentrations. Expectedly, the Cu and Zn contents in farmyard manure are roughly twice as high as in mineral and organo-mineral fertilizers. The reason is the use of these minerals as feed supplements in pig housing. With respect to mineral P fertilizers, it is striking that their B content is about 10 times higher than in farmyard manure.

The phosphate fertilizer database at JKI-PB is a typical example for a big number of cases and a big number of parameters. When looking into the correlations between the 45 elements in phosphate fertilizers the results show that out of more than 1000 possible pairings 36% are significant, but weak (>0.1). Only the combinations Be/Cr, Cu/Co, Cr/V, Se/Zn, U/V and all combinations of the light REE (La, Ce, Pr, Nd, Sm, Eu) show correlation coefficients >0.8. In other words, the variability of one variable explains the variability of its pairing partner by >64%.

Fig. 1 shows the ratio of phosphate concentrations in igneous rocks (*n*=22) to sedimentary rocks (*n*=128). I/S index is the ratio of phosphate content in igneous rocks to sedimentary rocks. The content of Mn, K, Ti, Fe, Mg, P, Co, Cu, Sr and Th in igneous phosphate is significantly higher than that in sedimentary phosphate. The content of Mn, K, Ti, Fe, Mg, P, Co, Cu, Sr and Th in phosphates of igneous rocks is higher than that of sedimentary rocks. The content of Ca, S, Cd, Co and U in sedimentary phosphate is much higher than that in igneous phosphate. The I/S of REE is >1, but it differs from light REE to heavy REE. With the increase of element ordinal number, the content of REE in sedimentary phosphate ores increases gradually. The two actinides, Th and U, are distinct, with Th enriched in igneous rock phosphate and U enriched in sedimentary rock phosphate.

3.2. Clustering effect of elements carried by phosphate fertilizers

Graphic displays are limited to only three PC, because the human brain can only visualize three dimensions in space. The extracted PC is located within the variable clusters. By means of mathematical procedure called varimax rotation the PC shifted from their squared distance minimizing position through the variable clusters into a squared distance maximizing position between the variable clusters. Fig. 2 shows the interrelationships of 45 elements analyzed from 150 phosphate rock samples in the first and second principal component plots extracted from the entire data set.

Most of the REE in the cluster have high loads (>0.8) on the first principal component, and the light REE (La, Ce, Pr, Nd, Sm and Eu) separated from the heavy REE (Gd, Dy, Ho, Er, Tm, Yb, Lu) and the actinide elements Th in the cluster. The core finding of PCA is that light and heavy REE behave differently in the phosphogenesis process. In contrast, the actinides U clustered with Be, Cd, and Cr with high loads (>0.8) on the second principal component (Fig. 2). Except for Cd, Zn, Cu, Be, Tl and Li, the other trace elements are located in PC1 region. The Macro elements are scattered across the three clusters, as shown in Fig. 2. REE are relatively concentrated in cluster III, and as the atomic number increases, the distribution of elements tends to PC2.

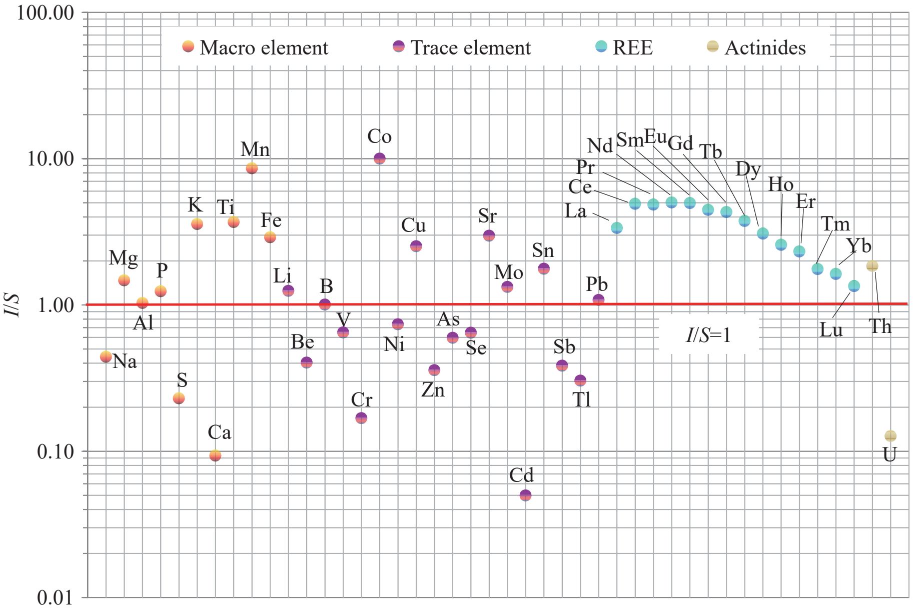

Fig. 1. Ratios of four different types of elements in phosphorus fertilizer in igneous and sedimentary rocks. I and S stand for igneous and sedimentary rocks respectively.

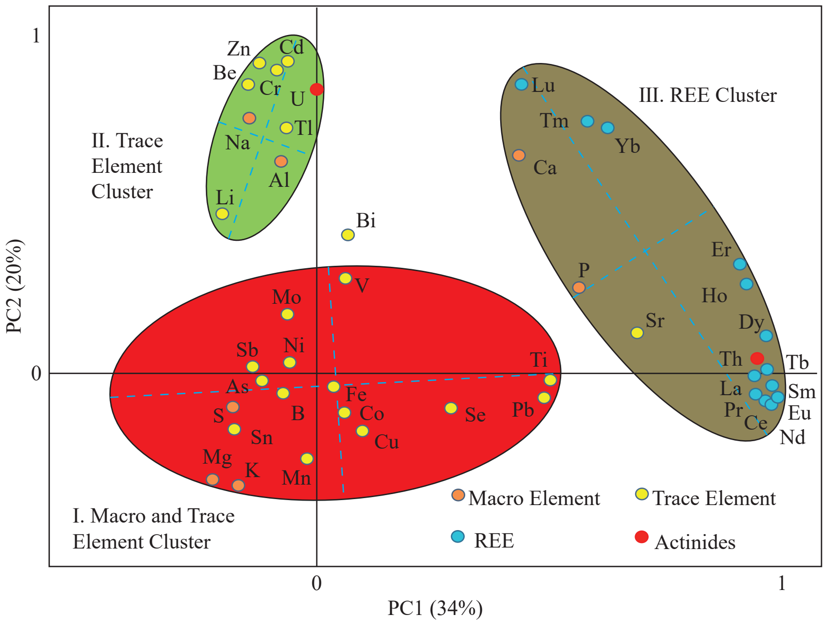

Fig. 2. Varimax-rotated display of the loads of 45 elements analyzed in 150 igneous and sedimentary phosphate rocks on the first two main components out of 11 with an eigenvalue > 1, representing 34% (component 1) and 20% (component 2) of the variability observed in the entire data set.

How to mitigate soil pollution caused by phosphate fertilizer, especially uranium pollution, is discussed below. This is due to the special coexistence relationship between Cd and U content. Therefore, by adjusting the Cd content in phosphate fertilizer, U will be similarly affected. However, the regression relationship between the two elements in different sample sets shows that phosphate will contain 12.5 mg/kg to 75.7 mg/kg U even though Cd content can reduce to near zero. They are 12.5 mg/kg, 12.7 mg/kg and 75.7 mg/kg in mineral P fertilizers, igneous rock phosphate and sedimentary rock phosphates, respectively. U as an inevitable element in any kind of fertilizer needs, therefore, to give a sufficient attention.

Mineral P fertilizers (Formula 2–4):

$$\mathrm{U(mg/kg)} = 4.62\ \mathrm{Cd(mg/kg)} + 12.5(n = 372; r = 0.825{*}{*}{*}) \tag{2}$$

Igneous rock phosphates:

$$\mathrm{U(mg/kg)} = 1.34\ \mathrm{Cd(mg/kg)} + 12.7(n = 22; r = 0.530{*}{*}) \tag{3}$$

Sedimentary rock phosphates:

$$\mathrm{U(mg/kg)} = 0.654\ \mathrm{Cd(mg/kg)} + 75.7(n = 128; r = 0.206{*}) \tag{4}$$

Where, n is the sample quantity; r is regression coefficient.

4. Discussion

4.1. Heavy metal loading of farmland due to the long-term application of phosphate fertilizers

To assess the effects of long-term application of phosphate fertilizer on agricultural soils, Figs. 3a–c shows the annual average load of mineral phosphate fertilizer on As, B, Cd, Cu, Li, Mo, Ni, U and Zn, as well as the contribution of heavy metals in German agricultural soils. These data were collected from the commercial fertilizers that also stocked at the JKI-PB back to the year 1950/1951. The calculations are based on long-term data of German agricultural statistics and include data from years in the past when high P rates were applied, as the common understanding in textbooks at that time was that the overall long-term utilization of fertilizer P by plants is limited to 75% (Schnug E and De Kok LJ, 2016).

The annual heavy metal load of As, Cd, Cu, Ni, Pb, Zn and U in German agricultural soils by applying phosphorus fertilizer was As 40.0 t/a Cd 22.1 t/a, Cu 95 t/a, Ni 54.1 t/a, Pb 11.2 t/a, Zn 431 t/a and U 114 t/a. The average contribution of phosphorus fertilizer application to the background concentration of farmland soil was As 2.7%, Cd 20.9%, Cu 1.12%, Ni 0.55%, Pb 0.18%, Zn 1.21%, U 12.9%, which is much higher than that of the Pb, Ni, and Cd in monoammonium phosphate fertilizer that commonly used in Rio Grande and other part of the world (Lottermoser BG, 2010).

Among all the elements, the concentration of Cd and U in soil showed the highest pollution contribution value. Its value is 6 times higher than Cd, 3 times higher than As, and about 10 times higher than Pb. However, the load of phosphate fertilizer on U is in the same order of magnitude as that of Cu, which is 6 times higher than Cd, 3 times higher than As, and about 10 times higher than Pb. Similarly, a Switzerland study showed that the average concentration of Cd and U in fertilized cultivated topsoil was 58% and 9% higher than in grassland topsoil (Bigalke M et al., 2017). Both elements are highly biotoxic and highly mobile in environmental systems, typically entering the food chain through soil-plant systems

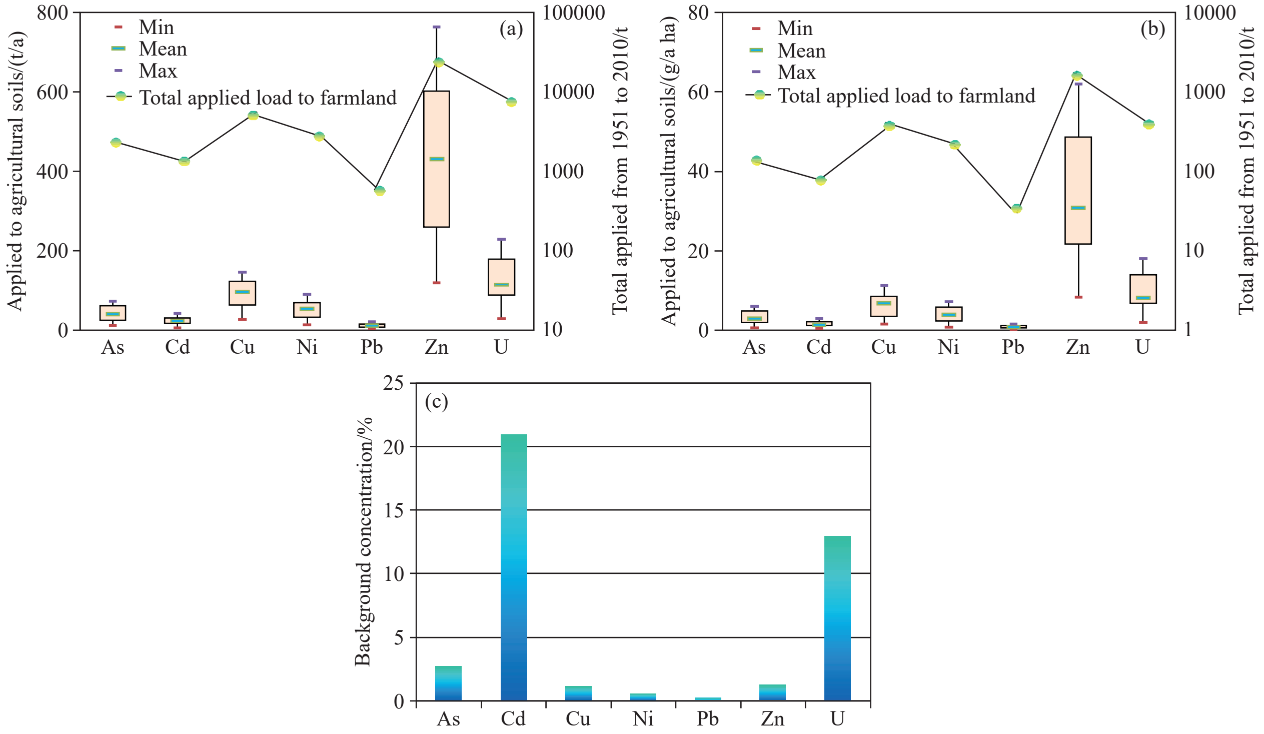

Fig. 3. Heavy metal concentrations and their loads to agricultural soils applied by mineral P fertilizers in Germany. P fertilizer samples were from the German market. The collection data back to samples from 1970 to 2010. a–loads applied to agricultural soils; b–application for per hectare; and c–proportion of soil background concentration from P fertilization.

(Cd) or drinking water (U) (Kratz S et al., 2016). Cd has long been the subject of social and scientific discussion, while U has received less attention in research (Windmann HGI, 2019). Cd and U differ significantly in the way they enter the food chain: Cd is highly non-mobile in the soil but is easily absorbed by plants, while U is highly mobile in the soil matrix and therefore easily enters the food chain via water routes (Hassoun R and Schnug E, 2011).

Based on Schnug E and De Kok LJ, 2016, fertilizer consumption data from the World Food and Agriculture Organization, and estimates by Lambers H et al. (2020) (assuming an average U content of 113 mg/kg P calculated by P_2O_5), an increase of about 707 t of U per year (2002–2013 average) was applied through mineral P fertilizer in 28 European countries. In fact, most of the world's phosphate mines produce uranium concentrations (about 200 mg/kg) greater than this data (Johnston AM, 2014). Liesch T et al. (2015) concluded that 26000 t of U (with the average of 325 t per year) had been applied in the U.S. due to the phosphate mined in last 80 years. The considerable amounts of application of phosphorus fertilizers resulted in the uranium recklessly spreading on agricultural soils and thus in the long-term endanger the food via U uptake by agriculture crops and livestock. Therefore, there is an important urgent need to limit the concentration of these elements in mineral fertilizers given that these heavy metals' toxicity and radioactivity causing harm to the environment and public health.

4.2. Element signatures to identify origins of phosphate rocks and fertilizers

The concentration of heavy metals and radio-nuclides in phosphate rocks depends strongly on the geographical area where they were mined (Hassan NM, 2016). In depositional environment studies, it recognized that the relative enrichment of heavy metals such as Be, Cd, Cr and U is a geochemical indicator of sedimentary phosphate rocks, while igneous materials tend to enrich Sr and Ti (Sattouf M, 2007). Accordingly, the first main component in Fig. 2 reflects the composition of igneous, the second main component the composition of sedimentary rock phosphates. These findings suggest that trace element patterns could be useful to distinguish between sedimentary or igneous phosphate rocks. However, it proved to be impossible to identify the precise origin of sedimentary phosphate rocks, because there is a large variation in trace metal concentrations, even in sedimentary phosphates from the same deposit (Table 1).

Isotope ratio techniques have been used as geochemical indictors to trace the origin of phosphate rock deposits. The three most commonly used elements for stable isotope analysis are oxygen (O), carbon (C) and sulfur (S), all being major structural components of francolite, which is the main mineral in phosphate rocks. Two other relevant radiogenic isotope tracers, strontium (Sr) and uranium (U) are constituents in the lattice of francolite that replace major elements (Jarvis I et al., 1995). Studies on stable C and S isotope ratios are mainly indicators of the depositional and diagenetic history of phosphate rocks rather than their geographic origin and therefore not pursued in this section (Morikiyo T et al., 1966).

Stable oxygen isotopes are commonly used as geochemical indicators. The major advantage of using the oxygen-isotope ratios in phosphate ($^{18}O_p$) is that isotope exchange between oxygen in phosphate and water is extremely slow in inorganic systems (Sattouf M, 2007). Therefore it is fair to assume that the $\delta^{18}O_p$ of sedimentary phosphate rocks provides information of its original palaeo-environment (Longinelli A and Nuti S, 1973). So, the application of $\delta^{18}O_p$ to sedimentary phosphate rocks has been used to estimate water paleo-temperatures and diagenetic conditions. The following phosphate-water temperature equation was formulated (Formula 5; Longinelli A and Nuti S, 1973):

$$T = 111.4 - 4.3(\delta^{18}O_p - \delta^{18}O_w) \tag{5}$$

where T is the average environmental temperature (°C), $\delta^{18}O_p$ is the natural oxygen isotope composition of phosphate and $\delta^{18}O_w$ is that of water. When comparing phosphate rocks of different ages, a temporal trend of decreasing $\delta^{18}O_p$ values (9‰–24‰) was found with increasing rock age (0.01–2000 Myr) (Shemesh A et al., 1983). This $\delta^{18}O_p$ time trend might be useful to help identify the deposit of phosphate rocks.

The residence time of Sr in seawater is with about 3 Myr several orders of magnitude longer than oceanic mixing times; thus it is fair to assume that Sr in ocean water is more or less homogenously mixed (Turner JT, 2015). The Sr ($^{87}Sr/^{86}Sr$) isotope composition of phosphate is in general agreement with the Sr isotope ratio ($^{87}Sr/^{86}Sr$) in contemporary seawater (Sattouf M, 2007). The Sr isotope content in seawater changed during the geological ages, so that the Sr isotope-age curve can be applied to date the age of marine sediments (Harris N, 1995), particularly for the Cenozoic (0–20 Myr) time period (Hodell DA et al., 1991). This procedure is most likely less precise when used to estimate the date of more ancient rocks. The attempts to date phosphogenesis by Sr isotopes have been made by Schnug E and De Kok LJ (2016), who found that age determinations for phosphorites from four different locations are in good agreement with their geological context and previous estimates. Subsequent research was conducted by (Kratz S et al., 2016), who successfully used the $^{87}Sr/^{86}Sr$ isotope ratios to separate phosphate rock samples into four distinct groups: (1) Igneous phosphate rock from Russia (Kola) and sedimentary rock from; (2) Algeria, Israel, Morocco, Tunisia and Syria; (3) the USA and finally (4) those from Senegal and Togo.

The U-series isotopes have the advantage in dating young phosphorites, because the modern ocean is isotopically uniform with a $^{234}U/^{238}U$ activity ratio of 1.144 ±0.004 (Jarvis I et al., 1995). In U-series studies of phosphorites deposits in the Peru-Chile and Namibian margins (Baturin GN et al., 1972), Western South Africa (Birch GF et al., 1983) and East Australia (Kress AG and Veeh HH, 1980), the $^{234}U/^{238}U$ activity ratios were close to that of present seawater, which indicates a forming during the same period. The more recent study by Sattouf M (2007) revealed that based on their R ($^{234}U/^{238}U$) values phosphate rock from the USA could be distinguished from that of the Middle East and North Africa. One reason is presumably the relatively younger age of the phosphate rocks originating from the USA.

It is important to note that changes in the overall elemental composition and isotopic ratio may occur during the fertilizer manufacturing process when isotopic signatures applied to directly trace the origin of P fertilizers (Laera A et al., 2019). The isotope ratio signatures in phosphate rocks are less susceptible to such alterations than the total element concentrations during the P-fertilizers production process. As mentioned earlier, $\delta^{18}O_p$ normally cannot be altered in abiotic systems. This means that $\delta^{18}O_p$ in P fertilizers keeps its inherent values of phosphate rocks during the manufacturing process. Sattouf M (2007) did test the reliability of Sr and U isotope signatures for detecting the origin of P fertilizers. The study showed that there was a linear, almost 1∶1 regression (r^2=0.989, p<0.05), between the Sr isotope ratio in phosphate rocks and in P fertilizers originating from these materials. The slightly higher values of R ($^{87}Sr/^{86}Sr$) in P fertilizers were most likely due to a kinetic isotope effect which happens during the digestion with sulfuric acid. The same author used the R($^{234}U/^{238}U$) ratio to verify the provenance of a certain fertilizer which was manufactured from phosphate rock mined in the USA (Sattouf M, 2007); further differentiation down to a specific P deposit proved to be not feasible because of the spatial variation of the isotope ratio within the deposit. In conclusion, it is evident that the origin and genesis do shape the large elemental and isotopic patterns of a particular phosphate rock. However, the inherent large variability in elemental concentrations makes source tracking difficult using specific elements or elemental ratios.

The analysis of isotopic patterns of U, Sr, O is an analytical tool with the ability of a partial separation of the phosphate rock origin. However, differences could be reflective of age of the phosphate rock rather than true sourcing. Further work still needed to be able to better and univocally pinpoint the phosphate rock origin. These assessments may include work on the unexplored stable isotope content in phosphate for elements such as B, Ni, Zn or Dy.

4.3. Reduction of heavy metal loads in phosphate fertilizers

4.3.1. Valorization

Valorization of mineral resources is the process of exploiting resource components with a view to optimize the value of the geological ore deposits and to create added-value products for market applications. Thus, valorization of fertilizer production aims: (1) To find alternative uses for wastes that accumulate during phosphate mining, mineral processing and fertilizer manufacturing; and (2) to extract resource ingredients other than phosphate from phosphate rock (by-products such as U) (Fig. 4).

Since the early 1900s, global annual mine production of

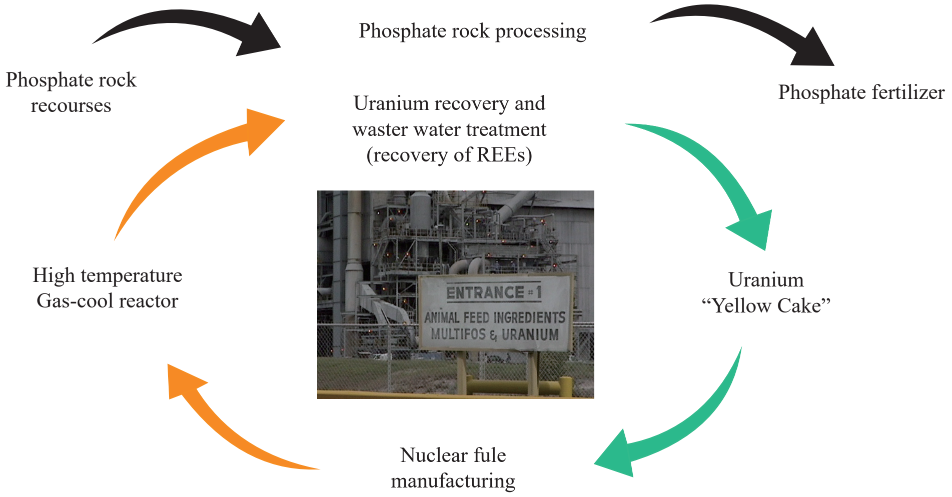

Fig. 4. In the early days of phosphate mining, extracting uranium (U) from phosphate rock for nuclear fuel and weaponry was a highly welcomed added value to the production of P fertilizers; IMC Agrico Phosphate Processing Plant, Florida - photograph by Connett (2001).

phosphate rock has steadily increased to a current peak of 263 Mt (Ulrich AE，2019). The phosphate content of phosphate rock varies greatly from about 1.75% to about 8.73% P (Lopes CM et al., 2021) and some of the mined phosphate is lost during mining, mineral processing and fertilizer manufacturing (López-Arredondo DL et al., 2014). Therefore, only a small proportion of the mined phosphate ore is being used as phosphate fertilizers, whereas the great majority (about 80%–96%) of the mined phosphate rock is presently discarded as waste throughout the whole fertilizer industry value chain (Braithwaite AC, 1987). In fact, the quantity of total solid waste produced can be high, but it varies significantly between mine sites and fertilizer plants. One study reports findings where, for one ton of phosphoric acid produced, 9.5 t of phosphate ore are required and 21.8 t of diverse wastes and 6.5 t of tailings are produced (Lottermoser BG, 2010).

The growth in phosphate production has led to an increasing amount of waste accumulated during mining and mineral processing. At mine sites, significant overburden and waste rock volumes need to be removed to access the phosphate ore and fine-grained tailings are generated during phosphate processing (Chowdhury SR and Yanful EK, 2010). These wastes are commonly placed into large engineered repositories. This growing volume of waste and related environmental concerns have prompted a great deal of research into additional resource recovery for phosphate rock. Research around the value-added of phosphate rock waste has shown that waste can serve as: (1) Dry cover in the capping of mine waste resource and vegetation restoration (Lottermoser BG, 2010); (2) additives in acid mine water treatment (Ouakibi O et al., 2013); (3) raw materials for the ceramic industry (Liu Y et al., 2017); and (4) construction industry resource materials (Ait-Ouakrim EH et al., 2023). Therefore, phosphate rock waste can be recycled and reused for various purposes. These activities will minimize potential environmental damage, reduce the footprint of phosphate mines, and lead to the development of other local industries.

The amount of waste accumulated in fertilizer plants is much larger, with phosphogypsum (PG) being by far the main waste product, accumulated during the hydrometallurgical treatment of phosphate ores (Lottermoser BG, 2010). Global PG production is estimated to be as high as 1239×10^{6} t per year (Lottermoser BG, 2010). PG consists primarily of calcium sulfate crystals, making it an attractive alternative to gypsum, suitable for construction and agricultural uses, and as a source of valuable products (sulfuric acid, ammonium sulfate). Over the past few decades, different PG value-added routes have been developed in the fields of agriculture, construction, environment and energy (Lottermoser BG, 2010). However, some PG may also contain residual phosphoric acid and hydrofluoric acid, heavy metals (Cd, Pb), and radio-nuclides (^{238}U, ^{232}Th, ^{226}Ra) (Wei FZ et al., 2015). In the United States, the Environmental Protection Agency is concerned about the presence of metals and radio-nuclides in PG and classifies PG as "Technologically Enhanced Naturally Occurring Radioactive Material" (Schnug E, 2023). This prevents large-scale reuse of PG. Therefore, in some countries such as the United States, PG is stored in large piles due to regulation of radioactivity levels, or because alternatives such as natural gypsum and flue gas are more competitive (Beretka J and Mathew PJ, 1985).

Phosphate deposits may contain elevated concentrations of valuable elements including U, Th and REE. Trace element concentrations of phosphate rock (U, B, Cr, Cu, Ga, Ni, Sc, Th, V, Zn) differ from region to region, with sedimentary phosphate ores containing in general higher trace element concentrations than igneous phosphate ores. In comparison, higher concentration of lanthanides can be found in igneous than sedimentary rock phosphates (Kratz S et al., 2011). Some U concentrations are high enough to be of commercial interest, and U recovered during fertilizer manufacturing at some locations (Ulrich AE, 2019). Metal recovery is possible through acid leaching or the application of organic solvents and subsequent recovery of valuable constituents applying ion exchange technology (Wu S et al., 2022). Thus, the extraction of by-products during fertilizer manufacturing is possible using established technologies. Such resource recovery would minimize potential environmental damage, reduce the environmental footprint of fertilizer plants, lead to the development of additional local industries and generate added-value products for market applications.

To date, scientists have identified multiple pathways for phosphate rock appreciation. Unfortunately, many of the proposed reprocessing, reuse and recycling routes are still at the research stage and have not been adopted by industry. As a result, most of U, Th, and REE still end up in waste streams or fertilizer value chains, and agricultural soils and underlying drinking water aquifers are increasingly contaminated with U and other elements (Liesch T et al., 2015; Schnug E et al., 2023).

There is no doubt that following the precautionary principle the future of sustainable P fertilization requires to cut the loads of hazardous elements to agricultural land. The wingspread definition of the precautionary principle says “When an activity raises threats of harm to human health or the environment, precautionary measures should be taken even if some cause and effect relationships are not fully established scientifically” (Defur PL and Kaszuba M, 2002). The main obstacle for employing environmental and health sound measures in agricultural production techniques is that they almost always add costs to the production chain and the inevitable social weighing of goods also almost always goes on the expenses of the vulnerable part, which is health and environment. A smart way out would be the valorization of the culprit: Make the hazardous components pay for their removal from the fertilizer.

4.3.2. Legal measures

Many research outcomes and concepts of resource recovery remain ideas that it cannot be implemented in fertilizer plants as current government regulations do not allow or stimulate such activities, and industry does not consider them as economical. In particular, legislation by government agencies in Europe and North America prevents the reprocessing and reuse of wastes (Amery F and Schoumans O, 2014). These authorities are obsessed with setting environmental risk limits for organic and inorganic substances. Adaptation of statutory requirements needed to ensure that regulations are based on scientific evidence and best practices. In particular, supportive government policies and constructive regulation are required (Wu S et al., 2022). Most of all, government authorities should not only set legal limits for contaminants like Cd and U in fertilizers but also thresholds for resource components that, when present above a certain concentration, have to be extracted from the mined ores. For phosphate rock in particular, thresholds for the compulsory recovery of by-products such as U and REE should be given, enforcing the valorization of phosphate rock.

It cannot be expected that P fertilizers with low concentrations in hazardous elements will appear on the market without significant financial advantages in their production through the valorization of by-products as benefits for health and the environment simply do not pay off (yet). The EU has assessed available legal measures and concluded that, as a classical steering tool in environmental policymaking, to control Cd a limit value would be the most practical and effective tool (Ulrich AE, 2019). The EU Cd rule, which is part of the revised EU Fertilizer Regulation, is among the most controversial regulations to apply to the agricultural sector in recent years, as the rule is more a matter of trade and geopolitics than of environmental and public health protection.

In 1997, the European Commission proposed limit values for Cd in mineral fertilizers at first, with the aim to reduce soil pollution and safeguarding food safety, profitability for farmers, and human health. For many years, hope remained high for a progressive reduction of the Cd content in fertilizers from 26.2 mg/kg to 8.73 mg/kg P over a transition period of 12 to 16 years. However, retrospectively this hope was unrealistic as the political and industrial realms were divided between fear of overly high costs, insufficient supply, geopolitical concerns, and environmental and public health concerns (Ulrich AE, 2019). A preliminary agreement on the limit finally reached in November 2018, to be confirmed by the EU Council of Ministers in 2019. As the lowest common denominator, a single limit value of 60 mg/kg Cd will be set three years after the entry of the new EU Fertilizer Regulation, and a voluntary green label for fertilizers, that contain less ⩽ 8.73 mg Cd/kg P will be put in place (European Parliament, 2018). The European Commission will then review this welcoming foundation for soil and public health protection from fertilizer-derived Cd seven years after the rule will have come into force. The EU bodies will then decide if there is a need to lower the limit to 40 mg and eventually 20 mg, as for instance Lutter S et al. (2016) indicated.

The Cd limit is a historical achievement that opens the way for demonstrating sufficient political courage and consistency in setting higher standards in the future. Notably, market realities had already surpassed the EU norm of 60 mg/kg Cd even before the implementation of the rule. Trade group data suggests that most fertilizers already comply with this limit (Ulrich AE, 2019). However, the agreement will only affect about 8% of products traded in the EU, which will have an impact on the exports of Senegal, Togo, and Tunisia and, to a lesser degree, Algeria, Israel, and Morocco (Financial Times, 2018). Swiss regulators demonstrated considerable political courage in 2018 by passing a Cd limit of 4.80 mg/kg P in phosphate fertilizers from secondary sources starting in 2019.

In addition, the issue of U will be monitored to learn if its content needs to be limited in the future. Although in much higher concentration and potentially much more harmful for human health and environment industry and lawmakers are afraid of regulating U in P fertilizers like the proverbial devil the holy water. A common disguise strategy to avoid another can worm to be opened was the misbelief that once the Cd content in fertilizers would be limited the U concentration would follow automatically. In compliance with the anticipated regulation of Cd for fertilizers with < 2.18% P a limit value of 1.5 mg/kg U in the fertilizer was proposed in order to protect agricultural soils from further accumulation of U (Kratz S, 2011).

4.4. Outlook

In the future, additional measures will need to be taken to give effect to the limit values for harmful elements in fertilizers. The control and monitoring of these restrictions is central to enforcement in the coming years, despite some of their notorious complications. Commonly, the national authorities in which the products are being marketed perform the inspections of P fertilizer products. At this stage, the different member states' control regimes are somewhat opaque and appear very heterogeneous.

It needs to develop guidelines for law enforcement assistance to determine (1) select the representative fertilizer; (2) the minimum number of tests; (3) the type of control parameters; (4) select the laboratory to use; (5) determine the test frequency; (6) specify the sampling and analysis methods; and (7) the allowable error range. Taking these steps will help ensure a minimum of comparability and consistency during the review (and thus an acceptable outcome). Labeling of hazardous element concentrations should be made mandatory in order to assist all relevant on-farm control measures for mineral elements.

Other tools are in use in addition to these measures, notably via the EU's Common Agricultural Policy, which is currently in the reform process. An increasing number of consumers are asking for environmentally friendly agricultural products and production. The use of subsidies for fertilizers low in hazardous elements would encourage safe fertilization and would contribute to safeguard soil resources.

The sustainable management of P along its value chain requires multifaceted cooperation similar to the phosphate nutrient stewardship, the 4Rs. From a regulatory perspective, such management involves trade, soil and water, chemicals, fertilizers, food, public health and waste legislation. Now P regulation is often pursued in an indirect and poorly linked manner. One potential intervention that bears the potential to overcome the dispersed nature of legislation, and reflects the complexity of real-world P governance, would be an EU Phosphate Directive, similar to the Nitrates Directive. Some EU member states already passed P legislation, which is focused exclusively on P losses and the subsequent risk of eutrophication. Nevertheless, an EU directive is required that regulates proper P governance and stewardship. Cleaner fertilizers result in cleaner soils, healthier food, cleaner waters, and cleaner atmosphere and finally yet importantly make fertilizer manufacturing more profitable.

5. Conclusions

Elemental concentrations of 150 phosphate rock samples obtained from fertilizer companies and traders or commercial batches of JKI-PB indicate that sedimentary phosphate contains more Bi, Cd, Ca, U, Cr, S, Tl, Zn, Sb, B, As, Se, and Ni than igneous phosphate. In comparison, there is more Fe, Mg, Al, Na, Co, Mn, Nd, Sm, Ce, Pr, Eu, Gd, Tb, Ti, K, La, Dy, Sr, Ho, Cu and Er in igneous phosphate rocks than in sedimentary rocks. After varimax rotation, the PCA displays the loads of 45 elements analyzed in 150 igneous and sedimentary phosphate fertilizers, with the first two main components representing 54% of the variability observed in the entire data set. The REE are plotted on the first principal component, with the light REE (La, Ce, Pr, Nd, Sm, and Eu) clustered together with the actinides Th and the heavy REE (Gd, Dy, Ho, Er, Tm, Yb, Lu). Light and heavy REE behave differently. The actinides U and Be, Cd and Cr have cluster high loads on the second principal component.

The average contribution of mineral fertilizer combined with heavy metals to agricultural land in Germany was 0.18%–20.9%, with an average of 5.65%, in which Cd and U contributed the most, 20.9% and 12.9% respectively. Compared with Cd, the toxicology and radiation hazards of U are of greater concern. In 28 European countries, approximately 707 t of U are added to agricultural soils annually through the application of inorganic phosphate fertilizer. Isotope ratio techniques can be used as geochemical indictors to trace the origin of phosphate rock deposits. The oxygen-isotope ratios in phosphate ($\delta^{18}O_p$) can estimate water paleo-temperatures and diagenetic conditions. The $^{87}Sr/^{86}Sr$ isotope ratios can be applied to date the age of marine sediments and separate phosphate rock samples. Moreover, $^{234}U/^{238}U$ ratios can be used to distinguish the phosphate rocks from different areas.

The new EU Fertilizer Regulation considers nine pollutants in fertilizers (Cr^{6+}, Hg, Ni, Pb, As, Cu, Zn, biuret, and perchlorate) and monitors the risk of toxicity and carcinogenicity of these contaminants, including fertilizer-derived U. It is important to note that the Cd limit will not automatically co-regulate U content in fertilizers as proposed. Depending which technological process is chosen, synergies may exist between removing two or more potentially harmful trace elements at the same time. However, a separate limit value for U would need to be established to really provide for safe long-term application.

CRediT authorship contribution statement

Lian-kai Zhang, Silvia H. Haneklaus and Ewald Schnug conceived of the presented idea. Xiang Liu, Ya-jie Sun and Heike Windmann carried out the experiment. Bernd G. Lottermoser and Roland Bol contributed to the conceptuliosation of the paper. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

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