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Letter

Tracing the Environmental Effects of Mineral Fertilizer Application with Trace Elements and Strontium Isotope Variations

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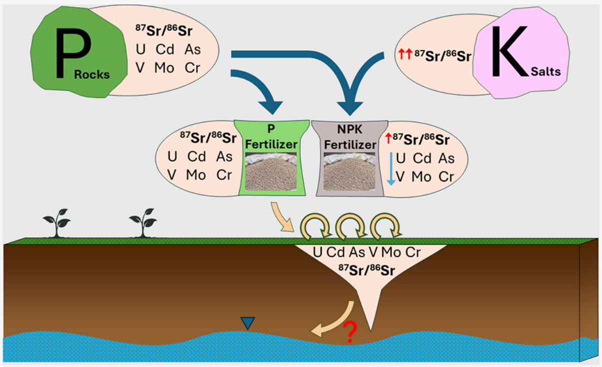

ABSTRACT: Fertilizer utilization is critical for food security. This study examines the occurrence of trace elements (TEs) and Sr isotope ($^{87}Sr/^{86}Sr$) variations in phosphate rocks and mineral fertilizers from a sample collection representative of major phosphate producing countries. We show high concentrations of several TEs in phosphate rocks ($n = 76$) and their selective enrichment in phosphate fertilizers ($n = 40$) of specific origin. Consistent with the concentrations in parent phosphate rocks, phosphate fertilizers from the U.S. and Middle East have substantially higher concentrations of U, Cd, Cr, V, and Mo than those in fertilizers from China and India. Yet, fertilizers from China and India generally have higher concentrations of As. The $^{87}Sr/^{86}Sr$ in phosphate fertilizers directly mimic the composition of their source phosphate rocks, with distinctive higher ratios in fertilizers from China and India (0.70955−0.71939) relative to phosphate fertilizers from U.S. and Middle East (0.70748−0.70888). Potash fertilizers have less Sr and TEs and higher $^{87}Sr/^{86}Sr$ (0.72017−0.79016), causing higher $^{87}Sr/^{86}Sr$ in mixed NPK-fertilizers. Selective extraction (Mehlich III) of soils from an experimental agricultural site shows relative enrichment of potentially plant-available P, Sr, and TEs in topsoil, which is associated with Sr isotope variation toward the $^{87}Sr/^{86}Sr$ of the local utilized phosphate fertilizer.

KEYWORDS: *Phosphate, Potash, Soil and Water Pollution, Agriculture*

1. INTRODUCTION

Fertilizer is an essential source of nutrients for sustained crop growth in agricultural systems. The main nutrients provided by fertilizer are nitrogen (N), phosphorus (P), and potassium (K). While N in fertilizers is commonly derived from atmospheric nitrogen via the Haber-Bosch process,[1] the P and K in mineral fertilizers are sourced from geological materials such as phosphate ores (for P) and evaporite deposits and brines (for K).[2,3] During processing, K-rich ores may undergo minimal physical or chemical separation to develop potash (K-fertilizer), such as potassium chloride (MOP) or potassium sulfate (SOP). Potash may be mixed with sulfuric acid or nitrate salts to create secondary MOP or SOP products.[2,4] The processing of phosphate rocks (PRs) is more energy intensive and requires calcination and physical separation, followed by sulfuric acid leaching to develop the phosphoric acid product, with phosphogypsum solid waste as byproduct.[5] The phosphoric acid may be used to generate phosphate fertilizers (P-fertilizers) of Single Super Phosphate (SSP), reacted further with PR to generate Triple Super Phosphate (TSP), or subsequently reacted with ammonia to generate mono- or diammonium phosphate (MAP/DAP).

Previous studies have shown that PRs are the primary source of trace elements (TEs) incorporated into mineral fertilizer, such as V, Cr, As, Se, Mo, Cd, and U.[6−34] Accumulation of some of these elements has been observed in agricultural soils and can be highly variable based on fertilizer utilization and soil chemical properties.[16,34−43] Several studies have investigated the Sr isotope ratio ($^{87}Sr/^{86}Sr$) in PRs,[44−50] and one study has shown the similarity between the $^{87}Sr/^{86}Sr$ ratio of PRs and mineral fertilizers originating from the same geographical region.[51] Additionally, a few studies have characterized and applied the Sr isotope ratio of fertilizer as a tracer for delineating their environmental impact.[27,51−54] However, these studies have investigated the occurrence of TEs and the utility of Sr isotopes only in specific case studies. The potential universal utilization of this tracer has not been established, which is the major objective of this study.

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Given the large variations in the $^{87}Sr/^{86}Sr$ of global PRs, this study aims to (1) utilize a global sample collection of PRs and mineral fertilizers to establish the Sr isotope fingerprint of P-fertilizers generated from major PR producing countries (Table S1) in comparison to that of K-fertilizers; and (2) use a subset of these samples, which are collected paired phosphate rock-fertilizer samples, to demonstrate the enrichment of TEs in phosphate rocks and mineral P-fertilizers. Strontium isotope geochemistry has been utilized to identify trace element contamination in the environment due to, for example, brine contamination, landfill leaching, coal ash, and fracking fluids.[55−64] Developing the $^{87}Sr/^{86}Sr$ fingerprint of fertilizers can aid in source attribution of TE contamination of soil and groundwater associated with agricultural systems. The co-occurrence of a distinctive Sr isotope ratio similar to the fertilizer source and elevated TE concentrations could indicate the impact of fertilizer application on soil and water quality. Using the occurrence of P as an indicator for P-fertilizer may not always be sufficient given the possibility of multiple P sources and its reactivity with soil and aquifer rocks. We hypothesize that the Sr enrichment and isotope ratio of P-fertilizers, if distinct from background soil, can be used as a proxy for delineating the occurrence of fertilizer-sourced contaminants in the environment.

2. METHODS AND MATERIALS

2.1. Sample Collection. This study presents analysis of a total of 76 PRs (Table S2) and 40 fertilizers (Table S3) from major global PR producing regions, including the western U.S., eastern U.S., China, India, North Africa, and the Middle East. A subset of these samples are rock-fertilizer pairs consisting of fertilizer(s) produced from the paired sedimentary PR (n = 7 pairs). PR samples have been collected directly from phosphate mines in addition to archived samples previously collected by the Julius Kühn Institute in Germany (Table S2). Information on the source of the ores was provided by the U.S. Geological Survey data set of the world phosphate mines.[65] Fertilizer samples (Table S3) were collected from mines and commercial sources. In addition, 12 soil samples were collected from experimental fields subject to differential P-fertilizer application rates at the Tidewater Research Station in Plymouth, Washington County of North Carolina (see details in Hu et al.[12]). This includes 4 soil samples each from 3 plots with varying fertilizer application, at intervals from surface to 70 cm depth.[12] In the experimental research site, plots FTS1, FTS3, and FTS5 were investigated, with most recent rates of P-fertilizer application of 0, 22.4 (adequately fertilized based on soil test recommendations), and 168.1 (overfertilized with respect to recommendations) kg P_2O_5 ha^{-1}/year, respectively, and a uniform K-fertilizer application rate of 16.8 kg K_2O ha^{-1}/year.[12,66]

2.2. Analytical Methods. A description of the analytical methods used in this study has been previously published elsewhere.[12,67] Briefly, PRs and fertilizers were dried, powdered, and fully digested with a heated nitric and hydrofluoric acid mixture. The plant-available fraction of soils was extracted via the Mehlich-III extraction method (see SI for more information).[12] Trace elements were measured on an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Fisher X-Series II), equipped with a collision/reaction cell device. The $^{87}Sr/^{86}Sr$ of samples was analyzed on a ThermoFisher Triton thermal ionization mass spectrometer, following separation of strontium via ion-exchange chromatography with a Sr-specific resin (Eichrom). The accuracy of analysis was assessed by repeated digestion and measurement of IRMM BCR-032. This yielded recoveries within 10% of certified standard values for P, V, Cr, Cd, and U and within 20% for As. The mean $^{87}Sr/^{86}Sr$ value from repeated measurements of the NIST SRM 987 was 0.710255 ± 0.000005 (1 SD, n = 58).

2.3. Statistical Analysis. All statistical calculations and analyses were performed in R (v 4.3.0).[68] Nonparametric analyses were conducted, including the Mann−Whitney test and Spearman's rank correlation test where Rho (ρ) evaluates the strength of the correlation. Statistical significance is based on p values, where $p < 0.01$ for a 99% confidence interval and $p < 0.05$ for a 95% confidence interval.

3. RESULTS AND DISCUSSION

3.1. Trace Element Occurrence in P-Fertilizers. The concentrations of K, Sr, and TEs (V, Cr, As, Mo, Cd, and U; reported in mg/kg of fertilizer) in P-fertilizers generally mimic the levels in their PR sources but can also be enriched (Figures S1 and S2). P-fertilizers and PRs from India and China have systematically lower concentrations of these TEs compared to P-fertilizers from the Middle East, North Africa, and Western and Eastern U.S. (Figure S1). However, PRs and P-fertilizers from China have similar or higher concentrations of As compared with P-fertilizers from all other regions (Figure S1). Fertilizers that contain potassium (NPK-fertilizers) have lower concentrations of these TEs. In comparing the TE concentrations in P-fertilizers to their concentrations in PRs from the same region, we show significant increases in Cr in P-fertilizers from eastern U.S. and India ($p < 0.01$ and <0.05, respectively); U in P-fertilizers from the western U.S. ($p < 0.01$); and Mo and V in P-fertilizers from the Middle East ($p < 0.05$) relative to their source PRs (Figure S1). In contrast, the concentrations of these TEs in K-fertilizers were significantly ($p < 0.01$) lower than those in P-fertilizers (Table S2).

The relatively large concentration of specific TEs and P in PRs is related to their geological setting; geologically younger sedimentary PRs (ages of mid-Miocene to Permian), which represent most phosphate producing countries, originated on a continental shelf environment under reduced conditions that resulted in paired enrichment of TEs and P in the mineral carbonate fluorapatite ($Ca_5(PO_4,CO_3)_3F$).[5] In contrast, sedimentary PRs of Devonian-aged or older, including those from China and India, were likely deposited in a different, peritidal depositional environment, resulting in lower TE concentrations.[5] Igneous PRs do not show the similar enrichment in these TEs, except for V and As, likely due to the capability of the mineral apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) to host P, V, or As (Figure S1).[5,69]

Given that these TEs and P are derived from sourced PRs, the percentage of P_2O_5 in fertilizers that includes both P and K (NPK-fertilizers) can be used to estimate the TE content of the fertilizer. Figure 1 shows the correlation between the advertised P concentration (as P_2O_5, based on the manufacture labeled N−P−K value) in NPK-fertilizers and the paired TE concentration (n = 11). In these fertilizers, there are significant relationships between the P content and concentrations of U, As, V, Cr, and Cd ($p < 0.01$; ρ = 0.93, 0.90, 0.88, 0.82, and 0.78, respectively), indicating that PR is the predominant source of these TEs in the NPK-fertilizers, which is consistent with the lower TE concentrations of K-fertilizers.

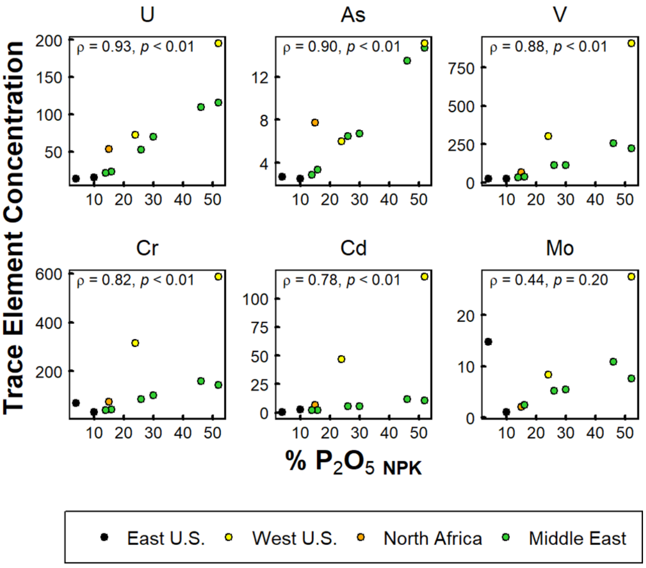

Figure 1. Concentrations of U, As, V, Cr, Cd, and Mo (mg/kg of fertilizer) versus labeled phosphate content (%) in NPK-fertilizers produced from sedimentary PRs from Western U.S. ($n = 2$) and Eastern U.S. ($n = 2$), North Africa ($n = 1$), and the Middle East ($n = 6$). In fertilizers from the Middle East, $\rho = 1$ for U and As ($p < 0.01$); $\rho = 0.94$ for V, Cr, and Cd ($p < 0.05$); and $\rho = 0.94$ for Mo ($p = 0.08$).

A further assessment of TE enrichment in P-fertilizers relative to their source PR, which was conducted by direct comparison of paired (co-occurring) PRs and P-fertilizers (Figure S2), illustrates the important role of fertilizer processing in its chemical composition. In a phosphate rock and SSP fertilizer pair from India, we found no significant difference in the TE concentration among the fertilizer−phosphate rock pair. Similarly, the SSP from the Middle East shows similar or lesser concentrations of TEs compared to the source PR, inferring no secondary enrichment of TEs associated with PRs.

By contrast, the TSP fertilizer from the Middle East has greater concentrations of U, V, and Mo relative to the source PR, likely due to the further processing with PR, resulting in mobilization of P and some TEs into TSP fertilizers. Similarly, the monoammonium phosphate (MAP) fertilizer from the Middle East is more enriched in Cd, V, Cr, and As relative to the source PR. In all 3 of the DAP fertilizer and rock pairs (2 from the Middle East and 1 from East U.S.), the fertilizer product has similar or lower concentrations of U than in the source rock but systematically higher concentrations of Cr, Cd, and V. These differences highlight the variation in TE enrichment in different P-fertilizers that apparently arises from different manufacturing processes in addition to the naturally occurring variations in the source PRs.

3.2. Sr Isotopes in P-Fertilizers and Phosphate Rocks.

The $^{87}Sr/^{86}Sr$ ratios of PRs vary based on the source of the PRs (sedimentary versus igneous) and the age of the sedimentary PRs (Figure S3). Apart from PRs from South Africa, igneous PRs have $^{87}Sr/^{86}Sr$ ratios lower than those of sedimentary PRs. The Sr isotope ratios of sedimentary PRs from the Middle East, North Africa, and eastern and western U.S. typically follow the secular Sr isotope seawater curve over geological time, whereas older sedimentary PRs from China and India, as well as igneous PRs from South Africa, generally have higher $^{87}Sr/^{86}Sr$ ratios (Figures 2 and S3). Subset rock−fertilizer pair data show that the Sr isotope composition of P-fertilizers directly mimics the Sr isotope composition of their parent PRs (Figure S4). Consequently, P-fertilizers originating from PRs in China and India typically have much higher $^{87}Sr/^{86}Sr$ ratio than P-fertilizers generated in the Middle East, North Africa, and eastern and western U.S. (Figure 2). Data of the $^{87}Sr/^{86}Sr$ ratio in PRs and P-fertilizers from the Middle East are consistent with almost identical $^{87}Sr/^{86}Sr$ ratios reported for wastewater and PRs from a P-fertilizer facility in Israel.[70] The consistency of the Sr isotope ratios in P-fertilizers with the isotope ratios of PRs from the same country provides a novel tool for the identification of the source of P-fertilizers, despite the differences in P-fertilizer manufacturing processes. This can

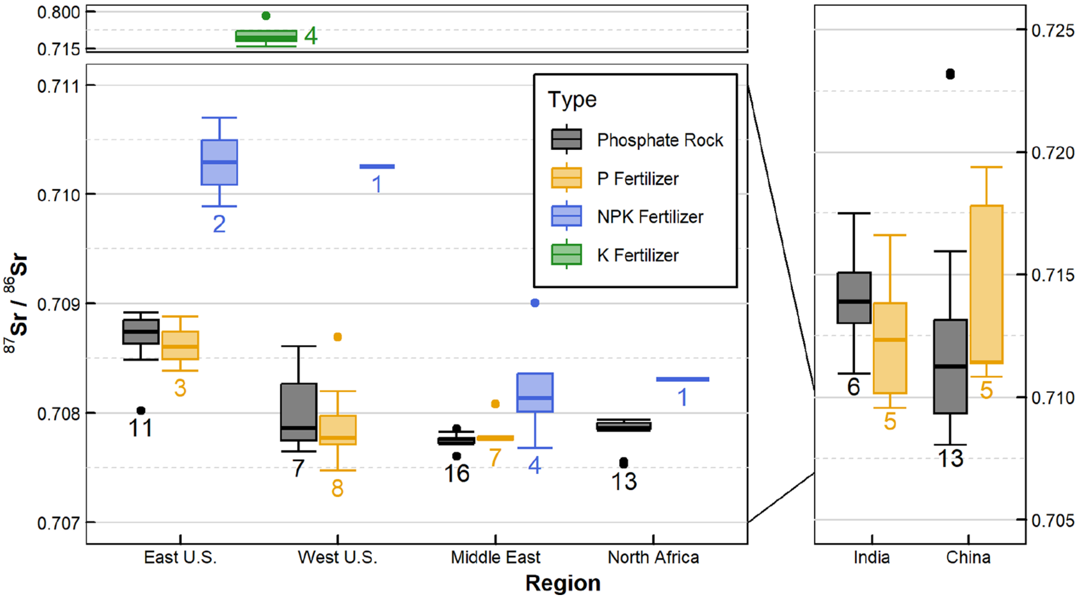

Figure 2. Box plots of $^{87}Sr/^{86}Sr$ of PRs and fertilizers from different global regions. Numeric values refer to the number of samples. K-fertilizers from the U.S. ($n = 4$) have distinctively higher $^{87}Sr/^{86}Sr$ ratios.

distinguish those from China that are characterized by relatively low TE contents and high $^{87}Sr/^{86}Sr$ from P-fertilizers originated from younger PRs from the U.S., North Africa, and Middle East with distinctively higher TE content and lower $^{87}Sr/^{86}Sr$ ratios.

Our data collection of K-fertilizers is restricted to the U.S. and the Middle East (Jordan). In the U.S., the $^{87}Sr/^{86}Sr$ ratios of K-fertilizers (0.720170−0.790156) are substantially higher than those of PRs and P-fertilizers from the U.S. (Figure 2). Most potash utilized in the U.S. is imported from K-bearing evaporite deposits (sylvite) in Canada.[71,72] The higher $^{87}Sr/^{86}Sr$ ratio is likely a result of high Rb associated with K in the evaporite salts,[73] resulting in a high proportion of ^{87}Rb that decays into ^{87}Sr. Therefore, higher $^{87}Sr/^{86}Sr$ ratios in NPK-fertilizers are observed due to the mixing of P and K source materials (Figure 2). These results are consistent with those of Böhlke and Horan who have shown greater $^{87}Sr/^{86}Sr$ ratios in K-fertilizers (0.83518) than in P-fertilizers (0.70882−0.70960), whereas the mixed NPK-fertilizer had an intermediate $^{87}Sr/^{86}Sr$ ratio of 0.71275.[53] In the case of the Middle East, the NPK-fertilizers have similarly higher $^{87}Sr/^{86}Sr$ ratios (0.708123−0.712094) relative to P-fertilizer (0.707750−0.707788) and PR (0.707606−0.707854) (Figure 2). Thus, the inclusion of more K-fertilizer to an NPK-fertilizer produces a fertilizer with a higher $^{87}Sr/^{86}Sr$ ratio.

3.3. Using Sr Isotopes for Tracing the Impact of P-Fertilizer in Agricultural Soil. Hu et al.[12] have investigated the accumulation of TEs in soils impacted by long-term utilization of P-fertilizers at the Tidewater Research Station in North Carolina. The study has shown that the levels of P and certain TEs in the upper soil layers directly depend on the magnitude of P-fertilizer application.[12] To investigate the possible use of $^{87}Sr/^{86}Sr$ ratio as a proxy for the impact of P-fertilizers on the soil quality, the isotope composition of Sr in the bulk (total dissolution) and the plant-available fraction (extracted by the Mehlich-III extractant[12,74]) in the three sampled plots (FTS1, FTS3, and FTS5; Figure 3) were analyzed. The concentration of Sr in the K-fertilizer (2.84 mg/kg, US-K4) was negligible compared with the higher Sr in the P-fertilizer (992 mg/kg, UW-F7) utilized on site (Table S2). While the Sr concentration of the bulk soil does not show any correlation with P, Sr in the plant-available soil fraction shows high correlation with P, reflecting the effect of P-fertilizers.[12] Similar to the patterns observed for other TEs, P and Sr from the plant-available soil fraction in the vertical profiles decrease with soil depth (Figure 3).[12]

Analysis of the applied P-fertilizer on site shows a distinguishable and lower $^{87}Sr/^{86}Sr$ ratio (0.707766) relative to the plant-available fraction of the background soil (a range of 0.710320−0.710595) and therefore may be used as a potential indicator of the occurrence and migration of TEs originated from P-fertilizers in the soil (Figure 3). The plant-available fraction of the FTS5 topsoil, the plot with the highest P-fertilizer application rate, has the highest Sr concentration and the lowest $^{87}Sr/^{86}Sr$ values relative to the other plots (Figure 3). Together with P levels, Sr concentrations in the plant-available soil fraction decrease with depth, while the $^{87}Sr/^{86}Sr$ ratio increases along the soil profile in all three experimental sites toward the background $^{87}Sr/^{86}Sr$ composition (Figure 3). These results suggest that Sr isotopes can be used as a proxy for the occurrence of TEs derived from P-fertilizers in impacted soils that are characterized by a Sr isotope ratio different from that of the applied P-fertilizer.

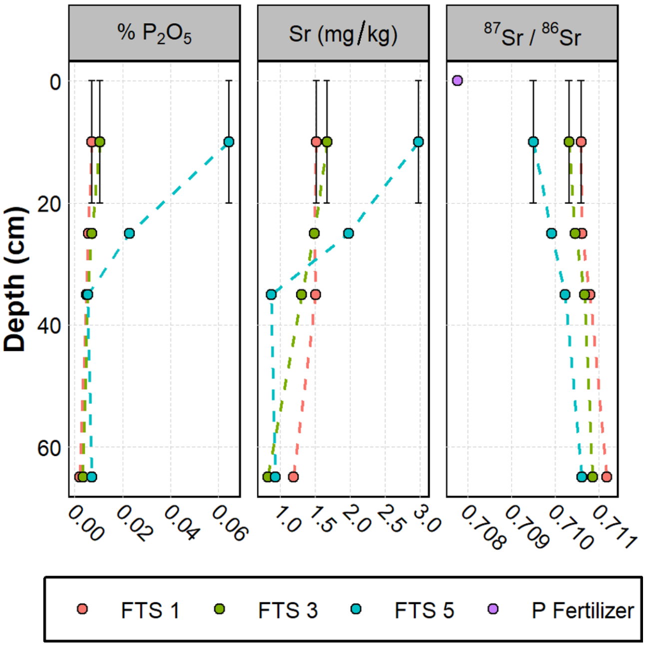

Figure 3. Vertical variations of P_2O_5, Sr, and $^{87}Sr/^{86}Sr$ from the soil plant-available fraction in three different plots treated with none (FTS 1), recommend amount (FTS 3, 22.4 kg P_2O_5 ha^{-1}/yr), and excessive (FTS 5, 168.1 kg P_2O_5 ha^{-1}/yr) amounts of P-fertilizer from the Tidewater Research Station in Plymouth, North Carolina. Uncertainties in the $^{87}Sr/^{86}Sr$ values are much smaller than those in the symbols (i.e., 10^{-6}).

Although K-fertilizers contain a higher $^{87}Sr/^{86}Sr$ (0.72017−0.79016) than P-fertilizers from the U.S. and the Middle East (0.70748−0.70888) or from China and India (0.70955−0.71939), the much higher Sr concentrations in P-fertilizers allow the $^{87}Sr/^{86}Sr$ ratio of the P-fertilizers to be the dominant fertilizer signature in cases of long-term application of both K- and P-fertilizer, as demonstrated at the Tidewater Research Station. Furthermore, P-fertilizers from the U.S. and the Middle East will have a greater impact on soil quality due to the higher average concentrations of U (132 vs 10 mg/kg), Cd (26.7 vs 1.2 mg/kg), Cr (210 vs 29 mg/kg), V (207 vs 38 mg/kg), and Mo (10 vs 1.2 mg/kg) as compared to P-fertilizers from China and India which only have higher concentrations of As (14.6 vs 7.8 mg/kg). Future studies should assess the impact of agricultural liming, gypsum, and other soil amendments with possible high Sr contents and distinct $^{87}Sr/^{86}Sr$ ratios,[75−77] which could mask the contribution of Sr from P-fertilizers. Overall, given the systematic enrichment of TEs in mineral P-fertilizers and their distinctive Sr isotope ratio demonstrated in this study, future studies should examine the role of P-fertilizers on TEs contamination (e.g., uranium) of soil and water resources associated with agricultural operations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.4c00170.

Additional experimental details; tabular sample data and information; figures of geochemical trends in phosphate rocks and fertilizers by rock age, region, and within paired rock-fertilizer samples (PDF)

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Notes

The authors declare no competing financial interest.

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