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Evidence for the accumulation of toxic metal(loid)s in agricultural soils impacted from long-term application of phosphate fertilizer

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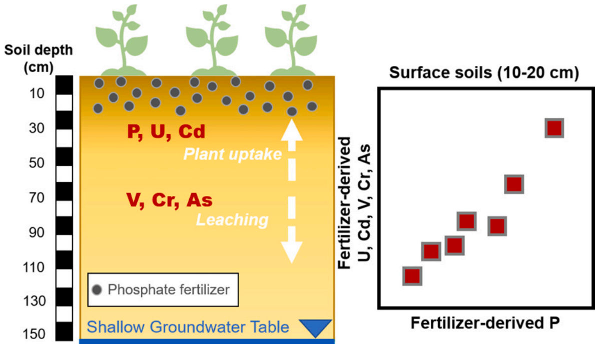
HIGHLIGHTS

- Application of P-fertilizer results in the enrichment of metal(loid)s in topsoils.
- Enrichment of metal(loid)s are directly linked to amount of P in impacted soils.
- Cd is of the greatest concern given its highest potential plant bioavailability.
- Bioaccumulation in crops and water contamination warrant future investigation.

GRAPHICAL ABSTRACT



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ABSTRACT

Phosphate fertilizers may contain elevated concentrations of toxic metals and metalloids and therefore, their excessive application can result in the accumulation of both phosphorus (P) and metal(loid)s in agricultural soils. This study aims to investigate the occurrence, distribution, and potential plant-availability of metal(loid)s originating from phosphate fertilizer in a long-term experimental field at the Tidewater Research Station in North Carolina, where topsoil (10–20 cm deep) and subsoil (up to 150 cm deep) samples were collected from five plots with consistent and individually different application rates of P-fertilizer since 1966. We conducted systematic analyses of P and metal(loid)s in bulk soils, in the plant available fraction, and in four sequentially extracted soil fractions (exchangeable, reducible, oxidizable, and residual). The results show that P content in topsoils were directly associated with the rate of P-fertilizer application ($\rho = 1$, $p < 0.05$). Furthermore, P concentrations were highly correlated with concentrations of Cd, U, Cr, V, and As in the bulk topsoil ($\rho > 0.58$, $p < 0.05$), as well as the potential plant-available fraction ($\rho > 0.67$, $p < 0.01$), indicating the accumulation of the fertilizer-derived toxic metal(loid)s in the topsoil. Significant correlations ($p < 0.001$) of metal(loid)s concentrations between the bulk soil and the potential plant-available fraction raises the possibility that P-fertilizer application could increase the accumulation of toxic metal(loid)s in plants, which could increase human exposure. Results from sequential leaching experiments revealed that large portions of the trace elements, in particular Cd, occur in the soluble (exchangeable and reducing) fractions of topsoil with higher P-fertilizer input, whereas the levels of

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redox-sensitive elements (As, V, U, Cr) were higher in the reducible and oxidizable fractions of the soils. Overall, the data presented in this study demonstrate the effect of long-term P-fertilizer application on the occurrence and accumulation of a wide range of toxic metal(loid)s in agricultural topsoil.

1. Introduction

Phosphorus (P) is an essential plant macronutrient and plays a major role in regulating primary productivity in ecosystems (Filippelli, 2008). Sufficient supply of soil P is critical to sustain crop production and thus food security for an increasing global population. Inorganic phosphate fertilizers are generally made via acid decomposition of grounded or pulverized phosphate rocks. In many cases, these phosphate rocks have been reported to contain elevated levels of potentially toxic metal(loid)s, such as uranium (U), cadmium (Cd), and arsenic (As), which could be incorporated into phosphate fertilizers (El Bamiki et al., 2021; Nziguheba and Smolders, 2008; Verbeeck et al., 2020).

Previous studies have identified that phosphate rocks and P-fertilizer are potential sources of the aforementioned toxic metal(loid)s in agricultural soils (Bergen et al., 2022; Bigalke et al., 2017; Jiao et al., 2012; Mortvedt, 1987; Nziguheba and Smolders, 2008; Suciu et al., 2022; Sun et al., 2020a, 2020b, 2022). Several studies have used long-term and experimental agricultural sites to evaluate the impact and accumulation of fertilizer-derived contaminants on the soils (Bracher et al., 2021; Jeng and Singh, 1995; Rothbaum et al., 1979, 1986; Sun et al., 2020a, 2020b, 2022; Takeda et al., 2006; Wetterlind et al., 2012). While most studies have mainly focused on Cd and U, the fate of other toxic metal(loid)s originating from P-fertilizer application in agricultural soils has not been well-studied. Furthermore, most studies have focused on detecting U and Cd accumulation in the topsoil (5–20 cm), but only a few have investigated their occurrence in deep soil profiles (Rothbaum et al., 1979; Sun et al., 2020b, 2022; Takeda et al., 2006). Although fertilizers are only applied at the surface, contaminants can potentially be mobilized into deeper soils and the underlying groundwater (Gardner et al., 2023; Kubier et al., 2019; Liesch et al., 2015; Lyons et al., 2020). Given that many trace elements' speciation and mobility depend on their reactivity with the soil and ambient redox conditions, the fate and transport of fertilizer-derived contaminants may be affected by the changes in edaphic properties (i.e. texture, mineralogy, organic content, and redox conditions) along the soil profile. In addition, the occurrence and distribution of P and metal(loid)s may vary within different phases

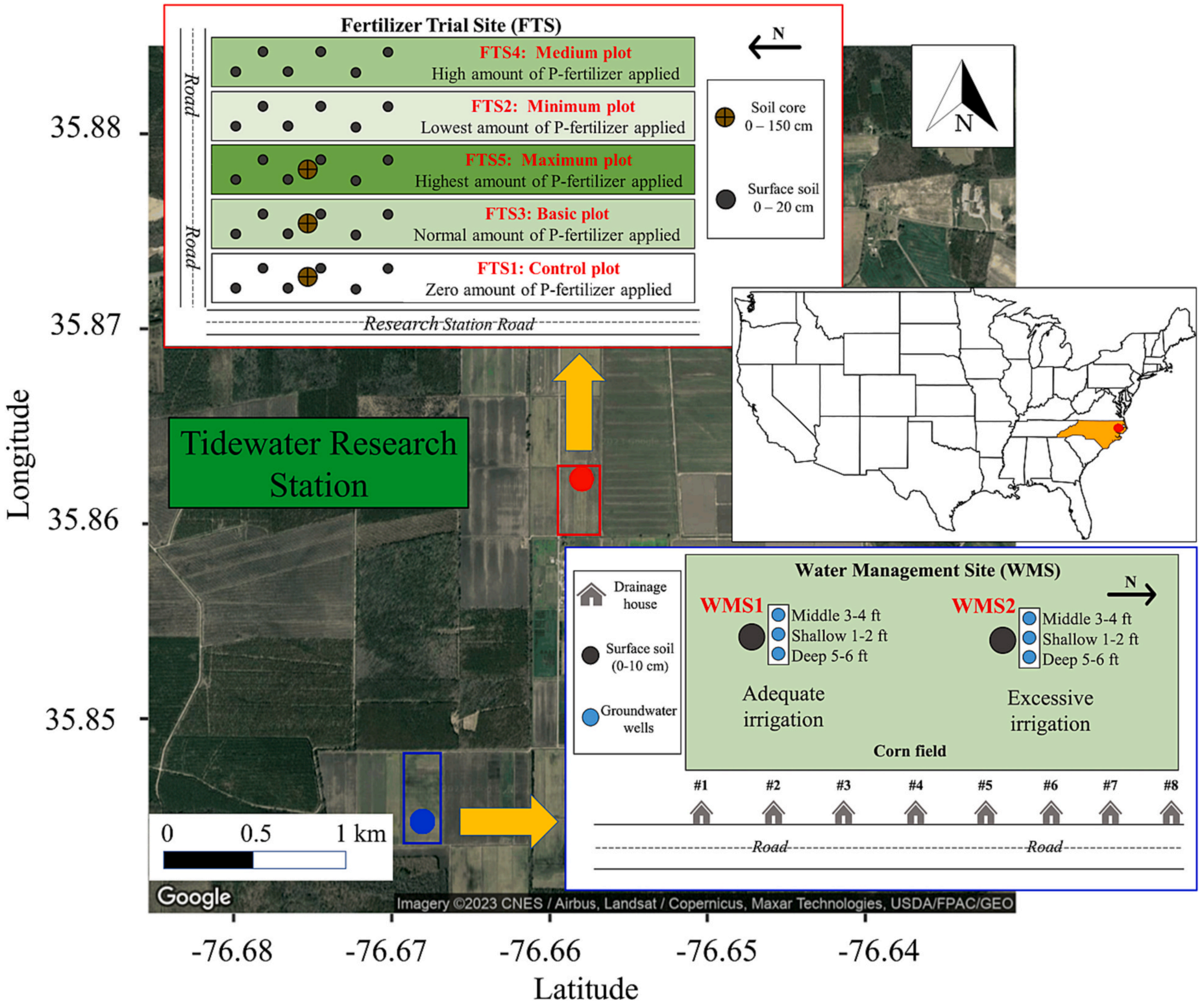

Fig. 1. Schematic illustration of the sampling locations at two sites (i.e., fertilizer trial site, FTS and water management site, WMS) of the Tidewater Research Station in eastern North Carolina, USA.

of the impacted soil such as the bioavailable or plant-available fraction. Furthermore, the occurrence of metal(loid)s in the natural bulk minerals in soils could mask the contribution of metal(loid)s derived from P-fertilizer applications (Filgueiras et al., 2002; Rapin et al., 1986). Therefore, it is important to consider the occurrence of metal(loid)s in different phases and fractions within the soil to isolate the impact of fertilizer-derived contaminants.

This study aims to determine the distribution and accumulation of selected P fertilizer-derived metal(loid)s in both surface (10–20 cm) and deep soils (up to 150 cm) from the Tidewater Research Station in eastern North Carolina, USA, a long-term experimental site in which soil in the plots were treated with different rates of P-fertilizer over several decades. Given that certain metal(loid)s are often enriched in P fertilizers, we hypothesize that higher rates of P-fertilizer application will increase the concentrations of these trace elements in the bulk and plant bioavailable fractions of the soils. Through systematic analyses of selected metal(loid)s in bulk soils and individual phases, including the potential plant-available fraction, we present new and novel data of differential occurrence and distribution of P and metal(loid)s in P fertilizer-impacted soils.

2. Methods

2.1. Study site and sample collection

The Tidewater Research Station (Fig. 1) was established in 1943 in Plymouth, Washington County, NC. The long-term experimental trial with P fertilizer application at Tidewater Research Station is located in the field E-4 (35.86° N, 76.66° W), which consists of 5.5 acres of agricultural soil cultivated with row crops and managed with minimum tillage or non-tillage (Morales, 2021). The soil type on site is poorly drained Portsmouth fine sandy loam with moderate organic matter content and available water capacity (Crozier et al., 2009). Based on the physical texture along the soil profile (Fig. S1), several distinct horizons can be identified; (1) the Ap (0 to 30 cm) and Eg horizons (30 to 50 cm), which are mostly characterized by dark-colored fine sandy loam; (2) the Btg horizon (50 to 90 cm), which is characterized by a brown sandy clay loam; (3) the BCg horizon (90 to 100 cm), which is composed of sandy loam; and (4) the 2Cg horizon (100 to the maximum depth of soil profile ~150 cm), which consists of loamy sand.

The long-term experimental trial commenced in 1966 and includes 60 plots, each 53 m long and 6.4 m wide (Morales, 2021). In this study, we collected soil samples from 5 plots with different rates of P fertilizer treatment at the Fertilizer Trial Site (FTS). Fig. 1 shows a schematic illustration of sampling locations at the site. FTS1 is a control plot, receiving no P-fertilizer; FTS2 is a plot with the lowest amount of P-fertilizer applied, at rates below the crop requirement; FTS3 is a plot with the adequate amount of P-fertilizer applied for the row crops cultivated in the region; FTS4 is a plot with P-fertilizer applied at rates moderately above the crop's requirement; and FTS5 is an over-fertilized plot, with the highest P fertilizer application. In 2020–2021, the rates of P fertilizer application were 0, 11.2, 22.4, 67.2, and 168.1 kg P_2O_5 ha^{-1}/year in FTS1, FTS2, FTS3, FTS4, and FTS5, respectively. The rates of P-fertilizers in the five fertilization regimes (FTS1 to FTS5) varied over the years to adjust the fertilization to different crop needs. The annual application of P since 1966 in the five plots are estimated to be 0, 1457, 2180, 3848, and 6196 kg P_2O_5 ha^{-1}. In addition, potash fertilizer has been applied to each plot at a constant rate of 16.8 kg K_2O ha^{-1}. Two sample collection campaigns were launched. In June 2022, when the corn plants were in the early stage, three soil profiles up to 150 cm deep were retrieved using an auger from FTS1, FTS3, and FTS5. Each soil profile was composed of 15 individual samples collected at 10-cm intervals. At all five plots, 10 surface soil samples were collected up to 20 cm deep and mixed as one composite sample. In September 2022, when the corn was ready for harvesting, surface soil samples were collected up to 10 cm deep from each of the five plots following the same sample protocol.

In addition, we collected two composite surface soils (0–10 cm) at the Water Management Site (WMS; Fig. 1) at TRS in June and September 2022, respectively. WMS 1 is the soil plot with regular irrigation, whereas WMS 2 is the soil plot with excessive irrigation. Fertilizers 18-46-0 (DAP; 18 % N, 46 % P, 0 % K) and 9-23-30 (NPK; 9 % N, 23 % P, 30% K) were applied in 2021 at rates of 120 lb./acre (~135 kg/ha) and 200 lb./acre (~224 kg/ha) in WMS 1 and WMS 2, respectively (Personal communication with Robert Walters, 2022). However, although it is known that WMS 1 and WMS 2 have been treated with similar amounts of fertilizer, we do not have the information about how long these specific fertilizers have been previously applied in those plots.

All the collected soil samples were oven-dried at 40 °C until reaching a constant weight. Plant residuals and gravels were manually removed, and the remaining soil was homogenized by passing it through a 2-mm stainless-steel sieve. Following coning and quartering, a portion of each sample was ground in a ceramic mortar and pestle until it could pass through a 200-mesh stainless steel sieve for later chemical analysis.

2.2. Sample processing

2.2.1. Bulk dissolution

To determine the total elemental concentrations in the soil, all soil samples were fully digested according to the following procedures: 52 ± 5 mg of air-dried and sieved (<2 mm) soil sample was weighed in 15 mL Teflon vials and digested overnight at 105 °C on a hotplate in a hydrofluoric acid (HF) and nitric acid (HNO_3) mixture (v/v = 2 mL:1 mL; optima grade). The solutions were then dried down completely and redissolved overnight at 105 °C in a mixture of 15 M HNO_3 (1 mL; optima grade), hydrogen peroxide (H_2O_2, 1 mL; optima grade), and deionized (DI) water (5 mL). Following the redissolution, ~ 50 μL aliquot of each solution was taken and diluted to 2 mL with DI water for the measurement of elemental concentrations on an inductively coupled plasma-mass spectrometer (ICP-MS), as described in Section 2.3 (Wang et al., 2022).

2.2.2. Mehlich-III extraction for plant-available fraction in the soil

The Mehlich-III extraction method has been commonly used to determine the bioavailable P in agricultural soil because the extracted P is highly correlated with plant uptake (Mehlich, 1984; Nduwamungu et al., 2009). The composition of Mehlich-III extractant includes 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.001 M EDTA, 0.2 M CH_3COOH, and 0.013 M HNO_3. The final pH was adjusted to 2.5 ± 0.1 using NH_4OH. Nitric acid (HNO_3) and ammonium nitrate (NH_4NO_3) can extract exchangeable base cations (e.g., Ca, Mg, and K), ethylene diamine tetra acetic acid (EDTA) and ammonium fluoride (NH_4F) can enhance the extraction of micronutrients (e.g., Cu, Zn, Mn, and Fe), and acetic acid (CH_3COOH) is used to prevent CaF_2 precipitation (Mehlich, 1984). In this study, we used these methods to determine the proportions of both macro-and micro-nutrients that are potentially available to plant uptake. For the extraction, 1.00 ± 0.05 g air-dried and sieved (<2 mm) soil sample was mixed with 10 mL Mehlich-III extractant in a 50 mL metal-free centrifuge tube. Samples were then placed on a horizontal shaker at 180 rpm for 5 min, followed by centrifugation at ~4200 rpm for 15 min to separate the supernatant and soil. The supernatant was immediately extracted using a metal-free syringe equipped with a 0.45 μm mixed cellulose ester (MCE) membrane filter unit to avoid further contact with soil. The extract was transferred into a 15 mL metal-free centrifuge tube and acidified with HNO_3 to prevent precipitation. Within 24 h after the Mehlich-III extraction, ~100 μL aliquot of each extract was taken and diluted to 2 mL with DI water and elemental concentrations were quantified by ICP-MS (Section 2.3).

2.2.3. Sequential extraction

To determine the distribution of trace elements in the different phases of the soil samples, a modified three-step sequential extraction

Table 1
The modified BCR sequential extraction procedure adopted in this study (Bakircioglu et al., 2011; Bracher et al., 2021; Rauret et al., 1999).

Step	Chemical phase	Extraction procedure
F1	Weak acid (HOAc) soluble	Dissolved 0.5 g of soil sample in 20 mL 0.11 mol L^{-1} of HOAc (CH_3COOH), pH ~ 4; 16 h shaking at room temperature
F2	Reducible	20 mL of 0.5 mol L^{-1} hydroxylamine hydrochloride ($NH_2OH{\bullet}HCl$) at pH ~ 1.5, 16 h shaking at room temperature
F3	Oxidizable	10 mL of 8.8 mol L^{-1} hydrogen peroxide (H_2O_2) (pH 2), 1 h shaking at room temperature and 1 h at 85 °C water bath. Then add 25 mL of 1 mol L^{-1} ammonium acetate (CH3COONH4) at pH ~ 2, 16 h shaking at room temperature
F4	Residual	See full digestion procedure (Section 2.2.1)

approach was adopted in this study (Table 1). The method was recommended by the European Community Bureau of Reference (BCR) to extract trace elements from different soil phases, including water and acid soluble and exchangeable phases (F1), reducible (bound to Fe/Mn oxides) phases (F2), oxidizable (bound to organic matter) phases (F3); and residual (bound to primarily silicate minerals) phases (F4) (Rauret et al., 1999). The extraction began by combining 0.50 ± 0.05 g air-dried and sieved (<2 mm) soil sample in a 50 mL metal-free centrifuge tube with 20 mL of reaction solution (see details below). It was then placed on a horizontal shaker at 180 rpm for 16 h at room temperature, then centrifuged at ~4200 rpm for 30 min. After the centrifuging, the liquid was immediately extracted using a metal-free syringe equipped with a 0.45 μm mixed cellulose ester (MCE) membrane filter unit to avoid further contact with soil. The extract was transferred into a 15 mL metal-free centrifuge tube and acidified with HNO_3 to eliminate solute precipitation while the residual solid was rinsed with DI water and centrifuged three times. This same procedure is followed for each sequential extraction step using HOAc for the first step (F1), $NH_2OH{\bullet}HCl$ for the second step (F2), CH_3COONH_4 for the third step (F3), and full digestion for the final step. Such procedure was repeated until the final residue was collected (F4). Following each extraction step, ~100 μL aliquot of extract was taken and diluted to 2 mL with DI water to measure elemental concentrations by ICP-MS (Section 2.3).

2.3. *Elemental measurement*

The concentrations of both major (i.e., Mg, Al, P, K, Ca, and Fe) and trace (i.e., V, Cr, Mn, Cu, Zn, As, Sr, Cd, and U) elements in soil samples, including the fully digested and selectively extracted soil solutions, were measured by a Thermo Fisher X-Series II inductively coupled plasma mass spectrometer (ICP-MS) at Duke University. To monitor and correct for instrumental drift, each solution aliquot was spiked with 10 mL internal standard solution containing In, Tm, and Bi. Each sample was analyzed in triplicate, from which mean value was reported and standard deviation was calculated to denote uncertainty. The National Institute of Standards and Technology (NIST) standard reference material (SRM) 2711a was used to assess quality assurance and quality control (QA/QC) for the total dissolution. The mean percent recovery for the majority of the reported elements in NIST 2711a from repeated measurements (n = 10) was >90 %, except that Cr was ~85 % for and U was ~79 %. The relative standard deviation was below 10 % for all the reported elements.

2.4. *Statistical analysis*

For the statistical evaluation, the non-parametric Spearman rank correlation test was conducted, where the Spearman correlation coefficient rho (ρ) ranged from −1 to 1 was used measure the extent of correlation between two variables, and the statistical significance was

Table 2
Mean bulk concentrations of major and trace elements in the composite surface soils (10–20 cm) and fertilizers used at the Tidewater Research Station. N/A refers to not applicable, bdl to below detection limit.

Sample ID	Sampling date	Sampling depth	Mg	Al	P	K	Ca	V	Cr	Mn	Fe	Cu	Zn	As	Sr	Cd	U
		cm	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
FTS 1	June 2022	20	686	17,320	152	7427	3277	27.2	15.9	214	5869	3.03	17.3	1.57	68.6	0.09	1.21
FTS 2	June 2022	20	709	18,864	165	8386	3530	31.2	19.4	264	7136	5.52	19.3	1.98	74.6	0.06	1.73
FTS 3	June 2022	20	710	18,235	275	8080	3732	34.6	22.0	255	7235	6.81	18.9	1.94	76.0	0.09	1.61
FTS 4	June 2022	20	757	17,888	433	8084	3941	34.4	20.3	269	7671	3.87	21.3	2.04	77.1	0.13	1.73
FTS 5	June 2022	20	721	18,700	504	8243	4008	32.1	18.9	258	6680	8.93	23.3	1.50	74.7	0.19	1.50
WMS 1	June 2022	10	1026	13,190	510	7984	3038	45.8	28.6	250	6180	8.21	9.06	2.73	60.8	0.22	1.80
WMS 2	June 2022	10	2042	25,644	1040	10,630	4544	78.9	55.5	188	9444	21.8	37.5	4.65	84.3	0.27	3.35
FTS 1	September 2022	10	568	20,025	127	7820	3216	28.0	14.8	255	6906	2.01	18.0	1.60	82.0	0.06	0.98
FTS 2	September 2022	10	540	18,992	155	7854	3031	26.2	13.3	240	6353	3.00	18.1	1.40	70.8	0.08	1.02
FTS 3	September 2022	10	686	21,092	269	8047	3253	27.7	16.9	221	5970	7.17	21.2	1.89	79.4	0.13	1.68
FTS 4	September 2022	10	575	21,084	307	8944	3131	28.9	14.6	279	6923	2.59	20.4	1.16	84.7	0.15	1.28
FTS 5	September 2022	10	595	17,682	358	6462	3453	25.0	14.9	241	6152	4.11	16.0	1.19	63.5	0.17	1.21
WMS 1	September 2022	10	1069	33,666	452	7555	3570	45.9	27.9	157	6494	8.34	30.5	2.46	64.4	0.22	1.93
WMS 2	September 2022	10	1628	48,290	771	7612	3572	59.3	41.9	132	7786	15.2	44.8	3.34	69.3	0.21	3.01
TSP fertilizer	June 2022	N/A	3439	1858	212,316	3767	164,250	179	132	25.8	1101	27.2	521	4.09	992	23.0	163
MOP fertilizer	June 2022	N/A	1045	101	156	363,808	665	0.27	0.19	4.69	362	1.86	bdl	0.10	2.84	0.04	0.06

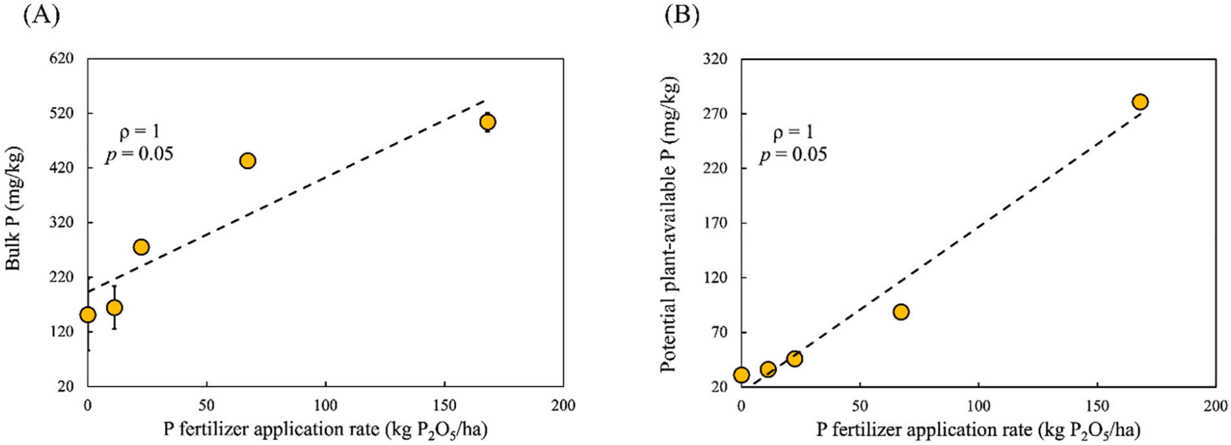

Fig. 2. Mean concentrations of P in the bulk (A) and potential plant-available fraction (B) in bulk surface soils (0–20 cm) from FTS and WMS plots of Tidewater Research Station versus the P-fertilizers applications rates in the FTS site soils. Error bars represent the standard deviation from triplicate analyses and are smaller than the data markers if not shown.

reflected by p-value. All statistical analyses were conducted with MATLAB (R2022b) (The MathWorks Inc., 2022).

3. Results and discussion

3.1. Fertilizers and soil quality characterization

3.1.1. Trace elements in fertilizers

Previous studies have reported elevated levels of trace metals such as uranium (U) and cadmium (Cd) in phosphate rocks, in particular in sedimentary phosphate rocks (Pufahl and Groat, 2017), as well as in associated P-fertilizers (Verbeeck et al., 2020). The mean concentrations of major and trace elements in the triple super phosphate (TSP) fertilizer as well as potash (MOP) fertilizer applied at TRS in 2021 are shown in Table 2. The concentration of P in this TSP fertilizer is 212.3 g/kg, which is equivalent to 48.5 % P_2O_5. Analysis of the TSP fertilizer shows that it contains high levels of U (163 mg/kg), Cd (23 mg/kg), V (179 mg/kg), and Cr (132 mg/kg). These results are in general consistent with data reported for P-fertilizers derived from sedimentary phosphate rocks (Verbeeck et al., 2020). The magnitude of trace elements enrichment in P-fertilizers depends on the phosphate rock source and fertilizer production processes. For example, P-fertilizers produced from sedimentary phosphate rocks usually have typically higher concentrations of U and Cd than P-fertilizers originated from igneous phosphate deposits (Gupta et al., 2014; McClellan and Van Kauwenbergh, 1990; Molina et al., 2009; Pufahl and Groat, 2017).

In contrast, the concentrations of these metal(loid)s in the potassium (K-) MOP fertilizer are significantly lower (Table 2 and Fig. S2). Although the magnitude of application of the P-fertilizer varied among the plots, the K-fertilizer was applied equally for all the five FTS plots (Fig. 2). To investigate the impacts of phosphate rocks, soil samples collected from the control plot FTS1 were regarded as background compared to those collected from the other plots. Given that the concentrations of trace elements in the TSP-fertilizer are much higher than that in the MOP fertilizer (Table 2; Fig. S2), we posit that any external input of trace metals to the soil would be derived primarily from P-fertilizers, with almost negligible contribution from the K-fertilizers.

3.1.2. Soil quality characterization

The mean concentrations of major and trace elements in the bulk surface soils of FTS 1–5 and WMS 1 and 2 are shown in Table 2. For the FTS site, the concentrations of P in the bulk surface soils correlate with P-fertilizers application rates ($\rho = 1$; $p < 0.05$; Fig. 2A). Consistently, V, Cr, As, Sr, Cd, and U are enriched in soils collected from the fertilized plots FTS 2–5 relative to the background soil from the control plot FTS 1, mostly for the samples collected in June, with the Cd and U showing the greatest extent of enrichment (Fig. S3). The relative lower enrichment and even slight depletion of trace elements in the soils collected in September (Fig. S3) may indicate loss to runoff and/or potential uptake by plants. The data show that the concentrations of P in the bulk surface soils significantly correlate with Cd ($\rho = 0.92$; $p < 0.001$), U ($\rho = 0.78$; $p < 0.001$), Cr ($\rho = 0.76$; $p = 0.003$), V ($\rho = 0.76$; $p = 0.003$), and As ($\rho = 0.58$; $p = 0.03$), but not with Sr ($\rho = -0.14$; $p = 0.74$; Fig. 3). While previous studies have reported the accumulation of Cd (Bigalke et al., 2017; Jeng and Singh, 1995; Jiao et al., 2012; Loganathan et al., 1996; Mortvedt et al., 1981; Mortvedt, 1987; Williams and David, 1973) and U (Bigalke et al., 2020; Rothbaum et al., 1979; Stojanovic et al., 2006; Sun et al., 2020a, 2020b, 2022; Takeda et al., 2006; Wetterlind et al., 2012) in surface soils treated with P-fertilizers, this study shows that Cr, V, and As in agricultural topsoils can also be derived from the application of P-fertilizers. The high statistically-valid correlations between P and the toxic metals(loid)s demonstrated in this study clearly indicate that the rate of P-fertilizer application controls the occurrence of a wide range of metals(loid)s in the impact topsoil.

In addition to surface soils, we investigated the variations of metal(loid)s along the soil profiles. Soil cores up to 150 cm deep (Fig. S1) were collected in plots FTS 1, FTS 3, and FTS 5, spanning from the unfertilized to the highest application rate. For each of these profiles, 10 cm segments were analyzed to study the vertical distribution of trace elements in the bulk soils. The data show that long-term intensive phosphate fertilizer application has significantly increased the P concentrations in the bulk pool in the 0–30 cm soil depth (Fig. 4A). However, lower P concentrations are observed in deeper (>30 cm) soil. Cadmium concentrations follow similar vertical variations with elevated Cd levels at the upper 30 cm of soils depth (Fig. 4B). The low Cd level in soil profiles below 30 cm depth is consistent with results reported in previous studies that show gradual decrease of Cd with depth (Kubier et al., 2019). In the top 10 cm of soil, the bulk Cd concentration in FTS 5 is higher than in FTS 3 and FTS 1. The result further confirms that Cd accumulation co-occurs with P accumulation, in which case topsoil would be most impacted by long-term application of P-fertilizers.

Uranium in the top 10 cm soil of FTS 5 has a higher concentration (composite value of the two sampling campaigns is 1.61 mg/kg) than that of FTS 1 (0.90 mg/kg) and FTS 3 (0.96 mg/kg) (Fig. 4C). The accumulation of U in the top soil samples in this study is consistent with previous works that have shown U accumulation in top soil due to P-fertilizer application (Bigalke et al., 2020; Rothbaum et al., 1979; Stojanovic et al., 2006; Sun et al., 2020b; Takeda et al., 2006; Wetterlind et al., 2012). There is, however, no systematic trend of U concentrations in deeper soils that can be related to the application of P-fertilizers.

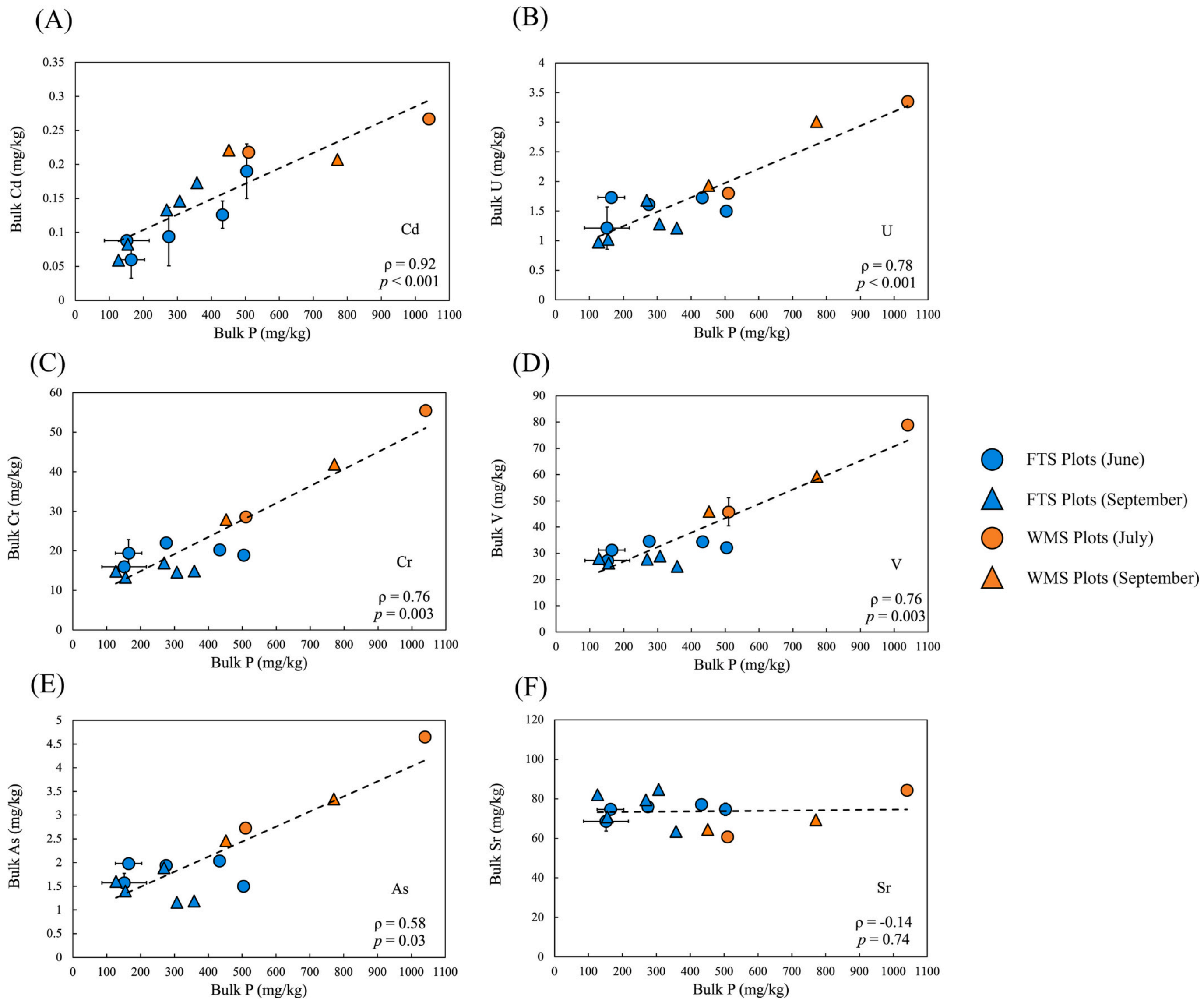

Fig. 3. Binary scatter plots of the mean concentrations of metal(loid)s vs. P in bulk surface soils (0–20 cm) from FTS and WMS plots of Tidewater Research Station (see Fig. 1 for their locations). Statistically significant correlations exist between P and (A) Cd, (B) U, (C) Cr, (D) V and (E) As concentrations ($p < 0.05$); no correlation was observed between P and Sr (F) concentrations. Error bars represent the standard deviation from triplicate analyses and are smaller than the data markers if not shown.

Similarly, little systematic variations in relation to P-fertilizer applications can be discerned for Cr, V, and Sr among the three soil profiles (Fig. 4).

In contrast, As is enriched in the deeper horizon of the soil profile (>100 cm) collected from FTS5, the plot with the highest rate of application (Fig. 4G), which coincides with the depth of the transition from sandy loam to a loamy sand texture and the depth of local water table (Fig. 4). The distinctive higher As concentrations in FTS 5 compared to the other two plots suggest that it is related to the long-term input of As from extensive P-fertilizer application. It is possible that long-term application of P-fertilizers has led to mobilization of As and its deeper soil in the water-saturated zone of the soil profile. Furthermore, the association of As with the saturated zone may suggest that dissolved As in the shallow groundwater was absorbed onto the deep soil, resulting in higher As concentrations. This scenario is also consistent with previous studies that have reported As leached out from contaminated topsoil to uncontaminated subsoil due to the P-fertilizer application (Davenport and Peryea, 1991; Peryea, 1991; Peryea and Kammereck, 1997).

3.2. *Potential plant-available fractions of metal(loid)s in soil*

3.2.1. *Potential plant availability*

The mean concentrations of metal(loid)s from the Mehlich-III extraction and their relative percent to the respective bulk concentrations are summarized in Table 3, which can indicate the potential plant availability of metal(loid)s in the soil. The concentrations of plant-available P are correlated with the amounts of P-fertilizer application (Fig. 2B). The plant-available fraction of P in the surface soil with the most extensive P-fertilizer application (FTS 5) is up to 56 % of the bulk and significantly higher than that in soils from the other 4 plots (17–21 %, Table 3), which show little difference between soils with and without P-fertilizer application. Similarly, the plant-available fraction of Cd is the highest in FTS 5 (65 %) among all the five plots. Yet, Cd has a higher plant-available fraction than U (Table 3). Previous studies have identified that Cd has substantial mobility and the propensity to accumulate in plants (Shahid et al., 2017; Yang et al., 2014), which is consistent with frequent reports of Cd in food products (Chunhabundit, 2016; Grant and Sheppard, 2008; Roberts, 2014). In contrast, other metal(loid)s

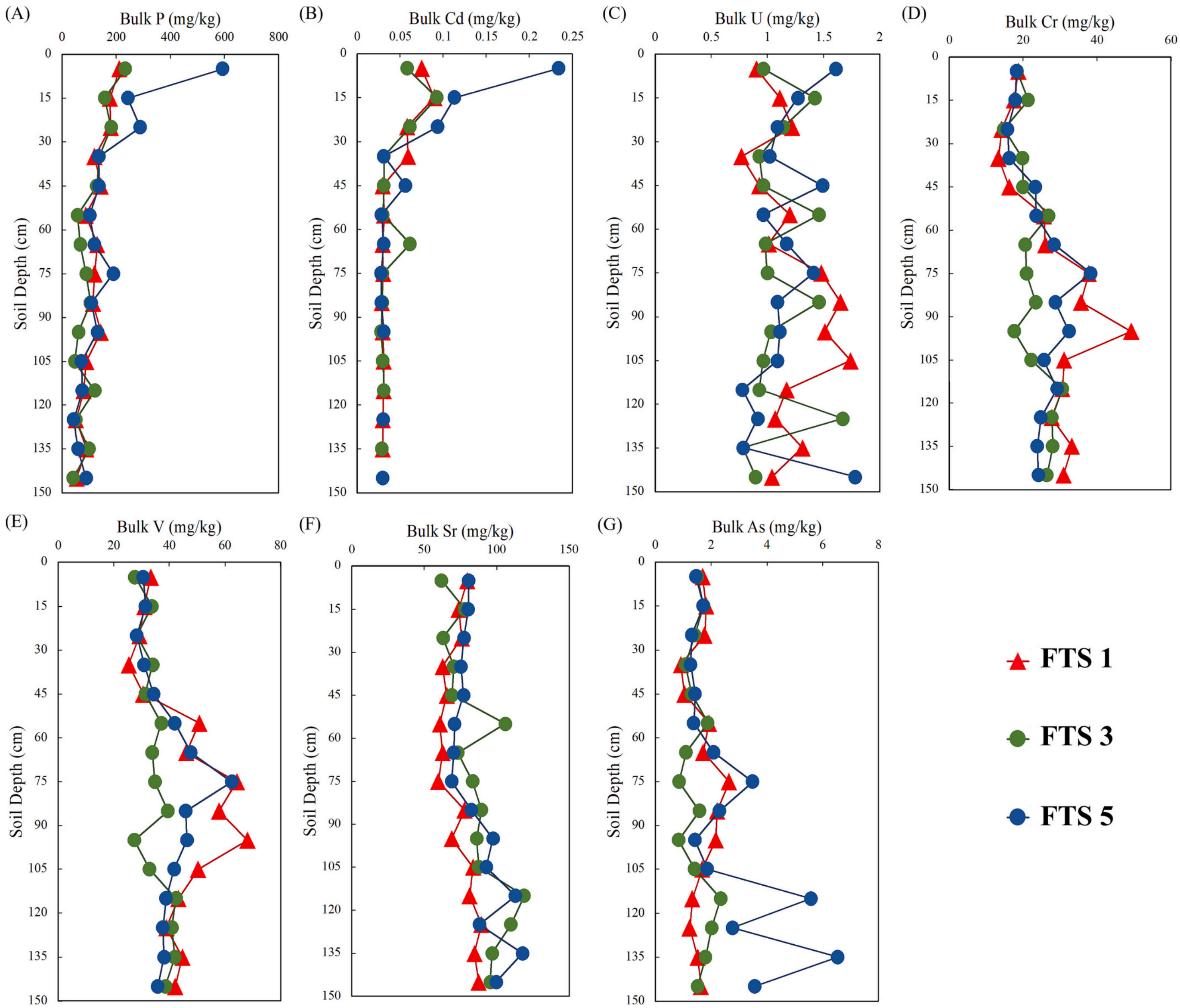

Fig. 4. Mean bulk concentration profiles of (A) phosphorous (P); (B) cadmium (Cd); (C) uranium (U); (D) chromium (Cr); (E) vanadium (V); (F) strontium (Sr); and (G) arsenic (As) in cores from the FTS site. Red triangles symbolize the unfertilized soil plots (FTS-1) and green and blue circles symbolize the fertilized soil plots from FTS-3 and FTS-5. Error bars represent the standard deviation from triplicate analyses and are smaller than the data markers if not shown.

including Sr, V, Cr, and As have a relatively low plant availability (0.4–12 %; Table 3). Interestingly, the Mehlich III extractable concentration correlated with the bulk concentration for Cd, Cr, V, and As in the bulk soils ($\rho > 0.63; p < 0.05$); in contrast, no correlation is seen between the Mehlich III extractable and bulk concentrations for U and Sr (Fig. 5).

3.2.2. *Correlation between P and metal(loid)s in Mehlich III extraction*

Phosphorus fertilizer has been shown to increase the plant available fraction of P in the surface soils (Fig. 2B). To test if P fertilization may also increase the occurrence of metal(loid)s in the potential plant-available fraction of soils, we compare their concentrations to P in the Mehlich III extractions (Fig. 6). The data show that the concentration of Mehlich III extracted P is significantly correlated with the concentrations of Mehlich III extractable Cd ($\rho = 0.96, p < 0.001$), U ($\rho = 0.71, p = 0.004$), Cr ($\rho = 0.88, p < 0.001$), V ($\rho = 0.93, p < 0.001$), As ($\rho = 0.67, p = 0.008$) and Sr ($\rho = 0.71, p = 0.006$) (Fig. 6). These correlations support our hypothesis that similar to P, the Mehlich III extractable metal(loid)s in the soils could be primarily derived from the long-term P-fertilizer application. These results are consistent with Sun et al. (2020b) who adopted a non-HF acid extraction method to estimate the bioavailable portions of U and found that the long-term P- fertilizer application can significantly increase the extractable U concentrations in the upper 0–24 cm (A horizon) of the impacted soil, with less impact on the U in the plant available fraction of deeper soil. Compared with unfertilized soil, fertilizer-derived U is usually associated with available soil organic matter and poorly crystalline Fe/Al mineral fractions (Sun et al., 2020b; Takeda et al., 2006; Yamaguchi et al., 2009).

Similarly, our data show that the concentration of Mehlich III extracted Cr in the FTS 5 surface soil is 0.28 mg/kg, which is four times higher than Cr extracted from the unfertilized FTS 1 soil (0.068 mg/kg), and three times higher than the regularly fertilized FTS 3 soil (0.084 mg/kg). These results are consistent with the high Cr in the P-fertilizer used on site (132 mg/kg; Table 2). The toxicity of Cr is highly dependent on its oxidation state: the trivalent species, Cr(III), is an essential nutrient with low solubility in water; however, the hexavalent species Cr(VI) composed of chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) are highly mobile, toxic, and carcinogenic (Unceta et al., 2010; Zhitkovich, 2011). It has been shown that Cr in several common commercial P fertilizers is

Table 3
The summary of mean P and trace elements concentrations (mg/kg) as well as the percent of potential plant-available fraction (i.e., the ratio of Mehlich III extractable concentration to the bulk soil concentration ×100) in Mehlich-III extracted (potential plant available) fraction.

Soil plot	P		Cd		U		Sr		V		Cr		As	
	Mehlich III extracted (mg/kg)	Potential plant-available	Mehlich III extracted (mg/kg)	Potential plant-available	Mehlich III extracted (mg/kg)	Potential plant-available	Mehlich III extracted (mg/kg)	Potential plant-available	Mehlich III extracted (mg/kg)	Potential plant-available	Mehlich III extracted (mg/kg)	Potential plant-available	Mehlich III extracted (mg/kg)	Potential plant-available
FTS 1	31.1	21 %	0.04	51 %	0.02	2 %	1.52	2 %	0.21	1 %	0.07	0.4 %	0.13	8 %
FTS 2	36.2	22 %	0.04	58 %	0.02	1 %	1.22	2 %	0.24	1 %	0.09	0.5 %	0.13	7 %
FTS 3	45.9	17 %	0.05	45 %	0.03	2 %	1.67	2 %	0.23	1 %	0.08	0.4 %	0.12	6 %
FTS 4	88.7	21 %	0.08	55 %	0.04	2 %	1.69	2 %	0.30	1 %	0.12	1 %	0.15	8 %
FTS 5	281	56 %	0.11	65 %	0.07	5 %	2.98	4 %	0.59	2 %	0.28	2 %	0.18	12 %

in the form of the toxic hexavalent chromium (Vogel et al., 2020). The German fertilizer ordinance has determined an upper limit value of 2 mg/kg of hexavalent chromium and 300 mg/kg total chromium in commercial fertilizers (Kruger et al., 2017; Vogel et al., 2020). Luo et al. (2009) estimated that 20 % of Cr inputs in the agricultural soil of China are derived from P-fertilizer application, and Li et al. (2020a, b) found that the Cr concentrations in soil were significantly correlated with the application rate of P fertilizers. In contrast, Watanabe (1984) found that the Cr concentrations in treated soils with long-term phosphate fertilizer application did not differ from unfertilized soil, and the soil minerals contribute to Cr concentrations. The chromate species has a similar structure to orthophosphate (PO_4^{3-}), and increasing P concentration could therefore displace adsorbed Cr from soil minerals (Gonzalez-Rodriguez and Fernandez-Marcos, 2021). Our results show that Cr was accumulated in both the bulk (Fig. 3C), and the bioavailable fraction of the soils (Fig. 6C), which are directly affected by the magnitude of P applications.

Vanadium is relatively abundant in the continental crust compared with other trace metals, but global anthropogenic emissions have exceeded the natural sources (Schlesinger et al., 2017). The V concentration in the TSP fertilizer is 179 mg/kg (Table 2). The concentration of Mehlich III extracted V in the FTS 5 surface soil is 0.59 mg/kg, which is approximately three times higher than in the unfertilized FTS 1 soil (0.21 mg/kg) and the regularly fertilized FTS 3 soil (0.25 mg/kg). Vanadium is an essential nutrient for some organisms, but large V concentrations may be toxic to humans and ecosystems. It is also a redox-sensitive element that has three oxidation states (III, IV, V); the vanadate ion ($H_2VO_4^-$) is the most stable and common form in oxic environments (Gustafsson, 2019; Schlesinger et al., 2017). Vanadate is strongly adsorbed on poorly crystalline Fe/Mn oxides and organic matter. Like chromate, phosphate may compete with vanadate for sorption sites, therefore, increasing P may cause the desorption of vanadate and potentially increase the mobility and plant availability of V in the soils (Gonzalez-Rodriguez and Fernandez-Marcos, 2021).

Likewise, the As concentration in the TSP fertilizer was higher than in the background soil (4.1 mg/kg versus 1.6 mg/kg; Table 2). The concentration of Mehlich III extracted As in the FTS 5 soil is 0.18 mg/kg, which is 40 % greater than that in the unfertilized FTS 1 soil (0.13 mg/kg), and 50 % higher than in the regularly fertilized FTS 3 soil (0.12 mg/kg). Arsenate (As (V)) and arsenite (As (III)) are two common inorganic As oxyanions occurring in oxic and reducing environments, respectively. Hartley et al. (2013) found As accumulation in archived soil before 1948 due to the long-term applications of arsenic-enriched phosphate fertilizer. The occurrence of arsenate under oxic conditions (e.g., AsO_4^{3-}or AsO_3^{3-}) could compete with the comparable orthophosphate ions (PO_4^{3-}) for plant uptake and/or Fe/Mn crystalline adsorption (Jiao et al., 2012; Manning and Goldberg, 1996; Strawn, 2018). Therefore, the P fertilizer application potentially increases the mobility and plant-availability of As in soils.

Overall, applying P-fertilizer could increase the potential plant-available metal(loid)s, which pose risks to the environment and human health even if their concentrations in P-fertilizers are low. In addition to being directly incorporated into plants, high concentrations of toxic metal(loid)s, particularly those easily mobilized, have also been shown to exert negative effects on the structure, diversity, and activity of microbial communities in agricultural soils. This can happen by reducing biodiversity, weakening metabolism, and increasing resistance of bacteria (Giller et al., 1998; Sazykin et al., 2023).

Strontium concentration in the TSP fertilizer used in Tidewater Research Station was high (992 mg/kg, Table 2). Sr is an alkaline earth metal that usually occurs as a divalent cation (Sr^{2+}) (Dubchak, 2018; Gupta et al., 2018), and this element is commonly enriched in phosphate rock, P-fertilizer, and phosphogypsum (El Bamiki et al., 2021; Németh et al., 2006; Rutherford et al., 1996). The bioavailable concentration of Sr in FTS 5 was 2.98 mg/kg, which is about two times higher than in FTS 1 (1.52 mg/kg) and in FTS 3 (1.67 mg/kg). It is interesting to note that

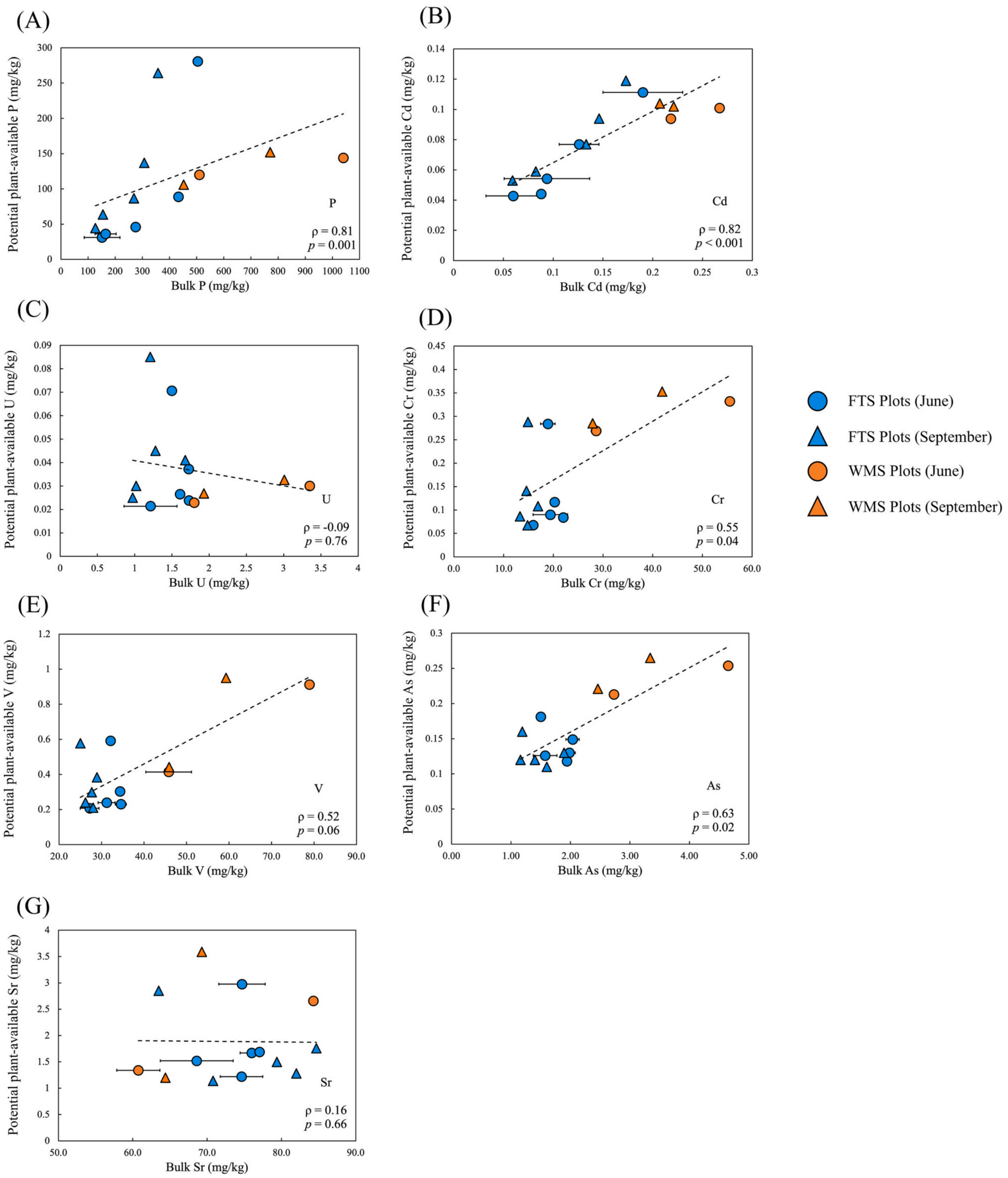

Fig. 5. Mean concentrations of potential plant-available trace elements (i.e., Mehlich-III extractable) versus their concentrations in the bulk soils from the FTS and WMS plots (see locations in Fig. 1). Statistically significant correlations exist for (A) P, (B) Cd, (D) Cr, and (F) As concentrations ($p < 0.05$); no correlation was observed for (C) U, (E) V, and (G) Sr concentrations. Error bars represent the standard deviation from triplicate analyses and are smaller than the data markers if not shown.

although Sr is not correlated to P in the bulk soil (ρ = −0.14; $p = 0.74$; Fig. 3F), Sr is highly correlated to P in the plant-available fraction (ρ = 0.71, $p = 0.006$; Fig. 6F), indicating only limited impact of the P-fertilizers applications. In contrast, Németh et al. (2006) found that both bulk and plant-available Sr in soil with large rates of P- fertilizer applications were significantly higher than those in a control plot.

Fig. 7 shows systematic high concentrations of Mehlich-III extracted P, Cd, U, Cr, V, and Sr in the upper 0–50 cm depth of the soil profiles. The greatest concentrations in the upper soils were in the site with the highest fertilizer application (FTS 5; Fig. 7). These trends are consistent with the trends observed for the concentrations of metal(loid)s in the bulk soils and reinforce our observation for metal(loid)s contribution

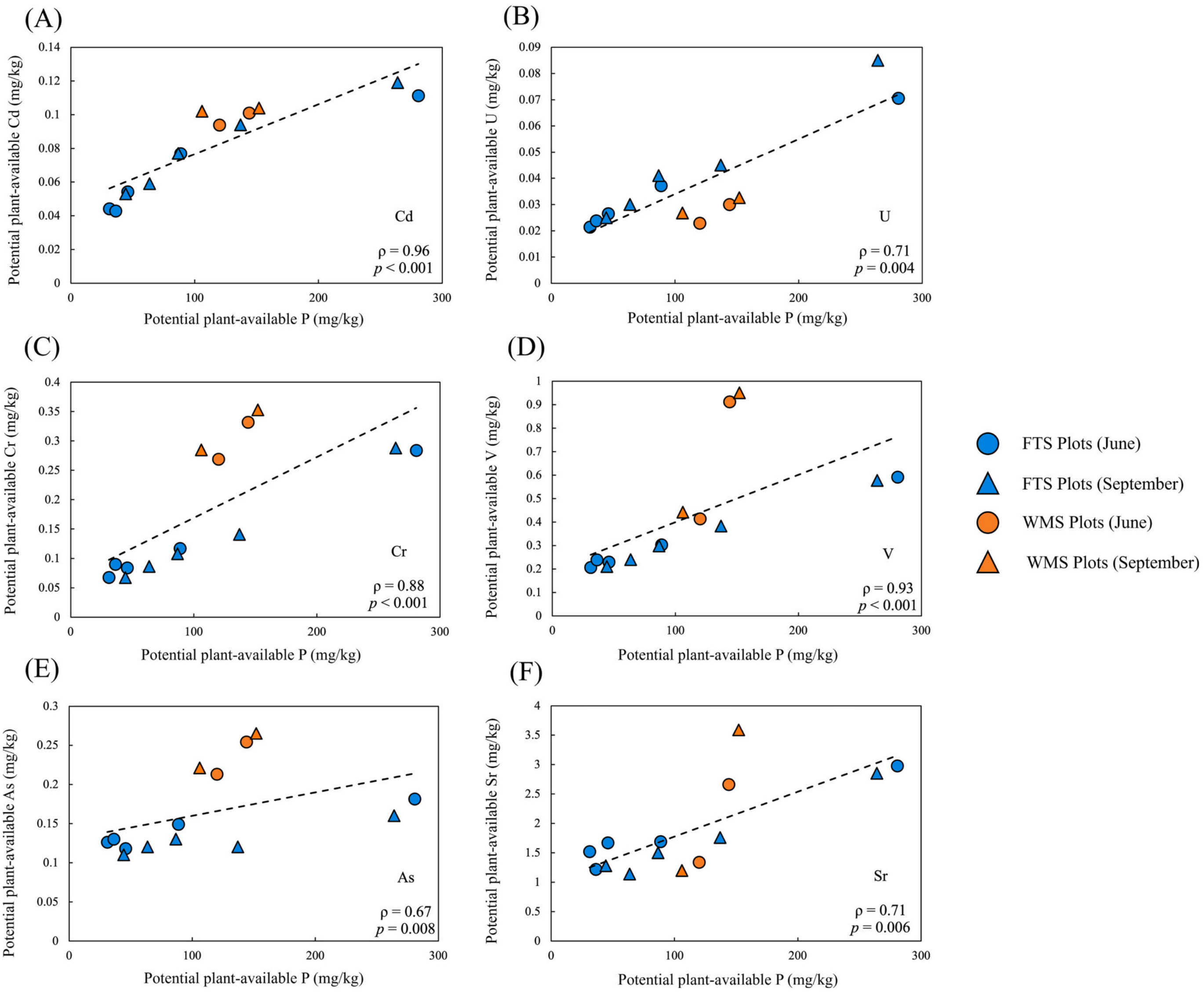

Fig. 6. Binary scatter plots of mean concentrations of trace elements versus P in the potential plant available fraction from the FTS and WMS plots of Tidewater Research Station (see locations in Fig. 1). Statistically significant correlations exist between P and (A) Cd, (B) U, (C) Cr, (D) V, (E) As and (F) Sr concentrations ($p < 0.01$). Error bars represent the standard deviation from triplicate analyses and are smaller than the data markers if not shown.

from the P-fertilizers in the upper part of the soils and the diminishing effects at deeper depth. These results are consistent with previous studies that showed the P fertilizer application would have limited impact on U variations in the deep subsoil (Rothbaum et al., 1979; Sun et al., 2020b, 2022; Takeda et al., 2006). In contrast, the As variation in the plant available fraction is consistent with the As variations in the bulk soils, showing higher values in the deeper section of the soil profile, with As levels in FTS 5 > FTS 3 > FTS 1 (Fig. 7).

3.3. Distribution of metal(loid)s in different soil fractions

In addition to the evaluation of metal(loid)s in the bulk and plant-available fraction of the soil, we conducted sequential leaching to determine the occurrence and distribution of metal(loid)s in other soil phases, including the exchangeable phase (F1), the reducible phase (F2), the oxidizable phase (F3), and the residual phase (F4). Metal(loid)s extracted from the acetic acid (HOAc) fraction (F1) are weakly adsorbed to soils and can be readily mobilized by ion-exchange process or by lowering the soil pH (Bakircioglu et al., 2011; Filgueiras et al., 2002). This fraction is considered as the most mobile and bioavailable for uptake to plants, which may also be mobilized into the environment (defined as F1). Metal(loid)s in the reducible phase (F2) are more likely to be released from soil under reducing conditions due to the reductive dissolution of Fe and Mn (oxyhydr)oxides (Gleyzes et al., 2002). Metal(loid)s in the oxidizable phase (F3) are mainly associated with organic materials and/or sulfides and are expected to retain in soils for a long time and can be released by microbial decomposition (Bakircioglu et al., 2011; Bracher et al., 2021). Finally, metal(loid)s in the residual fraction (F4) are considered inert and unavailable for plant or microbial communities, as this fraction is interpreted as tightly bound into mineral structures (Bracher et al., 2021; Gleyzes et al., 2002). The potential mobility and bioavailability of elements generally decrease from F1 to F4 in this sequential extraction.

The combined proportions of metal(loid)s in the more soluble (F1–F3) fractions in the surface soil of FTS 5, which has the highest P-fertilizer application rate, are the highest among all the tested surface soils (Fig. 8). For example, nearly 100 % of Cd is in the mobile fractions (F1–F3) of FTS 5 soil. Cadmium derived from P-fertilizer is mainly associated with the mobile acetic acid soluble fraction (F1) and reducible fraction (F2) of soil, which is consistent with the results reported in previous studies (Bracher et al., 2021; Li et al., 2010). It has also been suggested that Cd partitioned into F1 is the major source of plant-

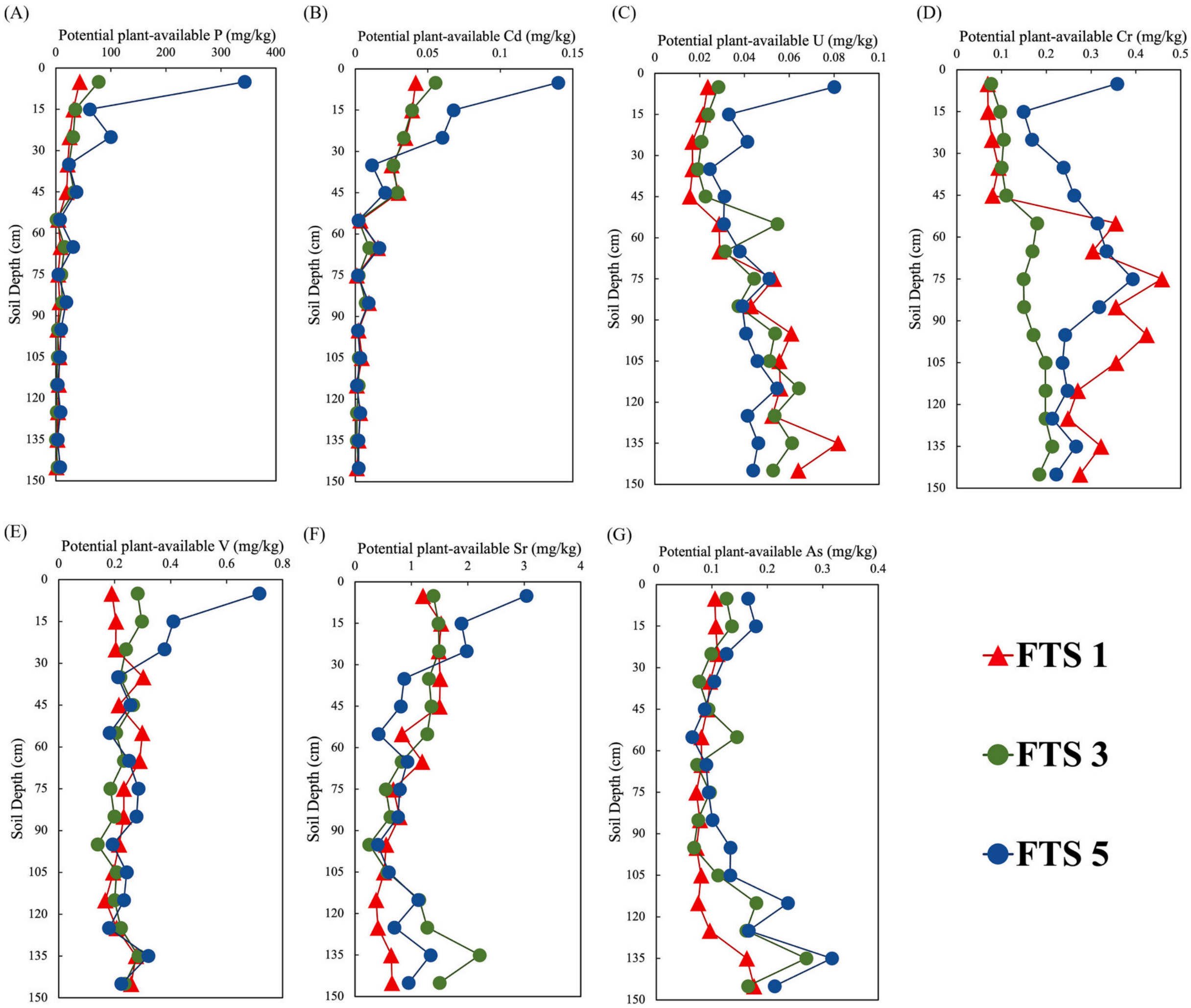

Fig. 7. Variations of mean concentrations of Mehlich III extracted (A) phosphorous (P); (B) cadmium (Cd); (C) uranium (U); (D) chromium (Cr); (E) vanadium (V); (F) strontium (Sr); and (G) arsenic (As). Red triangles symbolize the unfertilized soil plots and green and blue circles symbolize the fertilized soil plots.

available Cd for crops like wheat in that >80 % of Cd in this fraction was incorporated into the wheat (Bracher et al., 2021). In addition, acidic soil would be at increased risk with toxic metals like Cd because soil pH affects their sorption/desorption capacity, which control the mobility and availability of trace metals in soils (Filgueiras et al., 2002; Kicińska et al., 2022; Li et al., 2021). This is also consistent with the results of the Mehlich-III extractions showing that Cd has the greatest potential plant availability in the FTS 5 soil.

Strontium is dominantly present in the non-mobile residual fraction (F4: 95–97 %; Fig. 8), whereas the redox-sensitive oxyanion elements (U, Cr, V, As; Fig. 8) are in higher portions in the reducible and oxidizable fractions, reflecting their redox-dependent mobilization affinity. Potentially mobile As is mainly in the reducible fraction (F2; 12–17 %) (Fig. 8). When the soil matrix is exposed to reducing conditions (e.g., waterlogging), As bound to iron and manganese (oxyhydr) oxides is likely to be released. Vanadium has similar portions in the reducible (F2; 3–4 %) and oxidizable (F3; 4–6 %) fractions (Fig. 8). In contrast, potentially mobile U and Cr are largely in the oxidable form (F3), which account for 15–39 % and 8–11 % of their total concentrations, respectively (Fig. 8). The oxidizable fraction of an element is not considered to be easily bioavailable, since it is usually bounded to humic substances with a large molecular weight, which only slowly release small amounts of metals (Filgueiras et al., 2002). However, the fraction of oxidizable U is noticeably higher in soil with greater fertilizer application rates, indicative of its primary contribution from the long-term application of P-fertilizer. The fertilizer-derived U associated with soil organic matter was identified as an important pool of U as compared to U under oxic conditions (Yamaguchi et al., 2009).

4. Integration and conclusion

Based on the NuGIS dataset (the Fertilizer Institute), the average annual consumption of P-fertilizers in the U.S. between 1987 and 2016 was 4.17 million tons/year. Using the metal(loid)s to P ratios measured in the triple phosphate fertilizer (TSP) used in the Tidewater Research Station (Table 2), we estimate the overall annual flux of metal(loid)s introduced to the agriculture fields in the U.S. (Table 4). Different P-fertilizers derived from other source phosphate rocks might result in different metal(loid)s concentrations and thus different accumulation rates. The data suggest that large rates (Table 4) of toxic metal(loid)s are annually added to agriculture fields across the U.S directly from P-fertilizers application. The investigation of the abundance of metal(loid)s in agricultural soils from the experimental fields in the Tidewater Research Station of eastern North Carolina indicates that long-term application of P-fertilizers resulted in accumulation of toxic metal (loid)s, including Cd, U, Cr, V, and As in the top agriculture soils. We show that the magnitude of the application rates of the P-fertilizers controls the P and metal(loid)s concentrations in the topsoil. In spite of the different methods of P-fertilizers application and soil types between the FTS and WMS sites, the data show consistent relationships between P

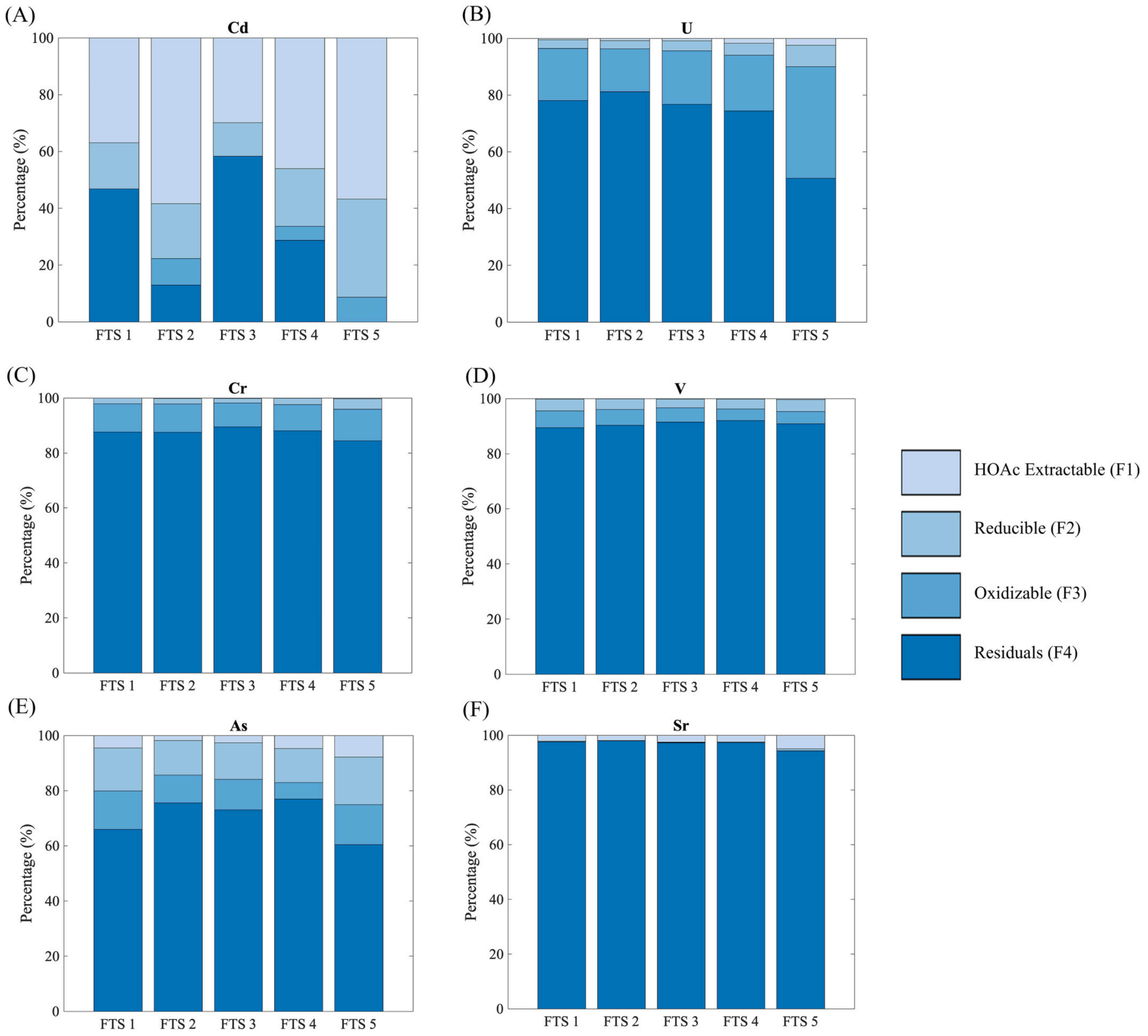

Fig. 8. Fraction of (A) cadmium (Cd); (B) uranium (U); (C) chromium (Cr); (D) vanadium (V); (E) arsenic (As); (F) strontium (Sr) in surface soils from FTS plots of Tidewater Research Station.

Table 4
Data of average annual P_2O_5 (million metric tons/year) in agriculture fertilizers consumed in the U.S. between 1987 and 2016 (Nu GIS web site). Conversion of the P_2O_5 to P and using the ratios of Cd, As, U, Cr, V, and Sr to P in the triple phosphate fertilizer (TSP) used in the Tidewater Research Station (Table 2) are used to estimate the annual fluxes of these metal(loid)s to the environment through utilization of P-fertilizers in the U.S.

Year	P_2O_5 ($\times10^6$ tons/ year)	Cd (tons/ year)	As (tons/ year)	U (tons/ year)	Cr (tons/ year)	V (tons/ year)	Sr (tons/ year)
Average	4.17	190	35	1360	1100	1500	8250

and metal(loid)s accumulation in the topsoil. Both the bulk and the Mehlich III-extractable fraction show strong and positive correlations between P and Cd, U, Cr, V, and As but not with Sr in the surface bulk soils (top 0–20 cm). Yet the deeper soil profiles show systematically lower concentrations of P and metal(loid)s with the exception of As, indicating that toxic metal(loid)s derived from P-fertilizers application preferentially accumulate in the topsoil and/or leach out to the underlying groundwater from the deep soil section. In contrast, we detected elevated levels of As in the deep (>100 cm) soil associated with the depth of the groundwater table, suggesting As mobilization from the topsoil followed by a secondary attenuation into the seep soil.

We also conducted Mehlich III and sequential extractions to detect the toxic metal(loid)s occurrences in the different soil phases, including the potential plant-available fraction. The P concentrations show significant positive correlations with U, Cr, V, As, and Sr in the potential plant-available fraction of the surface soils. This analysis indicates that long-term application of P-fertilizers increases the occurrence of toxic metal(loid)s in the potential plant-available fraction in the soils, and thus an increase in the probability of transforming of toxic metal(loid)s accumulated in the soil into the plant products and can have negative effects on microbial communities in agricultural soils (Giller et al., 1998; Sazykin et al., 2023). Given the direct positive corrections between the concentrations of some of the metal(loid)s in the bulk soil and the Mehlich III-extractable fraction, we posit that the accumulation of these toxic metal(loid)s in the topsoil increases the potential human exposure to these contaminants (Alengebawy et al., 2021). Sequential extractions show higher portions of Cd in the most mobile fractions (i.e., exchangeable and reducible) of soils with higher levels in soils with higher P-fertilizer application rates. Although other redox-sensitive elements (As, Cr, V, U) have predominant occurrence in the residual non-soluble fraction, they also show higher levels in the reducible and oxidizable fractions, reflecting their redox-dependent mobilization potential. The high P concentrations in the soils would likely increase the mobility of Cr, V, and As in the infiltrating fluids, because they occur as oxyanions that would compete with dissolved orthophosphate for sorption sites on the soils. Consequently, the potential bioavailability of these metal(loid)s would be affected by both the magnitude of P-fertilizer inputs and the phosphorous-metals exchange reactions.

Overall, the results of this study clearly demonstrate that long-term and excessive application of P-fertilizer results in the accumulation of a wide range of toxic metal(loid)s and P in topsoil, proportional to the rate of P-fertilizer application. A large proportion of these toxic metal(loid)s incorporate into the plant-available fraction in the soil, raising the potential of uptake by plants in agricultural fields. Future studies should evaluate the selective uptake and bioaccumulation of metal(loid)s in different agricultural crops and settings as well as the potential for mobilization and transport of the metal(loid)s to groundwaters and the environment.

CRediT authorship contribution statement

Jun Hu: Conceptualization, Methodology, Investigation, Writing – original draft and review & editing; Zhen Wang: Supervising, Conceptualization, Methodology, Investigation, Writing – original draft and review & editing; Gordon Williams: Investigation, Review & editing; Gary S. Dwyer: Investigation, Review & editing; Luke Gatiboni: Conceptualization, Methodology, Investigation, Review & editing; Owen W. Duckworth: Conceptualization, Methodology, Investigation, Review & editing; Avner Vengosh: Supervising, Conceptualization, Methodology, Investigation, Writing – original draft and review & editing;

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data are provided in the manuscript

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.167863.

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