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Impacts of fertilization on metal(loid) transfer from soil to wheat in a long-term fertilization experiment – using ^{87}Sr/^{86}Sr isotopes as metal(loid) tracer

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ABSTRACT

Fertilizers are widely used to sustain food production but can alter soil chemistry and potentially contribute toxic metal(loid)s to agricultural systems. For the first time, this study examined the occurrence of select metal(loid)s (Zn, Sr, V, As, Cd, Pb, and U) alongside the ^{87}Sr/^{86}Sr isotope ratio in agricultural soil– both total and mobile pools– and wheat grain. Samples were collected from one of four fertilization treatments– mineral (NPK), organic (manure), combined mineral+organic, and unfertilized controls– within the 120-year Static Fertilization Experiment in Bad Lauchstädt, Germany. Fertilization treatments altered soil pH and organic carbon resulting in mineral fertilization lowering pH and increasing cation mobility (Cd, Zn, Sr), whereas organic fertilization increased pH and enhanced the mobility of non-cationic elements (V, As). These effects translated into higher Cd in mineral-fertilized wheat grain and higher As in mineral+organic wheat grain. Fertilization shifted the ^{87}Sr/^{86}Sr ratios in soils and wheat grains toward that of the applied fertilizers, with mineral and mineral+organic wheat grains inheriting the triple super phosphate signature (0.70778) and organic wheat grains matching manure (0.70883). The ^{87}Sr/^{86}Sr ratio in the mobile soil pool was correlated with mobile As, V, and P, demonstrating that the ^{87}Sr/^{86}Sr ratio reflects both fertilizer source and the mobility of select co-occurring metal(loid)s. Overall, this study demonstrates metal(loid) enrichment in soil and wheat from fertilization and establishes ^{87}Sr/^{86}Sr ratio as a robust tracer of fertilizer impacts. These findings underscore the need for targeted fertilization strategies to reduce contaminant accumulation in agroecosystems.

1. Introduction

Fertilizer application is a regular agricultural practice used to optimize crop growth and meet global food demands by providing essential nutrients for plant growth, including nitrogen (N), phosphorus (P), and potassium (K). Traditionally, organic fertilizers derived from animal and plant-based carbon substances were the primary agricultural fertilizers (Bogaard et al., 2013). However, the increased use of inorganic N, P, and K salts, known as mineral fertilizers, greatly contributed to the Green Revolution in the 20th century, with 48% of yield increases globally in cereal grain, attributed to their application (Ladha et al., 2016). Yet, this yield boost came at the cost of soil health degradation, including acidification, N-eutrophication, reduced aggregation, and declines in micro-, meso-, and macro-life biodiversity (Gomiero, 2016). These concerns have fueled discussions on enhancing the role of organic fertilizers in agricultural management as it can improve aforementioned soil health parameters (Bebber and Richards, 2022; Gattinger et al., 2012; Köninger et al., 2021; Lin et al., 2019; Reganold and Wachter, 2016).

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Beyond yield quantity, food quality– defined by nutrient and contaminant concentrations– is a key aspect of food security (Pinstrup-Andersen, 2009). Metals, such as zinc (Zn) and vanadium (V), serve as essential micronutrients in humans by acting as enzyme cofactors that support immune function, antioxidant defense, energy metabolism, and connective tissue formation, but they can become toxic at excessive levels (Kabata-Pendias and Mukherjee, 2007). While these elements can be both essential and harmful, global food systems are more often challenged by deficiencies rather than toxicities, making micronutrient malnutrition a major health concern (Passarelli et al., 2024).

In contrast to that, certain metal(loid)s such as arsenic (As), cadmium (Cd), lead (Pb), and uranium (U) do not have known favorable metabolic functions in the human body but rather exert toxicity, including disrupting cellular processes, damaging organs, and increasing the risk of cancer and other chronic diseases upon long-term exposure (Chen et al., 2021; Tchounwou et al., 2012).

Some studies warn that the intensification of agriculture driven by the Green Revolution has led to a dilution of essential micronutrients in crops (Bhardwaj et al., 2024; Fan et al., 2008). Moreover, the application of mineral fertilizers has been associated with an increase in the occurrence of harmful metal(loid)s, such as As, Cd, and U in soils, which is primarily linked to their contents in phosphate rock used as a source of phosphorus (Hill et al., 2024; Azzi et al., 2017; Molina-Roco et al., 2018; Raven and Loeppert, 1997; Gupta et al., 2014). Organic fertilizers have also been shown to have increased concentrations of Pb, As, Cu, Mn, and Zn, due to mineral supplements in animal feed materials (Bolan et al., 2004; Lopes et al., 2011; Luo et al., 2009; Nookabkaew et al., 2016; Sager, 2007; Sheppard and Sanipelli, 2012). Alarmingly, it is estimated that 14–17% of cropland globally is affected by toxic metal pollution, placing approximately 0.9 to 1.4 billion people at health risk (Hou et al., 2025). Despite these concerns, metal(loid) regulations in fertilizers remain uncommon worldwide, with specific limits enforced only in select regions such as the European Union, Canada, and California (European Union, 2019; Government of Canada, 2025; State of California, 2024).

Once in the soil, metal(loid)s interact with soil components through adsorption, co-precipitation, and complexation, affecting metal(loid) mobility and availability for plant uptake (Lair et al., 2007; Rieuwerts et al., 1998). In oxic soils, this mobility is primarily regulated by soil pH and the availability of adsorption sites on minerals and organic carbon, which can be influenced by the type of fertilization (Palansooriya et al., 2020; Park et al., 2011). While more adsorption sites generally reduce metal(loid) mobility, pH effects vary with ionic charge of the metal (loid): at high pH, cationic species become less mobile, whereas anionic species become more mobile due to particle repulsion (Violante et al., 2010). Few studies have compared metal(loid) uptake in minerally versus organically fertilized crops under realistic farming conditions, with most focusing solely on Cd and Zn occurrence in plants (Grüter et al., 2019; Mäder et al., 2007; Sun et al., 2017; Xu et al., 2018; Zhen et al., 2020). Furthermore, aspects of these studies are often context dependent (e.g., soil pH, type of organic fertilizer used, texture, etc.) and therefore yield contradictory results, showing that organic fertilizers may have varying effects on metal(loid) concentrations in crops compared to mineral fertilizers. This highlights a gap in understanding the impact of organic versus mineral fertilizers on metal(loid) accumulation in crops, and therefore, the effects on metal(loid) accumulation in plants beyond Cd and Zn remaining poorly understood, emphasizing the need for comprehensive research on this topic.

In plant systems, strontium (Sr) isotopes are primarily used as a tracer proxy of calcium (Ca) to determine Ca flux in plants (Capo et al., 1998; Drouet et al., 2005; Oeser and von Blanckenburg, 2020; Pett-Ridge et al., 2009). The Sr isotope ratio (^{87}Sr/^{86}Sr) can also be used as a tracer for metal(loid) contamination due to (1) co-occurrences with Sr from the contaminant sources– such as coal ash, oilfield brines, or phosphate rock mining– and (2) a distinct isotope composition that is significantly different from the native environment (Harkness et al., 2018; Hurst et al., 1991; Peterman et al., 2010; Ruhl et al., 2014; Vengosh et al., 2022). Unlike metal(loid) concentrations alone, which can be altered by chemical processes, the ^{87}Sr/^{86}Sr ratio retains distinct source-specific signatures that allow differentiation between natural and anthropogenic inputs and can be used for source apportionment of cation contributions (Capo et al., 1998). However, due to its conservative nature, the Sr isotope ratio may not be suitable in directly quantifying geochemical mechanisms.

In addition to the enrichment of potentially toxic metal(loid)s, Sr is enriched in phosphate fertilizers, and the Sr isotope ratios in phosphate fertilizers are similar to their source phosphate rocks (Hill et al., 2024). A previous study has shown that in addition to metal(loid) enrichment from the application of phosphate fertilizers, the Sr isotope ratio of the mobile soil pool (via Mehlich III extraction) in agricultural soil was also reflective of the source and magnitude of phosphate fertilizer application (Hill et al., 2024; Hu et al., 2024). Another study was able to utilize the Sr isotope ratio to discriminate cereal grains grown in different soils amended with either marl or ash (Schmitt et al., 2023). Strontium isotopes do not fractionate in the environment and therefore preserve the original isotope fingerprint of the contamination source (Capo et al., 1998). Furthermore, Sr often co-occurs with contaminant metal(loid)s in the environment (Capo et al., 1998). In contrast, other isotope tracers, such as Cd isotopes, fractionate in the soil–plant system, causing ambiguity in its utility as an effective contaminant source tracer but may provide better quantification of mechanistic processes (Capo et al., 1998; Imseng et al., 2019; Wei et al., 2019). This study is the first to explore the utilization of ^{87}Sr/^{86}Sr as a tracer for metal(loid)s in the fertilizer-soil–plant cycle.

This study aims to assess the transfer of selected metal(loid)s from soil to crop under three commonly applied fertilization practices (mineral, organic, and mineral+organic) in comparison to an unfertilized control. To this end, we utilized the Static Fertilization Experiment (SFE) in Bad Lauchstädt, Germany, one of the world's oldest long-term fertilization trials, established in 1902 (Berti et al., 2016; Merbach and Schulz, 2013). We selected wheat as our model plant due to its global importance, providing 19% of dietary calories and 20% of proteins worldwide (Food and Agriculture Organization of the United Nations, 2018). Additionally, we focused on a set of representative metal(loid)s: (i) essential micronutrients with agronomic and nutritional relevance (Zn, V), and (ii) toxic metal(loid)s with no known biological function but documented occurrence in fertilizers and soils (As, Cd, Pb, U). This selection reflects both their agricultural significance and their potential to affect food quality and human health. Given that both mineral and organic fertilizers contain metal(loid)s (Gupta et al., 2014; Lopes et al., 2011; Luo et al., 2009), we hypothesized that total soil metal(loid) concentrations will be effected by fertilization; however, fertilization-induced differences in soil pH and organic carbon will lead to differences in metal(loid) mobility, which is also dependent on the ionic charge of metal(loid)s (Violante et al., 2010). Through analysis of selected metal(loid)s in the total and mobile soil pools, as well as the co-produced wheat grains, after over 100 years of different fertilization practices, we present realistic data on the impact of fertilization practices on soil and wheat grain quality. While soil geochemical changes control metal(loid) mobility and crop uptake, these data alone cannot disentangle whether accumulated metal(loid) in grains originate from soil background pools or from fertilizer additions. Given the enrichment of Sr with metal(loid)s in mineral fertilizers and the distinctive Sr isotope ratio of phosphate fertilizer (Hill et al., 2024), we posit that the Sr isotope ratio could be utilized as tracer for metal(loid) enrichment in agriculture systems.

2. Materials and analytical methods

2.1. *Sample collection and site description*

Dried, archived wheat grain and soil samples collected from 2000 to

2021 were retrieved from the Static Fertilization Experiment (SFE) in Bad Lauchstädt, Germany, which is set upon a Haplic Chernozem soil (Altermann et al., 2005) with unchanged fertilizer application regimes since 1902 (Merbach and Schulz, 2013). The total experimental area of 4 ha is divided into 8 stripes (Fig. S1). Each stripe is separated into 18 plots, each with a different fertilization treatment. Plant and soil samples were taken from stripes 3, 6 and 7, as they have not changed treatment since 1902 and have a similar pH range (Table S1). Each stripe represents a replicate in this study. The study followed a yearly crop rotation sequence of sugar beet (*Beta vulgaris*), summer barley (*Hordeum vulgaris*), potato (*Solanum tuberosum*), and winter wheat (*Triticum aestivum*). Since 2015, sugar beet and potato have been replaced by silage maize (*Zea mays*). For the present study, we analyzed only winter wheat samples collected between 2001 and 2021. During this period, five cultivars were grown: Pegassos (2001–2005), Cardos (2006–2008), Torrild (2009–2012), Glaucus (2013–2015), and RGT Reform (2016–2021) (Table S1).

Samples for the present study were collected from plots of the fertilization schemes: none, mineral, organic, or organic+mineral fertilization. Since fertilizers are not archived in the SFE, only those from 2023 were obtained. Mineral fertilizers at SFE enrich soil with phosphorus, potassium, and nitrogen, and include triple super phosphate (TSP), potash, and calcium ammonium nitrate (CAN), respectively (Table S2). Plots undergoing organic fertilization were treated with farmyard manure, for which the supplier has been consistent for decades (Table S2). Plots undergoing mineral+organic fertilization received a mixture of all four fertilizers. Yields were calculated based on the weight of 105 °C-dried wheat grain from a 49.8 m^2 plot area.

2.2. Wheat grain sampling and processing

Wheat grains were air-dried, separated from the remaining plant material, and stored in the dark at ambient temperature for archiving. The ground grain samples were digested using a heated HNO_3/H_2O_2 mixture (Muehe et al., 2019). In Teflon vials, approximately 200 mg of sample was combined with 5 mL of twice sub-boiled 7 N HNO_3 and 3 mL of concentrated Optima™ H_2O_2. The samples were heated in a hot block at 80 °C for 30 min, then at 105 °C for 6 h. The solution was dried down and reconstituted in a mixture of 1:1:5 (mL) of $H_2O_2/HNO_3/H_2O$ in preparation for analysis. The efficacy of wheat digestion and analysis was conducted by repeated digestion and measurement of IRMM ERM-CD281 Rye Grass standard, and the results were normalized to 105 °C-dried grain weight.

2.3. Soil and fertilizer sampling and processing

Soil samples were taken concurrent with wheat harvest. Approximately 25 individual cores were taken with an auger (1.9 cm inner diameter by 20 cm length), homogenized by plot, air dried, and kept in the dark at ambient temperature for archiving. Prior to experimentation, soil samples were sieved to 2 mm and dried at 105 °C until a constant weight was achieved and ground. Total metals of soils and fertilizers were determined *via* a heated *aqua regia* digestion (Melaku et al., 2005). In Teflon vials, approximately 100 mg of soil or fertilizer was combined with 3 mL of Optima™ HCl and 1 mL of twice sub-boiled HNO_3. Samples were allowed to pre-react overnight and then heated at 105 °C for 24 h. The solution was dried down and reconstituted in a mixture of 1:1:5 (mL) of $H_2O_2/HNO_3/H_2O$ in preparation for analysis. The efficacy of digestion and analysis was conducted by repeated digestion and measurement of NIST 2711a Montana II Soil standard. Mobile (i.e., potentially phytoavailable) elements in soil were approximated by a 15-minute extraction with 0.01 M $CaCl_2$ at a 1:6.67 w/v ratio at room temperature (Houba et al., 2000; Kim et al., 2015). Extracts were filtered through 0.45 μm filters (Millex™) in preparation for analysis. This extractant was chosen as it provides a conservative estimate of the readily exchangeable pool, thereby avoiding overestimation of contaminant mobility and bioavailability.

2.4. Analytical methods

Soil organic carbon (SOC) and total nitrogen (TN) contents of the total soil samples were determined in five replicates by combustion in a C/H/N analyser (Vario El III, Elementar Hanau, Hanau, Germany). The soil samples did not contain inorganic carbon in the form of carbonates (Multi N/C, Analytik Jena, Jena, Germany). Soil pH was measured in five replicates using a fresh soil-to-0.01 M $CaCl_2$ ratio of 1:2.5 (w/v) after 60 min of equilibration. Trace elements from plant and soil digestions and mobility extractions were measured on an inductively coupled plasma mass spectrometer (ICP-MS) at Duke University (Thermo Fisher X-Series II). Isolation of Sr in preparation for isotope analysis was conducted via ion-exchange chromatography with a Sr-specific resin (50–100 μm Eichrom SR-B100-S). The $^{87}Sr/^{86}Sr$ isotope ratios were measured on a thermal ionizing mass spectrometer (TIMS, ThermoFisher Triton) at Duke University. The mean $^{87}Sr/^{86}Sr$ ratio from repeated measurements of the NIST SRM 987 was 0.71025 ± 0.00001 (1 SD, $n = 43$) and of the IRMM ERM-CD281 was 0.70852 ± 0.00001 (1 SD, $n = 6$).

2.5. Statistics and data analysis

All statistical analysis and data visualization were performed using R v 4.4.2 (R Core Team, 2023). A linear mixed-effect model was fitted between metal(loid)s and fertilization schemes with year, stripe, and cultivar (for wheat grain) as random effects. The year term was included to capture interannual variation (e.g. weather), while cultivar and stripe accounted for repeated measures across genotypes and spatial replicates. Post hoc pairwise comparisons of estimated marginal means between treatments were performed using Tukey's adjustment for multiple testing, and significant differences ($p < 0.05$) were summarized using compact letter display. This information is visualized in box and whisker plots where the box represents the interquartile range (IQR), the whiskers extending to the data within 1.5*IQR, and outliers outside this range portrayed as black data points. Pearson correlations were conducted between select element and isotope constituents. The Pearson correlation coefficient (r) is used to assess the linearity of a modeled fit line and 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. The estimated flux of metal(loid)s over 120 years was calculated and is presented in detail in the Supplemental Information.

3. Results

3.1. Metal(loid) inputs from mineral and organic fertilizers

Among all fertilizers used in mineral fertilization, TSP contained the highest concentrations of Zn, Sr, V, As, Cd, and U, while Pb was higher in CAN (Table 1). In the potash fertilizers, concentrations of these elements were relatively low or were below the detection limit. Based on fertilizer application rates for the mineral fertilization treatment (Table S2), TSP accounted for over 90% of the fertilizer-derived input of Sr, V, Cd, and U into soils. For Zn and As, TSP contributed between 60–70% of the fertilizer-derived input, with the remainder primarily attributed to CAN. Lead was the only metal(loid) for which 97% of the fertilizer-derived input was due to CAN. Potash fertilizer is not a major contributor, contributing less than 3% of the fertilizer-derived input of each metal (loid) flux.

Although the organic-based fertilizer, farmyard manure, contained lower overall metal(loid) concentrations than TSP (Table 1), the total metal(loid) input to the soil was higher in the organic fertilization treatment compared to the mineral fertilization treatment, except for Cd and U, due to the high biannual application rate of manure (Table S2). Specifically, the annual input of Zn, Pb, As, and V into soil in organic

Table 1
Metal(loid) concentrations and Sr isotope ratio of applied fertilizers.

Fertilizer	Zn (ppm)	Sr (ppm)	V (ppm)	As (ppm)	Cd (ppm)	Pb (ppm)	U (ppm)	^{87}Sr/^{86}Sr
Manure†	66	34	1.8	0.4	0.1	1.9	0.1	0.70883
TSP	477	933	164	5.8	22.5	0.8	193	0.70778
Potash	1.1	19	bdl	0.1	bdl	0.2	0.1	0.71356
CAN	96	13	1.7	0.9	0.7	13.5	0.4	0.70851

bdl: below detection limit.

† Manure metal(loid) concentrations are reported based on fresh mass content.

fertilization was estimated to be 9-, 5-, 5-, and 1.1-times higher, respectively, compared to those of mineral fertilization, while U and Cd were 14- and 3-times lower, respectively.

In the mineral+organic fertilization treatment, the estimated metal(loid) input into soil through fertilization was slightly higher ($\leq$ 1.2-times) than in the organic fertilization treatment (Table S2). Uranium was an exception, with an annual input that was 3.8-times higher than that for organic fertilization, which was still below half the input of mineral fertilization. Over 80% of Zn, Sr, V, As, and Pb input into the soil in the mineral+organic fertilization treatment came from manure. For Cd, 58% of input originated from manure, 31% from TSP, and 11% from CAN, while for U, 26% came from manure, 72% from TSP, and 2% from CAN.

Strontium was detected in all fertilizers, with concentrations decreasing in the order: TSP (933 ppm), manure (34 ppm), potash (19 ppm), and CAN (13 ppm). However, the isotope ratio ^{87}Sr/^{86}Sr followed a different trend; decreasing in the order: potash (0.71356), manure (0.70883), CAN (0.70851), and TSP (0.70778).

3.2. *Metal(loid)s distribution and soil properties in total and mobile pools*

Similar patterns in Zn, Cd, and Pb were observed in total soil concentrations (Fig. 1, time-resolved data in Fig. S2), with the lowest concentrations found in unfertilized soil, followed by mineral-fertilized, organic-fertilized, and highest in combined mineral+organic-fertilized soils. Both As and U concentrations were significantly higher in mineral-fertilized and mineral+organic-fertilized soils, but not significantly different in organic-fertilized soils, compared to unfertilized soils. Total V concentrations for all treatments were unaffected by fertilization. The SOC of ~ 1.5% and TN of ~ 0.13% in unfertilized soils increased by 50–65% in both organic-fertilized and mineral+organic fertilized soils, and by 10–20% in mineral-fertilized soils (Fig. S3). Compared to soil pH of ~ 6.0 in unfertilized soils, mineral fertilization showed a lower soil pH of ~ 5.5 and organic- and mineral+organic-fertilization showed a significantly higher soil pH of ~ 6.8 and ~ 6.7, respectively (Fig. S3).

Fertilization influenced metal(loid) concentrations in the soil mobile pool (i.e., potentially phytoavailable, Kim et al., 2015), approximated by 0.01 M $CaCl_2$, revealing two distinct patterns for (1) Cd and Zn and (2) As and V (Fig. 2, time-resolved data in Fig. S4). Cadmium and Zn concentrations were highest in the mobile soil pool of mineral-fertilized soils, significantly exceeding those in unfertilized soils. Soil undergoing organic and mineral+organic fertilization had significantly lower Cd concentrations, while Zn concentrations were non-significantly different in the mobile soil pool, compared to unfertilized soils. Compared to unfertilized soils, As and V concentrations were significantly higher in the mobile soil pool of all fertilization treatments, with the highest levels detected in mineral+organic-fertilized soils, followed by organic-fertilized, and mineral-fertilized. Arsenic and V were strongly positively correlated with P in the mobile soil fraction ($r^2 > 0.90$; $p < 0.001$) (Fig. S5). Uranium and Pb were below the detection limit in all mobile

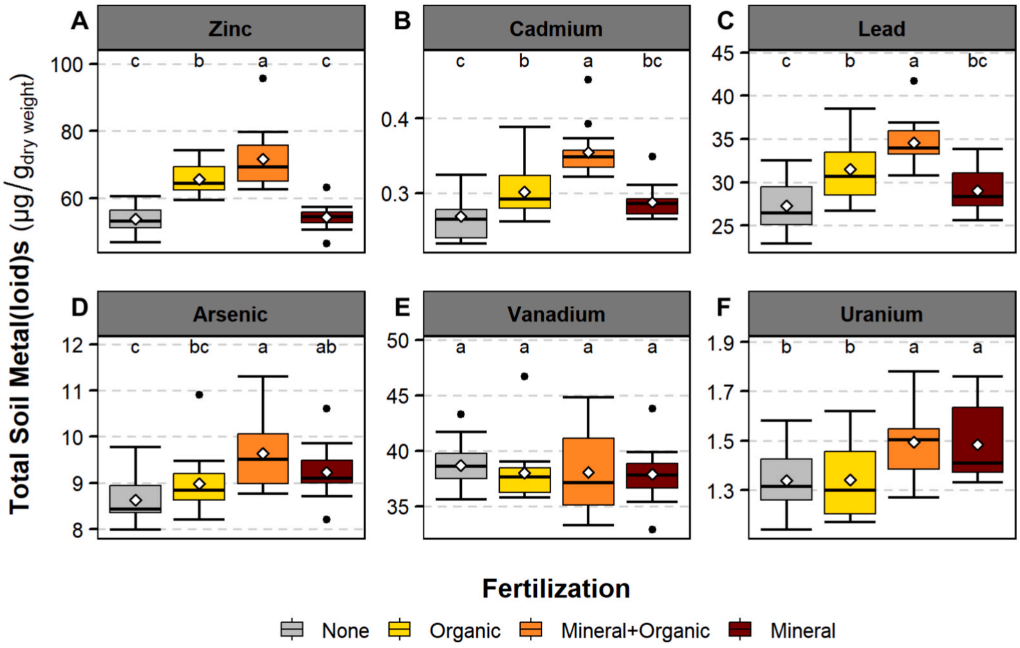

Fig. 1. Total metal(loid)s of historically differently farmed agricultural soils under four fertilization practices; from left to right: none (gray), organic (yellow), mineral+organic (orange), mineral (red) fertilization. Three replicates were sampled between years 2001 – 2020 (n = 14) and compared with each other using a linear mixed-effects model. Different lowercase letters denote groups with significantly different estimated marginal means within each metal(loid) based on Tukey-adjusted pairwise comparison (α = 0.05). The white diamond represents the mean value. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

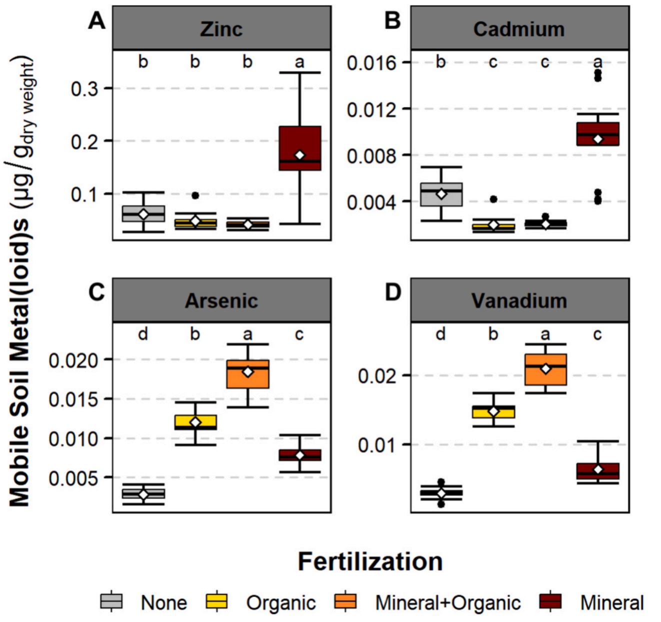

Fig. 2. Mobile metal(loid)s of historically differently farmed agricultural soils. 0.01 M $CaCl_2$-extractable metal(loid)s were quantified under four fertilization practices; from left to right: none (gray), organic (yellow), mineral+organic (orange), mineral (red) fertilization. Lead and U were not detected. Three replicates were sampled between years 2001 – 2020 (n = 14) and compared with each other using linear mixed-effects model. Different lowercase letters denote groups with significantly different estimated marginal means within each metal(loid) based on Tukey-adjusted pairwise comparison ($\alpha = 0.05$). The white diamond represents the mean value. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

soil pools.

3.3. Metal(loid) accumulation and yield in wheat grains

Cadmium concentrations were significantly higher in mineral-fertilized wheat grains, while significantly lower in organic-fertilized wheat grains, compared to unfertilized wheat grains (Fig. 3). The combined mineral+organic fertilization treatment resulted in Cd concentrations similar to those in unfertilized wheat. Zinc concentrations were significantly higher in mineral+organic fertilized wheat grains relative to unfertilized wheat grains, primarily due to higher Zn concentrations in one of the three duplicates (stripe 7, see time resolved data in Fig. S6). Arsenic concentrations were significantly higher in mineral+organic and mineral-fertilized wheat grain, and both exceeded concentrations in organic and unfertilized treatments, which did not statistically differ from each other. Fertilization significantly increased wheat yields, with a 2.4-fold increase for mineral and mixed fertilization, and a 2-fold increase for organic fertilization (Fig. S7). There was no significant difference observed in Pb concentrations between all treatments. Uranium and V were below the detection limit in all wheat grain.

3.4. Strontium and the $^{87}Sr/^{86}Sr$ in soil and wheat grain

Strontium concentrations in total soils, mobile soil pools, and wheat grains were significantly affected by fertilization, with unique patterns observed for the different sample types (Fig. S8, time-resolved data in Fig. S9). Compared to unfertilized soil, total soil Sr concentrations were higher under all fertilization treatments, with the greatest increase in mineral+organic-fertilized soils, followed by organic- and mineral-fertilized soils, between which there was no significant difference.

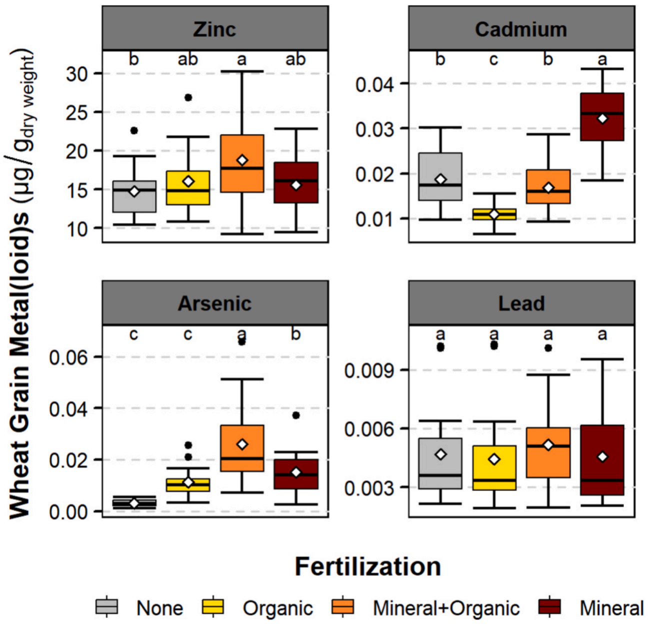

Fig. 3. Total metal(loid)s of historically differently farmed wheat grains grown on soils under four fertilization practices; from left to right: none (gray), organic (yellow), mineral+organic (orange), mineral (red) fertilization. Vanadium and U were not detected. Three replicates were sampled between years 2001 – 2021 (n = 16) and compared with each other using linear mixed-effects model. Different lowercase letters denote groups with significantly different estimated marginal means within each metal(loid) based on Tukey-adjusted pairwise comparison ($\alpha = 0.05$). The white diamond represents the mean value. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Likewise, Sr concentrations in the mobile soil pool were higher under all fertilization treatments, with the highest increase in mineral-fertilized soils, followed by mineral+organic-fertilized, then organic-fertilized soils. In wheat grain, Sr concentrations were significantly higher, to a similar degree for mineral- and mineral+organic fertilized, compared to unfertilized wheat grain.

The $^{87}Sr/^{86}Sr$ ratios approximately ranged between 0.711 and 0.716 in total soils, 0.706 – 0.709 in the mobile soil pool, and 0.707 – 0.710 in wheat grains (Fig. 4, time-resolved data in Fig. S9). Fertilization significantly decreased the $^{87}Sr/^{86}Sr$ ratio across all sample types (total soil, mobile soil pool, and wheat grain) compared to unfertilized samples. The greatest reduction occurred in both mineral and mineral+organic fertilization, for which there were no significant differences between the $^{87}Sr/^{86}Sr$ ratios in the mineral and mineral+organic fertilization treatments. Additionally, wheat grains from these two treatments had similar $^{87}Sr/^{86}Sr$ ratios to the TSP fertilizer (0.70778) (Fig. 4). Under organic fertilization, the $^{87}Sr/^{86}Sr$ ratios across all sample types were significantly lower compared to unfertilized samples but remained higher than mineral+organic and mineral-fertilized samples. Organic-fertilized wheat grains featured an $^{87}Sr/^{86}Sr$ ratio similar to the manure fertilizer (0.70883) (Fig. 4).

In the mobile soil pool, concentrations of As, V, and P were positively correlated with Sr within the organic- and mineral+organic-fertilized treatment groups (r = 0.69 – 0.88) and mineral- and none fertilized treatment groups (0.48 – 0.78) (Fig. 5). The $^{87}Sr/^{86}Sr$ ratio was negatively correlated with As, V, and P in the mobile soil pool of mineral+organic-fertilized soils (r = -0.84 – -0.85) and with As and V in the mobile pool of mineral-fertilized soils (r = -0.64 – -0.75) (Fig. 5). No significant correlation was detected between Cd and the $^{87}Sr/^{86}Sr$ ratio; however, mineral-fertilized soils were characterized by significantly higher Cd concentrations and lower $^{87}Sr/^{86}Sr$ ratios (Fig. 5). In the total soil, metal(loid) concentration generally does not correlate with the

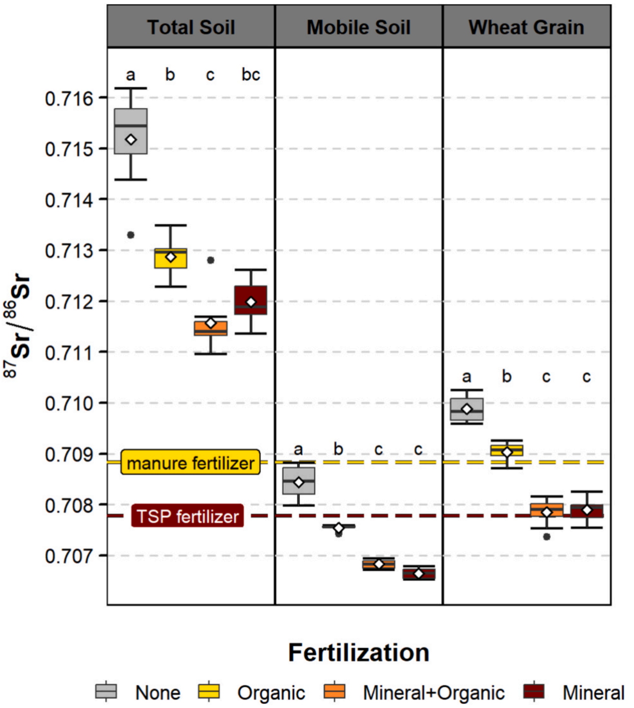

Fig. 4. Strontium isotope ratios ($^{87}Sr/^{86}Sr$) of historically differently farmed agricultural wheat and soil under four fertilization practices; from left to right: none (gray), organic (yellow), mineral+organic (orange), mineral (red) fertilization. The mobile soil pool was approximated by a 0.01 M $CaCl_2$ extraction. The dash lines represent the strontium isotope ratio in pure TSP and manure fertilizers. Two replicates were sampled for each sample type ($n_{total\ soil} = 7$, $n_{mobile\ soil} = 10$, $n_{wheat\ grain} = 10$) between 2001 and 2021 and compared with each other using a linear mixed-effects model. Different lowercase letters denote groups with significantly different estimated marginal means within each metal(loid) based on Tukey-adjusted pairwise comparison ($\alpha = 0.05$). The white diamond represents the mean value. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$^{87}Sr/^{86}Sr$ ratio (Fig. S10). As an exception, U and V show a significant positive correlation with the $^{87}Sr/^{86}Sr$ ratio only in nonfertilized soils ($r = 0.96$ and 0.85, respectively) and Sr shows a significant correlation with V in all treatments ($r = 0.86 – 0.95$, Fig. S10).

4. Discussion

4.1. *Fertilization-driven metal(loid) input and entry into wheat*

Due to fertilization, modern agriculture is a major source of metal(loid)s in soil and potentially in crops (Rodríguez Eugenio et al., 2018). Many studies have shown, including the results of our study, that mineral fertilizers, particularly TSP, contribute the highest concentrations of metal(loid)s to agricultural soils. Although farmyard manure contained lower levels of metal(loid)s, it is applied in greater quantities than mineral fertilizers and thus the resulting total metal(loid) input from organic fertilization may be comparable or even higher than mineral fertilization (Table S2). A notable exception to this trend is U, which is scarce in manure, due to its low presence in animal feed materials, but abundant in TSP due to the high concentrations of U in phosphate rock from which it is manufactured (Azzi et al., 2017; Hill et al., 2024; McBride and Spiers, 2001; Shtangeeva, 2010).

Despite differences in fertilizer metal(loid) inputs, total soil metal(loid) contents did not vary proportionally between mineral- and organic-fertilized soils. This is likely due to the vast difference in mass between the applied fertilizer and the receiving soil, which is mixed through tillage. Our estimates suggest that even after over 120 years of fertilization, metal(loid) differences between mineral- and organic-fertilized soils ranged from 0.2 to 106 kg/ha, which are much smaller compared to approximately 4,200 metric tons of soil per hectare in the tilled top 30 cm (Table S2). These values should be treated as rough estimates intended to illustrate observed trends, based on assumptions of a closed system without leaching or plant uptake and constant, uniform metal inputs same as in the assessment year. This approach does not account for long-term variability in fertilizer composition, soil redistribution through plowing, slight differences in management, crop uptake, atmospheric deposition, or weather-driven leaching, limiting the precision of a complete mass balance over 120 years. Vertical redistribution through carbonate leaching may also occur, but profile data from the same Haplic Chernozem at Bad Lauchstädt (to 190 cm depth) show accumulation of metal(loid)s in the topsoil, with the highest enrichment in the top 30 cm and markedly lower concentrations below (Altermann et al., 2005). This indicates that although some leaching and downward movement occur, the dominant accumulation of fertilizer-derived metal(loid)s remains in the plough layer.

The mobile soil pool, which is potentially phytoavailable (Kim et al., 2015), is more relevant for crop uptake than total soil metal(loid) concentration. In our study, a 0.5-unit soil pH decrease is observed in mineral-fertilized soils, resulting in increased metal(loid) concentrations in the mobile soil pool, particularly for cations such as Cd^{2+}, Zn^{2+}, and Sr^{2+} than for oxyanions like As and V in the predominant forms of $H_2AsO_4^-$ and $H_2VO_4^-$ (Fig. 2, Fig. S8). Although ICP-MS detects only total elemental concentrations, As and V are referred to as oxyanions here because the prevailing pH/Eh conditions of the studied soil indicate that $H_2AsO_4^-$ and $H_2VO_4^-$ are the dominant species (Brookins, 1988). Soil acidification can be driven by ammonium-based fertilizers, such as CAN, allowing soil minerals like carbonates and iron oxides to dissolve and release absorbed metal(loid)s into the mobile soil pool (Barak et al., 1997; Bolan et al., 2003; He et al., 2007; Schwertmann, 1991). In addition, acidification increases the surface charge of soil particles, further reducing cation binding due to electrostatic repulsion (Violante et al., 2010). Concurrently, protons released through ammonium oxidation, along with other fertilizer-derived ions (e.g., Ca^{2+}, NH_4^+, K^+, NO_3^-, $H_2PO_4^-$) compete for remaining adsorption sites or form soluble ion pairs, further enhancing metal(loid) mobilization (Rieuwerts et al., 2006; Violante and Pigna, 2002), as observed in the mineral-fertilized mobile soil pool reported in our study.

Once mobilized, metal(loid)s are passively transported toward plant roots via mass flow, where water movement, a non-selective process driven by plant transpiration (Šimůnek and Hopmans, 2009; Sterckeman and Thomine, 2020). In addition, plants actively take up essential metal(loid)s through specific transporters that toxic metal(loid)s can exploit due to their chemical similarity (Colangelo and Guerinot, 2006). For example, Cd^{2+} can enter the plants via Zn^{2+} or Fe^{2+} transporters, $H_2AsO_4^-$ via $H_2PO_4^-$ transporters, and Pb^{2+} and Sr^{2+} via Ca^{2+} transporters (Capo et al., 1998; Zhao et al., 2022). In our study, both the passive and active uptake mechanisms to the wheat were likely enhanced by the increase in the mobility of toxic metal(loid)s in the mineral-fertilized soil (Fig. 2, Fig. 3). Grain accumulation of non-essential elements such as Cd and As closely followed their mobility in soil, as also supported by soil–grain correlations (Fig. S11–S12). However, Zn was not enriched in the wheat grain despite its increased mobility in soil (Fig. 2, Fig. 3, Fig. S12) likely due to its function as an essential micronutrient in plants with tightly regulated uptake, allowing plants to maintain optimal internal Zn levels despite changes in soil availability pools (Stanton et al., 2022).

Farmyard manure contains complex carbon as functional groups or minerals, which can enhance metal(loid) scavenging via adsorption, precipitation, or complexation (Caporale and Violante, 2016; Lair et al., 2007; Park et al., 2011; Sun et al., 2017). Additionally, manure application can buffer soil pH by reversible protonation of organic acids and acid neutralization via manure-born carbonates and bicarbonates

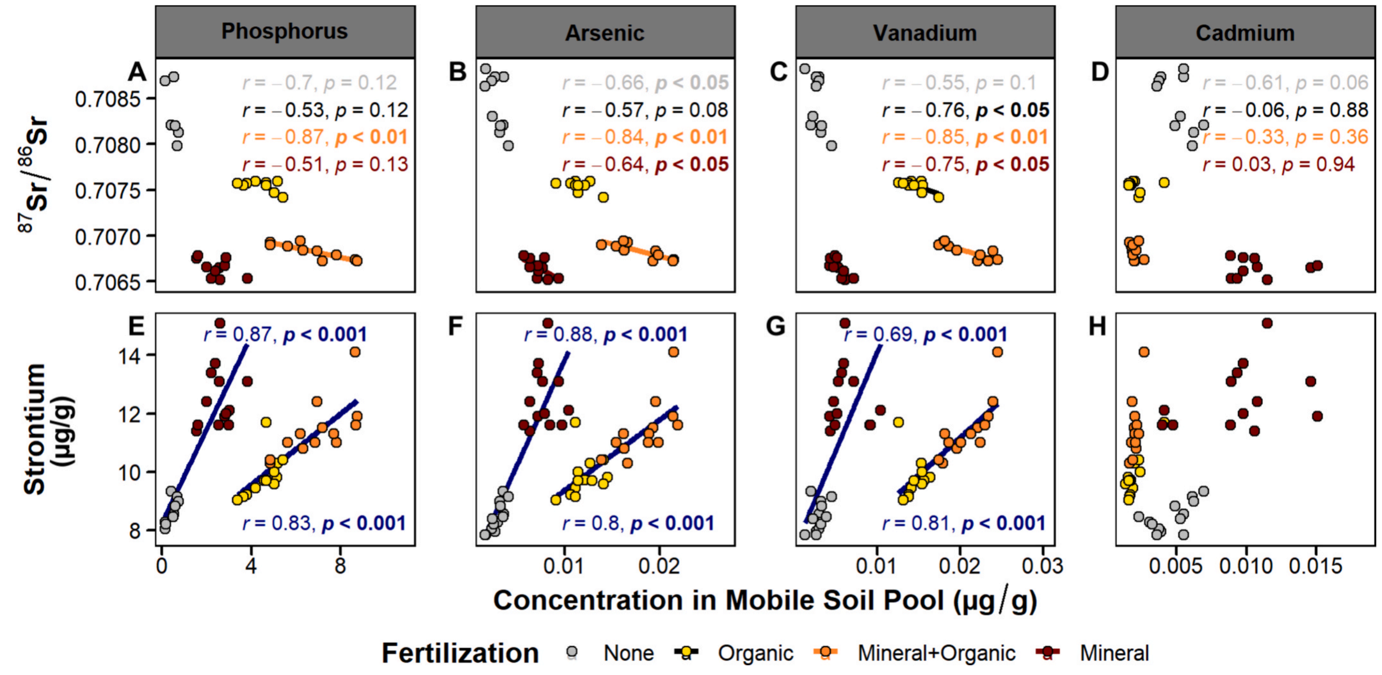

Fig. 5. (A:D) Relationship between P, As, V, and Cd and the strontium isotope ratio ($^{87}Sr/^{86}Sr$) and Sr concentrations in the mobile pool of historically differently farmed agricultural wheats and soils under four fertilization practices between years 2001 and 2021: none (gray), organic (yellow/black), mineral+organic (orange), mineral (red) fertilization. Pearson correlations were conducted between select elements and the $^{87}Sr/^{86}Sr$: the Pearson correlation coefficient (r) is used to assess the linearity of a modeled fit line and deemed statistically significant where $p < 0.05$ and best fit lines are plotted where significant trends are observed. (E:H) Similarly, Pearson correlations and modeled fit lines were conducted between elements with significant $^{87}Sr/^{86}Sr$ ratio trends (i.e., P, As, & V) and Sr, where combined significant trends were determined for fertilization treatments containing manure application (organic and mineral+organic) and those that do not (mineral and none). Three replicates were measured for elemental analysis and two replicates for isotope analysis.

(Eghball, 1999; Li et al., 2012; Naramabuye and Haynes, 2006; Whalen et al., 2000). In our study, organic fertilization increased soil OC by ~ 45% and pH by ~ 0.7 units relative to unfertilized soils (Fig. S3). Higher soil pH promotes cation binding and repels anions due to increasing negative surface charges on soil particles (Beiyuan et al., 2017; Violante et al., 2010). This is most pronounced in organic- and mineral+organic-fertilized soils by the decreased mobility of positively charged Cd^{2+} and increased mobility of negatively charged oxyanions such as $H_2AsO_4^-$ and $H_2VO_4^-$ compared to unfertilized soils (Fig. 2). Decreased Cd^{2+} mobility in the soil led to lower accumulation of Cd^{2+} in wheat grains compared to unfertilized ones (Fig. 2, Fig. 3). Zinc accumulation in wheat grains remained unchanged, likely due to its naturally high soil concentrations (Fig. 1), maintaining sufficient phytoavailability despite reduced mobility. In contrast, Pb is generally poorly mobile in soils due to its high molecular weight and electron charge density (Pourrut et al., 2011; Stanton et al., 2022), as evident by undetectable levels in the mobile pool even without fertilization (Fig. 2). This limits its transfer across the soil–plant barrier (Xiong et al., 2014); organic fertilization did not further reduce this already minimal transfer. Although organic fertilization increased $H_2AsO_4^-$ mobility in soil, this did not result in higher overall As accumulation in wheat grains. This is possibly due to As being bound to manure-derived organic matter, forming large complexes that were less available for root uptake (Kumar et al., 2021). Moreover, wheat roots have effective mechanisms to regulate As translocation within a plant, including As efflux, and sequestration via thiol complexation in the roots, which limit As movement to the grains (Shi et al., 2015).

In soil treated with both mineral and organic fertilizer, the binding site composition resembled that of solely organic fertilization, as indicated by similar SOC and pH levels and confirmed by clustering analysis (Fig. S3, Fig. S13). While organic matter typically reduces As bioavailability through sorption and complexation (Caporale and Violante, 2016), the combined application of mineral and organic fertilizers here counteracted this effect (Fig. 2), likely due to ions derived from the addition of mineral fertilizer, occupying more binding sites. Specifically, $H_2PO_4^-$ can displace $H_2AsO_4^-$ due to their similar size, increasing $H_2AsO_4^-$ mobility and following uptake by plant roots (Violante and Pigna, 2002). In contrast, this effect was less pronounced for cationic metals (i.e., Cd^{2+} and Zn^{2+}), likely due to the abundance of negatively charged soil particles maintaining strong metal retention. However, competition with NPK-derived cations could still weaken soil binding capacity for cationic metal(loid)s, which aligns with the observed increase in Cd accumulation in wheat grains compared to solely organic fertilization (Fig. 3).

4.2. Fertilization effect on wheat grain quantity and quality

While manure application supports long-term soil fertility by enhancing organic matter content and gradual nutrient release, NPK fertilizers provide readily available nutrients that boost immediate wheat yields (Crowder and Reganold, 2015; Seufert et al., 2012), as also observed in our study with a tendency for higher yields under mineral fertilization compared to organic fertilization. Balancing high yields with soil health has driven more recent discussions on integrating organic and mineral fertilization (Reganold and Wachter, 2016). Our results support this approach, showing that mineral+organic fertilization maintains wheat yields (Fig. S7) at the same level as mineral fertilization while improving soil parameters such as pH and organic carbon (Fig. S3). Furthermore, clustering analysis confirmed that grain metal(loid) concentrations were more closely associated with mobile soil metal(loid) pools and soil parameters than with total soil metal(loid) concentrations (Figs. S11-12, with confirmation with PCA in Fig. S13).

The concern that higher yields may lead to the dilution of essential micronutrients, such as Zn, has been discussed (Bhardwaj et al., 2024; Fan et al., 2008). However, our results do not support this concern. Regardless of fertilization type, wheat grain Zn concentrations (ug/g) did not decline under fertilization (Fig. 3). Across all treatments, grain Zn concentrations aligned with concentrations typically found in wheat grown on soils with sufficient Zn (20–30 μg/g grain), and in yield-corrected terms (g/ha), fertilized plots exported more Zn due to greater yields (Fig. S14) (Cakmak, 2008).

Among tested treatments, mineral+organic fertilization was most effective, increasing grain Zn concentrations by 28% compared to the unfertilized control. However, achieving the biofortification target of 37 μg/g grain to address widespread dietary Zn deficiency may still require selecting soils with naturally higher Zn mobility and/or wheat varieties with enhanced Zn uptake and translocation (Bouis and Saltzman, 2017). Resembling previous studies, our results suggest that Cd concentrations increase in soils and wheat grain under mineral fertilization. However, when considering both wheat quality and yield, mineral+organic fertilization might offer a balanced compromise. Even with mineral fertilization, Cd concentrations of wheat grains in our study (0.006 – 0.043 μg/g) were well below the maximum permissible Cd levels set by the Codex Alimentarius Commission and even the more stringent European Commission regulation (0.2 and 0.1 mg/kg, respectively) (Codex Alimentarius Commission, 2023; European Commission, 2023). However, it is important to note that the Chernozem soil in this study has a strong Cd adsorption potential and low natural Cd concentrations (Fig. 1) (Altermann et al., 2005), placing it in the lower range of Cd concentration across soils worldwide and highlighting the suitability of this soil for high agricultural productivity (de Vries et al., 2022; Hou et al., 2025). However, the observed 72% increase in Cd due to mineral fertilization in comparison with unfertilized wheat grain (Fig. 3) is still concerning, as it could render wheat unsafe in other soil types with higher background Cd concentrations and lower potential adsorption capacity.

Regional studies, such as those from China, Germany, New Zealand, Idaho (USA), show that Cd in wheat grains purchased from food markets can reach or slightly exceed the 0.1 and 0.2 mg/kg thresholds, potentially violating food safety regulations in the future with continuous mineral fertilization (Gao et al., 2022; Gray et al., 2019; Hüsken et al., 2024; Strawn et al., 2022). While these regional findings offer valuable insights, global assessments of Cd in food remain scarce, especially in areas undergoing deforestation and in vicinity of mining as these activities lower soil pH and organic matter content (Mgelwa et al., 2025; Rice and Herman, 2012). These conditions could lead to higher Cd mobility and plant uptake, underscoring the need for further investigation.

Arsenic accumulation is of more concern in crops cultivated in anoxic waterlogged soils (i.e., rice) rather than crops grown on oxic soils (i.e., wheat) due to redox-driven changes in bioavailability (Takahashi et al., 2004; Zhao et al., 2010). Consequently, multiple regulations exist for As concentrations in rice, while no specific limits have been set for wheat grains by the WHO or the EU (Codex Alimentarius Commission, 2023; European Commission, 2023). Our results show that all three types of fertilization treatments investigated here may increase As concentrations in wheat grains by up to an order of magnitude (up to 0.066 μg/g) compared to unfertilized wheat grain (0.003 ± 0.002 μg/g), particularly highest in mineral+organic fertilization (Fig. 3). This increase may be further enhanced under alkaline conditions, where arsenic mobility is typically elevated (Fendorf et al., 2010). We suggest that in our setting under mineral fertilization, elevated As accumulation was primarily driven by competition for sorption sites with NPK-derived ions. Whereas in mineral+organic treatments, this effect was likely compounded by the presence of organic matter, which may inhibit inner-sphere binding of As to soil minerals and thus maintain it in more mobile, plant-available forms. This finding serves as a cautionary note for rice studies where As solubility and plant uptake could be further enhanced by manure application (Tang et al., 2021). In light of the processes observed here, further research is warranted to explore the combined effects of mineral and organic fertilization on As accumulation in rice grains.

4.3. Utilizing the $^{87}Sr/^{86}Sr$ ratio to trace fertilizer-derived metal(loid) enrichment in the soil-wheat system

The ^{87}Sr/^{86}Sr variation in soils and plants is sensitive mostly to Sr-rich soil amendments (Drouet et al., 2005; Hill et al., 2024; Schmitt et al., 2023). In the present study, we found that elements of As, V, and P exhibit strong relationships with the ^{87}Sr/^{86}Sr in the mobile soil pool and that mineral fertilization significantly lowers the ^{87}Sr/^{86}Sr ratio and increases the Cd concentrations of wheat grain and the mobile soil pool (Fig. 5). In the soil–plant system, previous work has shown that the ^{87}Sr/^{86}Sr of vegetation is similar to that of the bioavailable pool in the soil in which it is rooted (Oeser and von Blanckenburg, 2020), and that the magnitude of mineral fertilization can have a synonymous effect on the Sr, P, and ^{87}Sr/^{86}Sr ratio in the mobile pool of agricultural soils (Hill et al., 2024). Unlike any previous studies, in this study we examined four different fertilization practices, including the characterization of the ^{87}Sr/^{86}Sr ratio of organic- and mineral+organic fertilized soils and crops. We found that fertilization significantly reduced the ^{87}Sr/^{86}Sr ratio of total soil towards the isotope ratio of the applied fertilizers (Fig. 4). Although fertilization increased total soil Sr, the ^{87}Sr/^{86}Sr ratio of total soils did not fully mimic that of the applied fertilizers unlike the wheat grain, likely due to the influence of a Sr flux inherent to the solid soil materials as exhibited by the isotope ratios in the unfertilized soils. This Sr isotope tracing is possible due to the fertilizer Sr isotope composition being significantly different from the background Sr isotope composition of the soil (Fig. 4).

In contrast, the ^{87}Sr/^{86}Sr fingerprint of the TSP fertilizer was inherited totally by the mineral-fertilized wheat grain, although potash and CAN were also applied (Fig. 4). The consistency of the isotope fingerprint of the mineral fertilizers within the wheat grain is confirmed by the Sr mass balance calculation. Considering the Sr flux (Table S2) and ^{87}Sr/^{86}Sr ratio of the mineral fertilizers (Table 1), the "applied ^{87}Sr/^{86}Sr ratio" in the mineral fertilization treatment is 0.70798, which is only slightly higher than that of the TSP. This is because the Sr flux from TSP fertilizer (139 g/ha/yr) is substantially higher than the Sr flux from either CAN (5.5 g/ha/yr) or Potash (4.37 g/ha/yr). Such a mass balance calculation for the mixed fertilization treatment is more complex due to the effects of organic fertilizer on the soil chemistry and mobility of Sr. The co-enrichment of Sr and Cd in mineral-fertilized wheat grain is accompanied by an ^{87}Sr/^{86}Sr ratio that is different from organic-fertilized and unfertilized wheat grain, which allows us to isotopically associate Cd enrichment in wheat grain with mineral fertilization (Fig. 5).

In addition to mineral-fertilized wheat grain, mineral+organic-fertilized wheat grain exclusively inherited the ^{87}Sr/^{86}Sr ratio of the TSP fertilizer. The TSP contained higher Sr concentrations than the manure and flux calculations showed higher annual application of Sr by the TSP compared to manure (Table S2). Sole observance of the TSP ^{87}Sr/^{86}Sr ratio in mineral+organic-fertilized wheat grain is likely due to Sr from the TSP being more mobile than that from manure, as shown by the 35% increase in mobile soil Sr in mineral+organic fertilization vs 16% in organic fertilization compared to no fertilization, even though the total absolute Sr flux from fertilizer in mineral+organic fertilization was only 6.5% higher than organic fertilization alone. Nonetheless, the enrichment of Sr in organic-fertilized wheat grain was accompanied by an ^{87}Sr/^{86}Sr ratio similar to that of the manure fertilizer (Fig. 4), which emphasizes the sensitivity of Sr isotope as a tracer for the sources of applied fertilizers in wheat grains.

Significant relationships were found in the mobile soil pool between the ^{87}Sr/^{86}Sr ratio and oxyanions (Fig. 5). In many cases in the mobile soil pool, greater enrichment of these elements was associated with further reduction of the ^{87}Sr/^{86}Sr ratio (Fig. 5). Thus, here the magnitude of mobile oxyanion enrichment may be associated with a greater influence of the ^{87}Sr/^{86}Sr ratio on the mobile soil pool. This relationship further extends to Sr concentrations, where significant positive correlations were observed between Sr and these oxyanions (Fig. 5). These correlations did not persist in wheat grain (Fig. S15) due to the different plant uptake pathways (i.e., Sr through Ca/cation pathways and As and V via phosphate/anion pathways) that are subject to unique physiological regulation.

Interestingly, the enrichment of Sr, present as Sr^{2+}, is unique for fertilization treatments receiving manure application and those that are not (Fig. 5), further showcasing the muffled Sr enrichment observed in organic and mineral+organic fertilization due to manure application. Differences in the trends of Sr^{2+}, Cd^{2+}, and Zn^{2+} in the mobile soil pool likely stem from the significantly larger radius of Sr^{2+} compared to the other cations, which allows Sr^{2+} to behave more like Ca^{2+} for which it is similar in size (Capo et al., 1998). Furthermore, while Zn^{2+} tends to form inner-sphere complexes in soils and Cd^{2+} a mix of inner- and outer-sphere complexes, Sr^{2+}, like Ca^{2+}, primarily forms outer-sphere associations, allowing its mobility to be less pH dependent than Cd^{2+} and Zn^{2+} (Appel and Ma, 2002; Gu and Evans, 2008; Kamel, 2010; Martínez et al., 2006; Sahai et al., 2000; Smičiklas et al., 2015). Thus, the level of Cd enrichment in the mobile soil pool cannot be reflected by the $^{87}Sr/^{86}Sr$ variations. However, it is significant that the enrichment of Cd in the mobile soil pool and wheat grain is accompanied by an $^{87}Sr/^{86}Sr$ ratio that is distinctive from the background isotope ratio and indicative of the TSP applied in mineral fertilization (Fig. 5).

Although the $^{87}Sr/^{86}Sr$ ratios of the mobile soil pools had a similar trend as the $^{87}Sr/^{86}Sr$ ratios in wheat grain (i.e., lower ratios for fertilized soils), the mean $^{87}Sr/^{86}Sr$ ratio in each fertilization type were 0.0011 – 0.0015 lower in the mobile soil pool compared to the wheat grain (Fig. 4). We approximated the mobile soil pool via an ammonium acetate (NH_4Ac) extraction method, as done in a previous study (Oeser and von Blanckenburg, 2020), and found no significant difference in the $^{87}Sr/^{86}Sr$ ratios of the mobile soil pool approximated by either the NH_4Ac or $CaCl_2$ extraction methods (Table S3), further showing that, for this soil, the mobile soil pool does not fully represent the wheat-available soil pool in regard to Sr. This discrepancy likely reflects the fact that chemical extractions emphasize exchangeable and carbonate-associated Sr, whereas plants integrate Sr uptake over the growing season from the rhizosphere solution. In our system, the dominant Sr source for wheat was the directly labile Sr in fertilizer or manure inputs, while other Sr sources contributed little to plant uptake because of high Ca:Sr competition and localized rhizosphere processes.

Fertilization affected soil $^{87}Sr/^{86}Sr$ via two coupled pathways: (1) direct addition of exogenous Sr carrying the fertilizer isotope signature, and (2) fertilization-induced changes in soil chemistry that alter the relative contribution of native Sr pools to the mobile fraction (e.g., enhanced mineral dissolution/exchange). The former is evident in the wheat grain while the latter is reflected in the mobile soil pool which shifted toward lower $^{87}Sr/^{86}Sr$ ratios and co-varied with specific mobile metal(loid)s. The $^{87}Sr/^{86}Sr$ isotope ratio is conservative and reflects mixing rather than isotope fractionation, limiting its utility in directly describing effects of geochemical changes (e.g., pH or SOC) but still provides valuable insight due to correlations with metal(loid)s reflecting shared geochemical controls. While metal(loid) concentration data alone may be sufficient to show that fertilization increases metal(loid) contents in wheat grain, they cannot distinguish whether Sr and co-occurring metal(loid)s are primarily derived from fertilizer inputs or mobilized soil reserves. Given that the wheat grain $^{87}Sr/^{86}Sr$ ratio mimics that of the applied fertilizers, our data supports the significant influence of soil amendments on the $^{87}Sr/^{86}Sr$ ratio of wheat grain and clearly demonstrates the utility of this approach for tracing contamination sources in wheat grain.

5. Conclusions

This 120-year fertilization trial shows that fertilization influences soil–plant metal(loid) transfer mainly through changes in soil chemistry rather than total soil concentrations. Shifts in pH and organic matter controlled the mobility of cationic metals (Cd, Zn) and oxyanions (As, V), thereby shaping their accumulation in wheat grains. The $^{87}Sr/^{86}Sr$ isotope ratio proved to be a robust tracer, distinguishing fertilizer-derived inputs from the soil background, such as for Cd, and reflecting shared geochemical controls with specific metal(loid)s, such as As, V, and P. Although the distinct difference in the $^{87}Sr/^{86}Sr$ isotope ratio between native soil and the fertilizers allowed for its utility as a tracer, this may not be possible for other systems where soil amendments and soil background contain similar Sr isotope ratios. The provenance information provided by the Sr isotope ratio can be particularly valuable in cases where the metal(loid) concentrations of soil amendments overlap with native soil concentrations, or where contamination sources in environments adjacent to agricultural operations are uncertain. However, these findings are based on a single Chernozem soil and should be validated in other soil types, particularly more acidic soils with lower organic carbon and clay contents where metal(loid) mobility may be greater. We therefore highlight the need for future research to validate these findings in other long-term experiments established on soils with different textures (e.g., sandy soils) and pH buffering capacities (e.g., acidic soils). Despite these limitations, the study provides valuable long-term reference data on how fertilization shapes soil and crop quality. It highlights that fertilizer composition affects not only nutrient supply but also contaminant transfer, with direct implications for management and regulation. The isotope-tracing framework introduced here offers a model for future studies and a potential tool for monitoring fertilizer-related contamination in agroecosystems.

CRediT authorship contribution statement

Robert C. Hill: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Aleksandra Pieńkowska:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ines Merbach:** Writing – review & editing, Methodology, Investigation, Data curation. **Thomas Reitz:** Writing – review & editing, Supervision, Methodology, Investigation. **E.Marie Muehe:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Avner Vengosh:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

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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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2025.109851.

Data availability

The data that support the findings of this study can be accessed at https://doi.org/10.7924/r40293w8x.

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