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Mitigation of the mobilization and accumulation of toxic metal(loid)s in ryegrass using sodium sulfide

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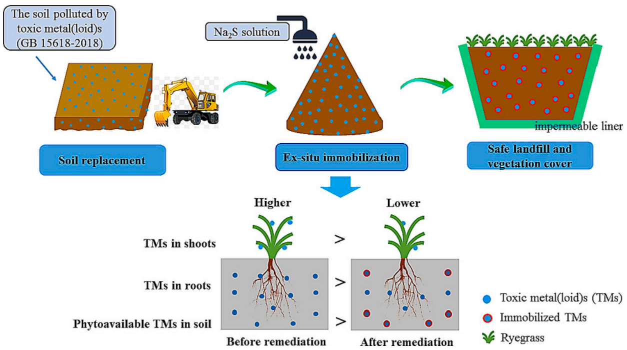
HIGHLIGHTS

- In two sites of field investigation, Na_2S immobilized soil toxic metal(loid)s (TMs).
- Na_2S lowered the leachability of As, Cd, Cu, Hg, Ni, Pb, and Zn from treated soils.
- Na_2S reduced the DTPA-extractable TMs down to 85.9 % compared to control.
- Na_2S decreased TM uptake by ryegrass and their root-to-shoot translocation.
- Na_2S has a great potential to remediate soils heavily polluted with TMs.

GRAPHICAL ABSTRACT



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ABSTRACT

Remediation of soils contaminated with toxic metal(loid)s (TMs) and mitigation of the associated ecological and human health risks are of great concern. Sodium sulfide (Na_2S) can be used as an amendment for the immobilization of TMs in contaminated soils; however, the effects of Na_2S on the leachability, bioavailability, and uptake of TMs in highly-contaminated soils under field conditions have not been investigated yet. This is the first

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Sulfur-rich amendments
Phytoavailability
Risk mitigation

field-scale research study investigating the effect of Na_2S application on soils with Hg, Pb and Cu contents 70-to-7000-fold higher than background values and also polluted with As, Cd, Ni, and Zn. An ex situ remediation project including soil replacement, immobilization with Na_2S, and safe landfilling was conducted at Daiziying and Anle (China) with soils contaminated with As, Cd, Cu, Hg, Ni, Pb and Zn. Notably, Na_2S application significantly lowered the sulfuric-nitric acid leachable TMs below the limits defined by Chinese regulations. There was also a significant reduction in the DTPA-extractable TMs in the two studied sites up to 85.9 % for Hg, 71.4 % for Cu, 71.9 % for Pb, 48.1 % for Cd, 37.1 % for Zn, 34.3 % for Ni, and 15.7 % for As compared to the untreated controls. Moreover, Na_2S treatment decreased the shoot TM contents in the last harvest to levels lower than the TM regulation limits concerning fodder crops, and decreased the TM root-to-shoot translocation, compared to the untreated control sites. We conclude that Na_2S has great potential to remediate soils heavily tainted with TMs and mitigate the associated ecological and human health risks.

1. Introduction

The Tongguan County is one of the main gold production areas in China, and its gold mining, metallurgy and separation activities can date back to 200 BCE (Liu et al., 2021). Atmospheric deposition, slag accumulation, weathering processes, insufficient protective technical diffusion barriers, and a rather relaxed regulation enforcement framework have inevitably led to heavily contaminated surrounding soils with potentially toxic metal(loid)s (TMs), which has been documented previously (Khan et al., 2021; Qi et al., 2022; Liu et al., 2021). The Chinese State Council has proposed a plan, the Soil Pollution Prevention and Control Action Plan (namely Soil Ten Chapters), to prevent soil pollution. With this, a series of massive soil remediation projects to restore contaminated soils have been launched (CSC, 2016). At present, the remediation projects of the contaminated sites in China are characterized by high pollutant removal rates, short construction periods, and adequate budgets; thus ex situ restoration technologies have been widely applied in industrial and mining polluted sites (Song et al., 2022; Yang et al., 2023). For heavily polluted soils, the most widespread decontamination method is soil excavation followed by its transportation to a safe landfill location (Guemiza et al., 2017; O'Brien et al., 2021; Ok et al., 2020; Yang et al., 2023).

Recently, immobilization and phytoremediation technologies have also been highly recommended for TMs remediation of polluted sites in China and worldwide, which is also acknowledged as the optimal treatment for disposal of 57 species of wastes by the U.S. EPA (Kumar et al., 2022; Wang et al., 2021a, 2021b; Menhas et al., 2023). Meanwhile, a large number of soil amendments for immobilization of TMs in contaminated soil have been emerged (He et al., 2021; Palansooriya et al., 2020; Shi et al., 2023; Wang et al., 2021a, 2021b; Xu et al., 2022; Grammenou et al., 2023). For example, organic amendments (e.g., processed animal wastes, biochar, biosolids/sewage sludge, and compost/plant residues) and inorganic amendments (such as clay minerals, ashes, liming materials, metal oxides/red mud, phosphorus compounds, and inorganic sulfides) have been identified as immobilization agents, due to their ability to reduce TMs mobility in soil (Abukari et al., 2022; Kumpiene et al., 2019; Man et al., 2021; Shaheen et al., 2023; Xiao et al., 2022; Xing et al., 2022; Yang et al., 2021). Among these, sodium sulfide (Na_2S) has a strong affinity for TMs, owing to Lewis acid and base soft-soft interactions and to the smaller solubility product constants of the produced metal sulfides (Wang and Mi, 2017). To date, Na_2S has been recognized as a metal precipitant and frequently applied in soil to achieve decontamination (Lu et al., 2017; Zhang et al., 2020). For instance, Zhang et al. (2020) demonstrated that 0.25 % (w/w) Na_2S application considerably reduced DTPA-extractable Pb and Zn in soils that were mildly and seriously contaminated. Moreover, efficient immobilization and a decrease in soil Cr(VI) were reported by Yuan et al. (2018) after Na_2S incorporation with mechanochemical treatment. However, most of these studies were carried out under laboratory pot culture and artificial addition of TMs in unpolluted soils. Furthermore, the effect of Na_2S addition on TMs uptake by cultivated plants in multi-element contamination has not been sufficiently explored, especially under field conditions. Hence, it is imperative to investigate the impact of Na_2S on the immobilization and phytoavailability of TMs in a field study.

Moreover, due to the distressing situation of climate change, the world, and especially China, is facing a decrease in arable land productivity; hence, the focus of the global attention should be the rational utilization of restored resources (Ye et al., 2022; Wang et al., 2023). In this regard, Zang et al. (2017) proposed that plants that act as TM stabilizers (i.e., with edible parts able to have TM content below the safety regulation limits) could be a viable solution for cultivating soils seriously contaminated with TMs. Ryegrass (*Lolium perenne* L.), widely used as a fodder crop for pigs, cattle, sheep and other large livestock animals, is frequently cultivated in many parts of China due to its high yield and nutrient content (Mori, 2021). Therefore, ryegrass was selected in this study to investigate its accumulation of TMs under Na_2S application. Song et al. (2019) reported that metal sulfides, i.e., ZnS and MoS_2, significantly reduced the uptake of Cd, Pb, As, Cr, Cu, Ni, and Zn by roots, stems, and leaves of cucumber, and this was attributed to the strong complexation of the sulfides and their high affinity with soil TMs. Therefore, in this study we hypothesized that Na_2S application may decrease soil acid (sulfuric-nitric)-leachable and DTPA-extractable TMs, allowing TMs in the excavated soil to be stabilized in the soil matrix and ryegrass shoots to have sufficiently low TM contents to satisfy fodder regulation standards. Hence, the objectives of this study were (i) to evaluate soil pollution and map the soil spatial and vertical distribution characteristics of TMs (As, Cd, Cu, Hg, Ni, Pb and Zn); (ii) to quantify the efficacy of Na_2S in immobilizing soil TMs (i.e., reducing the leachable and DTPA-extractable TM concentrations) and in affecting soil properties; and (iii) to investigate TM uptake and translocation in ryegrass and how these are affected by Na_2S. This study is novel because it is the first field-scale research study investigating the effect of Na_2S application on soils with Hg, Pb and Cu concentrations 70-to-7000-fold higher than background values and also polluted with other TMs including As, Cd, Ni, and Zn.

2. Materials and methods

2.1. Experimental site and remediation processes

The study site was located in Tongguan County, Shaanxi Province (110°09′–110°25′E, 34°23′–34°40′N). One of the dominant pollution sites in the county was a series of industrial production parks at the Daiziying site, which was the main gold production location in Tongguan County and the most heavily-polluted site for TMs, and was closed down by the government for several years; the other was the mining tailing pond named the Xitongyu No. 3 Bridge at the Anle site, which was used for depositing tailings or other industrial wastes from gold mines after ore sorting; therefore, the soils at both the Daiziying and Anle sites were seriously threatened by TM pollution. The Daiziying and Anle sites belong to the warm temperate zone of continental monsoon climate, and the basic properties of the contaminated soils at Daiziying and Anle sites are shown in Table S1 (Supplementary Information). To preserve the ecological environment and human health, the whole remediation project was ordered by the Chinese Central Government in

2019. The complete set of treatments included soil replacement, ex situ restoration, safe landfilling and vegetation cover. The remediation processes of the Daiziying and Anle sites were carried out separately, i.e., landfills were established at each of the two sites. The description of the whole remediation process is shown schematically in the Supplementary Materials (Fig. S1; Supplementary Information), and the details were as follows: i) In August 2020, the TM-polluted soils at a depth of 1 m were excavated and transported to a passivation center; ii) In October 2020, the air-dried soils were transferred to the mixing equipment with a loader, and fully mixed with sodium sulfide (Na_2S) solution (1000 L of water at 50–60 °C containing 500 kg of sodium sulfide) that was homogeneously sprayed through a metering pump in the soil at a mixing ratio of 1:200 (solution: soil); iii) In January 2021, the treated soils were transported to the landfill; before that, an anti-seepage system was fitted at the bottom of the landfill, including laying geotechnical cloth (200 g m^{-2} and 600 g m^{-2}) and 1.5-mm HDPE impervious membrane, and then backfilled using the layered roller compaction method (Fig. S2, Supplementary Information); iv) In March 2021, perennial ryegrass (*Lolium perenne* L.) was planted on the top of the backfill site in disperse form, and cultivated with a seeding rate of 150 kg ha^{-1} and fertilizer rate of 750 kg ha^{-1} of calcium-magnesium phosphate—this treatment was labeled as “After remediation.” Meanwhile, a portion of the excavated soil was treated in the same way as mentioned above except for Na_2S application, and planted with ryegrass at the same planting density and management patterns of water and fertilizer, which was labeled as “Before remediation,” namely the control treatment. The mature state of ryegrass before and after remediation treatment was shown in the Supplementary Information (Fig. S3). Ryegrass planted on Na_2S-treated soil grew better than that without Na_2S application, and its leaves were greener and fuller. Furthermore, the Na_2S applied in this study was in the form of light yellow flakes, with a purity >60 %, a pH value of 12, a relative density (d164) of 1.43, and a melting point of 950 °C; it was purchased from Yaan City of southwest China's Sichuan Province. Additionally, it is easily soluble in water, and its aqueous solution is alkaline. Perennial ryegrass is known to be harvested multiple times per year. Hence, the whole ryegrass plants were collected in May and October 2021, and were thereafter referred to as the “First harvest” and “Last harvest,” respectively.

2.2. Sampling and analysis

Field sampling of the soil in the studied sites was conducted in August 2019, i.e. before the remediation project. Soil samples at depths of 0–5 cm, 5–20 cm, 20–40 cm, 40–60 cm and 60–100 cm were obtained from 30 profiles (20 profiles at the Daiziying site and 10 profiles at the Anle site). In addition, 39 topsoils at the Daiziying site and 18 top-soils (0–20 cm) at the Anle site were also collected. After being excavated, the air-dried soils were fully mixed by a mixing equipment, and used for further characterization analyses, DTPA-extractable TMs, and leaching toxicity of TMs before mixing with Na_2S solution. In May and October 2021, the shoot and root samples of the harvested ryegrass (as explained in the previous section) were washed and dried in an 80 °C oven. Additionally, after the second harvest of ryegrass, landfill soil samples were obtained, air-dried, and ground to fine and homogenous particles of a size of <0.147 mm for further analyses. Soil pH, electrical conductivity (EC), organic matter (SOM) and cation exchange capacity (CEC) were determined following soil testing standard methods (MAPRC, 2006). The total Cd, Cu, Ni, Pb and Zn content were extracted using HCl-HNO_3-HF-$HClO_4$ digestions, while the As and Hg contents were digested with a mixture solution of HCl-HNO_3-dionized water (3:1:4 v/v/v).

Furthermore, plant samples were digested with a HNO_3-$HClO_4$ mixture (Zhu et al., 2018a). The potentially bioavailable TM concentrations in soil were extracted by 0.005 M DTPA - 0.01 M $CaCl_2$ - 0.1 M TEA solution at pH = 7.3 (Wang et al., 2019b). The leaching toxicity test was conducted following the sulfuric-nitric acid method (USEPA, 2007a). Specifically, the preparation of the extractants was as follows: approximately 2 drops of the mixture of concentrated sulfuric and nitric acids with a mass ratio of 2:1 were added to 1 L deionized water to bring the extractants to a final pH of 3.20 ± 0.05. The TM contents were determined by atomic absorption spectrophotometry (Hitachi, FAAS Z-2000, Japan) for Cd, Cu, Ni, Pb and Zn. The detection limits were 0.06 mg kg^{-1} for Cd, 4 mg kg^{-1} for Cr, 1 mg kg^{-1} for Cu, 3 mg kg^{-1} for Ni, 10 mg kg^{-1} for Pb and 1 mg kg^{-1} for Zn (MEEPRC et al., 2019). The contents of As and Hg were determined by the atomic fluorescence spectrometry (Haiguang, LC-AFS-8530, China). The detection limits for As and Hg were 0.01 mg kg^{-1} and 0.002 mg kg^{-1}, respectively (GAQSIQPRC and NSMCPRC, 2008). In this study, standard reference materials (GBW07403), provided by the National Research Center for Certified Reference Materials of China, were used to control the accuracy of the analysis, and TM recoveries were in the range of 92.9 %–106.4 %. SPSS 22.0 software was used for the statistical analysis of the results, and the relative standard deviation of duplicate samples was <5 %.

2.3. Quantification of soil and plant pollution

The soil TM contamination status was quantitatively evaluated by three indices: (a) geo-accumulation index (I_{geo}) to assess soil metal pollution by comparing metal concentrations in the investigated soils against their background concentrations, (b) potential ecological risk index (*PERI*) to evaluate the ecological risks posed by TMs in soil, and (c) Nemerow integrated pollution index (*NIPI*) to characterize the overall pollution status for the soils. The translocation of TMs from roots to aerial parts of ryegrass was calculated using the translocation factor ($TF_{\text{root-to-shoot}}$) (Antoniadis et al., 2017; Xiao et al., 2019; Ma et al., 2020). The calculation formulas are shown in in the Supplementary Materials (Table S2).

3. Results and discussion

3.1. Characteristics of TM distribution in the studied soils

3.1.1. Spatial distribution patterns and potential risk evaluation

The variations in the TM contents in the surveyed regions are presented in Table 1. The mean TM content (mg kg^{-1}) of As was 9.53, while that of Cd = 4.79, Cu = 2.18×10^3, Hg = 93.1, Ni = 22.0, Pb = 5.37×10^3, and Zn = 559.9 in Daiziying site; while in the Anle site the mean TM content (mg kg^{-1}) was As = 11.6, Cd = 7.18, Cu = 2.36×10^3, Hg = 87.4, Ni = 22.5, Pb = 9.61×10^3, and Zn = 726.1. Some of the studied elements had large coefficients of variation (CV > 20 %), i.e., Cd (42.2 %), Cu (57.0 %), Hg (63.4 %), Pb (69.8 %) and Zn (42.8 %) in the Daiziying site and Hg (35.4 %) in the Anle site, showing a heterogeneous distribution; on the other hand, some TMs exhibited lower variability of <20 %. Cadmium, Cu, Hg, Pb, and Zn far exceeded the corresponding background values in Shaanxi Province; this was especially the case for Hg, which was 398–7.34×10^3 times higher in Daiziying and 2.08×10^3–4.58×10^3 times higher in Anle (background = 0.03 mg kg^{-1}; CNEMC, 1990). Apart from As and Ni, TM contents surpassed the risk screening values in almost all cases in the studied sites. In Daiziying, Cd was higher than its risk intervention level by 75.5 %, while Hg was higher by 100 % and Pb was higher by 78.2 %; for Anle, all three elements were higher than their risk intervention values by 100 % (MEPRC, 2018).

Pollution assessment was conducted for soil TMs by I_{geo} and *NIPI* values on the basis of the environmental quality standard of soils in China (CEPA, 1995). Meanwhile, potential ecological risk index (*PERI*) was applied to clarify the relative sensitivity of biological communities to the hazardous TMs (Mazumder et al., 2023). As shown in Table 2, the descending order of I_{geo} and *NIPI* in both studied soils was Hg > Pb > Cu > Cd > Zn > As > Ni. The overall I_{geo} and *NIPI* values indicated that Hg, Pb, Cu and Cd exhibited a case of extremely strong pollution (as judged

Table 1
Descriptive statistics of soil toxic metal(loid)s contents in the studied soils of Daiziying and Anle sites, and soil background values of Shaanxi Province and related soil quality standards.

Statistical parameter	As	Cd	Cu	Hg	Ni	Pb	Zn
Daiziying site							
Max (mg kg^{-1})	13.9	6.59	3.70 × 10^3	220.3	26.2	9.74 × 10^3	782.6
Min (mg kg^{-1})	7.66	1.26	245.8	12.0	17.5	574.2	150.4
Median (mg kg^{-1})	8.69	5.71	2.60 × 10^3	94.0	22.5	5.75 × 10^3	662.5
Mean (mg kg^{-1})	9.53	4.79	2.18 × 10^3	93.1	22.0	5.37 × 10^3	559.9
Standard deviation	1.77	2.02	1.24 × 10^3	59.1	2.51	3.75 × 10^3	239.9
Coefficient of variation	18.6	42.2	57.0	63.4	11.4	69.8	42.8
Anle site							
Max (mg kg^{-1})	12.5	7.42	2.52 × 10^3	137.3	25.2	1.04 × 10^4	763.5
Min (mg kg^{-1})	10.8	6.95	2.28 × 10^3	62.5	19.3	8.65 × 10^3	645.6
Median (mg kg^{-1})	11.3	7.20	2.31 × 10^3	73.1	23.4	9.65 × 10^3	746.3
Mean (mg kg^{-1})	11.6	7.18	2.36 × 10^3	87.4	22.5	9.61 × 10^3	726.1
Standard deviation	0.73	0.19	104.2	31.0	2.40	630.9	48.2
Coefficient of variation	6.28	2.65	4.41	35.4	10.7	6.57	6.64
Background values[a]	11.1	0.094	25.9	0.03	28.8	21.7	73
Risk screening values[b]	25	0.6	100	3.4	190	170	300
Risk intervention values[c]	100	4.0	–	6.0	–	1000	–

[a] Soil background values of Shaanxi Province (CNEMC, 1990).
[b] Risk screening values for soil contamination of agricultural land in China (GB15618-2018; MEPRC, 2018).
[c] Risk intervention values for soil contamination of agricultural land in China (GB15618-2018; MEPRC, 2018).

by I_{geo} of >5) or heavy pollution ($NIPI > 3$), while Zn was found to be moderately enriched as judged by I_{geo} ($3 > I_{geo} > 2$) or strongly enriched ($3 > NIPI > 2$), which was 100 % in the soil samples collected from the Anle site compared to the Daiziying site. As and Ni were at safe levels ($I_{geo} < 0$ and $NIPI < 1$) in both studied soils. Furthermore, according to the toxicity response coefficients of TMs (40 for Hg, 30 for Cd, 10 for As, 5 for Cu, Ni, and Pb, and 1 for Zn) proposed by Hakanson (1980), soil TMs in both the Daiziying and Anle sites, had the following order of their ecological risk values: Hg > Cd > Pb > Cu > As > Zn > Ni. Specifically, Hg, Cd, Pb and Cu in the surveyed regions were at significantly very high polluted levels ($PERI > 320$), and As, Ni and Zn were at low potential ecological risk ($PERI < 40$). Given the abovementioned factors, Hg, Cd, Pb and Cu posed a serious threat to eco-environmental safety at both the Daiziying and Anle sites, and it is suggested that there is an urgent need to remediate these heavily-polluted soils.

3.1.2. *Vertical distribution of TMs*

As shown in Figs. 1a and b, Cu, Hg, Pb, and Zn exhibited similar downward trends: they were enriched in the top layer (0–5 cm) and gradually declined with soil depth owing to their low mobility and vertical migratory aptitude in soil (Cui et al., 2021). Specifically, the mean contents of these metal(loid)s were reduced by 17.0 %–20.1 % and 48.9 %–59.5 % at soil depths of 5–20 cm and 40–60 cm, respectively, compared to the top layer (0–5 cm). For Cd, the mean content dropped from 12.20 mg kg^{-1} (0–5 cm) to 5.58 mg kg^{-1} (5–20 cm) and 2.25 mg kg^{-1} (60–100 cm) with reduction rates of 54.3 % and 81.5 %, respectively. This could be explained by atmospheric deposition, as well as the strong combination of the presence of cationic metals in the top layer, which was consistent with the study of Bai et al. (2019). As for As and Ni, they showed the opposite distribution pattern, as they slightly increased with increasing soil depth, which might be attributed to the weak adsorptive capacity of soil for As and Ni, and wet deposition and eluviation (Azam et al., 2023). The average pH of ~7.8, as well as the low SOM and CEC values of the soils, indicated negligible adsorption interactions between anionic As and soils (Sosa-Rodríguez et al., 2020). Additionally, the low leachability and DTPA-extractable values of soil As and Ni suggested that a low amount of Ni was sorbed into the surface soils, as will be discussed in Sections 3.3 and 3.4. Meanwhile, wet deposition, for example, rain erosion, might cause the transfer of weakly bound As and Ni from the topsoil to the deeper soil; thus, soil As and Ni concentrations were slightly enhanced with increasing soil depth. Similarly, Rajmohan et al. (2020) reported an increase in Ni content with soil depth (0–100 cm) in seasonally waterlogged soil. It should be noted that the mean Cd, Cu, Hg and Pb concentrations still exceeded the risk screening and intervention values throughout the 0–100 cm soil profile (MEPRC, 2018).

3.2. *Changes in selected soil properties*

The changes in soil pH, EC, SOM, and CEC after remediation are presented in the Supplementary Materials (Fig. S4). Soil pH increased from 7.79 to 8.92 in Daiziying and from 7.90 to 8.85 in Anle. This result might be ascribed to the hydrolysis of Na_2S, i.e., $Na_2S + H_2O \rightarrow NaHS + NaOH$, the product of which, NaOH, could cause high consumption of

Table 2
Soil toxic metal(loid)s contamination status evaluated by the calculated Geo-accumulation index (I_{geo}), potential ecological risk index (*PERI*) and Nemerow integrated pollution index (*NIPI*) values.

Parameter	Study site	Statistical value	As	Cd	Cu	Hg	Ni	Pb	Zn
Geo-accumulation index (I_{geo})	Daiziying	Range [Mean]	(−1.12)–(−0.26) [−0.80]	3.16–5.55 [5.09]	2.66–6.57 [5.81]	8.05–12.3 [11.0]	(−1.31)–(−0.72) [−0.97]	4.12–8.22 [7.37]	0.46–2.84 [2.35]
	Anle	Range [Mean]	(−0.62)–(−0.41) [−0.52]	5.62–5.72 [5.67]	5.87–6.02 [5.93]	10.4–11.6 [10.9]	(−1.17)–(−0.78) [−0.94]	8.05–8.31 [8.21]	2.56–2.80 [2.73]
Potential ecological risk index (*PERI*)	Daiziying	Range [Mean]	6.9–12.5 [8.6]	402–2.10 × 10^3 [1.53 × 10^3]	47–713 [422]	1.59 × 10^4–2.94 × 10^5 [1.25 × 10^5]	3.0–4.5 [3.8]	132–2.24 × 10^3 [1.24 × 10^3]	2.1–10.7 [7.7]
	Anle	Range [Mean]	9.8–11.3 [10.5]	2.22 × 10^3–2.37 × 10^3 [2.29 × 10^3]	439–487 [456]	8.34 × 10^4–1.83 × 10^5 [1.16 × 10^5]	3.3–4.4 [3.9]	1.99 × 10^3–2.39 × 10^3 [2.21 × 10^3]	8.8–10.5 [9.9]
Nemerow integrated pollution index (*NIPI*)	Daiziying		0.48	9.60	30.3	49.7	0.13	46.3	2.27
	Anle		0.48	12.2	24.4	33.8	0.13	58.8	2.48

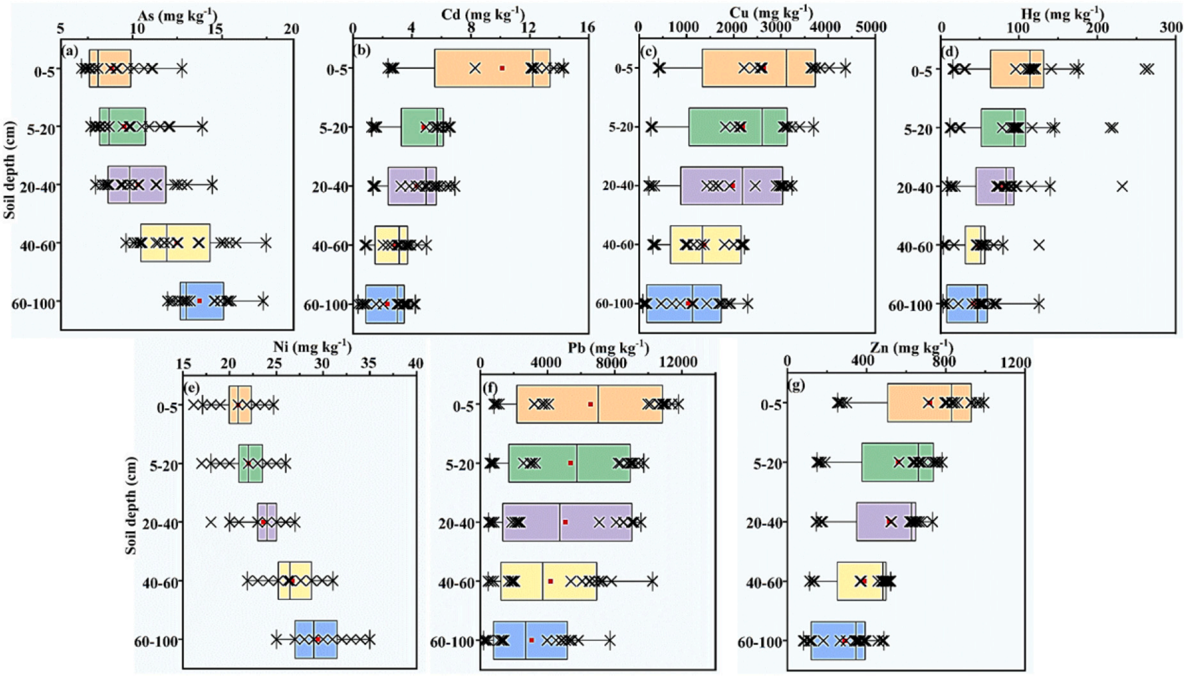

Fig. 1a. Vertical distribution of As (a), Cd (b), Cu (c), Hg (d), Ni (e), Pb (f) and Zn (g) along soil profiles (0–100 cm) of the Daiziying site, respectively. And "×" symbols represent the soil samples collected from the Daiziying site.

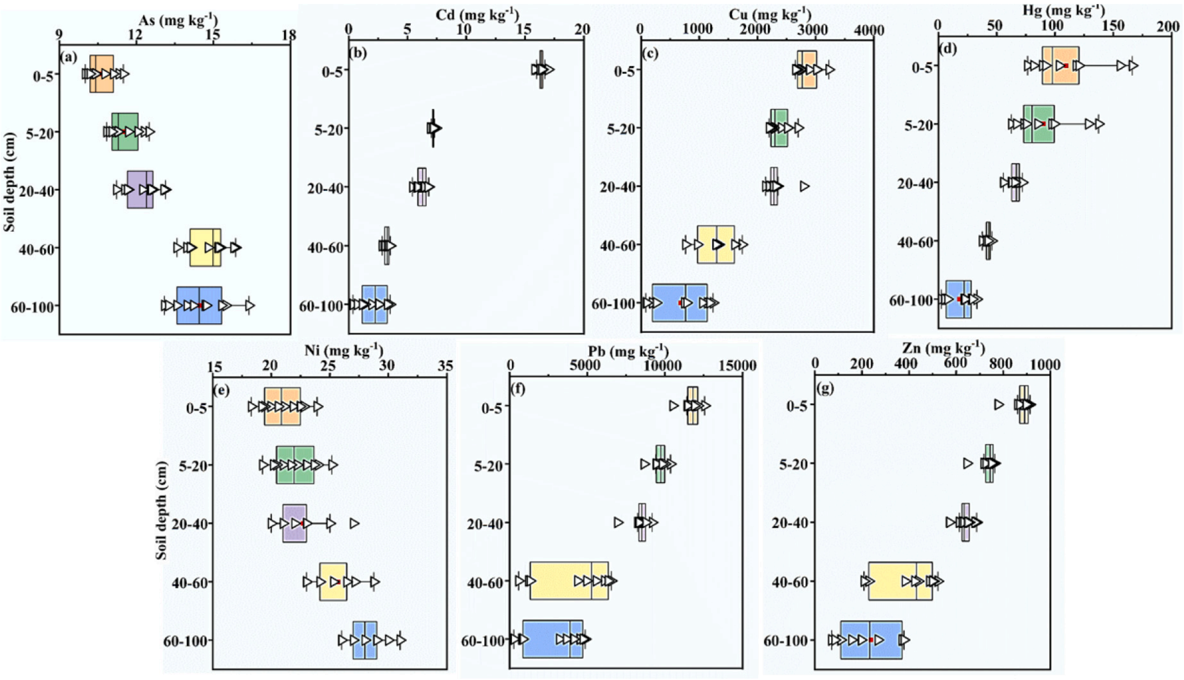

Fig. 1b. Vertical distribution of As (a), Cd (b), Cu (c), Hg (d), Ni (e), Pb (f) and Zn (g) along soil profiles (0–100 cm) of the Anle site, respectively. And "▷" symbols represent the soil samples collected from the Anle site.

hydrogen ions and an increase in soil pH (Li et al., 2020). Na_2S has long been considered to have the advantage of raising soil pH (Zhang et al., 2020). Soil EC was increased by an average of 36.8 % in Daiziying and 29.0 % in Anle after remediation, owing to the generation of soluble Na ions (Shi et al., 2019). However, SOM and CEC at the two sites had negligible changes after remediation. A slight increase in SOM content might be ascribed to the growth promotion of ryegrass through the added nutrients after Na_2S application (Holland et al., 2018). A similar study from Shen (2017) found that added Na_2S at rates of 0.2 %, 0.6 % and 1 % had little effect on soil CEC after crop maturation (soybean, oilseed rape, maize and wheat). Therefore, the significant enhancement in soil pH and EC, as well as the slight increase in soil SOM caused by Na_2S application, might have influenced the solubility and mobility of soil TMs (Zhang et al., 2020; Padhye et al., 2023).

3.3. *Changes in TM leachability*

After remediation, the mean concentrations (mg L^{-1}) of TMs leached from the soil in Daiziying were reduced from 51.9 to 13.9 for Cu, from 2.51 to 0.034 for Hg, from 0.21 to 0.19 for Ni, from 13.57 to 3.68 for Pb, from 9.35 to 7.38 for Zn, and from 0.056 and 0.15 to undetectable values for As and Cd, respectively (Fig. 2a). Notably, the extractable Hg and Pb in all untreated contaminated soil samples significantly exceeded the leaching toxicity identification standard values in China, while the remediation treatment decreased TM leaching concentrations to levels below the limit values (As = 5, Cd = 1, Cu = 100, Hg = 0.1, Ni = 5, Pb = 5 and Zn = 100 mg L^{-1}; USEPA, 2007a, 2007b). Similar results were obtained from the restored soils in Anle where the mean TM concentrations (mg L^{-1}) were reduced from 84.4 to 50.6 for Cu, from 2.98 to 0.075 for Hg, from 0.16 to 0.11 for Ni, from 20.4 to 4.29 for Pb, from 10.7 to 8.96 for Zn, and from 0.075 and 0.26 to undetectable values for As and Cd, respectively (Fig. 2b). It is worth noting that TM leachability followed the sequence Cd > Cu > Hg > Zn > Ni > As > Pb both before and after the remediation treatment, which might be ascribed to the high heterogeneity of TM solubility in soils, the initial contaminant concentration and effectiveness in immobilization of various TMs under the Na_2S application (Paniagua-López et al., 2021). As discussed in Section 3.1.1, Hg, Cd, Pb and Cu posed a serious threat to eco-environmental safety at both the Daiziying and Anle sites due to their high initial concentration and toxicity, while, unlike the other three TMs, Pb leaching content was the lowest. This result is attributed to the lower solubility of soil Pb, as well as the strong inverse correlation between soil pH and Pb, and the smaller solubility product constants (K_{sp}) of PbS (Pastor-Jáuregui et al., 2020; Sun et al., 2018). Meanwhile, the remediation treatment resulted in the complete immobilization of Cd and As, and a low content of other metal(loid)s, following the descending order of immobilization efficiency of Hg > Pb > Cu > Ni > Zn. According to the Lewis acid and base soft-soft interactions, it is likely that soft acid-type Cd^{2+} and Hg^{2+} rapidly formed strong bonds with soft base-type S^{II} in preference to hard-medium-soft acid-type metals Pb^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} (Wang and Mi, 2017). This significant downward trend in released metal(loid)s was primarily due to the precipitation of insoluble sulfide species (Sun et al., 2018). For As, S^{II} could first be bound with natural organic matter to form sulfhydryl groups, and then with soil As and inhibit its leachability (Peřestá et al., 2022).

3.4. Changes in DTPA-extractable TMs

The immobilization treatment had different effects on various TMs regarding their DTPA extractability (Fig. 3). Specifically, the highest reduction in the remediated soils was observed in DTPA-extractable Hg (79.9 %), followed by Cu (68.3 %), Pb (58.6 %), Cd (34.9 %), Zn (31.0 %), Ni (29.9 %) and As (15.7 %) in Daiziying. In Agle the highest reduction was for Hg (85.9 %), followed by Cu (71.4 %), Pb (71.9 %), Cd

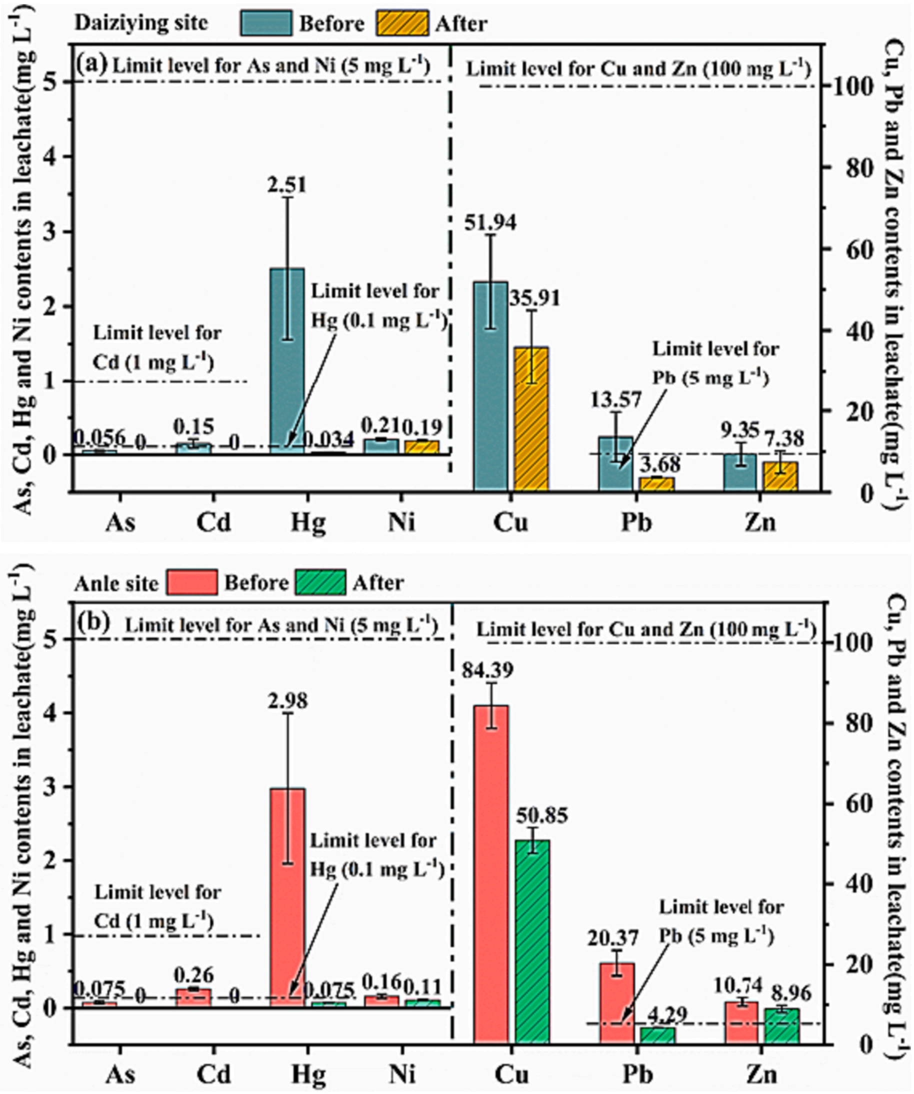

Fig. 2. The changes in leaching contents of toxic metal(loid)s before and after remediation in the Daiziying site (a) and the Anle site (b).

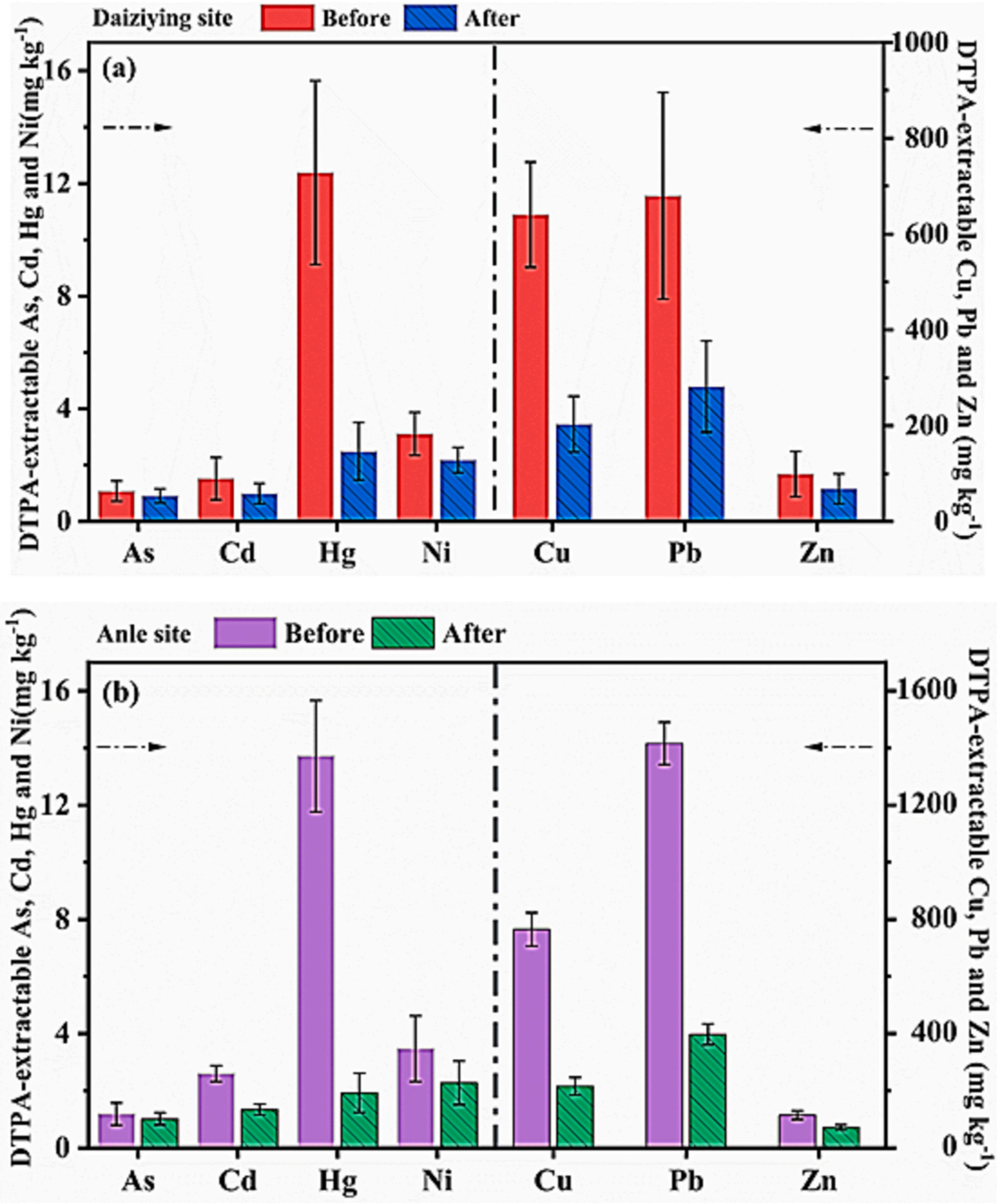

Fig. 3. The changes in DTPA-extractable contents of toxic metal(loid)s before and after remediation in the Daiziying site (a) and the Anle site (b).

(48.1 %), Zn (37.1 %), Ni (34.3 %) and As (14.3 %) compared with the untreated soils. This descending order might be mainly attributed to the solubility product constants (K_{sp}) of the studied TMs with S^{-II} which are as follows: HgS (4×10^{-53}) < CuS (6.3×10^{-36}) < PbS (8×10^{-28}) < CdS (8×10^{-27}) < ZnS (1.6×10^{-24}) < NiS (3.2×10^{-19}) (Sun et al., 2018). Other works agree that Na_2S application has a stronger affinity for soil Cu and Pb than for Zn owing to the difference in K_{sp} values (Zhang et al., 2020; Zheng et al., 2022). Additionally, Sun et al. (2018) found that Hg was preferentially precipitated with S^{-II} over Pb, Cd and Zn. Significantly, Na_2S addition hindered the release of bioavailable TMs under severe pollution in this study, which indicated that Na_2S application might immobilize soil TMs to inhibit their toxicity to ryegrass (Zhang et al., 2020). Therefore, the enhanced immobilization efficiency of TMs might be ascribed to (i) the increased soil pH under Na_2S application significantly decreasing the solubility of soil TMs (Paniagua-López et al., 2021) and (ii) metal sulfide precipitation. Specifically, soil metal(loid)s can react with S^{-II} ions and be converted into insoluble sulfide complexes that precipitate out of solution (Chen et al., 2019; Rinklebe et al., 2016; Shaheen et al., 2017). These metal(loid)s, except for Ni, are thiophile (chalcophile) elements, whose mobility and toxicity can be easily inhibited by metal sulfides (Na_2S, FeS, CuS and MoS_2) (Smieja-Król et al., 2022; Song et al., 2019; Huang et al., 2021; Zheng et al., 2022). Furthermore, the minimal As extraction efficiency in comparison with other TMs was due to the relative inability of anionic As to create complexes with DTPA (Zheng et al., 2022). Furthermore, the reduction in As bioavailability was due to the formation of sulfhydryl groups by the combination of Na_2S and organic matter in soil, as already described in Section 3.3.

3.5. *Changes in TM uptake*

3.5.1. *Changes in TM content in ryegrass shoots and roots*

At the first harvest, Cd, Hg and Pb in ryegrass shoots considerably exceeded the thresholds proposed for fodder crops (As = 2, Cd = 1, Hg = 0.1, and Pb = 30 mg kg^{-1}; no limits reported for Cu and Zn), while TM contents in the shoots at the last harvest were all lower than the limits of the fodder standards (AQSIQ, 2017) (Fig. 4). Notably, the inhibited availability of soil TMs after Na_2S application seemed to have affected

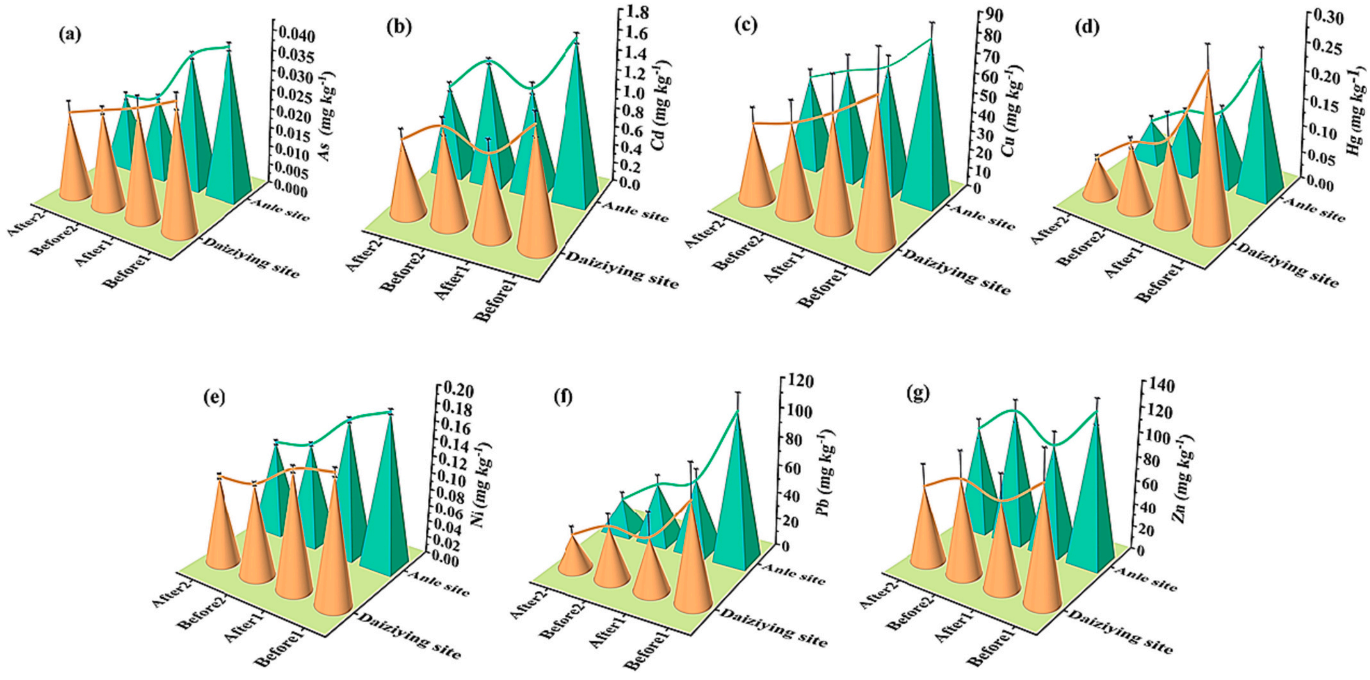

Fig. 4. The changes in uptake of As (a), Cd (b), Cu (c), Hg (d), Ni (e), Pb (f) and Zn (g) by ryegrass shoots before and after remediation, respectively. And “Before1”and “After1” represent the first harvest of ryegrass before and after remediation, “Before2” and “After2” represent the last harvest of ryegrass before and after remediation, respectively.

the TM contents in ryegrass shoots at both the first and last harvest. At the first harvest, the decline of As concentration in ryegrass shoots was 12.5 %, that of Cd = 30.9 %, Cu = 19.9 %, Hg = 46.4 %, Ni = 6.7 %, Pb = 46.4 % and Zn = 24.5 % in Daiziying. At the last harvest the TM concentrations in ryegrass shoots under Na_2S remediation were slightly lower than those at the first harvest. Specifically, the rate of decrease of As was 12.0 %, that of Cd = 22.6 %, Cu = 13.7 %, Hg = 41.7 %, Ni = 4.6 %, Pb = 36.0 % and Zn = 19.0 %. These decreasing rates were similar to those of the TM concentrations of ryegrass shoots in Anle.

A similar inhibitory effect of Na_2S application on the root uptake of TMs is shown in Fig. 5. At the first harvest, the decrease in Cd concentration of ryegrass roots was 22.6 %–34.6 %, that in Cu = 13.7 %–22.4 %, Hg = 35.7 %–45.8 %, Pb = 34.6 %–64.3 % and Zn = 17.3 %–27.4 %, while As and Ni contents in ryegrass roots decreased at the rates of 2.1 %–4.4 % and 4.8 %–9.3 %, respectively, in both sites. At the last harvest, the reduction rates of TMs in ryegrass roots were only 0.6–0.8 times for Pb, Hg, Cu, Cd and Zn, and 0.3–0.4 times for Ni and As, which is in accordance with the results regarding shoot uptake. Similar findings were reported by Song et al. (2019), where added metal sulfides, i.e., ZnS and MoS_2, significantly reduced the uptake of Cd, Pb, As, Cr, Cu, Ni and Zn by cucumber roots, stems and leaves—an effect attributed to the strong complexation of metal sulfides and subsequent reduced plant absorption of TMs. Nevertheless, the decline in uptake of TMs was largely affected by plant selectivity (Munir et al., 2020). Wang et al.

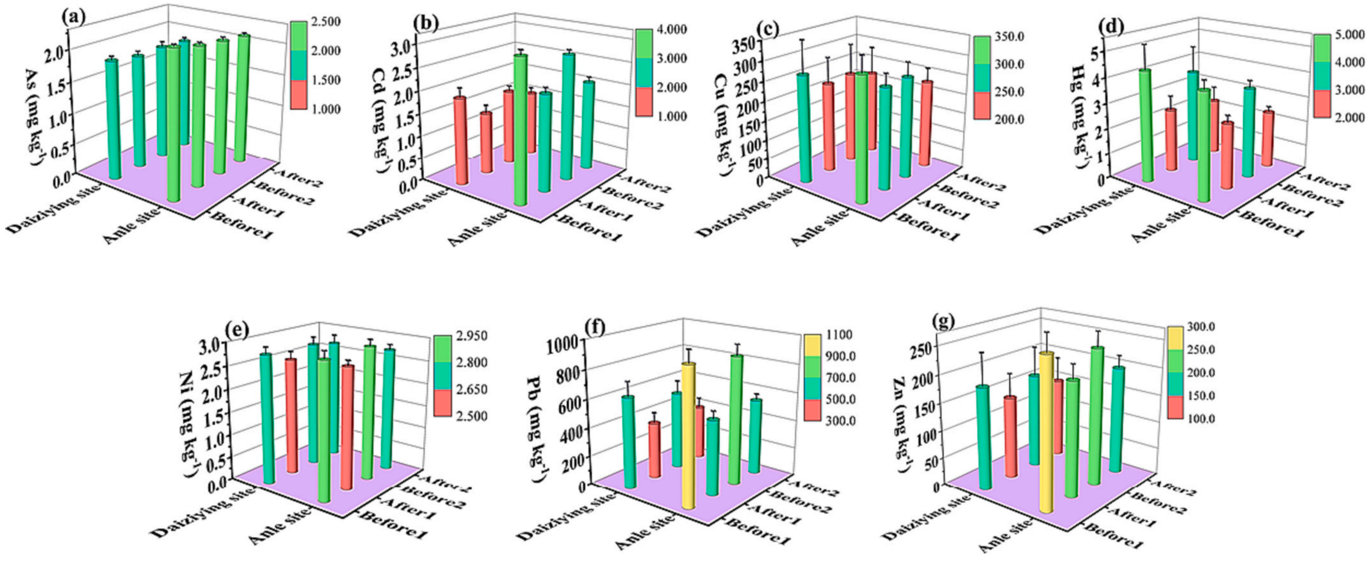

Fig. 5. The changes in uptake of As (a), Cd (b), Cu (c), Hg (d), Ni (e), Pb (f) and Zn (g) by ryegrass roots before and after remediation, respectively. “Before1”and “After1” represent the first harvest of ryegrass before and after remediation, “Before2” and “After2” represent the last harvest of ryegrass before and after remediation, respectively.

(2019c) showed that the uptake of essential metals such as Cu, Zn, Mn and Ni by *Pinus massoniana* Lamb leaves was stronger than that of toxic metal(loid)s, such as Pb, Cr and As. Additionally, plants usually take less time to accumulate the essential elements such as Mn, Fe and Cu from contaminated soils than non-essential metal(loid)s such as Hg (Thakur et al., 2022). Therefore, the decrease in uptake of TM contents by ryegrass due to added Na_2S was different: the reduction in uptake of essential elements was moderate, while that of non-essential elements was more pronounced. This difference in TM uptake by ryegrass under Na_2S remediation was predicted by both TM selectivity of ryegrass itself and the chemical speciation of the sulfide complexes as discussed earlier.

Combined with the decreased phytoavailability of soil TMs (Section 3.4), the declining uptake in ryegrass roots and shoots could likely be ascribed to the improvement of the retention capacity of TMs and downward movement of plant-available metal(loid) contents in the Na_2S-treated soils, which agrees with the results reported by Song et al. (2019). Notably, Na_2S can be dissociated into NaHS in the soil solution; it then reacts with H^+ to form H_2S; hence, Na_2S is extensively used as an exogenous hydroxyl sulfide (H_2S) releaser (Yu et al., 2019; Zhu et al., 2018b). In this study, the alkaline soil condition inhibited the conversion of NaHS into exogenous H_2S gas, hence, H_2S molecules in plants mainly come from endogenous sources, which can simultaneously strengthen the antioxidant system of plants, alleviate TM stress, and inhibit the uptake of TMs by plants (Arif et al., 2021). TM stress in plants may result in oxidative stress injury induced by excessive generation of reactive oxygen species (ROS; Hou et al., 2022). Additionally, H_2S can be synthesized as a scavenger of ROS in multiple cellular organelles, primarily in chloroplasts, to alleviate this threatening effect. On the other hand, H_2S may reduce the uptake of TMs in four ways: (i) H_2S can reduce TM uptake by inhibiting the expression of some transporter protein genes of TMs in plants (Zhu et al., 2018b); (ii) H_2S is involved in regulating the release of organic acids from plant roots, and TM uptake is decreased by complexing TMs in surrounding soils with organic acids (Wang et al., 2019a); (iii) H_2S can reduce polysaccharide components, mainly pectin and hemicellulose, in the plant root cell wall, further reducing TM contents in plants (Zhu et al., 2018b); and (iv) H_2S can reduce the flow of TMs to protoplasts by regulating calcium channels in plants (Arif et al., 2021). Meanwhile, the studies of Valivand and Amooaghaie (2021) and Fang et al. (2019) confirmed that NaHS application could reduce Pb and Cd contents in zucchini and alfalfa tissues. Taken together, the regulation of stress tolerance of ryegrass to TMs and inhibition of uptake of TMs by ryegrass caused by H_2S, and passivation of TMs in soil after Na_2S application, in addition to plant selectivity, might have jointly decreased TM uptake by ryegrass.

3.5.2. *Changes in TM translocation*

The $TF_{\text{root-shoot}}$ values of the seven TMs after Na_2S application declined when compared with the control treatment (Table S3), indicating the inhibiting effect of Na_2S addition, thereby guaranteeing the safety of the edible parts of fodder grass. The $TF_{\text{root-shoot}}$ values of TMs at the last harvest were significantly lower than those at the first harvest, while all the $TF_{\text{root-shoot}}$ values were <1, indicating the strong retention ability of ryegrass roots to TMs (Ma et al., 2020). The changes in $TF_{\text{root-shoot}}$ values after Na_2S treatment might be explained by the following: (i) the greater retention of TMs in the root systems due to the alkalinization of soil ($Na_2S + H_2O \rightarrow NaHS + NaOH$) and formation of metal sulfides with small K_{sp} values after Na_2S application (Kujawska and Pawłowska, 2022; Hamid et al., 2020), as discussed in Section 3.4; and (ii) the inhibitory effect of H_2S generated from Na_2S application on the expression of translocators (i.e., non-protein thiols and metallothioneins) and uptake of TMs by ryegrass roots as discussed in Section 3.5.1 (Fang et al., 2019). Similarly, Hamid et al. (2020) confirmed that the transfer of Cd, Pb and Cu from underground to aboveground parts was inhibited by some remediation agents, namely lime, fly ash and sepiolite, due to soil alkalinization. In addition, Yu et al. (2019) and Zhou et al. (2020) verified that the increased H_2S produced by Na_2S could inhibit the root-to-shoot translocation of Cd.

4. Conclusions

Ex situ treatments including soil replacement, immobilization with Na_2S, and safe landfilling were applied in two field sites; then, a one-year growth experiment with ryegrass was conducted. Na_2S application lowered the leachability, phytoavailability, uptake, and translocation of the studied elements in ryegrass. This is the first field-scale research study investigating the effect of Na_2S application on soils with Hg, Pb and Cu concentrations 70-to-7000-fold higher than background values and also highly polluted with other TMs. The Na_2S treatment evidently reduced the leaching and DTPA-extractable contents of TMs in the treated soils. Immobilization of the studied TMs varied due to the Lewis acid and base soft-soft interactions with S^{-II} and the solubility product constants of the complexes of metal sulfides that were formed. The TM uptake by, and the root-to-shoot translocation in, ryegrass also decreased with added Na_2S. The shoot TM contents in the ryegrass last harvest were lower than the TM regulation limits concerning fodder crops. In conclusion, Na_2S application ensured the passivation of the studied soil TMs, and the safety and feasibility of the cultivation of ryegrass in such seriously contaminated soils. Na_2S has great potential to remediate soils contaminated with toxic elements. These findings will offer nuances on how well Na_2S and similar immobilizing agents can be utilized to immobilize TMs in heavily contaminated soils and other regions grappling with severe contaminants. On a broader scale, the outcomes from this study could have profound implications for policy-making and local agricultural practices. By establishing a clearer connection between sulfur rich compounds application and TMs leachability and phytoavailability, stakeholders and policymakers can be equipped with evidence-based insights, enabling them to draft and implement more effective measures for managing soil health and ensuring sustainable agricultural productivity and mitigation of the ecological and human health risks. Furthermore, this study can serve as a foundation for future research efforts, focusing on refining sulfur rich compounds as a tool or exploring other innovative solutions that address TMs contamination in the agricultural soils. Therefore, this study is of great environmental concern. However, the impact of sodium salts on soil salinity should be further investigated. Additionally, more field trials are needed, under different environmental and experimental conditions, to confirm and validate the effect of Na_2S in different plants of economic interest.

CRediT authorship contribution statement

Han Zhang: Performing the experiments, investigation, analysis, data collection, methodology, Conceptualization, and writing the draft manuscript.

You Li: Investigation, Creating tables and figures. Writing - original draft.

Ronghua Li: Methodology, Visualization, Software, Writing - review & editing.

Weilong Wu: Investigation, Methodology, Formal analysis, Investigation, Creating tables and figures.

Hamada Abdelrahman, Jianxu Wang, Samir G. Al-Solaimani, Vasileios Antoniadis, and Jörg Rinklebe: Revising, editing, and proof reading for the entire manuscript.

Sang Soo Lee: Revising, editing, and proof reading for the entire manuscript, and co-corresponding.

Sabry M. Shaheen: Scientific concept, coordination, experimental guiding, data treatment, writing, editing, proof reading for the entire manuscript, and co-corresponding author.

Zengqiang Zhang: Supervision, conceptualization, research idea, project administration, visualization, experimental guiding, technical facilities, foundation, review, editing and corresponding author.

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

Data will be made available on request.

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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.2023.168387.

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