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Research article

Phragmites australis elevated concentrations of soil-bound heavy metals and magnetic particles in a typical urban plateau lake wetland, China

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ABSTRACT

Vegetation change significantly altered the hydrological processes and soil erosion within riparian ecosystems. It is unclear how change in managed vegetation types affect the geochemical behavior of heavy metals (HMs) and magnetic particles in karst riparian areas. Two soil depths of 0–20 cm and 20–40 cm were taken in alien species *Phragmites australis* (*P. australis*), native species *Juncus effuses* and *Schoenoplectus tabernaemontan* in a typical urban plateau Lake wetland, Caohai lake, China. Low-frequency mass magnetic susceptibility (χ_{LF}), anhysteretic remanent susceptibility (χ_{ARM}), isothermal remanent magnetization, Cd, Cr, Cu, Sb, Ni and Zn were determined. Compared with *Juncus effuses* and *Schoenoplectus tabernaemontani, P. australis* habitat had the higher values of HMs, χ_{LF}, χ_{ARM}, and isothermal remanent magnetization in top-soils. Frequency-dependent magnetic susceptibility ranged from 4.84 % to 10.87 % in top-soils and 6.82 %–9.95 % in sub-soils, lithogenic/pedogenic factors mainly masked the contribution of anthropogenic factors to magnetic signal enhancement. The correlation between variations of Cu and Sb with χ_{ARM} and isothermal remanent magnetization was found to be significant in top-soils, but not in sub-soils. *P. australis* tended to promote the enrichment of HMs and enhancement of magnetic signal, the impact of *P. australis* expansion on the distribution of soil HMs and magnetic particles in Caohai riparian wetland should be not disregarded.

1. Introduction

Wetlands are fragile areas with various hydrological, biological, and physical processes [1–3]. Changes in land-use in wetlands caused by anthropogenic activities evidently affect the structure and function of this ecosystem [1,3]. The alteration of wetlands through drainage, reclamation, and conversion into cropland elevated the concentration of HMs in cultivation fields [4]. The presence of elevated levels of HMs in wetlands has been found to contribute to the depletion of soil nutrients [5] and the deterioration of soil biology [6]. Thus, accurately estimating the abundance of HMs could provide useful information for the pollution control of those elevated elements in the wetlands [5,7,8].

Plants have the ability to partially mitigate the contamination caused by soil HMs [9]. The processes of soil flooding promote the

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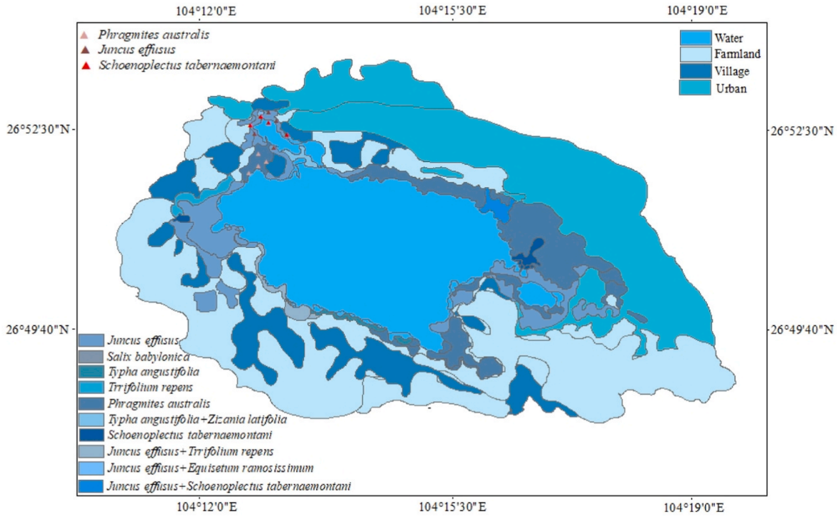

Fig. 1. Sampling sites in a typical urban plateau Lake wetland, Caohai lake, China.

enrichment of HMs [10] as well as the degradation of ferrimagnetic particles [11–13]. Soil χ_{LF} under the floodplain trees was substantially lower than that in the adjacent upland trees [11]. Studies have concentrated on the effects of ecosystem changes or land-use types on soil HMs associated with magnetic phases in the urban areas [14–16] and coastal wetlands [17]. The increased anthropogenic activities coupled with external metal nanoparticles inputs altered the geochemical behaviors of magnetic minerals and HMs in soils. It has been found that elevated levels of metal nanoparticles can have negative impacts on human health, as highlighted by [46]. To date, few studies have focused on the effect of vegetation type changes on soil HMs and magnetic particles in the karst urban plateau areas.

Previous studies have demonstrated that *Phragmites australis* (*P. australis*) has the capacity to mitigate shoreline soil erosion, facilitate soil accretion, and promote HMs accumulation [18]. This high abundance of alien *P. australis* in Caohai wetlands, Guizhou province, China has resulted in a decline in local plant species and poses a threat to the habitat of *Grus nigricollis* [18]. Alterations in the dominant plant species in the wetlands play a significant role in shaping the distribution patterns of HMs in soils [19] and the levels of HMs accumulated in plant tissues [20]. Numerous recent studies have been undertaken to ascertain the spatial patterns and contamination characteristics of specific HMs [20,21,45], the determinants influencing the dispersion of HMs [22,23], and the reactions of microorganisms to HMs [6]. We hypothesize the expansion of *P. australis* facilitated HMs enrichment and magnetic signal enhancement in Caohai riparian wetland. We examined (1) the influence of vegetation type changes on the distribution of soil HMs and magnetic particles in the karst riparian wetlands; and (2) the potential associations between the abundance of HMs and magnetic parameters.

2. Materials and methods

2.1. Study area

Caohai karst riparian wetland is part of the Caohai Karst National Nature Reserve (26°49′–26°53′N, 104°12′–104°18′E) [24]. Caohai lake is the largest natural karst dammed freshwater lake in Guizhou Province, China [25]. The region experiences a mean annual temperature of 10.9 °C [24], and a mean annual precipitation of 1000 mm [22,45]. The dominant plant community in the riparian areas is *P. australis*, *Juncus effuses*, *Salix babylonica, Typha angustifolia, Trrifolium repens, Zizania latifolia, Schoenoplectus tabernaemontani* (*S. tabernaemontani*) *and Equisetum ramosissimum*. The underlying bedrock primarily consists of sedimentary carbonate rock [25] and most of the riparian soil in Caohai riparian wetland is yellow-brown loam with a high pH, relative humidity and organic matter content [25], while peat swamp soil is located in the perennially flooded areas.

In August 2022, soil samples were collected at two depths of 0–20 cm and 20–40 cm under alien species *P. australis* in dry areas, native species (*Juncus effuses* and *S. tabernaemontani*) in alternating wet and dry areas (Fig. 1). Four soil sampling points were obtained at each vegetation habitat, with each sampling point consisting of a composite sample comprising four sub-samples from the same layer. A total of 24 soil samples (3 vegetation habitats × 2 soil depths × 4 spatial replicates) were collected. The collected samples were freeze-dried using a Labconco-18 freeze dryer (LABCONCO, USA) and subsequently sieved using a 100-mesh nylon sieve [21].

2.2. Laboratory analyses

Magnetic susceptibility was measured with a Bartington Instruments MS2B sensor at frequencies of 0.47 kHz (χ_{LF}) and 4.7 kHz (χ_{HF}) [26]. χ_{LF} is an indicator of the abundance of all magnetic minerals [26]. The frequency-dependent magnetic susceptibility (χfd%) permits identification of magnetite and maghemite of ultrafine in both magnetic and non-magnetic components [26] and estimated

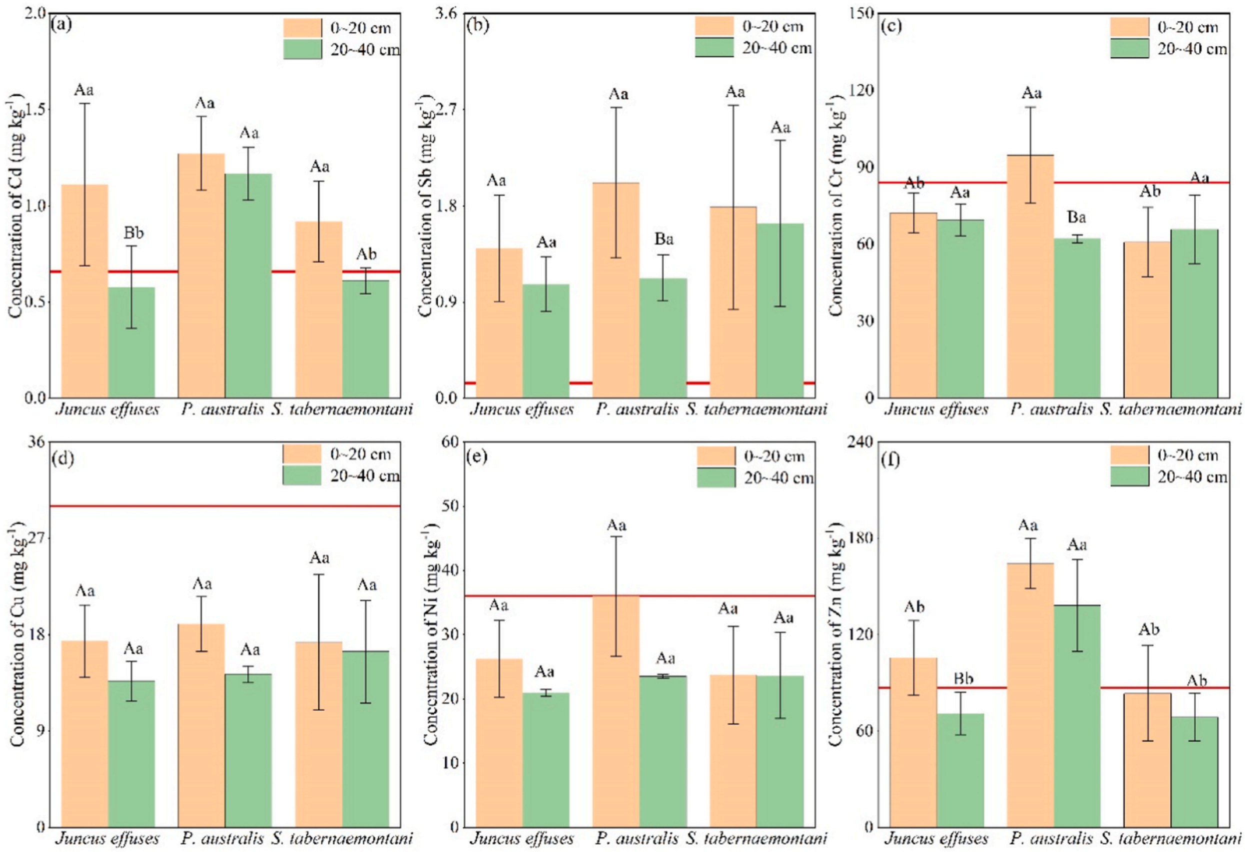

Fig. 2. Concentration of heavy metals at different soil depths under three vegetation habitats. The red lines are the values of local geochemical background. Lowercase letters in the same layer refer to significant differences at $P < 0.05$, uppercase letters indicate significant differences between topsoil and subsoil at $P < 0.05$.

using equation (1).

$$\chi fd\% = \frac{\chi_{LF} - \chi_{HF}}{\chi_{LF}} \times 100 \tag{1}$$

Anhysteretic remanent susceptibility (χ_{ARM}) is related to the stable single-domain ferrimagnetic grains ranging from 0.02 to 0.4 μm [27,28]. This parameter was quantified using an ASC D2000 alternating-field demagnetizer, employing a constant direct-current biasing field of 0.05 mT and an alternating field of 100 mT, and then determined using an AGICO JR6 spinner magnetometer [27]. An MMPM10 pulse magnetizer induced isothermal remanent magnetization in a magnetic field of 1000 mT (Saturation Isothermal Remanent Magnetization, SIRM) and −300 mT (IRM_{-300}). The abundance of ferrimagnetic and canted anti-ferromagnetic minerals in mixed assemblages is closely associated with SIRM [27,28], while the concentration of high-coercivity magnetic substances can be inferred from hard isothermal remanent magnetization (HIRM) [27,28]. The determination of magnetic mineralogy can be obtained through both χARM/SIRM and χARM/χfd [27]. S_{-300} is typically enhanced when a higher proportion of low-coercivity magnetic substances is present in relation to SIRM [27]. The equations are as follows:

$$HIRM = \frac{IRM_{-300} + SIRM}{2} \tag{2}$$

$$S_{-300} = \frac{IRM_{-300} + SIRM}{2SIRM} \tag{3}$$

Geochemical analysis of the samples was obtained using a Germany Spectro Arcos Eop inductively coupled to a plasma mass spectrometry. The soil sample was digested in an acid mixture of $HClO_4$+ HNO_3+HF [17] in Teflon tubes. Reagent blanks, triplicates, and standard reference materials (GBW07445) were used to assess quality assurance. The recovery rates were 90∼106 % for Cd, 91–105 % for Cu, 96–107 % for Cr, 90–110 % for Sb, 90–108 % for Ni, and 93–108 % for Zn, respectively.

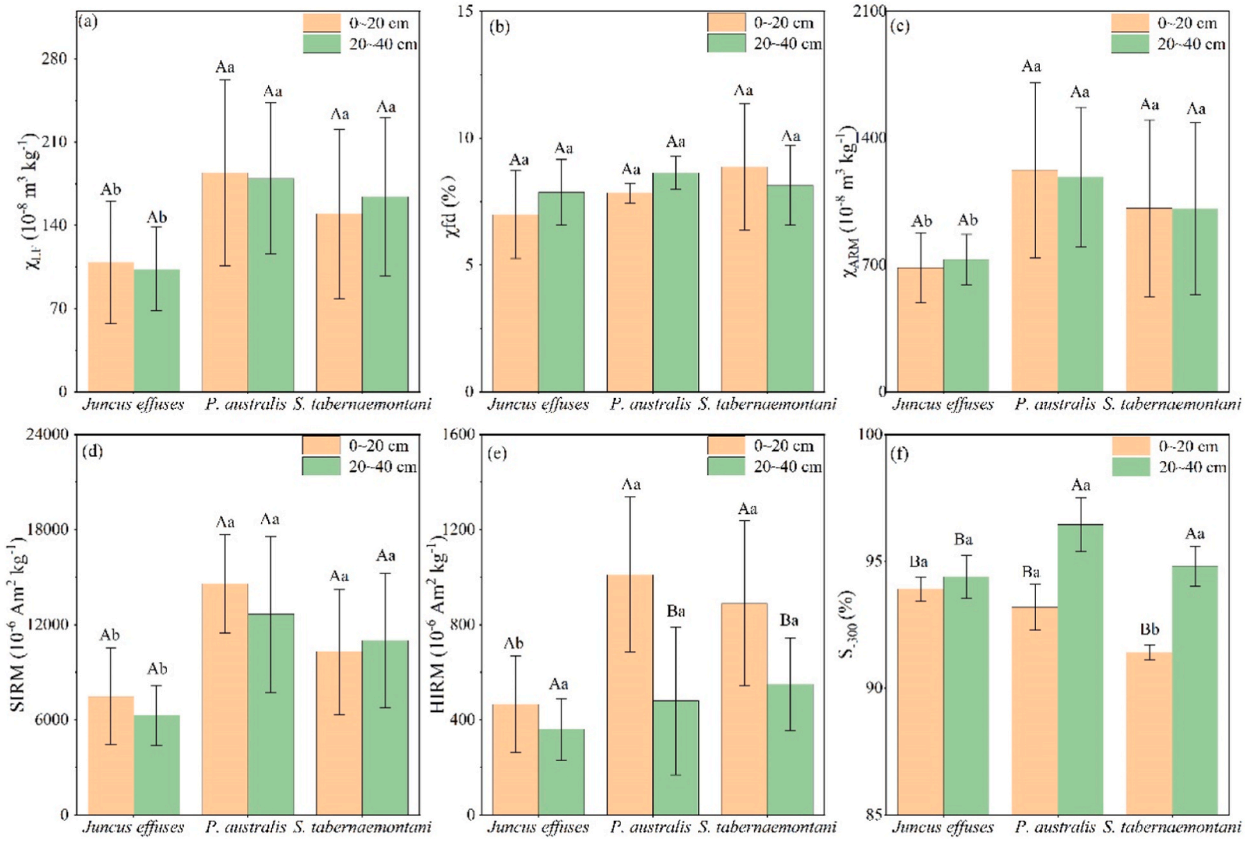

Fig. 3. Comparing magnetic characteristics of topsoil and subsoil at different vegetation habitats.

2.3. Data processing

The significant differences among vegetation types for the same soil layers were determined at the 5 % level using a Tukey–Kramer posthoc tests. Pairwise t-tests were used to examine the significant distinctions between top-soils and sub-soils within the same vegetation. Pearson correlation and linear regression analysis were employed to determine the relationships between HMs abundance and magnetic variables in soils.

3. Results

3.1. Variability of heavy metals in soil

As shown in Fig. 2, the levels of Cd, Sb, Cu, and Zn concentrated in top-soils across three vegetation habitats, whereas the concentrations of Cr in top-soils were marginally lower than that in sub-soils in *S. tabernaemontani*. *P. australis* demonstrated the highest levels of Cd, Sb, Cr, Ni and Zn in top-soils, as well as Cd and Zn in sub-soils (Fig. 2).

3.2. Variability of magnetic parameters in soil

χ_{LF}, χ_{ARM}, and SIRM in *P. australis* were slightly higher than those in other vegetation habitats in top-soils and sub-soils (Fig. 3). At the 0.05 significance level, no significant difference in χ_{fd}% was found at different vegetation (Fig. 3b). HIRM ranged from 466.67 ± 203.75 to 1010.43 ± 326.52 and 359.91 ± 130.75 to 550.02 ± 194.30 × 10^{-6} Am^2 kg^{-1} in top-soils and sub-soils, respectively (Fig. 3e). S_{-300} ranged from 91.41 ± 0.31 % to 93.90 ± 0.48 % in topsoil layer and 94.39 ± 0.84 % to 96.45 ± 1.05 % in subsoil layer (Fig. 3f). χ_{ARM}/χ_{fd} were higher in *Juncus effuses* (Fig. 4a), while χ_{ARM}/SIRM were slightly lower in *P. australis* (Fig. 4b).

3.3. Correlation between heavy metals and magnetic variables

At the 0.05 significance level, top-soils results showed a noteworthy positive correlation between χ_{LF} and Sb, χ_{LF} and Cu, χ_{ARM} and Sb, and χ_{ARM} and Cu (Fig. 4c). Conversely, the correlation between magnetic variables and HMs in the sub-soils was found to be

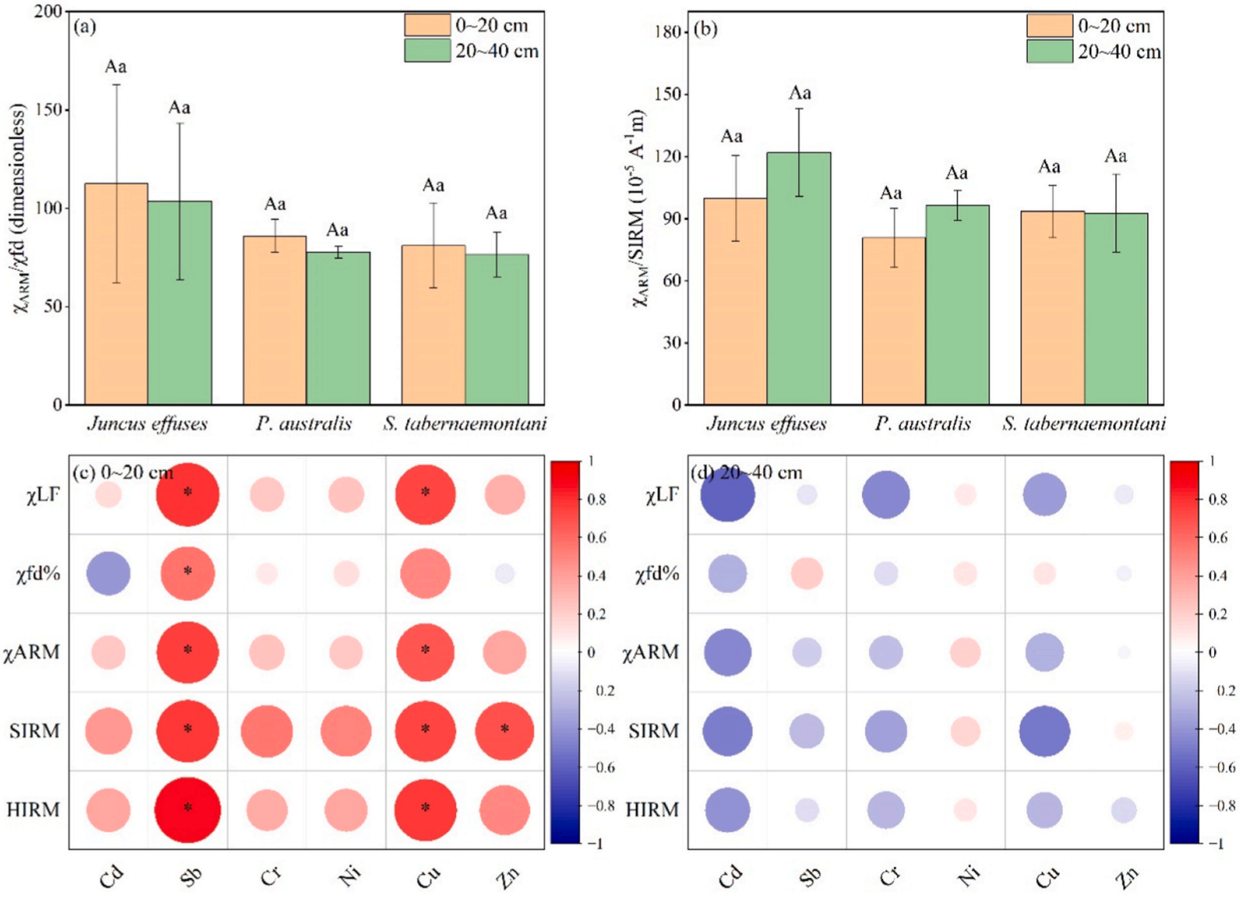

Fig. 4. Distribution of χ_{ARM}/χ_{fd} (a) and χ_{ARM}/SIRM (b) under vegetation habitats and correlation plot between heavy metal and magnetic parameters in topsoil (c) and subsoil (d). *P < 0.05.

insignificant (Fig. 4d).

4. Discussion

4.1. Influence of vegetation type change on HMs dynamics

All HMs in the habitats of *P. australis*, *Juncus effuses* and *S. tabernaemontani* were found to be slightly higher in top-soils than in sub-soils (Fig. 2a–f). The existence of elevated HMs concentrations in soils were associated with the contribution of exogenous HMs inputs and geogenic/pedogenic processes [29–31]. Top-soils experienced stress anthropogenic activities, resulting in the accumulation of significant quantities of HMs [30–32]. Geogenic processes primarily influence the presence of HMs in the sub-soils, with minimal migration of HMs from the top-soils to the sub-soils [7]. Previous research has also demonstrated that soil adsorption reduces the introduction of exogenous HMs into the sub-soils [7,32]. Compared with local geochemical background values [20], the maximum levels of Cd and Sb in top-soils were 1.92 folds and 14.39 folds above the limits, respectively (Fig. 2). A high concentration of Cd and Sb was also recorded in Caohai riparian soils, ditch, and lake sediments [20,21,45]. The proportion of Cd in secondary phase were higher than those of primary phase [22], while Sb predominantly occurred in residual fractions [45]. The cultivation of corn, potato, grains, and vegetables in cropland was prevalent, leading to the application of agricultural chemicals and pesticides. This practice resulted in an increased concentration of Cd and Sb in riparian ecosystems [10,33]. The presence of Cd can be attributed to the indigenous zinc smelting. Given a historical Pb–Zn smelting located approximately 15 km in Caohai riparian wetland [22,23], the contribution of Pb–Zn smelting to Cd enrichment cannot be disregarded.

P. australis was found to be a significant contributor to the accumulation of HMs in top-soils. Soils with a high organic matter content have been shown to provide sufficient sorption sites for HMs [1]. In terms of geochemical fractions of HMs, the concentration of Zn, and Sb were in residual-bound fraction > Fe-Mn oxides-bound fraction > organic matter–bound fraction in Caohai lake wetland [23,45]. Earlier studies have demonstrated that the well-developed root system and radial oxygen loss might promote the formation of iron plaque in the roots of *P. australis* [34]. The formation of iron plaque tended to prevent the absorption and enrichment of HMs in the

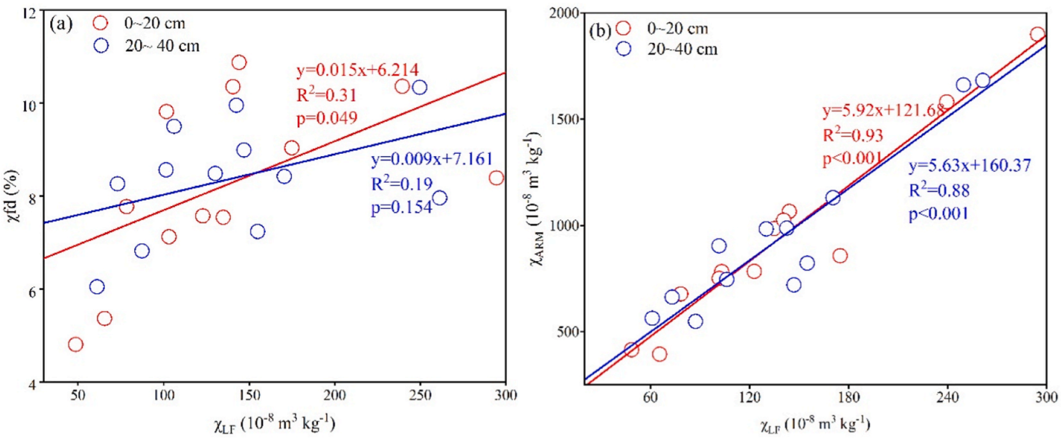

Fig. 5. Scatter plots of χ_{LF} vs χfd% (a) and χ_{LF} vs χ_{ARM} (b).

roots of *P. australis*, thus elevated those HMs in soils [35]. Given the high SOC and iron plaque in *P. australis* [34], this case had indicated *P. australis* might have higher concentration of some HMs than *Juncus effuses* and *S. tabernaemontani*. The level of selected HMs in soils was found to be higher in the alien plant, e.g. *Spartina alterniflora,* compared to the wetland with local plant species [19]. The distribution of HMs in the riparian ecosystem may have been influenced by changes in plant community components [1,10].

4.2. Influence of vegetation type change on HMs associated with iron-bearing minerals

The χ_{fd}% values were sensitive to the superparamagnetic (SP) size magnetic phases of pedogenic processes [36,37]. In poorly drained or waterlogged soils, SP ferrimagnetic minerals were found to be the least stable [38,39]. The decline in χ_{fd}% and χ_{LF} in poorly-drained soils can likely attributed to the anaerobic dissolution of inherited magnetite and soil-formed ferrous compounds [38]. Soil χ_{fd}% in dryland were much higher than that of paddy fields [39]. The mean values of χ_{fd}% ranged from 6.99 % to 9.32 % and there were no significant differences observed between *P. australis* and local plant species (Fig. 3b). These χ_{fd}% values align with those values reported in Caohai lake sediments [40] and ditch sediments [21]. The lithogenic and pedogenic processes obscured the impact of exogenous magnetic particles on magnetic signal enhancement in ditch soils [21]. At the 0.05 significance level, the R^2 values between topsoil χ_{LF} and χ_{fd}% were found to be 0.31 (Fig. 5a), whereas no significant statistically difference was observed in the relationship between subsoil χ_{LF} and χ_{fd}% (Fig. 5a). The contribution of superparamagnetic magnetic phases to the enhance χ_{LF} was relatively higher in top-soils. The positive relationship between χ_{LF} and χ_{ARM} ($R^2 = 0.88$–0.93, $p < 0.001$, Fig. 4b) highly meant the contribution of magnetic phases of single-domain to χ_{LF} [28]. The ratios of χ_{ARM}/χfd% and χ_{ARM}/SIRM were found to be higher in *Juncus effuses* and *S. tabernaemontani* compared to *P. australis* (Fig. 4a–b), the magnetic grains in *P. australis* were slightly coarser than those in *Juncus effuses* and *S. tabernaemontani*. Variations of $\chi_{LF,}$ χ_{ARM}, and SIRM were sensitively with the vegetation effect on the presence of soil-bound magnetic minerals accretion of stable domain grains.

The co-occurrence of HMs enrichment and magnetic signal enhancement in wetlands was found to be non-simultaneous [17,21]. Regional investigations have demonstrated that exogenous HMs are primarily associated with magnetic particles of coarser grain sizes [41,42], whereas pedogenic HMs are more likely to be lined to magnetic phases of SP/SD sizes [36,37]. The introduction of elevated exogenous HMs inputs has been shown to promote the enhancement of magnetic signals [15,41]. The close linkage of HMs abundance and magnetic signal characteristics partially favored the integration of HMs into the crystalline structure of iron-rich magnetic particles or their adsorption onto the surface of magnetic particles [43,44]. Present studies have indicated that the coexistence of pedogenically-produced magnetic particles and anthropogenic HMs exhibited a poor linages χ_{LF} between and those elements in Caohai lake [21]. This phenomenon reflected a minor influx of exogenous HMs associated with magnetic particles [21]. All selected HMs exhibited a weak association with magnetic variables in the sub-soils (Fig. 4b) and the magnetic enhancement of sub-soils did not correspond proportionally to the enrichment of those elements. Topsoil χ_{fd}% showed no significant relationship with HMs, but the correlation coefficient between χ_{LF} and Sb, χ_{LF} and Cu, χ_{ARM} and Sb, and χ_{ARM} and Cu were found to be 0.80, 0.73, 0.76, 0.67, respectively (Fig. 4a). Alterations in the circumstances of sampling sites may have an effect on the linkages between iron-bearing minerals and HMs. The different chemical phases of iron oxide had inconsistent effects on the geochemical behavior of HMs with the various environments, further studies should track the internal linkages between the various phases of iron oxide and exogenous HMs in soil minerals.

5. Conclusions

Across the examined regions, the *P. australis* was observed to have a tendency to enhance the prevalence of HMs and magnetic particles in soils. Findings from magnetic investigation suggested that lithogenic/pedogenic processes on magnetic signal characteristics outweighed that of anthropogenic loading in Caohai karst riparian ecosystems. Variations in Cu and Sb exhibited significant correlations with χ_{ARM}, SIRM, and HIRM in top-soils. The absence of correlation between magnetic variables and HMs was also recorded in sub-soils. It is necessary to carry out high-resolution spatial sampling and analysis to understand the biogeochemical processes of iron oxides and HMs in Caohai wetlands.

CRediT authorship contribution statement

Xin Yang: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Conceptualization. **Na An:** Software, Methodology, Investigation, Data curation. **Huipeng Luo:** Visualization, Software, Methodology, Investigation. **Jiao Zheng:** Visualization, Validation, Methodology, Investigation. **Jianlan Wu:** Visualization, Software, Methodology, Investigation, Formal analysis. **Dan Yang:** Supervision, Project administration, Funding acquisition, Conceptualization.

Data availability

Data will be made available on request.

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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