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Labile iron associated trace metals and REEs in estuarine surface sediments

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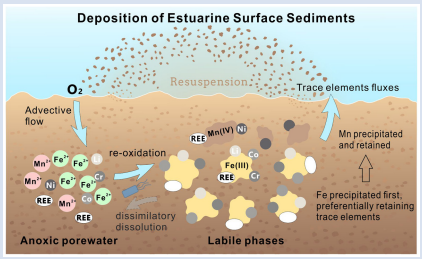
Abstract



Estuarine surface sediments experience frequent redox oscillations due to dynamic depositional environments, potentially altering key element cycles at the sediment-water interface. To examine the associations of elements in the most redox sensitive fractions, we applied flow through time-resolved analysis (FT-TRA) and batch dissolution dynamics to surface sediments collected from the Changjiang Estuary with diluted HNO_3. Our results revealed strong correlations in the release patterns of Fe with REEs, Cr, Co, and Li, as well as Mn with Ni. Additionally, light REEs (LREEs) showed enrichment in labile Fe oxyhydroxides, such as ferrihydrite, likely due to their high adsorption affinity for LREEs. Labile Fe plays a dominant role in bonding and fractionating trace elements in estuarine surface sediments, owing to its abundance and rapid reoxidation and coprecipitation. We propose that trace elements associated with labile Fe have high mobility and could be pumped out under dynamic depositional environments and the coupled redox oscillation. Fe served as the main switch of this "redox pump", regulating the net benthic fluxes and consequently the terrestrial inputs of trace elements to the marginal seas.

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Introduction

Iron (Fe) and manganese (Mn) oxyhydroxides are essential mediators in the benthic cycling of rare earth elements (REEs) and trace metals in dynamic marginal seas (Yang *et al.*, 2002; Borch *et al.*, 2010; Deng *et al.*, 2022; Lafrenière *et al.*, 2023). Their redox sensitive nature and high capacity for adsorption and co-precipitation drive their critical roles in the retention and release of trace elements (Yang *et al.*, 2002; Yuan *et al.*, 2004; Borch *et al.*, 2010). This role becomes particularly pronounced in estuarine environments, where redox oscillation in surface sediment prevails, modulated by coupled controls of hydrodynamic disturbance, benthic fauna, microbial activity, and organic matter inputs, *etc.* (Peiffer *et al.*, 2021; Zhou *et al.*, 2023). The frequency of redox oscillations across distinct spatio-temporal scales from minutely to monthly, amplifying the complexity of Fe and Mn cycling and their influence on trace element fluxes at the sediment-water interface (Borch *et al.*, 2010; Peiffer *et al.*, 2021; Song *et al.*, 2022; Hu *et al.*, 2024).

During steady state early diagenesis, Mn(IV) and Fe(III) oxyhydroxides are successively used by microbes as electron acceptors for organic matter remineralisation. The dissimilatory reduction of Fe and Mn phases and the complexation of organic ligands facilitates the release of adsorbed or coprecipitated trace metals (*e.g.*, Co, Ni, Cr) and REEs into porewaters, enabling their liberation from sediments *via* diffusion (Liu *et al.*, 2022; Zhu *et al.*, 2022; Zhang and Shields, 2023). Conversely, in the oxic sediment layer, as well as the reoxidation caused by sediment resuspension or bioturbation, dissolved Fe(II) and Mn(II) can be reoxidised forming oxyhydroxides that scavenge trace elements from porewater *via* coprecipitation and adsorption (Stolpe *et al.*, 2013; Zhou *et al.*, 2023). This cyclic dissolution and precipitation directly control the benthic fluxes of trace elements at the sediment-water interface, ultimately influencing terrestrial inputs of REEs and trace metals to marginal seas. Furthermore, these cyclic processes can cause fractionation of REEs or trace metals, producing distinctive geochemical signatures that reflect sedimentary redox histories and broader environmental conditions (Wu *et al.*, 2020; Peiffer *et al.*, 2021; Ma and Wang, 2023).

Although many studies have highlighted the quantitative importance of Fe-Mn oxyhydroxides in preserving trace elements (Manceau *et al.*, 2007; Chang *et al.*, 2016; Su *et al.*, 2017), large fractions of these oxyhydroxides are relatively unreactive during the redox oscillations of surface sediments (Poulton and Canfield, 2005). Only the labile fractions are susceptible to frequent redox oscillations and subsequently influence benthic fluxes at the sediment-water interface (Laufer *et al.*, 2020; Peiffer *et al.*, 2021). However, the geochemical properties of trace elements in the labile Fe-Mn oxyhydroxides and their potential recycling processes remain underexplored.

This study focuses on the labile fractions in surficial sediments of the Changjiang Estuary. In addition to the conventional batch dissolution dynamics, this study employed flow through time-resolved analysis (FT-TRA) to resolve compositional evolution at sub-minute resolution. The co-releases of Fe, Mn, REEs,

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and trace metals were closely monitored and compared using these two approaches. We aimed to investigate the distribution and associations of REEs and trace metals in the labile fractions of Fe and Mn oxyhydroxides, providing crucial insights into the benthic cycling processes during non-steady state early diagenesis. Understanding these dynamics is essential for evaluating the benthic fluxes of trace metals and REEs to coastal marine systems.

Materials and Methods

Sediment sampling. Surface sediment samples were collected from six stations along a salinity gradient in the Changjiang Estuary during research cruises in August and October 2023 (Fig. 1, Table S-1). Sediments from the upper 2 cm of the seabed, recognised by their yellowish colour, were retrieved using a box sampler. After collection, samples were immediately stored at 4 °C and freeze dried within one week. The dried sediments were sieved to remove particles larger than 125 µm. The sieved sediments were analysed for grain size distribution using a laser diffraction particle analyser (Malvern Mastersizer 3000). Total organic carbon (TOC) content was measured with a TOC analyser (Elementar vario EL cube). Total Fe content and other elements were quantified using HNO_3/HF digestion followed by measurement with inductively coupled plasma-optical emission spectrometry (ICP-OES, IRIS Advantage) and mass spectrometry (ICP-MS, Agilent 7900 Quadrupole).

Batch leaching experiments. For each station, 500 mg of sediment sample were extracted with 50 mL of 1 M $MgCl_2$ for two hours to remove exchangeable fractions. After centrifugation, the remaining solid was resuspended in 50 mL 0.5 M HNO_3 (double distilled) and stirred at 120 rpm. Labile Fe-Mn oxyhydroxides, which are most sensitive to redox oscillation and are potentially bioavailable, were expected to be leachable under these conditions. The suspension was sampled at regular intervals, centrifuged, and filtered through 0.22 µm filters. The filtrates were diluted 50 fold with 0.1 M HNO_3 and analysed using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900 Quadrupole). During ICP-MS measurements, a helium collision cell was used. Concentrations of Mn, Fe, Co, Ni, Cd, Li, and rare earth elements (REEs) were determined (McCurdy and Woods, 2004). The total REE concentration (∑REE) was calculated as the sum of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. REEs were further categorised into Light REEs (LREEs: La, Ce, Pr, Nd), Medium REEs (MREEs: Eu, Gd, Tb, Dy), and Heavy REEs (HREEs: Er, Tm, Yb, Lu). Internal standards (^{103}Rh and ^{115}In) were monitored to ensure precision, with count rate stability maintained below 3 % relative standard deviation (RSD). Double charging and oxide effects were minimised to below 1.7 % and 2.1 %, respectively.

Flow through time-resolved Analysis (FT-TRA). To avoid artifacts inherent to closed system reactors (*e.g.*, surface re-adsorption, secondary precipitation), a continuous flow through configuration was employed to leach the sediments, enabling phase discrimination through time-resolved elution signatures. To prepare for FT-TRA, 100 mg of sediment sample were initially extracted with 10 mL of 1 M $MgCl_2$ for two hours to remove the exchangeable fraction. After centrifugation, the solids were resuspended in 10 mL of ultrapure water. From this suspension, 10 mg of sediment were filtered onto 0.22 µm filters (Millipore Co.) and mounted in a flow through leaching system connected to an ICP-MS (Agilent 7900 Quadrupole) (Börner *et al.*, 2017). During the operation of FT-TRA, a constant flow rate of 0.5 mL/min was maintained using a gradient pump. Sequentially, 10 mL of 0.1 M and 0.5 M HNO_3 (double distilled) were pumped through the sediments. These HNO_3 solutions showed comparable Fe extraction capacity with HCl based on our pre-tests, and were chosen to target labile fractions of Fe-Mn oxyhydroxides, while optimising the matrix for real time measurement with ICP-MS. Similar ICP-MS methods and set-ups to those described above were used. Analytical reproducibility was confirmed using certified reference materials (GSR-6 limestone) and periodic testing of blank solutions. Analytical precision was ensured by replicating experiments under identical conditions. More information about our experiments, such as total amount of leached elements and correlation analysis, can be found in the Supplementary Information.

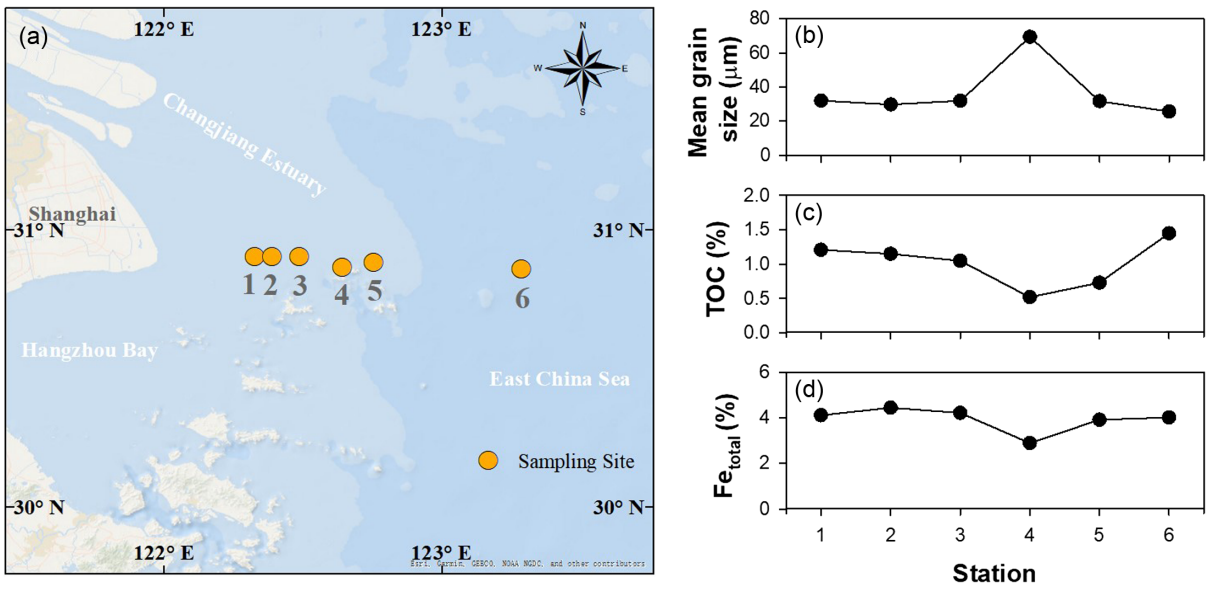

Figure 1 **(a)** Map of sampling stations in the Changjiang Estuary, **(b)** the mean grain size, **(c)** total organic carbon, and **(d)** total Fe weight percentage in sieved surface sediments of each station.

Results and Discussion

Sediment characteristics. The average grain size of the studied sediment fractions was 30.1 ± 2.7 μm across stations, except at station 4, where larger grains (69.4 μm) suggest a potential influence from nearby topography (Fig. 1). TOC content averaged 1.02 ± 0.34 %, and total Fe content averaged 3.93 ± 0.54 %, both showing stronger correlations with grain size than with distance from the estuary (Fig. 1). The total amounts of Fe extracted by batch leaching and FT-TRA were 4.3 ± 0.68 and 3.5 ± 1.05 mg/g sediment, which were comparable with each other and accounted for about 10 % of the total Fe (Table S-2).

Compared with traditional sequential Fe extractions (Poulton and Canfield, 2005), our extractions likely included carbonate-associated Fe and a large fraction of easily reducible oxides (*e.g.*, ferrihydrite, lepidocrocite), which were quantitively consistent with previous studies using sediments from a similar area of the Changjiang Estuary (Xu *et al.*, 2024). Approximately 0.35 ± 0.03 mg/g sediment of Mn were leached by batch leaching and FT-TRA. The abundance of Mn was less than one tenth that of Fe, implying Fe's greater role in trace element cycling. These labile Fe-Mn fractions are potentially the most susceptible to redox oscillations, reflecting the effects of complex biogeochemical processes during non-steady state early diagenesis (Laufer *et al.*, 2020; Peiffer *et al.*, 2021).

Trace metals associations with labile Fe-Mn oxyhydroxides. In both batch leaching and FT-TRA, the six stations exhibited consistent elemental release patterns with minor quantitative variations. The amount of trace metals extracted by these two approaches were comparable, with 16 % of Co, 17 % of Ni, 5 % of Cr, and 5 % of Li extracted from the sediments, respectively (Table S-2).

In the batch leaching, 92 % of Mn was released within 8 minutes, while Fe release was more gradual, with 52 % of Fe released within the same time frame (Fig. 2a). The extracted Ni, Co, Cr, and Li showed similar release patterns to Fe (Fig. 2a). Further Pearson correlation analysis revealed that Co and Ni correlated with both Fe and Mn, though Fe showed a stronger correlation than Mn as indicated by the *R* value (Fig. 2, Table S-3). Cr and Li only showed correlations with Fe.

In FT-TRA, more detailed associations were observed due to higher time resolution and different leaching gradients. Labile Mn was rapidly depleted by 0.1 M HNO_3, displaying a sharp release peak, with no further significant Mn release in subsequent 0.5 M HNO_3 leaching (Fig. 3a). In contrast, Fe exhibited a more gradual release, with higher peak intensity and a strong tailing effect during 0.1 M HNO_3 leaching. Further Fe release continued in 0.5 M HNO_3 leaching, albeit at reduced intensity (~0.38 times lower). Co and Li displayed strong correlations with Fe only during 0.1 M HNO_3 leaching ($R = 0.97$, $p < 0.01$), while Cr aligned closely with Fe in both leaching stages. Ni, on the other hand, was more strongly associated with Mn (Fig. 4, Table S-4). Combining the FT-TRA and batch leaching results, we suggest that in the labile fractions of estuarine surface sediments, Cr, Li and Co are primarily associated with Fe oxyhydroxides (*e.g.*, ferrihydrite), while Ni is preferentially associated with Mn oxides (*e.g.*, birnessite).

These observations align with prior studies where Ni was efficiently complexed with Mn oxides, particularly on the octahedral vacancy sites present on the birnessite [001] face, and further incorporated into the crystal structure of birnessite and buserite in marine sediments (Peacock, 2009; Shi *et al.*, 2024). Mn(IV) can oxidise Cr to highly soluble Cr(VI) species, limiting its association with Mn oxides (Liang *et al.*, 2021). Additionally, Cr(III) shares a high structural similarity with Fe(III), and may replace or incorporate preferentially into the lattices of labile Fe oxyhydroxides like ferrihydrite (coherent scattering domain size ~27 Å) (Tang *et al.*, 2010). The different Cr/Fe ratios in 0.1 M and 0.5 M HNO_3 extractions potentially reflect varying extents of structural replacement in Fe(III) oxyhydroxides with different crystallinities (Fig. 4c). Co and Li exhibited preferences for more labile and redox sensitive fractions of Fe oxyhydroxides, such as ferrihydrite, rather than more crystalline Fe forms extractable only in 0.5 M HNO_3 (Fig. 4a,d).

REEs association and fractionation by labile Fe. The amounts of REEs extracted by batch leaching and FT-TRA were comparable with each other, with 30.5 ± 1.5 % of REEs in sediments extracted, showing their enrichment in labile Fe fractions (Table S-2). In the batch leaching, 89 % of the release occurred within the first 8 minutes, while the compositions of REEs shifted with further releases of REEs and Fe (Fig. 1b). Notably, the ratio of LREE to HREE increased over time, indicating a stronger association of LREE with Fe oxyhydroxides. Correlation analysis revealed that REEs associate with both Fe and Mn (Fig. 2g,h), though FT-TRA provided more precise differentiation.

In FT-TRA, REEs release closely mirrored Fe release, with a relatively stable ∑REE/Fe ratio (~0.02) during 0.1 M HNO_3 leaching that decreased in 0.5 M HNO_3 leaching (Figs. 3a, 4e). This suggests that more labile fractions, such as amorphous Fe and ferrihydrite, are more efficient at retaining REEs. The correlation between Fe and ∑REE reached 0.94 ($p < 0.01$) and 0.93 ($p < 0.01$) for 0.1 M and 0.5 M HNO_3 leaching, respectively (Fig. 4e). Additionally, the LREE/∑REE ratio increased as Fe release progressed, stabilising around 0.75 after substantial Fe release (Fig. 4f). These results demonstrate Fe's dominant role in binding REEs and offer direct evidence for the preferential retention and fractionation of LREEs in labile Fe oxyhydroxides. This finding is consistent with the higher affinity of LREEs for Fe oxyhydroxide surface sites, where stable inner sphere complexes (a mixture of eight fold and nine fold coordination) resist rapid dissolution (Ohta *et al.*, 2009).

PAAS-normalised REE patterns revealed distinctions between conventional batch leaching and FT-TRA (Fig. S-3). The patterns from batch leaching were enriched in MREEs, resembling the characteristics found in the labile phases of Changjiang river and estuary sediments (Zhang *et al.*, 1998; Wang and Liu, 2008). However, the patterns obtained by FT-TRA were enriched in HREE, resembling the porewater characteristics (Deng *et al.*, 2022). We highlight the advantages of FT-TRA in avoiding surface re-complexation and secondary precipitation, reflecting more accurate elemental spatial distribution than batch dissolution in closed system. The resemblance of REE patterns with porewater may reflect the frequent aqueous-solid exchange under dynamic redox conditions, showing the high mobility of trace elements in the labile fractions.

Implications for trace element cycling in estuary sediments. This study underscores the role of labile Fe oxyhydroxides as primary drivers of trace metal and REE retention in estuarine surface sediments. The controlling influence of Fe could be intensified by the dynamic redox condition characteristic of these environments (Yuan *et al.*, 2004; Borch *et al.*, 2010; Shi *et al.*, 2024). In diffusion dominated settings, the Mn redox transition zone is typically closer to the sediment-water interface than Fe, thus Mn often regulates trace element fluxes from sediments (Deng *et al.*, 2022). However, in estuarine sediments, physical disturbances (*e.g.*, tides, waves, offshore currents) and bioturbation frequently disrupt redox stratification, leading to bulk sediment re-oxygenation in daily to monthly frequency (Song *et al.*, 2022). The faster reoxidation of Fe(II) compared to Mn(II) prioritises Fe(III) oxyhydroxides in coprecipitating and trapping trace

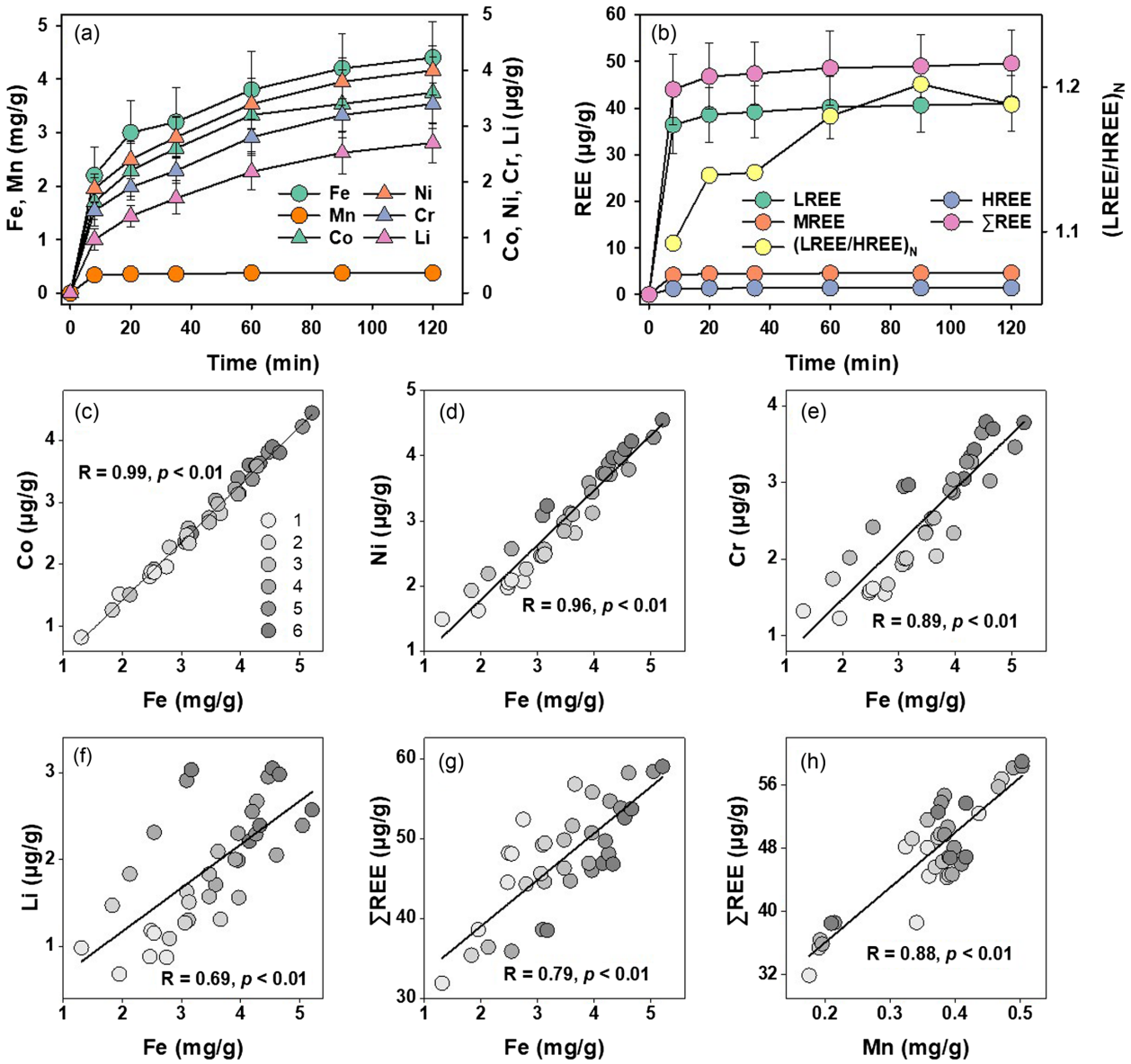

Figure 2 The release of **(a)** Fe, Mn, Co, Ni, Cr, and **(b)** REEs during the sediment leaching with 0.5 M HNO_3, as well as the cross plot of **(c)** Fe *vs.* Co, **(d)** Fe *vs.* Ni, **(e)** Fe *vs.* Cr, **(f)** Fe *vs.* Li, **(g)** Fe *vs.* ∑REE, **(h)** Mn *vs.* ∑REE over the releasing processes. In **(a, b)**, each point represents the mean ± standard deviation of values measured in sediments from six stations. $(LREE/HREE)_N$ represents the value that was PAAS normalised.

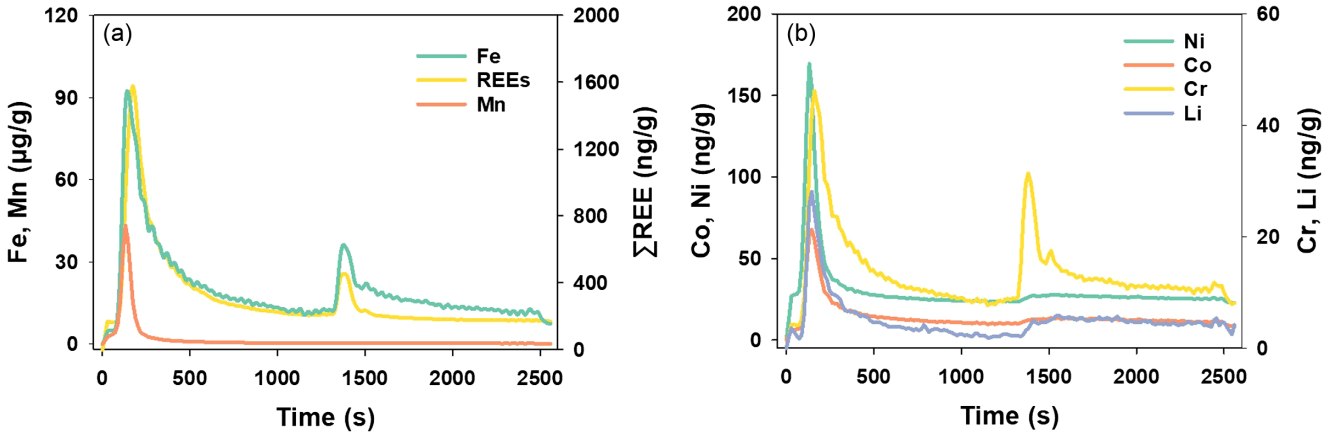

Figure 3 The dynamics of **(a)** Fe, Mn, and ∑REE, and **(b)** Co, Ni, Cr, and Li in the FT-TRA, during which 0.1 M and 0.5 M HNO_3 sequentially flowed through the sediments. The data points represent average values measured in six stations.

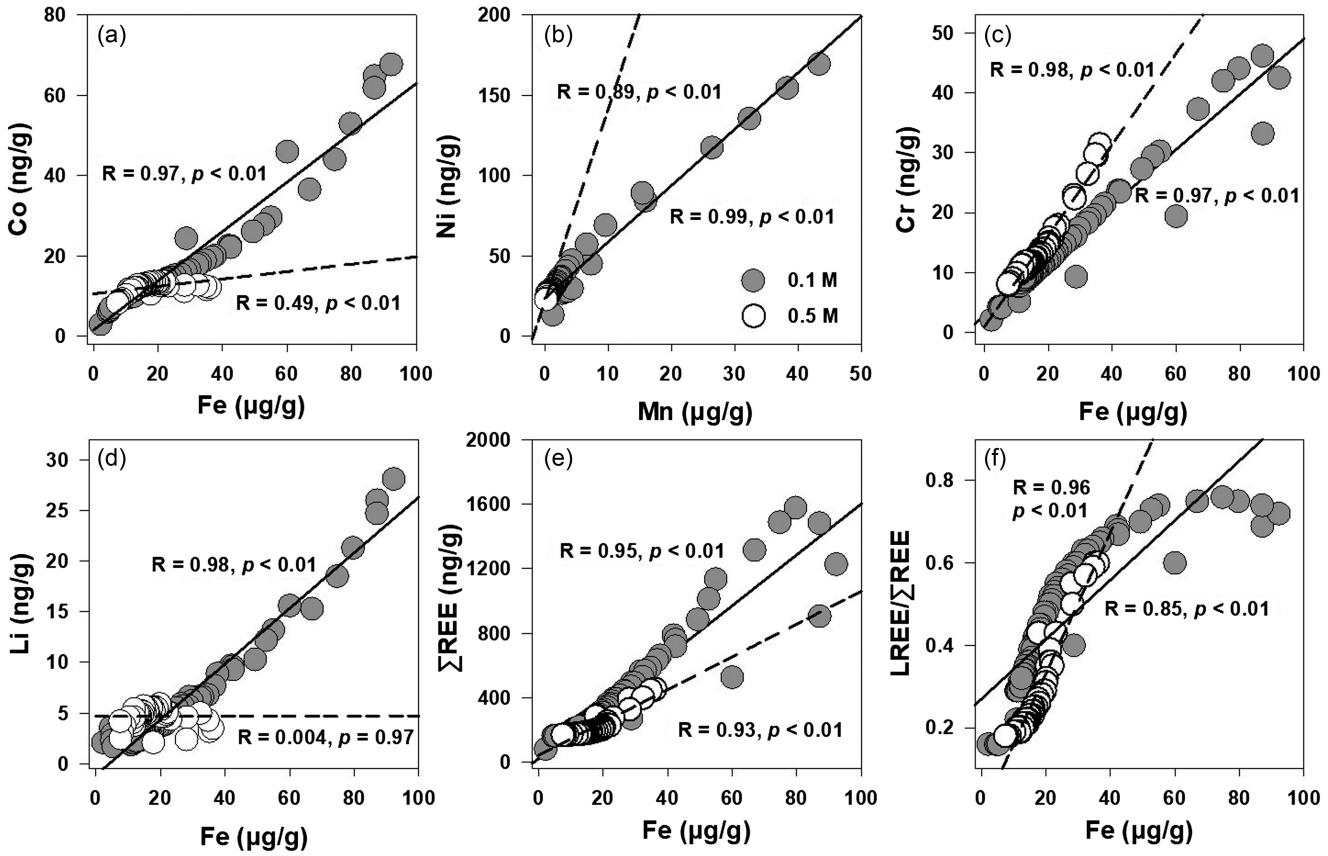

Figure 4 The cross plot of **(a)** Fe *vs*. Co, **(b)** Mn *vs*. Ni, **(c)** Fe *vs*. Cr, **(d)** Fe *vs*. Li, **(e)** Fe *vs*. ∑REE, and **(f)** Fe *vs*. LREE/∑REE in the effluent of FT-TRA. Solid and dashed lines represent the linear regression line in 0.1 M and 0.5 M HNO_3 leaching, respectively.

metals and REEs, thereby diminishing Mn's role in their retention (Peiffer *et al.*, 2021; Zhou *et al.*, 2023). This mechanism aligns with our findings that trace elements are preferentially associated and fractionated by Fe in the labile fractions of estuarine surface sediments.

Estimating benthic fluxes using porewater data from static cores often fails to include the output of dynamic depositional environments, particularly those driven by redox oscillation. Trace elements associated with labile Fe oxyhydroxides can be liberated during reductive dissolution using organic carbon as electron donor. These liberated trace elements can partially escape from capture by Fe reoxidation and coprecipitation/adsorption during advective discharge, thus contributing to benthic trace element fluxes (Zhou *et al.*, 2023). We hypothesise that this "redox pump", powered by non-steady state early diagenesis, increased the general mobility of trace elements preserved in the temporal sink of labile Fe oxyhydroxides, making them potential sources for benthic-pelagic exchange. Although the abundance of iron and trace elements in labile fractions is very limited (≤10 %), their role in trace elements solid-aqueous exchange is magnified under redox oscillation.

The power of the "redox pump", reflecting on the induced interactions between labile Fe and trace elements and their net fluxes, exhibits pronounced spatiotemporal variabilities in the estuarine environment. It is shaped by the sedimentary geochemical properties (*e.g.*, OC, Fe bioavailability) and the frequency of redox oscillation, which is further determined by the interplay of hydrodynamics, microbial activities, *etc*. Anthropogenic disturbances (*e.g.*, dredging, trawling) further disturbed sedimentary redox stratification, potentially amplifying the fluxes of trace metals liberated from labile Fe into the water column.

In summary, this study highlights the complexity of biogeochemical processes in estuarine surface sediments and emphasises the critical role of labile Fe in regulating trace element cycling. We suggest that the dynamic depositional environments, particularly the induced redox oscillations, can improve the mobility of trace elements associated with labile Fe, increasing their benthic fluxes and ultimately the overall fluvial inputs into the marginal sea. We highlight the importance of labile fractions in estuarine sediments, and encourage further application of FT-TRA to deepen insights into the co-evolution of elemental abundances and compositions during source to sink processes in the dynamic estuarine environments.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2515.

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References

Borch, T., Kretzschmar, R., Kappler, A., Cappellen, P.V., Ginder-Vogel, M., Voegelin, A., Campbell, K. (2010) Biogeochemical Redox Processes and their Impact on Contaminant Dynamics. *Environmental Science & Technology* 44, 15–23. https://doi.org/10.1021/es9026248

Börner, N., De Baere, B., Francois, R., Schwalb, A. (2017) Application of flow-through time-resolved analysis (FT-TRA) to isolate the elemental composition in ostracod calcite. *Chemical Geology* 467, 53–63. https://doi.org/10.1016/j.chemgeo.2017.07.019

Chang, C., Li, F., Liu, C., Gao, J., Tong, H., Chen, M. (2016) Fractionation characteristics of rare earth elements (REEs) linked with secondary Fe, Mn, and Al minerals in soils. *Acta Geochimica* 35, 329–339. https://doi.org/10.1007/s11631-016-0119-1

Deng, K., Yang, S., Du, J., Lian, E., Vance, D. (2022) Dominance of benthic flux of REEs on continental shelves: implications for oceanic budgets. *Geochemical Perspectives Letters* 22, 26–30. https://doi.org/10.7185/geochemlet.2223

Hu, C., Liu, M., Li, Y., Li, J., Che, X., Wang, H. (2024) Sedimentation and transformation of heavy metals during the transport from the Yellow River estuary to the sea: Evidence from surface sediments of the Yellow River subaqueous delta. *Marine Pollution Bulletin* 207, 116862. https://doi.org/10.1016/j.marpolbul.2024.116862

Lafrenière, M.-C., Lapierre, J.-F., Ponton, D.E., Guillemette, F., Amyot, M. (2023) Rare earth elements (REEs) behavior in a large river across a geological and anthropogenic gradient. *Geochimica et Cosmochimica Acta* 353, 129–141. https://doi.org/10.1016/j.gca.2023.05.019

Laufer, K., Michaud, A.B., Røy, H., Jørgensen, B.B. (2020) Reactivity of Iron Minerals in the Seabed Toward Microbial Reduction – A Comparison of Different Extraction Techniques. *Geomicrobiology Journal* 37, 170–189. https://doi.org/10.1080/01490451.2019.1679291

Liang, J.L., Huang, X.M., Yan, J.W., Li, Y.Y., Zhao, Z.W., Liu, Y.Y., Ye, J.Y., Wei, Y.M. (2021) A review of the formation of Cr(VI) via Cr(III) oxidation in soils and groundwater. *Science of The Total Environment* 774, 145762. https://doi.org/10.1016/j.scitotenv.2021.145762

Liu, W., Lu, G., Wang, W.X. (2022) *In situ* high-resolution two-dimensional profiles of redox sensitive metal mobility in sediment-water interface and porewater from estuarine sediments. *Science of The Total Environment* 820, 153034. https://doi.org/10.1016/j.scitotenv.2022.153034

Ma, L., Wang, W.-X. (2023) Dissolved rare earth elements in the Pearl River Delta: Using Gd as a tracer of anthropogenic activity from river towards the sea. *Science of The Total Environment* 856, 159241. https://doi.org/10.1016/j.scitotenv.2022.159241

Manceau, A., Lanson, M., Geoffroy, N. (2007) Natural speciation of Ni, Zn, Ba, and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. *Geochimica et Cosmochimica Acta* 71, 95–128. https://doi.org/10.1016/j.gca.2006.08.036

McCurdy, E., Woods, G. (2004) The application of collision/reaction cell inductively coupled plasma mass spectrometry to multi-element analysis in variable sample matrices, using He as a non-reactive cell gas. *Journal of Analytical Atomic Spectrometry* 19, 607–615. https://doi.org/10.1039/b312250f

Ohta, A., Kagi, H., Nomura, M., Tsuno, H., Kawabe, I. (2009) Coordination study of rare earth elements on Fe oxyhydroxide and Mn dioxides: Part I. Influence of a multi-electron excitation on EXAFS analyses of La, Pr, Nd, and Sm. *American Mineralogist* 94, 467–475. https://doi.org/10.2138/am.2009.2986

Peacock, C.L. (2009) Physiochemical controls on the crystal-chemistry of Ni in birnessite: Genetic implications for ferromanganese precipitates. *Geochimica et Cosmochimica Acta* 73, 3568–3578. https://doi.org/10.1016/j.gca.2009.03.020

Peiffer, S., Kappler, A., Haderlein, S.B., Schmidt, C., Byrne, J.M., Kleindienst, S., Vogt, C., Richnow, H.H., Obst, M., Angenent, L.T., Bryce, C., McCammon, C., Planer-Friedrich, B. (2021) A biogeochemical–hydrological framework for the role of redox-active compounds in aquatic systems. *Nature Geoscience* 14, 264–272. https://doi.org/10.1038/s41561-021-00742-z

Poulton, S.W., Canfield, D.E. (2005) Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chemical Geology* 214, 209–221. https://doi.org/10.1016/j.chemgeo.2004.09.003

Shi, M., Li, Q., Wang, Q., Yan, X., Li, B., Feng, L., Wu, C., Qiu, R., Zhang, H., Yang, Z., Yang, W., Liao, Q., Chai, L. (2024) A review on the transformation of birnessite in the environment: Implication for the stabilization of heavy metals. *Journal of Environmental Sciences* 139, 496–515. https://doi.org/10.1016/j.jes.2023.06.019

Song, S., Santos, I.R., Yu, H., Wang, F., Burnett, W.C., Bianchi, T.S., Dong, J., Lian, E., Zhao, B., Mayer, L., Yao, Q., Yu, Z., Xu, B. (2022) A global assessment of the mixed layer in coastal sediments and implications for carbon storage. *Nature Communications* 13, 4903. https://doi.org/10.1038/s41467-022-32650-0

Stolpe, B., Guo, L.D., Shiller, A.M. (2013) Binding and transport of rare earth elements by organic and iron-rich nanocolloids in Alaskan rivers, as revealed by field-flow fractionation and ICP-MS. *Geochimica et Cosmochimica Acta* 106, 446–462. https://doi.org/10.1016/j.gca.2012.12.033

Su, N., Yang, S.Y., Guo, Y.L., Yue, W., Wang, X.D., Yin, P., Huang, X.T. (2017) Revisit of rare earth element fractionation during chemical weathering and river sediment transport. *Geochemistry, Geophysics, Geosystems* 18, 935–955. https://doi.org/10.1002/2016GC006659

Tang, Y.Z., Michel, F.M., Zhang, L.H., Harrington, R., Parise, J.B., Reeder, R.J. (2010) Structural Properties of the Cr(III)−Fe(III) (Oxy)hydroxide Compositional Series: Insights for a Nanomaterial "Solid Solution". *Chemistry of Materials* 22, 3589–3598. https://doi.org/10.1021/cm1000472

Wang, Z.-L., Liu, C.-Q. (2008) Geochemistry of rare earth elements in the dissolved, acid-soluble and residual phases in surface waters of the Changjiang Estuary. *Journal of Oceanography* 64, 407–416. https://doi.org/10.1007/s10872-008-0034-0

Wu, Y.J., Fan, D.D., Wang, D.L., Yin, P. (2020) Increasing hypoxia in the Changjiang Estuary during the last three decades deciphered from sedimentary redox-sensitive elements. *Marine Geology* 419, 106044. https://doi.org/10.1016/j.margeo.2019.106044

Xu, P., Su, N., Lian, E., Wang, R., Yang, S. (2024) Enrichment effect and environmental control of clay reactive iron in the Changjiang River estuary and East China Sea. *Marine Geology & Quaternary Geology* 44, 54–64. https://doi.org/10.16562/j.cnki.0256-1492.2024030301

Yang, S.Y., Jung, H.S., Choi, M.S., Li, C.X. (2002) The rare earth element compositions of the Changjiang (Yangtze) and Huanghe (Yellow) river sediments. *Earth and Planetary Science Letters* 201, 407–419. https://doi.org/10.1016/S0012-821X(02)00715-X

Yuan, C.-G., Shi, J.-B., He, B., Liu, J.-F., Liang, L.-N., Jiang, G.-B. (2004) Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environment International* 30, 769–783. https://doi.org/10.1016/j.envint.2004.01.001

Zhang, C., Wang, L., Zhang, S., Li, X. (1998) Geochemistry of rare earth elements in the mainstream of the Yangtze River, China. *Applied Geochemistry* 13, 451–462. https://doi.org/10.1016/S0883-2927(97)00079-6

Zhang, K., Shields, G.A. (2023) Early diagenetic mobilization of rare earth elements and implications for the Ce anomaly as a redox proxy. *Chemical Geology* 635, 121619. https://doi.org/10.1016/j.chemgeo.2023.121619

Zhou, Z., Henkel, S., Kasten, S., Holtappels, M. (2023) The iron "redox battery" in sandy sediments: Its impact on organic matter remineralization and phosphorus cycling. *Science of The Total Environment* 865, 161168. https://doi.org/10.1016/j.scitotenv.2022.161168

Zhu, L., Zhang, X., Zhang, J., Liu, T., Qiu, Y. (2022) Saltwater intrusion weakens Fe-(oxyhydr)oxide-mediated (im)mobilization of Ni and Zn in redox-fluctuating soil–groundwater system. *Water Research* 221, 118799. https://doi.org/10.1016/j.watres.2022.118799