



Methods for investigating trace metal speciation and partitioning in mangrove sediments: a systematic quantitative literature review

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Abstract

Purpose Mangrove rhizosphere sediments are strong sinks for trace metals, yet conventional sampling and analytical approaches often lack the resolution to capture the fine-scale biogeochemical processes driving metal immobilisation. This review evaluates the limitations of common methodologies used to study trace metal speciation and partitioning in mangrove sediments and provides recommendations for best practices.

Methods A systematic quantitative literature review was conducted on peer-reviewed articles published between 1991 and 2026. Searches across four databases yielded 667 articles, of which 187 met the selection criteria and were coded to evaluate global methodological trends and identify key limitations and opportunities for improvement.

Results Most studies were conducted in Asia, followed by Brazil and Australia, with *Avicennia marina* the most frequently studied species. The most frequently reported metals were Cu, Zn, Pb, Fe, Ni, Cr, Cd, and Mn, reflecting industrial relevance and toxicity. Sequential extraction methods were applied in 45% of studies; however, anoxic sample handling, critical for preserving redox-sensitive phases, was rarely reported. High-resolution techniques such as DGT and DET were seldom used despite their capacity to resolve fine-scale biogeochemical processes.

Conclusion Conventional sampling and analytical approaches often fail to capture the fine-scale, redox-driven processes driving trace metal sequestration and partitioning in mangrove sediments. Adoption of methods to preserve in-situ redox conditions and the application of high-resolution analytical approaches to study fine-scale biogeochemical processes will enhance our understanding of trace metal mobility and ecological risk in mangrove ecosystems.

Keywords Mangrove · Sediment · Metal · Partition · Redox · Speciation

1 Introduction

Mangroves are a woody halophyte (salt tolerant plant) that grow in shallow intertidal estuarine regions of tropical, subtropical, and temperate climates where water temperatures typically range from 12 °C to 32 °C (Andersen and Kristensen 1988; Hogarth 2015; Tomlinson 2016). In 2020, mangrove forests were estimated to cover 145,068 km² of coastlines globally, with Indonesia, Brazil, and Australia hosting the largest areas (Jia et al. 2023). These forests

include approximately 70 species, which have evolved various mechanisms to tolerate salinities ranging from brackish to hypersaline (Liang et al. 2008; Alongi 2009; Parida and Jha 2010). Their widespread distribution and adaptive abilities emphasise their pivotal role in coastal biogeochemical cycles and habitat stability (Kathiresan and Bingham 2001; Hogarth 2015).

Mangroves provide a wide range of valuable ecosystem services to coastal environments (Alongi 2009; Tomlinson 2016; Kathiresan 2021; Wang and Gu 2021). Their intricate root systems act as a natural wave energy buffer, reducing coastal erosion and protecting shorelines from extreme weather events such as storm surge and flooding (Wang and Gu 2021). Additionally, mangroves improve water quality by trapping suspended particulates, promoting sediment deposition, and sequestering contaminants (Zhang et al. 2014; Wang and Gu 2021). Mangroves remove carbon dioxide from the atmosphere via photosynthesis and

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facilitate the efficient storage of organic carbon within their rhizosphere sediments, making them one of the world's most effective blue carbon sinks (Suratman 2008; Alongi 2012; Inoue 2019). Despite their ecological significance, global mangrove coverage declined by 39% between the 1970s and 2014 due to anthropogenic pressures, prompting increased efforts in restoration and conservation to counteract habitat loss and mitigate climate change impacts (Kodikara et al. 2017; Worthington and Spalding 2018; Lovelock et al. 2022).

Trace metals and metalloids occur naturally at low concentrations in the environment, typically in the $\mu\text{g/L}$ range (Pacyna et al. 1995; Pacyna and Pacyna 2001; Tchounwou et al. 2012). While trace metals are essential for various biological processes and critical for sustaining life, elevated concentrations can pose significant ecological risks due to their toxicity and ability to accumulate in ecosystems (Mertz 1993; Morel and Price 2003). Natural sources of trace metals in estuaries primarily stem from weathering and erosion of geological substrates, while anthropogenic activities, such as wastewater discharge, agricultural runoff, and industrial emissions, have significantly increased their flux to these environments (Pacyna and Pacyna 2001; McComb et al. 2014; Kolarova and Napiórkowski 2021). The growing demand for critical minerals, driven by the development of sustainable technologies, has raised concerns over the environmental impact of mining, transport, and disposal of emerging metal contaminants (Moss et al. 2011; Sauvé and Desrosiers 2014; Rhodes 2019; Batley and Campbell 2022). In mangrove ecosystems, the dense root systems and reduced water flow promote sedimentation, making these environments critical sinks for trace metals, highlighting their importance in mitigating metal contamination in coastal systems (Harbison 1986; Van Santen et al. 2007; Adame et al. 2010).

Sedimentation in mangrove forests can be up to ten times higher than in comparable unvegetated sediments, contributing to a substrate rich in organic matter, fine sediments, and reactive minerals such as iron and manganese oxyhydroxides (Janat Augustine and Chandramohanakumar 2002; Van Santen et al. 2007). These fine particles, with high surface area and enhanced metal adsorption characteristics, lead to considerably higher concentrations of trace metals in mangrove sediments compared to un-vegetated sediments (Lacerda et al. 1993; Janat Augustine and Chandramohanakumar 2002). Despite the elevated rates of sedimentation, mangrove sediments typically have unique redox profiles compared to other coastal sediments (Clark et al. 1998; Ferreira et al. 2007). This is due to the high organic content and fine particle composition, which limit oxygen diffusion and promote rapid microbial consumption of available oxygen, resulting in a thin oxic layer, at the sediment surface, that

quickly transitions to anoxic conditions within millimetres (Alongi 2005; Sarker et al. 2021; Jørgensen et al. 2022). The shallow depth of the oxic-anoxic interface is a key feature that influences biogeochemical processes such as carbon sequestration, nutrient cycling, and the reduction of metal oxyhydroxides in mangrove ecosystems (Clark et al. 1998; Du Laing et al. 2009; Alongi 2021).

Redox zonation in mangrove sediments is shaped by microbial respiration, where different electron acceptors are consumed sequentially in order of their energy yield. The typical order of consumption is, oxygen, nitrate, manganese and iron oxyhydroxides, sulfate, and carbon dioxide (Froelich et al. 1979; Burdige 2007, 2012; Hargrave et al. 2008; Huerta-Diaz and Reimer 2010; Ucar et al. 2017). Sulfate reduction often dominates the bacterial anaerobic metabolism in mangrove sediments and plays a key role in trace metal sequestration through pyritization, which incorporates metals into relatively stable sulfide minerals (Alongi et al. 2000; Müller et al. 2002; Grant et al. 2018). Bioturbation by benthic infauna and radial oxygen loss from mangrove roots further influence redox conditions and trace metal behaviour by creating oxygen-rich microsites and facilitating metal adsorption, complexation, and precipitation, which may also vary with tidal oscillations and sediment permeability (Choi and Park 2004; Kusky 2008; Middelburg and Levin 2009; Vidal Dura 2017; Jørgensen et al. 2019; De Santana et al. 2021). The highly dynamic nature of mangrove sediments creates a complex environment, where redox zonation and trace metal partitioning occur on a micro-scale spatial resolution making it challenging to accurately assess trace metal geochemistry (Lacerda et al. 1993; McComb et al. 2014; de Lacerda et al. 2022; Harmesa et al. 2022; Pan et al. 2023).

The majority of studies to date have investigated trace metal geochemistry in mangrove sediments using conventional sampling techniques such as sediment coring, which typically provide low spatial resolution, often limited to core slices of 0.5–1 cm in depth (Janaki-Raman et al. 2007; Qiu et al. 2011; Natesan et al. 2014). However, numerous studies have demonstrated that biogeochemical zonation in mangrove sediments can be heterogeneous at sub-millimetre spatial scales (Robertson et al. 2008; Kankanamge et al. 2020; Pan et al. 2020). Furthermore, most investigations into the geochemistry of major trace metal host phases, such as iron sulfides and organically bound sulfur, have relied on selective or sequential extraction methods. These methods are inherently operational in nature and often result in incomplete recovery of target species, while potentially co-extracting multiple species within a single fraction (Prietz et al. 2003, 2011). Given that the fate of trace metals in sediments is closely linked to major biogeochemical processes (e.g., iron oxidation and reduction, sulfate reduction, iron sulfide precipitation) that can alter their speciation, it is

essential to examine trace metal behaviour at comparably fine spatial scales to accurately characterise the mechanisms driving trace metal sequestration in mangrove sediments.

The objective of this systematic quantitative literature review is to evaluate the range of sampling methodologies and analytical techniques used to investigate trace metal speciation and partitioning in mangrove sediments globally. This comprehensive analysis will provide valuable insights into the limitations of common sampling and analytical approaches applied to study trace metals in mangrove sediments. Identifying the key limitations of existing research on trace metal speciation and partitioning in mangrove sediments will enable us to establish a clear set of recommendations for the optimal field sampling techniques and analytical methodologies to apply to study trace metals in mangrove ecosystems.

2 Materials and methods

2.1 Systematic quantitative literature review

The present literature review applies the Systematic Quantitative Literature Review (SQLR) methodology (Pickering and Byrne 2014) to analyse scientific literature. The SQLR method bridges the gap between the traditional narrative review and meta-analysis (Carlini et al. 2021). It systematically selects relevant scientific peer-reviewed literature from various databases and quantifies their information to identify research gaps within the literature (Pickering and Byrne 2014; Carlini et al. 2021; Humphries et al. 2021; Lee et al. 2023). The data that is coded into a database can include bibliographic information, study location, research objective, methodologies employed, and results. This is a robust and reliable analytical approach that delivers quantifiable, reproducible results, ensuring high confidence in the literature findings. (Carlini et al. 2021).

2.2 Data compilation

Four commonly used online databases (JSTOR, ScienceDirect, Scopus and Web of Science) as described by Lee et al. (2023) and Pickering and Byrne (2014) were searched in February 2026 to compile peer reviewed articles that focused on trace metal speciation and partitioning in mangrove sediments. The search terms used were metal* AND sediment* AND mangrove* AND (partition* OR sequential OR redox OR speciation OR cycl*). The search was not limited to a specific range of publication years. The search identified a total of 667 articles (JSTOR ($n=5$), ScienceDirect ($n=93$), Scopus ($n=217$) and Web of Science ($n=352$)) which were entered into a custom database (Zotero), where

irrelevant articles (e.g. reviews, full text unavailable, language or non-academic literature) ($n=27$) and duplicates ($n=241$) were excluded. A title scan was then performed to identify and remove articles that did not relate to both mangrove sediments and metals ($n=75$), followed by an abstract scan to identify and exclude articles that did not explore the speciation or partitioning of metals within the mangrove sediments, for example, environmental monitoring studies that simply evaluated total metal concentrations ($n=80$). The remaining 244 articles were entered into Excel for full text screening and subsequent systematic quantitative analysis.

2.3 Coding

During the full text screen, a further 57 articles were excluded as they were identified as non-relevant to the research question. The remaining 187 articles were coded in Excel based on criteria such as bibliographic details, geographic data, mangrove taxonomy, metals analysed, sampling methodology (e.g. retrieval method, anoxic sample handling), metal extraction methodology (e.g. single step vs. sequential extractions) and analytical instrumentation used to characterise trace metals. The coding criteria are outlined in detail in Table 1 and in the coding database provided as Supplementary Information.

3 Results and discussion

The 187 articles included in this review were published between 1991 and 2026 (Fig. 1). Over the 23-year period from 1991 to 2013, the average annual publication rate was less than two articles ($n=38$). However, from 2014 to 2026, the average increased to 12.4 articles per year ($n=149$), reaching a maximum of 19 articles published in 2022. The recent surge in studies is likely attributed to the increasing recognition of the mangrove plants' role in climate change mitigation, particularly their exceptional ability to offset greenhouse gasses and sequester large amounts of carbon in their sediments (Song et al. 2023). Additionally, mangrove sediments are recognised sinks for sediment bound contaminants such as trace metals (Harbison 1986; de Lacerda et al. 2022). Increased attention on mangrove restoration and newly constructed mangrove wetland projects (Charoenlerkthawin et al. 2024) may have contributed to the rise in publications over the past decade.

The studies evaluated in this review were carried out in 24 different countries spanning four geographic regions (Fig. 2). Out of the 187 studies more than 64% were done in Asia ($n=121$), predominantly in China ($n=50$) and India ($n=37$) followed by Malaysia ($n=11$), Vietnam ($n=6$),

Table 1 Classification and information criteria used for data coding

Category	Variables	Description
Publication	Author(s)	Name of Author(s)
	Year	Year published
	Title	Article name
	Journal	Journal name
Geographic	Region	Geographic region
	Coordinates	Latitude and longitude
	Country	Country
	Climate zone	Tropical, sub-tropical, temperate
Taxonomic	Target family and species	Mangrove species
Elements	Trace metal	Aluminium (Al), Arsenic (As), Silver (Ag), Boron (B), Barium (Ba), Beryllium (Be), Bismuth (Bi), Bromine (Br) Calcium (Ca), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Caesium (Cs), Copper (Cu), Iron (Fe), Germanium (Ge), Hafnium (Hf), Mercury (Hg), Iridium (Ir), Potassium (K), Lithium (Li), Magnesium (Mg), Manganese (Mn), Molybdenum (Mo), Sodium (Na), Niobium (Nb), Nickel (Ni), Osmium (Os), Lead (Pb), Palladium (Pd), Platinum (Pt), Rubidium (Rb), Rhodium (Rh), Ruthenium (Ru), Sulfur (S), Antimony (Sb), Scandium (Sc), Selenium (Se), Tin (Sn), Strontium (Sr), Tantalum (Ta), Thorium (Th), Titanium (Ti), Thallium (Tl), Uranium (U), Vanadium (V), Tungsten (W), Yttrium (Y), Zinc (Zn) and Zirconium (Zr)
Methodology	Sediment sampling	Sampling method; depth of sample; profile resolution methods
	Anoxic sample handling	Sample handling
	Extraction method	Single step; sequential; x-ray; two-dimensional high resolution
	Analytical instrumentation	AAS, ICP-MS and ICP-OES

Indonesia ($n=3$), Saudi Arabia ($n=3$), Thailand ($n=3$), Bangladesh ($n=3$), Borneo ($n=1$), Cambodia ($n=1$), Iran ($n=1$), Taiwan ($n=1$) and United Arab Emirates ($n=1$). Approximately 21% of the studies were done in North and South America ($n=39$), the majority taking place in Brazil ($n=31$). Smaller numbers were done in Martinique ($n=2$),

Venezuela ($n=2$), French Guiana ($n=1$), Guadeloupe ($n=1$), Puerto Rico ($n=1$) and USA ($n=1$). Studies in Oceania accounted for approximately 11% ($n=21$), primarily in Australia ($n=10$) and New Caledonia ($n=10$) with a single study from New Zealand. Finally, approximately 4% ($n=5$) of the studies were done in the African countries of Egypt ($n=4$), Mayote ($n=1$), Nigeria ($n=2$) and Tanzania ($n=1$). Over 77% of the studies were done in tropical climate zones ($n=144$), with approximately 22% and 2% of studies in sub-tropical and temperate zones, respectively.

Across the 187 articles, trace metal distributions in the sediments inhabited by 32 mangrove species were examined (Fig. 3). The majority of these studies focused on areas with multiple species ($n=71$), while 25 articles examined areas with only a single species. Notably, over one-third of the studies ($n=71$) did not specify the specific mangrove species inhabiting the area, likely due to challenges in identifying individual species in mixed-species forests, where root and rhizome systems often intersect.

Avicennia marina was the most frequently examined species among the studies ($n=48$), followed by *Aegiceras corniculatum* ($n=25$) and species in the *Rhizophora* genus ($n=60$). The prominence of these species aligns closely with our current understanding of mangrove species distribution (Duke et al. 1998, 2002; Fazlioglu et al. 2020; Takayama et al. 2021; Ma et al. 2022; Martínez-Díaz and Reef 2023). *Avicennia marina* is recognised as the most widely distributed mangrove species globally (Duke et al. 1998; Martínez-Díaz and Reef 2023), while *Aegiceras corniculatum* and *Rhizophora* also have widespread species distributions (Duke et al. 2002; Deng et al. 2009; Fazlioglu et al. 2020; Takayama et al. 2021; Zhang et al. 2022; Samal et al. 2023). These species are especially dominant in the Indo-Pacific biogeographic region (Duke et al. 1998, 2002; Deng et al. 2009; Takayama et al. 2021; Zhang et al. 2022; Samal et al. 2023), which accounts for the majority of the studies. Their broad distribution highlights their essential roles in sediment stabilisation and biogeochemical cycling, making them important subjects for research on trace metal distribution within mangrove sediments.

3.1 Metals

This review identified a total of 51 trace metals (including rare earth elements (REEs) as a single group) from the articles examined (Fig. 4). The most commonly studied trace metals were copper [Cu] ($n=135$), zinc [Zn] ($n=138$), lead [Pb] ($n=109$), nickel [Ni] ($n=99$), iron [Fe] ($n=96$), chromium [Cr] ($n=92$), cadmium [Cd] ($n=92$) and manganese [Mn] ($n=88$). Over the 35-year period that the articles were published, these metals were frequently studied. This is likely due to their industrial association, widespread use,

Fig. 1 Number of articles on the topic of trace metal geochemistry in mangrove sediments published annually between 1991 and 2026

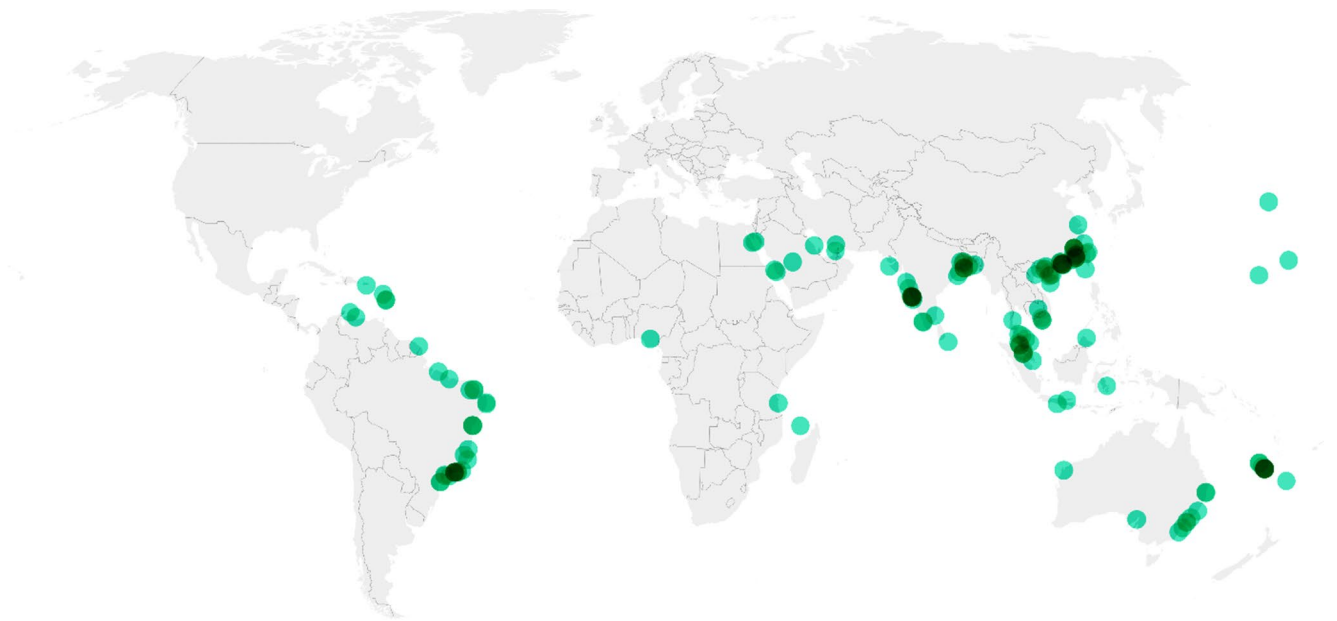
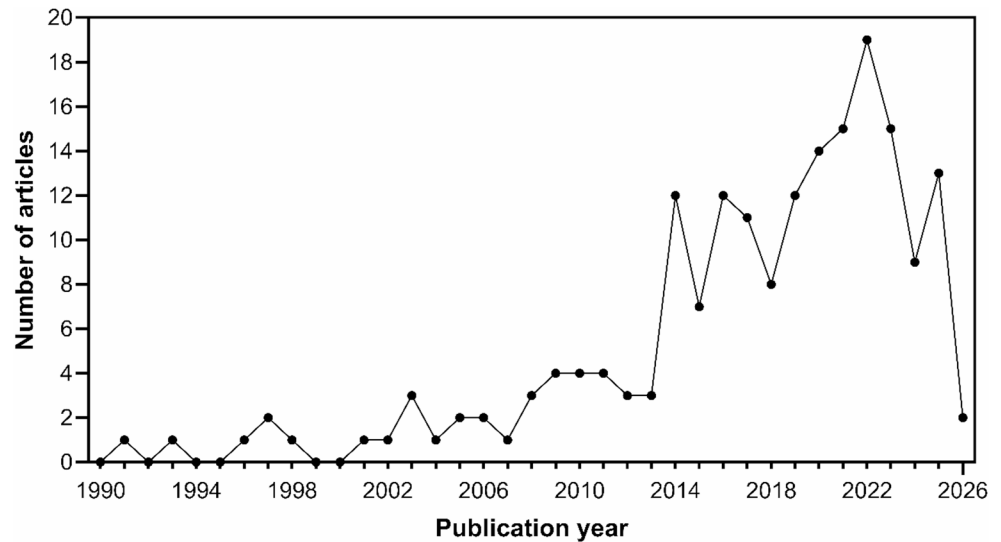


Fig. 2 World map showing the reported study locations in this review

high concentration in municipal discharge and recognised toxicity (Han et al. 2002; Häder et al. 2020). For example, the rise in human activities such as mining, construction, agriculture, industry and effluent discharge, elevate emissions of trace metals to the aquatic environment (Goldberg et al. 2012; Akhtar et al. 2021; Shah 2021). Although many trace metals are essential for biological processes, they can become harmful when present at concentrations elevated above background levels (Mishra et al. 2019; Rahman and Singh 2019; Kolarova and Napiórkowski 2021). Furthermore, many trace metals can bioaccumulate in the food chain, posing significant risks to humans who consume contaminated plants or animals (Peralta-Videa et al. 2009; Rehman et al. 2018; Ali and Khan 2019).

To a lesser extent, studies have also been done on arsenic [As] ($n=51$), cobalt [Co] ($n=41$) and mercury [Hg] ($n=27$). Cobalt, in particular, is of significant interest due to its application in sustainable technologies, such as lithium-ion batteries (Jones et al. 2020; Zhang et al. 2021; Earl et al. 2022; Savinova et al. 2023). Consequently, Co has been classified as a critical mineral and an emerging metal contaminant (i.e. of concern due to potential toxicity and an increased rate of extraction to meet growing industrial demand), with its projected global demand exceeding that of any other critical mineral (Jones et al. 2020; Savinova et al. 2023). This trend raises significant concerns regarding the potential impact to surrounding aquatic ecosystems (Paustebach et al. 2013; Ziwa et al. 2021). The increasing demand and potential

Fig. 3 Number of articles examining the different mangrove taxonomy in this review

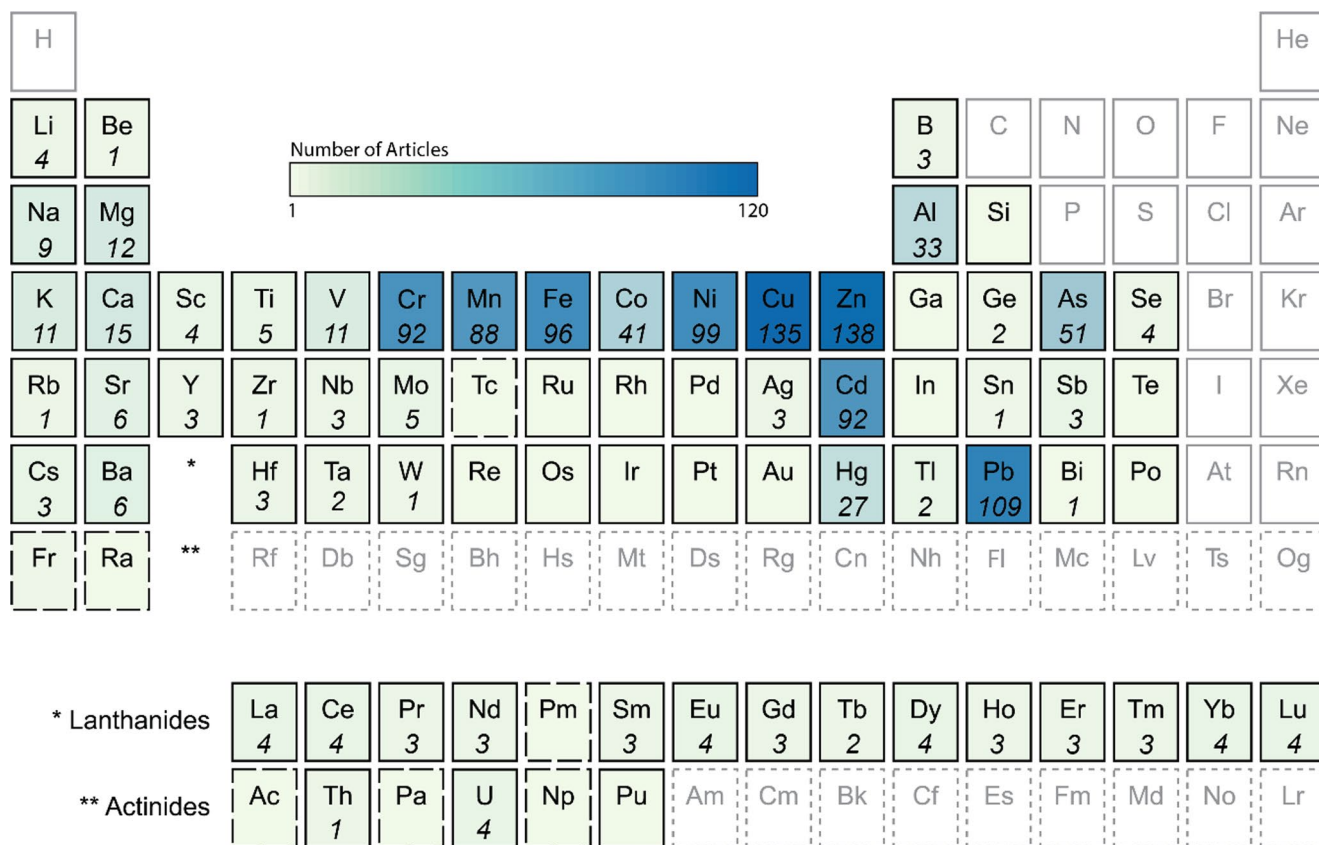
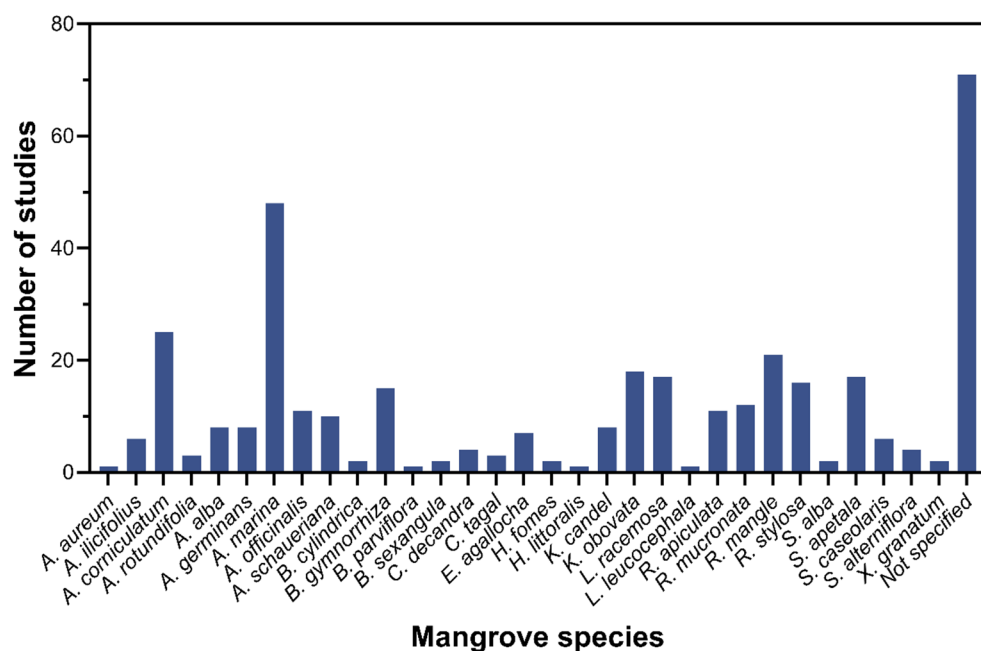


Fig. 4 Number of articles that analysed each trace metal in this review. The number of articles is shown by the number below the element symbol and colour scale

future environmental implications are reflected in the fact that 32 of the 41 studies examining Co were published within the last decade. In contrast, other emerging metal contaminants such as vanadium [V] ($n=11$), antimony [Sb] ($n=3$), tungsten [W] ($n=1$), and REEs ($n\leq 4$) have been relatively understudied. Furthermore, platinum group elements are an emerging environmental concern and have not been studied at all. The lack of understanding regarding these emerging contaminants highlights the need to address this gap in future research.

3.2 Methodological trends

3.2.1 Sediment sampling

Sediment sampling approaches varied across the reviewed studies, with most studies collecting either bulk surface samples (48%) or sediment cores (52%). Bulk samples were collected over depths ranging from 2 to 40 cm. However, most were taken from the top few centimetres and homogenised after collection, providing an integrated measure of trace metal concentrations. This approach does not capture vertical variability in metal concentrations or redox-sensitive processes within the sediment profile (Morford and Emerson 1999; Bennett and Canfield 2020). Furthermore, homogenising greater depths increases the likelihood of misrepresenting in situ conditions, as biogeochemical zones that occur over small vertical scales are mixed (Lessin et al. 2018; Devereux et al. 2019).

Core sampling was used in slightly more studies allowing vertical profiling of metal distributions and redox-sensitive zones within the sediment column. Sediment core depths ranged from 6 to 650 cm and slicing intervals differed among studies. Typical core lengths ranged from 10 to 50 cm, and sections were commonly sliced at intervals of 1–5 cm, with 1 cm slices being the most frequent in shallow sediments. These fine intervals were intended to provide higher vertical resolution of trace metal profiles and associated sediment properties to gain a better understanding of trace metal speciation and partitioning in the highly dynamic sediment environment. However, slicing cores at 1 cm intervals can still disrupt the natural sediment structure. In mangrove sediments, redox and biogeochemical gradients occur over millimetre scales due to animal bioturbation, radial oxygen loss, and microbial activity driven by high organic matter inputs (Sarker et al. 2021; Booth et al. 2023). For example, Andersen and Kristensen (1988) used micro-sensors to determine that the oxygen penetration depth in an *Avicennia marina* mangrove sediment was less than 2.5 mm and that the oxygen released from the pneumatophores via radial oxygen loss was consumed in approximately 0.5 mm. Therefore, typical core slices inevitably mix sediment

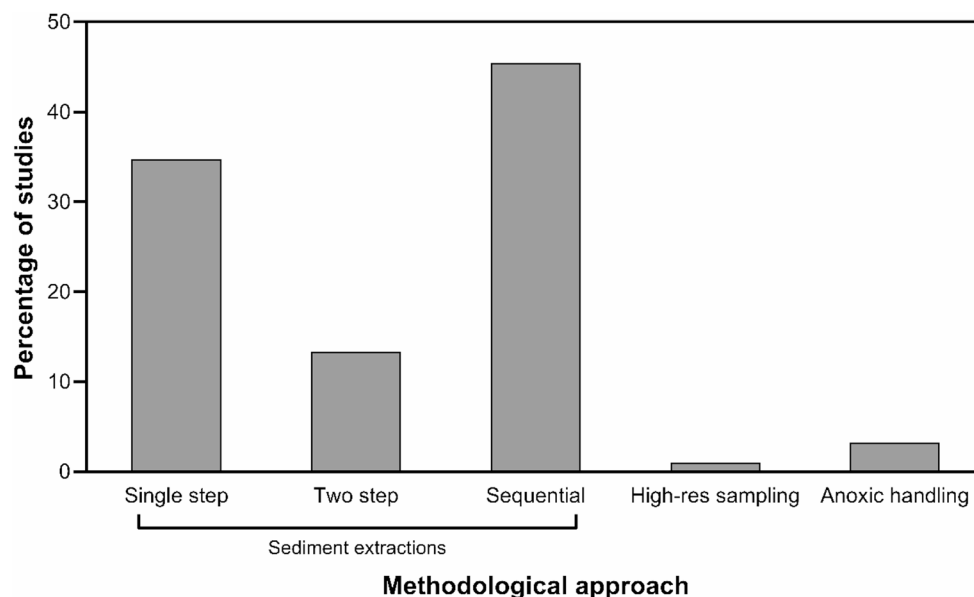
from distinct redox zones, potentially altering the measured speciation and partitioning of trace metals and obscuring fine-scale biogeochemical processes. This limitation highlights the challenge of capturing true in situ conditions and suggests that even core slicing at 1 cm may fail to accurately capture mangrove sediment biogeochemistry.

3.2.2 Anoxic sample handling

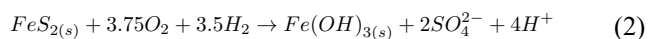
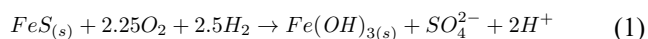
Only 3.2% ($n=6$) of studies transported and processed their samples under anoxic conditions (e.g. inside a nitrogen-sparged glove bag or a glove box with active catalytic oxygen removal), with only three of the 85 studies involving sequential extraction procedures following this important quality control step (Fig. 5). While the presence of oxygen is unlikely to affect the extraction and measurement of total metal concentrations in sediments, it is critical that oxygen is excluded in methods targeting specific metal fractions (such as the exchangeable, reduceable and oxidisable fractions commonly extracted by sequential extraction procedures). The oxidation of reduced metal-host phases (e.g. iron sulfides, organic matter) can modify their chemical form and the extractability of associated trace metals (Martin et al. 1987; Charriau et al. 2011), potentially leading to inaccurate assessments of trace metal speciation, partitioning and potential environmental risk. Therefore, maintaining anoxic conditions during sample processing is essential when studying the speciation and partitioning of trace metals, particularly in reducing environments such as mangrove sediments where metal behaviour is often strongly linked to redox-sensitive host phases (Keene et al. 2014; Harmesa et al. 2022).

The introduction of oxygen during sediment collection and processing can promote oxidation of iron sulfides (e.g. FeS, Eq. 1 or FeS₂, Eq. 2), resulting in the dissolution of sulfide minerals and the release of associated trace metals (Rickard et al. 1995; Schippers and Jørgensen 2002; Rickard and Luther 2007; Monachon et al. 2019). The oxidation of iron sulfides also produces dissolved Fe(II), which can further oxidize to Fe(III) and precipitate as iron oxyhydroxide (Eqs. 1–2). Iron oxyhydroxides have a strong affinity for some trace metals (Morse and Luther 1999; Billon et al. 2001; Jørgensen et al. 2019), so metals released from iron sulfide minerals during oxidation may repartition to newly-formed iron oxyhydroxides. These reactions caused by the introduction of oxygen can drastically impact the measured speciation and partitioning of trace metals and thus severely compromise the interpretation of metal transport and fate in mangrove sediments. For example, a recent study in Ras Mohammed National Park, Egypt (Younis et al. 2025) used a Peterson grab sampler and Tessier sequential extraction methods to study the partitioning of Cd, Cu, Fe, Mn, and

Fig. 5 Percentage of articles that used various methodological approaches to analyse trace metals in mangrove sediment samples



Pb in mangrove sediments. They concluded that Mn had the highest association with Fe-oxides, representing up to 41% of the total Mn partitioning. However, sediment samples were exposed to oxygen from collection through to the processing stages, which may have introduced artefacts where the proportion of Fe oxides in the samples is overestimated due to oxidation of reduced phases (e.g. dissolved Fe(II), solid Fe monosulfide) and repartitioning of Mn during sample processing. This has implications for understanding the potential for Mn mobilisation from the studied sediments and the role of Mn as a host phase for other metals. Furthermore, a study in the Zuari estuarine mangroves, India (Chakraborty et al. 2016) utilised sediment coring and sequential extraction using the BCR method to study partitioning of Cd in mangrove sediments. They concluded that 13.9–27.0% of Cd was associated with Fe-Mn oxyhydroxides. However, sediment samples were not handled under oxygen-free conditions, which may have resulted in an overestimation of Fe oxyhydroxides versus iron sulfides in the studied sediments due to oxidation of reduced Fe sulfides during prolonged exposure to oxygen.



3.2.3 Selective chemical extractions

Analytical methods used to determine trace metal concentrations in sediment vary depending upon the designated target fraction (Hlavay et al. 2004; Förstner 2004). 35% ($n=65$) of the 187 studies were limited to analysing a single

trace metal fraction and 13% ($n=25$) of studies targeted two fractions. These methods ranged from weak acid extractions that target the exchangeable, bioavailable fraction (i.e. weak hydrochloric acid or acetic acid extraction), through to methods using hydrofluoric acid that target the total metal concentrations in the sediment by dissolving the complete sediment matrix.

The most mobile and bioavailable portion of trace metals in the environment can be quantified by measuring exchangeable fractions, which allows for the evaluation of their potential immediate impact on surrounding ecosystems (Tessier and Campbell 1987; Kolarova and Napiórkowski 2021). This fraction is particularly important as it reflects the likelihood of trace metals being transferred into water, soil, or biological systems, posing risks to environmental and human health (Tessier and Campbell 1987; Nematollahi et al. 2021). However, this does not allow us to assess the potential impact that environmental factors (i.e. changes to redox conditions) may have on the less mobile fractions. Total concentrations are useful for examining broad trends, however, they do not reflect the complex metal speciation in sediments that can impact metal bioavailability and, ultimately, environmental and ecological risks (Rao et al. 2008). A recent study in Hainan Island, China (Wang et al. 2026) applied a single-step extraction using 8 mL HNO_3 and 2 mL HF, followed by microwave-assisted digestion, to determine trace metal concentrations in shade-dried mangrove sediments. The authors concluded that Pb, Mn, Ni, Cd, and Cr posed moderate to considerable ecological risks. However, a significant portion of these metals may have been present in the less mobile residual fractions, strongly bound to silicate minerals, which would limit their immediate bioavailability and ecological impact. This suggests that

the reported risk may overestimate the actual mobility and highlights the importance of sequential extraction methods used to consider the metal speciation and partitioning when assessing environmental risk.

Sequential extraction methods are commonly applied to investigate trace metal partitioning in mangrove sediments (Okoro et al. 2012). These methods extract metals from the sediment sample with a sequence of progressively stronger chemical extractants that target specific host phases. For example, the conventional BCR method uses a three-step procedure in which metals are operationally separated into acid-extractable (exchangeable and carbonate-bound), reducible (associated with Fe and Mn oxyhydroxides), and oxidisable (bound to organic matter and sulfides), through the sequential application of weak acid, reducing and oxidising reagents (Rosado et al. 2016). 45% ($n=85$) of studies used either the Community Bureau of Reference (BCR) method ($n=32$), Tessier method ($n=41$) or a custom sequential extraction technique ($n=12$). The BCR method traditionally follows a three-step extraction procedure, whereas the Tessier method follows a four-step procedure (Tessier et al. 1979; Liu et al. 2018; Kumkrong et al. 2021). However, some studies have modified these procedures by adding or removing extraction steps (Oyeyiola et al. 2011; Wijaya et al. 2022). Sequential extractions are particularly well-suited for estimating metal mobility under environmentally relevant conditions, making them more effective in assessing the ecological risk of sediment-bound trace metals compared to conventional single step extraction methods (Passos et al. 2010; Canuto et al. 2013).

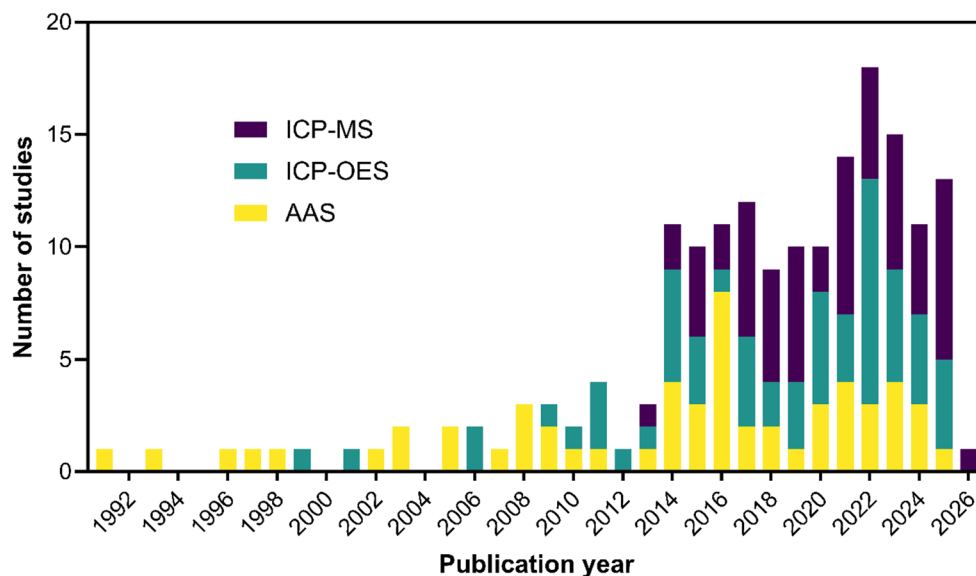
3.2.4 Two-dimensional high-resolution approaches

The aforementioned techniques are frequently used for understanding the overall trace metal speciation and partitioning in bulk sediments, including the likely host phases and potential release mechanisms (Martin et al. 1987; Carrillo-González et al. 2006; Rao et al. 2008). However, sequential extractions of bulk sediment samples do not account for the fine scale biogeochemical processes occurring in the mangrove rhizosphere. Mangrove sediments are typically anoxic, featuring a thin oxic layer to a few millimetres below the sediment surface (Alongi 2005). The introduction of oxygen to the anoxic zone can initiate redox reactions that significantly influence trace metal speciation and partitioning, and their consequent mobility and bioavailability (Middelburg and Levin 2009). In addition to diffusion of oxygen across the sediment water interface, oxygen can be introduced into anoxic sediments through two additional pathways: bioturbation and plant radial oxygen loss (ROL) (Murray 2006; Kusky 2008). Bioturbation is primarily driven by burrowing fauna such

as crustaceans, molluscs and worms (Gabet et al. 2003; Kusky 2008; Baranov 2018). Their burrowing activities disturb sediment layers, creating a network of tunnels that facilitate gas exchange, allowing oxygen to mix with sediment porewater and impact redox reactions and microbial activity on millimetre to micrometre scales (Kristensen and Kostka 2005; Vincent et al. 2024). Radial oxygen loss involves oxygen diffusion through the mangrove roots via the aerenchyma—a low-resistance pathway in their outer tissues (Pi et al. 2009; Cheng et al. 2015). This can result in relatively high oxygen concentrations in the sediments surrounding mangrove roots (Andersen and Kristensen 1988). These processes not only regulate the redox state but also influence the chemical speciation and the partitioning of trace metals and their host phases, potentially altering their mobility (Bartlett and Ross 2005; Carrillo-González et al. 2006; Keene et al. 2014; Sarker et al. 2021; Alongi 2021).

Capturing the fine-scale heterogeneity introduced into mangrove sediments by bioturbation and radial oxygen loss is challenging with conventional sampling techniques, such as coring and slicing (Robertson et al. 2008; Natesan et al. 2014; Pan et al. 2020). These techniques are limited to one dimensional profiles, typically at centimetre resolution, which is insufficient to resolve the complex, two-dimensional biogeochemistry occurring in mangrove sediments at much finer spatial scales (Robertson et al. 2008; Kankanamge et al. 2020; Pan et al. 2023). Diffusive gradients in thin films (DGT) and diffusive equilibration in thin films (DET) are advanced solute imaging techniques developed to enable high-resolution, two-dimensional measurements of porewater solute distributions (see (Santner et al. 2015), for a comprehensive review). Despite their demonstrated capability in capturing the fine-scale biogeochemistry of sediments, only two of the studies examined in this review employed these methods. This highlights a significant gap in the application of high-resolution sampling techniques in mangrove sediment research, where microscale redox gradients are critical to unravelling complex trace metal behaviour. Recent studies have modified gel based solute imaging methods to develop solid phase gel-based samplers to capture mineral transformations in marine sediments, followed by high-resolution analysis of metal speciation using synchrotron-based X-ray spectroscopy (Kraal et al. 2020; Haase et al. 2024). These techniques offer considerable potential for resolving trace metal speciation and partitioning in mangrove sediments at the fine spatial scales necessary to accurately characterise the mechanisms governing trace metal sequestration and remobilisation in these dynamic environments. However, their application in mangrove settings remains unexplored.

Fig. 6 Number of articles each year that used inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and atomic absorption spectroscopy (AAS) to analyse trace metals in mangrove sediment samples



3.2.5 Analytical instrumentation

Three analytical methods were used to determine trace metal concentrations in the majority of studies in this review (Fig. 6). Inductively Coupled Plasma Mass Spectrometry (ICP-MS; $n=60$), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; $n=60$), and Atomic Absorption Spectroscopy (AAS; $n=57$). Although these methods were used relatively evenly across the studies, a temporal trend was evident, with AAS more commonly applied in earlier studies, ICP-OES becoming increasingly adopted during the mid-2000s, and ICP-MS used regularly from 2013 onwards. ICP-MS typically provides higher sensitivity due to mass-based detection of ions, allowing reliable quantification of trace metals at sub- $\mu\text{g/L}$ concentrations (Moldovan et al. 2004; Tanase et al. 2014), whereas ICP-OES is often favoured for routine environmental analyses where detection limits in the $\mu\text{g/L}$ range are sufficient (Dymott 1995). In comparison, AAS provides only single-element analysis and detection limits that are typically orders of magnitude higher than ICP-MS, which has contributed to its reduced use as more sensitive techniques have become more widely available (Zhuravlev et al. 2016). This shift likely reflects improvements in the cost and availability of ICP-MS instruments and the increasing demand for lower detection limits, multi-element capability, and more efficient sample processing in environmental trace metal studies.

Several specialised analytical methods were reported less frequently across the reviewed studies. Cold Vapor Atomic Absorption Spectroscopy (CV-AAS; $n=5$) and Cold Vapor Atomic Fluorescence Spectroscopy (CV-AFS; $n=5$) are specialised analytical techniques used for the quantification of mercury (Hg) in sediments due to their high sensitivity and selectivity. Anodic Stripping

Voltammetry (ASV; $n=3$) is a sensitive electrochemical method used to determine trace metals at sub- $\mu\text{g/L}$ levels, involving preconcentration of metal ions on a working electrode followed by oxidation to produce a current proportional to concentration (March et al. 2015). The absence of Synchrotron-based X-ray absorption spectroscopy (XAS) in the reviewed studies was unexpected, especially given the growing availability and accessibility of Synchrotron facilities. Techniques such as X-ray absorption near edge structure (XANES) spectroscopy, for example, are powerful tools for probing the speciation (e.g. oxidation state and coordination environment) of trace metals associated with solid host phases in sediments (Hettiarachchi et al. 2017). Future research should aim to utilise XAS methodology to improve our understanding of trace metal speciation in mangrove sediments.

4 Study limitations

This review did not aim to provide a review of trace metal concentrations or behaviour in mangrove systems – this has been done recently by multiple authors e.g. (Yadav et al. 2023; Koka et al. 2025; Szafranski and Granek 2023). Rather, our objective was to evaluate the methodologies used in studies of metals in mangrove sediments – a critical aspect of reliable and reproducible research not discussed by existing reviews in this area. Although we utilised four databases for our systematic search, we did not perform manual forward or backward citation searches, which may have led to the omission of some relevant articles. Our selection criteria focused exclusively on peer-reviewed journal articles, which may have resulted in the exclusion of significant research found in books, book chapters,

conference papers, and theses. Additionally, by doing keyword searches in specific fields such as titles, abstracts, and keywords, we inadvertently excluded articles that were indirectly relevant. Nonetheless, the use of multiple databases combined with broad initial search terms ensured that our search was comprehensive and that our findings accurately reflect current trends in the literature on this topic. Finally, our review was limited to articles published in English, potentially excluding studies published in other languages which may result in an underrepresentation of research from certain regions.

5 Conclusion

This review highlights the increasing global focus on trace metal speciation and partitioning in mangrove sediments. Despite the growth of research over the past decade, most studies rely on bulk or low-resolution techniques that cannot resolve the fine-scale, redox-sensitive processes controlling trace metal sequestration and remobilisation. Few studies handled sediments under anoxic conditions, which can lead to oxidation of reduced phases, such as iron sulfides, altering metal speciation and partitioning. Sequential extraction methods, essential for understanding metal bioavailability and partitioning, were inconsistently applied. Advanced high-resolution approaches, such as gel-based mineral samplers coupled with synchrotron analysis, offer the potential to capture trace metal speciation and partitioning at sub-millimetre scales but have not yet been utilised in mangrove sediments. Future research should prioritise redox-preserving, high-resolution sampling methodologies with sequential extractions to better characterise trace metal speciation and partitioning, improving our understanding of their environmental fate and ecological risk in these dynamic ecosystems.

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Declarations

Competing interests The authors declare no competing interests.

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