Modeling transport and fate of heavy metals at the watershed scale: state-of-the-art and future directions

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Abstract

A predictive understanding of the source-specific (e.g., point and diffuse sources) land-to-river heavy metal (HM) loads and HM dynamics in rivers is essential for mitigating river pollution and developing effective river basin management strategies. Developing such strategies requires adequate monitoring and comprehensive models based on a solid scientific understanding of the watershed system. However, a comprehensive review of existing studies on the watershed-scale HM fate and transport modeling is lacking. In this review, we synthesize the recent developments in the current generation of watershed-scale HM models, which cover a wide range of functionalities, capabilities, and spatial and temporal scales (resolutions). Existing models, constructed at various levels of complexity, have their strengths and weaknesses in supporting diverse intended uses. Additionally, current challenges in the application of watershed HM modeling are covered, including the representation of in-stream processes, organic matter/carbon dynamics and mitigation practices, the issues of model calibration and uncertainty analysis, and the balance between model complexity and available data. Finally, we outline future research requirements regarding modeling, strategic monitoring, and their combined use to enhance model capabilities. In particular, we envisage a flexible framework for future watershed-scale HM models with varying degrees of complexity to accommodate the available data and specific applications.

Keywords

Heavy metals, catchment-scale, fate and transport model, point and diffuse source pollution, heavy metal land process, in-stream heavy metal process

1 Introduction

Elevated concentrations of heavy metals (HMs) are a global threat to aquatic systems and human health owing to their potential accumulation, biomagnification, and toxicity. The 'heavy metals' is a collective term used here to represent a group of metals and metalloids such as cadmium (Cd), mercury (Hg), copper (Cu), arsenic (As), lead (Pb), chromium (Cr), zinc (Zn), and nickel (Ni) that cause toxicity and ecotoxicity. Although there still exist debates concerning the imprecise use of the term 'heavy metals' and its alternatives, including 'toxic metals', 'trace metals', 'trace elements', and 'potentially toxic trace elements' (Duffus, 2002), we used the term 'heavy metals' consistently in this review for convenience. HMs are ubiquitous in the environment as naturally occurring elements. For example, As pollution from geogenic sources is a major problem in South Asia (e.g., Winkel et al., 2008). Meanwhile, HMs, such as Cd, Hg, Cu, As, Cr, and Pb, have contaminated river systems in many parts of the world as a by-product of industrialization (Johnson et al., 2018; Mason, 2013). For example, the signature of Pb mining and smelting activities by ancient Greeks and Romans have been documented in the Greenland ice cores (Hong et al., 1994). Moreover, over 100,000 abandoned or inactive mining sites are spread over 2,000 km^2 in the United States

(U.S.EPA, 1997). England and Wales have over 3,000 abandoned metal mines (Jarvis et al., 2007). In China, a nationwide survey of soil contaminants during 2005–2013 revealed that 16.1% of the soil samples exceeded the soil quality standards mainly because of high HM concentrations (MEPPRC and MLRPRC, 2014).

Knowledge of the HMs released from contaminated soils and sites in the upland and their subsequent migration in river networks is critical for assessing environmental risks, as well as developing effective pollution control and river basin management strategies. (Byrne et al., 2012; Le Roux et al., 2020). HMs can enter river systems via various diffusion pathways, including surface runoff, subsurface flow, groundwater flow, and soil erosion. Meanwhile, many biogeochemical processes greatly influence and regulate HM's mobility (Carrillo‐González et al., 2006). These mechanisms involve sorption, complexation, precipitation, redox reactions as well as weathering processes influenced by environmental factors such as pH, redox potential, and temperature (Borch et al., 2010; Degryse et al., 2009). Extensive studies, including field measurements, have been performed on the mechanisms of different soil biogeochemical reactions at the plot and field scales (Selim and Kingery, 2003). However, when it turns to the watershed scales, a quantitative and complete description of metal migration may be hindered by the strong spatial heterogeneity and temporal variability of HM production, transformation, and transport processes (Li, 2019). To fully understand the complex mechanisms of HMs transport at a watershed scale, a large amount of time- and resource-consuming fieldwork is needed. Watershed-scale

HM models are increasingly used as essential tools for assessing and restoring surface waters because they can serve several aims: manifesting and examining pollutant transport mechanisms or hypotheses (Aim 1, improving scientific understanding); assessing the environmental risk (Aim 2, risk assessment); estimating pollutant fluxes and locating critical source areas (Aim 3 Identifying critical source areas); and evaluating the impacts of climate change and mitigation scenarios on water quality (Aim 4, scenario analysis).

Over the last few decades, water quality models concerning the quantification of nutrients (e.g., nitrogen and phosphorus) dynamics at the watershed-scale have been extensively reviewed (Robson, 2014; Rode et al., 2010; Wellen et al., 2015). In contrast, reviews on HM dynamics models remain scarce (Ouyang et al., 2017; Qiao et al., 2023). Previous reviews have focused mainly on the spatiotemporal distribution of HMs in soil and river systems, their transformation and partitioning at solid-liquid interfaces (e.g., Degryse et al., 2009), and plot, field, and river-scale numerical transport models (e.g., Carrillo-González et al., 2006; Garneau et al., 2017). To our knowledge, a holistic description of watershed HM processes accounting for natural and anthropogenic inputs, terrestrial delivers into streams, and in-stream dynamics is lacking. The last significant and most relevant review came from a USEPA workshop in 2007 (Caruso et al., 2008), which gathered experts from academia and the government to explore state-of-the-art models for simulating metal fate and transport from different scales and application domains, such as equilibrium, stream, and watershed models. Caruso et al. (2008) stated that existing watershed models require further testing and evaluation using more field data, and a truly calibrated watershed HM model did not exist. In the last 15 years, new HM watershed models have been developed (Meng et al., 2018; Motovilov and Fashchevskaya, 2019; Sui et al., 2022), and monitoring methods have advanced (Byrne et al., 2021; Frau et al., 2018; Hanhauser et al., 2020). However, no follow-up review has been conducted till date. Therefore, we present a contemporary analysis of existing watershed pollution models by comparing the differences in functionality and underlying assumptions to highlight the challenges and opportunities for future model research and development.

Owing to the complexity of natural environmental systems, models are always necessarily simplified descriptions of reality. Moreover, models are often constructed at different levels of complexity in terms of structure, function, and processes depending on scientific knowledge, purposes, and data availability. Therefore, we evaluate models' strengths and weaknesses in this review according to their diverse intended uses. The remainder of this review is organized as follows. Section 2 outlines the primary sources, transformation mechanisms, and transport pathways of HMs in the natural environment. Section 3 reviews contemporary HM watershed models and highlights their basic assumptions, simplifications, components, and distinctions. Section 4 summarizes the research gaps and challenges in watershed HM modeling and applications. Finally, Section 5 concludes with future research needs in HMs monitoring, modeling, and their combined use.

2 Fate and transport of HMs in the real world

2.1 Sources of HMs in the environment

There are two main categories of HM sources: natural and anthropogenic. Natural sources mainly include bedrock weathering, volcanic eruptions, and atmospheric deposition. Anthropogenic sources (e.g., industrial, agricultural, and municipal) have dramatically changed HM concentrations in the natural environment compared with pre-industrial times (Chen et al., 2008). For example, HM pollution in soil and water is often associated with metal mining and smelting, chemical production, dyeing and printing, and burning fossil fuels (Rauch and Pacyna, 2009). In addition, applying fertilizers, pesticides, manure, and wastewater irrigation has substantially increased HM fluxes to local water bodies near agricultural land (Shi et al., 2018). Domestic sewage discharge from treatment plants in urban areas can also contribute significant quantities of HMs to aquatic environments (Zhou et al., 2018). Vehicular exhaust and wear and tear of tires are other important HM sources (Werkenthin et al., 2014). For example, Zn isotopes in sediment cores of eight lakes across the United States indicated that vehicle emissions are the most significant source of Zn (Thapalia et al., 2015). Finally, it should be noted that human activities are deeply intertwined with natural processes, sometimes blurring the boundaries. For example, HMs emitted from industrial activities are transported through the atmosphere, deposited in the soil, and then transported to water bodies via runoff and erosion (Andronikov et al., 2021).

Water pollutants come from either point sources or dispersed sources. Thus, HM sources can also be divided into the point and nonpoint sources. A point source of pollution is discharged directly from a discernible source, such as a discharge pipe from a factory or sewage plant. For example, the Seine (Chen et al., 2008) and Rhine (Stigliani et al., 1993) river basins in Europe and Dongting Lake in China (Li et al., 2013) receive most of their HM pollution from point sources. Unlike point sources, diffuse (nonpoint) sources do not originate from a specified location. Instead, they are characterized by intermittent occurrences and spatial heterogeneity, such as runoff from agricultural land during rainfall, which makes them challenging to trace and control (Patterson et al., 2013).

2.2 Transformation mechanisms

HM's mobility and bioavailability in terrestrial and aquatic systems depends on chemical speciation (van Leeuwen et al., 2005). In the most simple sense, chemical speciation refers to whether a metal exists in a dissolved/solute form or a solid/particle-contained form (Fig. 1). In the natural environment, several reactions can change HM speciation, such as sorption (adsorption/desorption), complexation (association/dissociation), precipitation/dissolution, diffusion into carbonates and oxyhydroxides (Degryse et al., 2009). In the solid phase, HMs are present as labile (M_l), non-labile (M_n), or inert metal (M_{inert}) species. Labile metal can exchange rapidly with the solution phase. Furthermore, metals in the labile pool in the solid phase can slowly transfer from/to a non-labile pool, which is a slow process taking years or longer (Buekers et al., 2008; Crout et al., 2006). In contrast, inert metals in parent minerals are unlikely to be released to a solution phase. In the solution phase, metals appear as free ions (M^{n+}), complexes with inorganic or organic ligands (ML), or associated with mineral colloids (ML_{inert}) (Honeyman and Santschi, 1988). Generally, the free ions in the solution tend to react most actively with the solid phase. However, similar to inert solid metals, some metals in solution, such as those in colloidal minerals, may also be non-reactive. Metals complexes with inorganic or organic ligands could be divided into labile and non-labile ML (ML_{labile} and $ML_{\mathrm{non\text{-}labile}}$) according to the dissociation rate of these complexes.

Soil HM's solubility and mobility are governed by soil properties such as soluble ligands in soil pore water, soil matrix composition (e.g., oxides, clay, and organic matter), pH, temperature, and redox potential (Young, 2013). In soil solutions, HM species are significantly affected by the presence of different organic and inorganic ligands. The soil solid phase consists of various constituents (clay minerals, organic matter, iron, and aluminum oxides); HM species in the solution react with these constituents via different mechanisms. Soil pH is considered the most critical factor influencing metal speciation in soils, thus the master variable affecting metal behavior in soil systems. In addition, the increase/decrease of soil redox potential (Eh) could regulate a series of biogeochemical reactions. For example, some variable-valence HMs such as Hg, As, Cr, and Fe could undergo valence changes within the range of redox potentials (Carrillo - González et al., 2006). Biomethylation could occur under anaerobic conditions, transforming the inorganic forms of Hg and As into methylated forms.

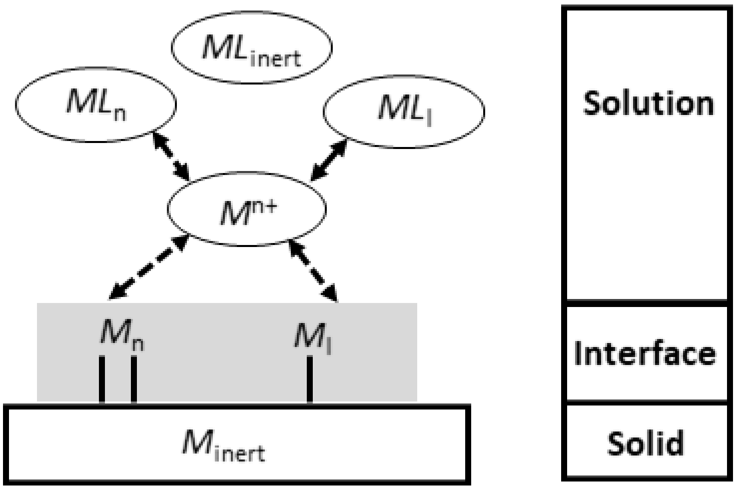

Fig. 1 Schematic representation of metal species and reactions between the solid and solution phases. Broken and solid reversible arrows represent kinetically constrained and 'instantaneous' reactions, respectively Young (2013).

2.3 Transport pathways

HMs can enter river systems via various diffusion pathways, such as surface runoff, soil leaching, subsurface flow, groundwater flow, erosion, and atmospheric deposition (Fig. 2) (Foster and Charlesworth, 1996). Surface runoff occurs when the soil becomes saturated or rainfall intensity exceeds the infiltration rate (Yang et al., 2015). The amount and rate of metal fluxes in surface runoff depend on metal speciation and concentration in the soil, rainfall intensity, and watershed characteristics. Surface runoff moves quickly to the stream channel. Thus, the immediate response of the stream's metal concentrations to increased streamflow is an indicator of the surface runoff process because they have an immediate effect on the solutes of the stream (Runkel et al., 2016).

After water infiltrates the soil, it undergoes the processes of vertical leaching and lateral flow, with the concomitant of dissolved metals. Soil leaching is the downward movement of dissolved metals in the soil profile via percolating water. Subsurface lateral flow refers to soil water processes where infiltrating water accumulates and moves laterally downslope along the upper surface of a less permeable layer in the soil. Subsurface lateral flow is abundant at the interface between the soil and bedrock, where permeability changes dramatically. A range of terms are used to refer to subsurface lateral flow, including throughflow, subsurface runoff, and interflow. The relative contribution of soil leaching or subsurface lateral flow to HM transport varies largely depending on the soil attributes and topographic and meteorological conditions. Xia et al. (2014) found that soil leaching is the dominant export pathway of soil HM in the southern Song-nen Plain of Northeast China. The subsurface flow from acid mine drainage in Cement Creek, Colorado, is the largest contributor to Zn loads in the watershed (Kimball et al. (2002). A national-scale modeling in the Netherlands reported that soil leaching was the most important contributor of Cd (20%), Zn (40%), and Pb (40%) to surface water (Bonten et al., 2008). Enhanced metal leaching is associated with acidic drainage due to high metal solubility and sulfide weathering rates under acidic conditions (RoyChowdhury et al., 2015).

Groundwater discharge is another possible input of HMs into surface waters. Groundwater containing dissolved contaminants migrates from the soil into subjacent aquifers and finally enters adjacent streams. Several hydrological and biochemical factors determine the amount of metal transported from the groundwater to streams. Generally, HM fluxes via groundwater discharge are significant in mountainous mining areas. Polluted aquifers act as long-term pollution sources for the surrounding rivers, even after mining activities have stopped (Wang et al., 2019). For example, the inputs of Cd (43%) and Zn (28%) to the Riou Mort River in France are mainly through groundwater discharge (Coynel et al. (2007). In contrast, fieldwork in the Gilt Edge Mine, South Dakota, USA, showed that metal loads from bedrock fractures contributed <1% of the total load to the creek (Caruso and Dawson, 2008). Additionally, the slow groundwater movement and HM attenuation in aquifers due to sorption could reduce the metal loads to the streams. Thus, HM transport in subsurface environments can be significant within certain landscapes and geology.

Soil erosion plays an important role in the biogeochemical cycles of HMs. Scientometric analysis has revealed that erosion-induced transport is the most influential factor in HMs mitigation mechanisms (Ouyang et al., 2018). A recent national-scale study across China revealed the ubiquitous prominence of soil erosion contributions to land-to-river metal fluxes (e.g., As, Cd, Cr, Cu, Ni, Pb, Zn, and Hg) (Liu et al., 2019).

In the absence of local anthropogenic inputs, atmospheric deposition is the most significant HM input to terrestrial environments (Lofts, 2007). For example, an inventory study of HM inputs to agricultural soils in China showed that atmospheric deposition accounted for 43–85 % of the total As, Cr, Hg, Ni, and Pb inputs (Luo et al., 2009). Atmospheric deposition contributes more Zn, Ni, and Pb to European agricultural soils than phosphate fertilizer application (Nziguheba and Smolders, 2008).

After HMs enter rivers, a number of physical (e.g., convection, diffusion, erosion and deposition of sediments), chemical (e.g., sorption, complexation, precipitation), and biological (e.g., bioturbation) processes could influence the fate of HMs in aquatic systems to some degree (e.g., Mason, 2013). The scavenging of HMs in river water depends largely on the solid-liquid distribution and the presence/properties of suspended/riverbed sediments (Honeyman and Santschi, 1988). Most HMs entering the rivers may be immobilized and stored by adsorption onto the riverbed sediments (Peng et al., 2009). A portion of HMs that adsorbed on fine suspended solids (e.g., hydrous oxides, clays) could transport downstream over long distances (Hochella et al., 2005). In addition, "big events", such as large storms and floods, have been shown to significantly affect HMs' remobilization and transportation (Ciszewski and Grygar, 2016; Peraza-Castro et al., 2016).

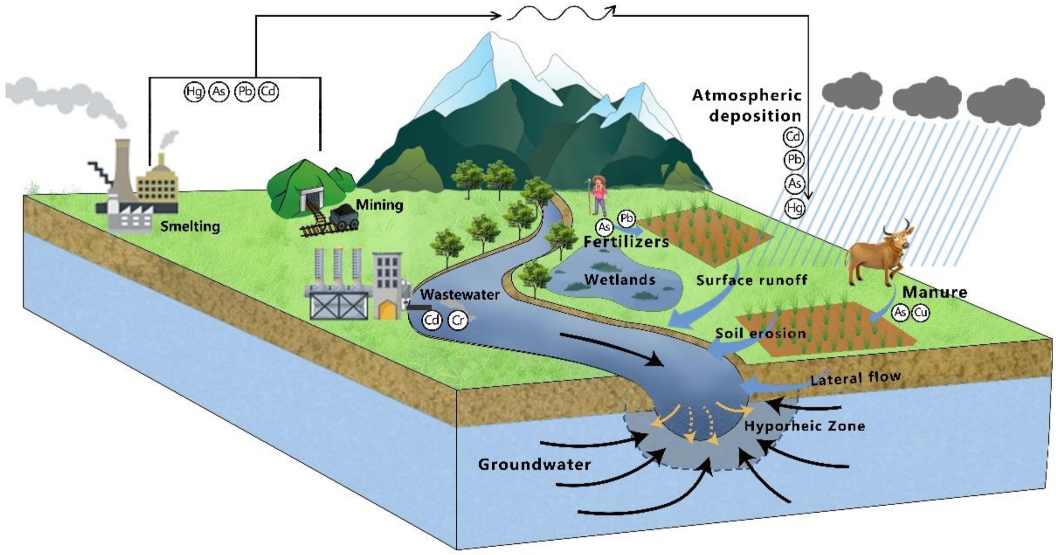

Fig. 2 A schematic diagram of the heavy metal cycle at the watershed scale.

3 Overview of watershed-scale HM fate and transport models

3.1 Existing representative models

Nine representative models were selected based on a thorough literature evaluation: L-THIA (Park et al., 2013), METALPOL (Vink and Peters, 2003), WARMF (Chen et al., 2000), ECOMAG-HM (Motovilov and Fashchevskaya, 2019), SWAT-HM (Meng et al., 2018), INCA-Metals (Whitehead et al., 2009), CTT&F (Johnson et al., 2011), TREX (Velleux et al., 2008), and TOPKAPI-ETH (Sui et al., 2022). A detailed description of each model is provided in SI. It is not intended to be an exhaustive list of all available watershed scale HM models. These representative models were selected because they are capable of simulating metal fate and transport processes at the watershed scale with various spatial and temporal resolutions. The manner of HM fate/transport description varies among the models, ranging from simple export coefficient models (e.g., L-THIA and METALPOL) to more complex integrated watershed models (e.g., SWAT-HM and TOPKAPI-ETH). It should also be noted that urban watershed models, such as SWMM model, were not included in this review. Urban models focus more on the buildup and washoff of pollutants from impervious surfaces and subsequent transport and transformation processes in the urban water infrastructure systems. Though urban area is usually a significant part of a watershed, the prominent particularities of urban models render them incomparable with general watershed models which mainly target the natural to less urbanized environments. Useful reviews on urban water quantity and quality modeling can be found in Zoppou (2001).

As mentioned in Section 2, metal behavior in the natural environment is highly complex in terms of various pollution sources, transformation reactions, and transport pathways. Therefore, models are always simplified descriptions of environmental systems with different levels of complexity. Furthermore, models have evolved over time, becoming increasingly detailed in terms of spatiotemporal resolution and the number of components and processes included. The selected models have been developed for a range of different objectives. They reflect a broad spectrum of concepts and assumptions, which can be categorized according to various criteria, including representation of processes (e.g., empirical, conceptual, process-based, or physically-based), spatial scale (e.g., plot, field, or watershed), spatial discretization (e.g., lumped, semi-distributed, and fully-distributed), and temporal scales (e.g., event-driven or long-term simulation). However, it is accepted that these categories are sometimes vague, and in practice, many models include elements of different categories. Generally, two main processes (contaminant partitioning and transformation and contaminant transport) are considered in watershed-scale metal models. The contaminant transport component commonly consists of three processes: (1) overland hydrological processes, (2) soil erosion and sediment transport, and (3) in-stream processes. The main features and components of the reviewed models and associated references are summarized in Table 1, with additional comparisons in Sections 3.2 and 3.3.

Table 1 Existing metal models at different spatial and temporal scales considered in this review.

Model	Metal speciation and transformation	Hydrology	Soil erosion	In-stream	Space discretization	Temporal scale	Distinguishing features and applicability	Main developers and key references
L-THIA	Total metal concentration	SCS-CN; do not consider the spatial route of NPS pollution	None	None	Fully-distributed	Daily, yearly	Large-scale and long-term total metal loads where surface runoff pathway dominates.	Purdue University, USA (Park et al., 2013)
METALPOL	Total metal concentration	A water balance model based on Rhineflow	Modified USLE, sediment delivery ratio (SDR), and the specific enrichment ratio model	None	Fully-distributed	Yearly	Export coefficient method, large-scale and long-term total metal loads considering multiple pathways but ignoring in-stream processes.	Vrije University Amsterdam, Netherlands (Vink and Peters, 2003)
WARMF	Two-phase equilibrium partitioning	Overland Flow using Manning's equation Lateral flow using Darcy's Law	ANSWERS model	Continuously stirred tank reactor (CSTR) model	Lumped	Daily	Continuously stirred tank reactor (CSTR) model	Electric Power Research Institute (EPRI), USA (Chen et al., 2000)
TREX	Three-phase equilibrium partitioning	Diffusive wave approximation	CASC2D-SED model	Diffusive wave approximation	Fully-distributed	Variable time step	High-resolution and event-based simulation models for small-scale applications	Colorado State University, USA (Velleux et al., 2008)
SWAT-HM	Three-phase equilibrium partitioning and reaction	SCS-CN	MUSLE	Variable storage method or Muskingum method	Semi-distributed (HRU)	Daily	Long-term continuous models with reasonable model structure and computational efficiency suitable for meso-scale and large-scale watershed, easy to	Beijing Normal University, China (Meng et al., 2018)

							couple with other processes such as carbon cycle.	
CTT&F	Four-phase equilibrium partitioning	Designed for use within existing hydrological modeling systems	Designed for use within existing hydrological modeling systems	Designed for use within existing hydrological modeling systems	Fully-distributed	Variable time step	Metal fate and transport modeling at small watershed scale such as arms firing ranges	US Army Corps of Engineers (Johnson et al., 2011)
INCA-Metals	Two-phase equilibrium partitioning	Quick flow, soil water flow and groundwater flow.	Erosion is by splash detachment and flow erosion of bulk sediment; five grain size classes are considered for in-stream processes	Nonlinear reservoir model	Semi-distributed (landscape units)	Daily	Process-based representation, minimized data requirements and model structural complexity, easy to couple with other processes such as carbon cycle.	Reading university, UK (Whitehead et al., 2009)
ECOMAG-HM	Two-phase equilibrium partitioning	ECOMAG hydrological model	None	Kinematic wave equation	Semi-distributed	Daily	Accounts for process of dissolution by melt and rainwater, suitable for snow-dominated watershed	Russian Academy of Sciences, Russia (Motovilov and Fashchevskaya, 2019)
TOPKAPI-ETH	Four-phase equilibrium partitioning and reaction	Kinematic wave approximation	Overland flow erosion using transport capacity approach	Kinematic wave approximation	Fully-distributed	Variable time step	Physically explicit representation of the major hydrology-sediment-metal processes with a reasonable computational efficiency suitable for small-scale watersheds.	ETHZ, Switzerland (Sui et al., 2022)

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3.2 Representation of metal partitioning and transformation

3.2.1 Existing metal transformation schemes

Existing models generally have four levels of complexity for reaction mechanisms (Fig. 3) (Degryse et al., 2009). The level 4 scheme (Fig. 3a) represents all the main metal species and transformation processes mentioned in Section 2.2. Although conceptually appealing, it requires extensive input information, often unavailable in routine research. The level 3 scheme does not consider the differences between non-labile and inert metals in the solid and solution phases. However, it requires simultaneous modeling or observation of dissolved organic matter (DOM) owing to its explicit modeling of metal complexes. The level 2 scheme consists of three metal pools: dissolved metal (M_d), labile metal (M_l), and non-labile metal (M_n), in which free metal ions (M^{n+}) and metal complexes (ML) in solution are regarded as M_d. The last and most simplified level 1 scheme consists of two pools: M_d and particulate metal (M_p), in which M_l and M_n are further regarded together as M_p.

As discussed above, metal partitioning and transformation in the natural world are highly complex. Several mechanistic models (also called equilibrium and geochemical models), such as MINEQL (Westall et al., 1976), MINTEQA2 (Allison et al., 1991), WHAM (Tipping, 1994), and ORCHESTRA (Meeussen, 2003), have been developed to describe metal partitioning between solid and solution, or metal speciation in solution only. For example, the WHAM model could describe metal sorption on organic matter by nonspecific electrostatic sorption and specific competition sorption (protons and metals compete for binding to two types of sites: carboxylic and phenolic groups) (Tipping, 1998). However, watershed-scale studies rarely provide such detailed input or validation information required for these mechanistic models. Most watershed-scale models employ the simpler level 2 and level 1 schemes that conceptually capture the dominant mechanism. For level 2, the HM transformation model considers two major reactions: (1) sorption and (2) slow reactions.

Sorption

Sorption refers to the adsorption-desorption processes between the dissolved metal in the solution phase and the labile metal in the solid phase. Several studies have demonstrated that adsorption-desorption is the most important process affecting the mobility and bioavailability of metals (Degryse et al., 2009). Dissolved metals (solution phase, [M_d]) are reversibly adsorbed onto solids and become labile adsorbed metals (solid phase, M_l). The solid-solution partition coefficient (K_d) is defined as the ratio of labile metal concentration in the solid phase to dissolved metal concentration in the solution phase when equilibrium is attained:

$$K_{\mathrm{d}} = \frac{M_{\mathrm{l}}}{[M_{\mathrm{d}}]} \tag{1}$$

where K_d is the solid-solution partition coefficient (L kg^{-1}), and M_l and [M_d] denote the labile metal concentration in the solid phase (mg kg^{-1}) and the dissolved metal concentration in the solution phase (mg L^{-1}), respectively.

It should be noted that K_d is an apparent (lumped) partition coefficient for describing the equilibrium speciation of metals between solid and solution phases, as it describes both the sorption and complexation of free ions in solution rather than a single mechanism. Moreover, because K_d is a strict equilibrium concept, equilibrium is implicitly assumed when adopting the K_d-based model. Nevertheless, the K_d approach is often used in the existing watershed model for the following reasons. (1) K_d value can be determined from an extensive literature search (e.g., Allison and Allison, 2005) or estimated through laboratory adsorption/desorption batch tests. (2) Regression models can be incorporated with the K_d concept to reflect the spatial variability of soil K_d. For example, most regression models involve a multivariate linear relationship between log K_d and the routinely measured soil properties (e.g., pH and soil organic carbon) (De Groot et al., 1998).

Slow reaction

"Slow reaction" refers to all the slow chemical processes (between labile and non-labile phases) in the solid phase, such as the intra-particle diffusion of metals in carbonates and oxyhydroxides. It is modeled as a reversible conversion between labile adsorbed metals (M_l) and their non-labile counterparts (solid phase, M_n) with kinetic rates (k_1, k_{-1}).

$$\begin{aligned} \frac{dM_l}{dt} &= -k_1 M_l + k_{-1} M_n \\ \frac{dM_n}{dt} &= k_1 M_l - k_{-1} M_n \end{aligned} \tag{2}$$

where k_1 and k_{-1} are the forward and backward rates of the slow reaction (d^{-1}).

Slow reaction is included in the SWAT-HM and TOPKAPI-ETH models because it plays an important role in long-term simulations (Buekers et al., 2008; Crout et al., 2006). For example, using synthetic numerical experiments, Sui et al. (2022) demonstrated the influence of slow reactions on the transport of dissolved Cd from uplands to rivers over longer timescales (>5 years), highlighting the non-labile metal as a long-lasting source of HM pollution.

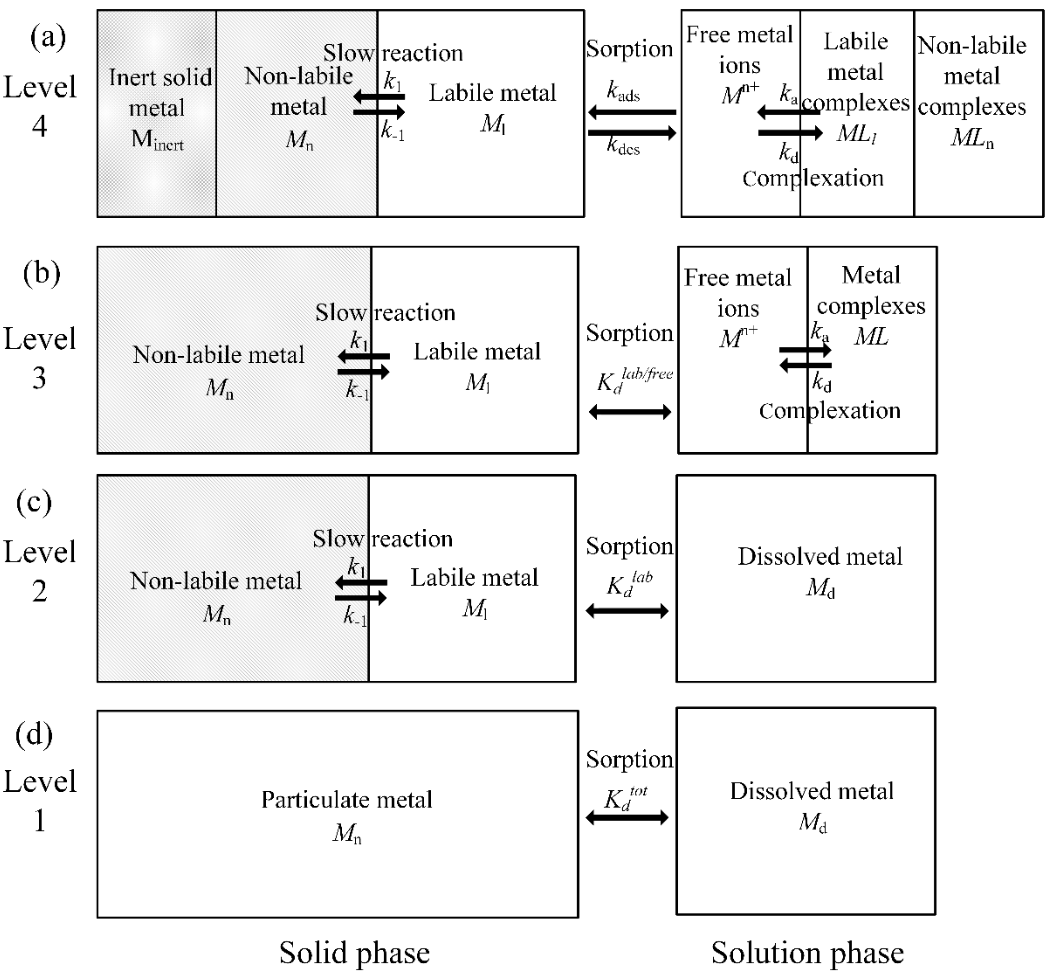

Fig. 3 Graphical descriptions of the metal transformation model in the soil-water environment with different levels of complexity. K_d, k_a, k_d, k_{ads}, k_{des}, k_1 and k_{-1} denote the equilibrium and rate constants. Modified from Degryse et al. (2009).

3.2.2 Equilibrium approach versus kinetic approach

The equilibrium-based (K_d) approach is commonly used for watershed-scale water quality models in Caruso et al. (2008) review. Recently developed models (e.g., SWAT-HM and TOPKAPI-ETH) have examined the equilibrium assumption adopted in the previous models to propose a new scheme (i.e., kinetic approach) to enhance their applicability. Specifically, the equilibrium assumption between the solution and solid phases without considering the slow reaction (transformation between labile and non-labile pools) may not reflect reality, especially in long-term metal simulations (Sui et al., 2022). The slow reaction is described as a reversible, first-order kinetic process with kinetic constants. However, it should be mentioned that mechanism-based principles have not yet been incorporated into the existing watershed HM models, although the development of reactive transport models (RTMs) in the subsurface geochemistry community has advanced rapidly since the 1980s (Steefel et al., 2015). The reactions in RTMs models include both kinetically controlled (e.g., microbe-mediated redox reaction, mineral dissolution, and precipitation) and equilibrium-controlled ones (e.g., ion exchange, surface complexation (sorption) and aqueous complexation) (Li, 2019). A few attempts (e.g., Bao et al., 2017) have been made to bring the RTMs from the "closed" groundwater systems into the "open" watersheds.

3.3 Representation of watershed-scale transport processes

3.3.1 Spatial discretization and temporal scale

A spatially distributed representation of the hydrology and contamination transport processes is necessary for watershed management. Thus, the watershed model simulates water flow and contaminant dynamics across discretized landscape units. The models differ in how they account for heterogeneity within each sub-basin. In watershed-scale models, spatial representation (discretization) is typically classified into three types: (1) lumped, (2) semi-distributed, and (3) fully-distributed models (Fig. 4). The lumped spatial approach does not discretize the sub-basins and represents them using average lumped parameters to represent the physical processes within each sub-basin. The WARMF model follows this lumped approach (Chen et al., 2001). Semi-distributed approaches are based on properties of land use, soil type, and topography, such as slope. Examples of such models are the SWAT model, which uses Hydrologic Response Units (HRUs) (Arnold et al., 2010), and the 'landscape units' in INCA-Metals (Whitehead et al., 2009). However, as the semi-distributed model, SWAT-HM fails to show the interaction between the HRUs, as they are not internally linked within the sub-basin but are routed individually to the basin outlet. The fully-distributed approach divides the watershed and sub-basins into hydraulically connected elements, such as grid cells, to substantiate cell-to-cell transport. Each cell has unique properties, such as slope, land cover, and soil, in a fully-distributed model. Such an approach is implemented in TREX (Velleux et al., 2008) and CTT&F (Johnson et al., 2011). A principal advantage of a fully-distributed watershed model is the opportunity to identify the critical source areas (Aim 3) within the watershed and sub-basin, such as waste piles that contribute the most to HM transport. However, owing to the computational burden and high demand for data, applying a fully-distributed model is limited to the small and mesoscale scale. The decreased spatial resolution of the semi-distributed model allows for a coarser calculation time step (e.g., daily), thus effectively reducing computational resources. The decreased spatial resolution of semi-distributed models allows for a coarser calculation time step (e.g., daily), thus effectively reducing computational resources. Semi-distributed models are still widely used for sub-basins prioritization when accurate location is not demanding. For instance, Chen et al. (2014) developed a framework integrating a watershed model with the Markov chain theory to pinpoint priority sub-basins.

For temporal scale, watershed-scale models can be divided into two categories: event and continuous models. Event models simulate watershed responses to a single rainfall event with a fine time resolution, like an hour or minutes, and are thus suit short-term simulating needs. In contrast, continuous models simulate the inter-rainfall environmental processes in the watershed as well as the rainfall events *alone*; thus, they usually simulate with daily timestep and suit long-term simulating needs. Among the 9 selected models, TREX and TOPKAPI-ETH have the single-event simulation capability. Other models, such as INCA-Metals and SWAT-HM, are able to analyze the long-term effects of hydrological changes and water management practices. The daily time step is likely one of the best temporal resolutions for the ease of computation and availability of datasets while maintaining the capability to manifest temporal variation. The daily time resolution is probably adequate for larger creeks or rivers that are not "flashy" (i.e., the hydrograph peaks and falls back to normal flow quickly within 24 hours). However, the daily time step may not be adequate to determine pollutant loads from flashy systems. Concerning toxicity modeling (Aim 2, , risk assessment), if acute toxicity is of primary concern and the metal concentration dynamic fluctuates on an hour- or minute-scale, event models become necessary to perform reliable risk assessments. On the other hand, if chronic toxicity is an issue that does not appear until a longer exposure, such as several days, weeks, or even months, the daily time step is likely adequate. It should also be noted that although most applications of SWAT have been on a daily time step, recent modifications make the sub-daily calculation operational (Brighenti et al., 2019). These modifications include adding Green and Ampt infiltration equations using rainfall input at any time increment and channel routing at an hourly time step.

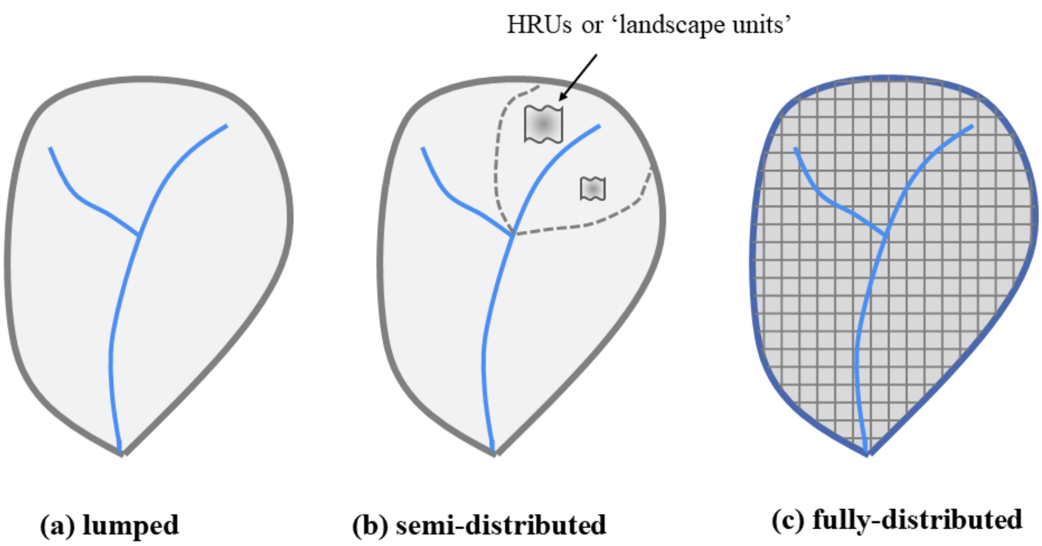

Fig. 4 Spatial discretization of the watershed model: (a) lumped, (b) semi-distributed, and (c)fully-distributed. HRUs are hydrological response units.

3.3.2 Overland hydrological processes

Modeling surface and subsurface hydrological processes is a prerequisite for process-based metal transport models because runoff drives soil HM deliveries into streams. Hydrological submodels in existing watershed-scale metal models can be divided into physically-based and conceptual. Every hydrological model requires two essential components: runoff generation and runoff routing. TREX and TOPKAPI are typical physically-based models that use the Green-Ampt equation to simulate infiltration and surface runoff generation. In contrast, the SCS-CN (curve number) method is widely used in models such as SWAT-HM and L-THIA to compute surface runoff. TREX and TOPKAPI route runoff using mass conservation-based continuity equations. The former uses diffusive wave approximation to simulate two-dimensional overland flow (i.e., surface runoff), while the latter uses kinematic wave approximation. They are both simpler forms of the St. Venant equations, also called dynamic wave equations.

In contrast, INCA-metals use storage-based (nonlinear reservoir) equations for flow routing. Subsurface hydrological processes (e.g., interflow, groundwater flow) are the most variable hydrologic components among the watershed models. Existing models use different approaches, ranging from ignoring all forms of subsurface fluxes (e.g., L-THIA) to empirical methods (e.g., INCA-Metals) to physically based equations (e.g., TOPKAPI-ETH). It should also be mentioned that all the reviewed models either lack groundwater modules or adopt simple ones. Regarding HMs, the convection–

diffusion–reaction equation (the conservation of solute mass) is the basic equation to simulate the movement of HMs driven by the hydrological flow and biogeochemical reactions (Steefel et al., 2005). Some simplifications are made in the reviewed HM models. For example, the HM transport in grid-based TOPKAPI-ETH is approximated as an advection process, neglecting the diffusion process. For semi-distributed models, the HRU or 'landscape unit' is used as the basic calculation unit to calculate the mass balance equations assuming spatial uniformity.

3.3.3 Soil erosion and sediment transport

As a major part of soil HM is tightly adsorbed to mineral particles, bound with organic matter, or present in parent minerals, soil erosion is the primary pathway of soil HMs to water bodies and has been studied at various scales (plot, watershed, and national scales) under natural or simulated conditions (Huang et al., 2019a; Quinton and Catt, 2007; Zheng et al., 2016). More recent studies have highlighted the important role of the water erosion pathway in the movement of HM from soils to surface waters (Liu et al., 2019). Moreover, erosion is a highly selective process that enriches the detached material with small-sized silt, clay, and organic carbon. The enrichment ratio (ER) of HM is the key variable representing the mechanisms and is defined as

$$ER = \frac{C_i}{C_0} \tag{3}$$

where C_0 denotes the concentration in the original soil, and C_i represents the mean concentration in the eroded sediment.

Several soil erosion and sediment yield models are available in the existing watershed-scale metal models with different process complexity and data requirements. The erosion and transport of particle HMs are directly coupled to corresponding fluxes of sediment particles. Soil erosion models quantify the amount of soil removed from a defined area over a given period. In contrast, the sediment yield models compute the amount of soil transported to water bodies over a defined area in a given period. Therefore, it is critical to account for all erosion and sediment transport processes within a basin to assess the sediment yield. The Universal Soil Loss Equation (USLE) and its descendants (e.g., RUSLE) are empirical models widely used for predicting soil erosion. However, USLE series models do not consider sediment deposition or route sediment in a spatial context; thus, they cannot be directly used to predict watershed sediment yield.

In many cases, USLE/RUSLE is applied to simulate hillslope erosion, along with sediment delivery ratios (SDRs), to determine the sediment delivered from the hillslope to water bodies. For example, METALPOL employed a modified USLE with the SDR to calculate the soil loss in river basins. The SWAT-HM uses the modified USLE (MUSLE) to simulate the sediment yield at the washed scale. MUSLE replaces the rainfall energy factor in the USLE using a runoff rate factor, fulfilling the sediment yield prediction for a single storm event by considering the runoff characteristics. Physically-based models (e.g., TREX and TOPKAPI-ETH) integrate a spatially distributed soil erosion and suspended sediment transport module. This module simultaneously accounts for 4 main sediment transport processes, advection, dispersion, erosion and deposition on a two-dimensional overland plane; the latter two processes are determined by the local transport capacity, which depends on the overland flow discharge and surface slope (Battista et al., 2020; Prosser and Rustomji, 2000). Additionally, ECOMAG-HM does not contain a sediment component; therefore, it is unsuitable for erosion-prone areas.

3.3.4 In-stream processes

Current watershed metal models employ significantly different levels of complexity in modeling in-stream processes. Most models (e.g., TREX and TOPKAPI-ETH) assume a one-dimensional transport along a stream reach for simplicity. Models such as SWAT-HM and WARMF assume a well-mixed water column for each channel. Regarding channel flow, TREX and TOPKAPI-ETH use diffusive wave approximation and kinematic wave approximation under the overland flow modeling. SWAT-HM provides the variable storage and Muskingum methods for water routing in the channel network. Physically-based models commonly consist of two sediment transport processes in rivers/streams: (1) advection and dispersion and (2) erosion and deposition. A simplified stream power equation calculates the maximum sediment load in river channels in SWAT-HM. Concerning the metal module, the CTT&F model includes a four-phase equilibrium partitioning (dissolved, precipitated, sorbed to sediment particles, and complexed with the dissolved organic carbon (DOC)). In contrast, some models (e.g., METALPOL) do not explicitly consider the in-stream processes but quantify the "apparent" retention behavior of metals in river systems by computing the difference between the measured load of metals at a specific river station/section and the sum of all point and diffuse (nonpoint) sources of metal emissions, which represent the inputs into a watershed.

3.3.5 Point sources and atmospheric deposition

There are generally two methods for quantifying point source emissions: the measurement method and the emission factor method when the source locations are identifiable and time series of effluent discharges and metal concentrations are available. Representing the point sources in the model is relatively easy. However, detailed observations are not available in most cases. Multiplying the estimated discharge (inhabitants connected to the point source × water volume used per person per day) by the average HM concentration could be a reliable way to estimate the daily HM loads (Liu et al., 2018). Notably, this approach cannot account for short-term fluctuations in HM concentrations and loads. Moreover, detailed locations and point source emissions are unavailable in some large-scale applications. Therefore, a bottom-up approach combining the activity levels of various industry sectors with HM-specific emission factors have been preferred to evaluate the aqueous emissions of HMs (Huang et al., 2019b; Wu et al., 2018). In compliance with the spatial resolution of model watershed models, the technical implementation of point source modeling differs in semi-distributed model from that in fully distributed models. Semi-distributed models add point source loads to the inlets of the reaches receiving the discharge for the balance calculation, whereas fully-distributed models have the sink/source term of the river solute from the external point source appended to the transport continuity equation in a river channel reach.

Atmosphere deposition is typically considered as the model input for watershed-scale water quality models. That is to say, most watershed models do not simulate atmospheric deposition processes, but instead use the measured fluxes of atmospheric deposition or simulated fluxes derived from air quality models. For example, modeling studies have mapped the global atmospheric concentrations and regional atmospheric deposition of priority heavy metals like Hg, Cd, and Pb under the United Nations' Convention on Long-Range Transboundary Air Pollution (Ilyin et al., 2022). Mosses have been used successfully as biomonitors to map the spatial patterns of HM deposition across Europe (e.g., Harmens et al., 2010).

4 Current challenges and research needs

4.1 Improving the model representation of real-world processes

4.1.1 Integrating with a carbon cycle module

The terrestrial and aquatic carbon cycles play a critical role in the biogeochemical cycling of HMs in natural environments (Warren and Haack, 2001). For example, the decomposition of soil organic matter (SOM) and its associated processes directly influence soil carbon, oxygen, and nitrogen cycles, and indirectly regulate soil HM cycles by modulating Eh and pH. SOM decomposition reactions have long been recognized as complex and mostly microbe-mediated. Among the development and applications of 9 reviewed models, only a few works has explicitly considered the dynamic linking between SOM and HM (Du et al., 2019). In soil solutions, Metals such as Cu and Pb may mostly be present as metal complexes, while Cd and Zn are usually present as free ions or labile complexes (Nolan et al., 2003). From the perspective of transport modeling, the total solution concentration, and not the metal speciation (e.g., free-ion and metal complex concentrations) in the solution, must be known. When the objective is to predict metal risk and toxicity (Aim 2, risk assessment), it is crucial to identify which metal species are taken up since bioavailability is influenced by the activity of free metal ions and "labile" metal complexes pool (Parker et al., 2001). However, DOM/DOC is an often-overlooked variable in data collection and modeling despite its importance in metal risk and toxicity assessments (Caruso et al., 2008). SWAT and INCA are capable of characterizing metal complex dynamics because these model families have been developed for a range of water quality variables, including organic carbon. For example, Futter et al. (2007) presented a process-based model for simulating DOC in soil and river water called the Integrated Catchments Model for Carbon (INCA-C), and Zhang et al. (2013) developed the SWAT-C model to simulate the mass balance of soil organic carbon. In addition, recent studies have enhanced the SWAT model by introducing microbe-mediated SOM turnover processes based on Microbial Kinetics and Thermodynamics model using dual Michaelis-Menten kinetics (Bhanja et al., 2019a; 2019b). Thus, SWAT-HM and INCA-metals are the most prospective model among the 9 models due to their amenability to integrate the SOM/DOM-HM interaction by taking the advantage of the existing carbon modules.

4.1.2 Reflecting on the role of the hyporheic zone

The hyporheic zone is defined as the portion of a streambed that contains a mixture of surface water and groundwater (Fig. 2). All of the nine models mentioned above ignore the metal attenuation (sink) and release (source) processes in the hyporheic zone. Thus, the metal attenuation and release processes in the hyporheic zone should be incorporated to understand the transport mechanisms in the river (Aim 1, improving understanding). Biogeochemical processes (both chemical and microbial) occurring within the hyporheic zone can significantly influence the fate and transport of HMs (Boano et al., 2014; Gandy et al., 2007). For example, the Mn oxide formation in the hyporheic zone could uptake the HMs and decrease the metal loads (Fuller and Harvey, 2000). In contrast, microorganisms' respiration may deplete the hyporheic zone's dissolved oxygen (Bourg and Bertin, 1993). The induced redox change could promote the dissolution of iron and manganese oxides and the adsorbed metals, causing their release into the solution and making the hyporheic zone a metal source (Coynel et al., 2007). Hyporheic zones are closely dependent on riverbed morphology and hence vary with higher spatial resolution. Meanwhile, the river morphology could affect the physicochemical properties of river sediment and floodplain soil and thus contribute to the further redistribution of HMs (Wei et al., 2022). Integrating hyporheic zones into the watershed model may be cumbersome for semi-distributed models because of their predefined flow direction and usually an inadequate resolution of the reach channel. On the other hand, fully-distributed models with grid cell discretization have better potential to model hyporheic exchange in detail. Integrating the transient storage reach-scale models (e.g., OTIS) within the fully-distributed watershed framework could be a solution. However, it is still challenging because of the high data requirements to reflect the remarkable heterogeneity of hyporheic exchange across the river network.

4.1.3 Refining the solid/liquid distribution (K_d) in rivers

In rivers, the fate of HMs depends on their solid/liquid distribution between water and suspended solid (SS) phases and the behavior of these two phases according to hydro-sedimentary processes. The solid/liquid fractionation is usually modeled with the fixed "K_d" using the recommended screening values or finite field measurements. However, the K_d variability is in the order of magnitudes depending on several environmental factors, such as SS, DOM/DOC content, and pH (Lu and Allen, 2006). None of the existing HM models has the capability to reflect the dynamic changes in K_d values under different hydrological conditions. Recently, Tomczak et al. (2019) compiled a database containing 8564 K_d values from 50 elements with their potential explanatory factors and determined the K_d distributions for *in situ* water/SS conditions as a function of SS, DOC, and pH. For example, assuming a log-normal distribution, the changes of geometric mean (K_d) and geometric standard deviation (K_d) were identified as power laws of m/V (ratio of solid mass to water volume) for Cd, Cu, Hg and Pb (Fig. 4 in Tomczak et al. 2019). Adding such relations to existing models could reduce the global variability of K_d values.

4.2 Gearing toward mitigation practices and climate change

Measuring pollution loads from all pathways within a watershed and evaluating the effectiveness of mitigation practices through actual implementation in the field is time-consuming and resource intensive. Numerical models can be valuable tools for developing targeted remediation strategies and assessing the impact of climate change on water quality. However, only a few watershed-scale HM models have considered mitigation practices. For example, Whitehead et al. (2009) investigated a range of cleanup scenarios considering point source reductions to evaluate the effects of mine restoration on water quality. Nonpoint source control measures should be evaluated in future watershed management plans because numerous studies suggest they play an important role in metal transport at the watershed scale (Liu et al., 2019; Zhou et al., 2023). For example, soil conservation measures (e.g., terracing, contour farming, and strip cropping) are common management operations for soil pollution control. Additionally, the extensive use of nitrogen fertilizers has resulted in significant soil acidification in several areas of China over the last three decades. This has contributed to increased metal availability and metal loss in soil (Guo et al., 2010). Field experiments have shown that liming can effectively reduce Cd accumulation in rice grains, as it increases soil pH and reduces Cd's bioavailability ($CaCl_2$-extractable) in the rhizosphere (Chen et al., 2018). Therefore, further investigations are required to represent mitigation practices in watershed-scale HM models for effective management decisions.

Climate change is modifying metal deliveries from soil to water due to changes in hydrological processes (Byrne et al., 2012). For example, in the Snake River watershed in the Rocky Mountains, USA, intensified generation of Acid Mine Drainage has been linked to warmer summer air temperatures and earlier drying of shallow soils, which expands weathering fronts and promotes oxidation (Rue and McKnight, 2021). In UK watersheds where low river flows are expected to occur more frequently and severely due to climate change, metal-rich groundwater may significantly influence stream metal concentrations (Byrne et al., 2020). Thus, assessing metal transport dynamics and responses to climate change scenarios is essential to develop effective watershed management strategies.

4.3 Reforming model calibration and uncertainty analysis

In the watershed-scale models, except for the physical parameters, some parameters are difficult to measure directly; therefore, they must be estimated from the collected data through a calibration procedure (Herrera et al., 2022). Calibration can be conducted manually by trial and error or automatically through a computer-based procedure or a combination of the two. Currently, the general sequence for calibrating a watershed-scale HM model is as follows:1) calibration of hydrological parameters, focusing on the proportion of surface runoff and baseflow; 2) calibration of sediment parameters, focusing on the ratio of upland and channel erosions; and 3) calibration of metal parameters, focusing on the land-to-river metal fluxes and riverine metal concentrations and loads (Meng et al., 2018; Sui et al., 2022).

Although numerous algorithms and tools exist for parameter calibration, the non-uniqueness feature (equifinality) in calibration makes the estimation of a unique or best parameter set meaningless (Abbaspour, 2022; Beven, 2006). Given the various types and sources of uncertainty, no calibration problem in the hydrology and water quality domain is uniquely solvable. In other words, if a single model (a best parameter set) fits the measurements well, many models (multiple parameter sets) exist that can achieve statistically similar model accuracy. For example, a model may exhibit satisfactory statistical agreement with measured streamflow data while misrepresenting flow pathways (e.g., surface runoff, lateral flow, and baseflow).

Mitigation of the non-uniqueness problem may be partially achieved by: (1) improving model representation and developing more robust models (discussed in Section 4.1), (2) implementing thorough parameter sensitivity analyses prior to calibration, (3) collecting more and better quality data (e.g., incorporating soft data) and extracting more information from the collected data, and (4) obtaining unconditional parameters through multi-variable, multi-objective calibration procedures. For example, sensitivity analysis can reduce the number of parameters for calibration by identifying the parameters with negligible influence on the output, thereby reducing the combinations of parameter sets that produce similar results. Some studies have separately calibrated surface runoff and baseflow (Zhang et al., 2011). Calibrating metal parameters using both dissolved and total metal concentrations could also improve parameter identifiability. For example, a long-term and high-frequency estimation of metal concentrations and fluxes in rivers could be obtained by analyzing the relationship between sporadic sampled (dissolved/particulate/total) metal concentrations and continuously monitored proxy indicators (e.g., discharge/SS/turbidity) (Nasrabadi et al., 2016).

Moreover, tracer and isotope data may assist watershed-scale model calibration because they provide information on both hydrologic pathways and specific contaminants (Jensen et al., 2018). Multi-objective (e.g., multi-criteria and multi-variable) calibration routines have been proposed to estimate model parameters using multiple types of data (Bennett et al., 2013). The use of soft data in automated calibration procedures is also recommended to constrain the model equifinality and improve the model's realism (Arnold et al., 2015). Typical soft data for metal modeling could be long-term average sediment yield, event mean concentration, and source apportionment using isotope analysis.

Recognizing and quantifying model uncertainties are vital for applying watershed HM models. As mentioned above, the uncertainties could be introduced by model validation data (e.g., limited data) and model structures (e.g., different representations of metal transformation). It should also be noted that model input (e.g., precipitation, DEM, digital elevation model) is another non-negligible source (Shen et al., 2012). The precision of the DEM is expected to affect the delineation of watersheds and the calculation of terrain factors (e.g., slope, slope length), which will further influence models' simulations of flow, sediment, and metal transport processes (Wechsler, 2007). Most HM model studies have been calibrated against HM concentrations in river water but occasionally report model uncertainty. Zhou et al. (2020) applied the SUFI-2 algorithm (Abbaspour et al., 2007) and behavioral simulations (e.g., model performance above a threshold of one/multiple objective functions) to represent the metal flux uncertainty. Thus, further research is needed to quantify uncertainty and its relative source strengths to support robust decision-making. Some existing long-term and high-frequency datasets in experimental watersheds (e.g., Neal et al., 2013) provide a valuable opportunity for model comparison, testing, and reducing model uncertainty.

4.4 Balancing model complexity and data requirements

In Section 3, the problems of model complexity and data requirements have been raised. Well-informed modeling relies on a well-designed monitoring network. However, an enormous amount of input and calibration data is required to build and calibrate complex water quality models. Moreover, the data requirements of water quality models vary with model complexity and purpose. Thus, in addition to collecting more and better quality monitoring data, it is necessary to determine the amount of data (Ledergerber et al., 2019) and the value of the data (Abbaspour et al., 1996) to be collected. The optimal experimental design (OED) technique is a useful tool for identifying data shortages and maximizing available information behind the measurement data. For example, suppose a new dataset is to be collected; model-based OED can evaluate the informational gain from the perspective of model calibration from a bundle of proposed experiments and help reach a cost-effective experimental design (Vanrolleghem et al., 1995).

Regarding better quality monitoring data, existing monitoring protocols by environmental regulators often collect grab samples, which cannot detect dynamic changes in HM concentrations, particularly during high-flow periods (Neal et al., 2012). Future research should incorporate the new advancements in sampling and analytical technologies which enable more representative and efficient measurement of HMs in soil and water. For instance, Frau et al. (2018) investigated the possibility of using novel electromagnetic wave sensors for the real-time and continuous monitoring of HMs in surface water. Moreover, several studies have applied the tracer injection and synoptic sampling (TISS) method to quantify the spatially detailed point and nonpoint metal fluxes to streams, which could be crucial data for multi-objective calibration in watershed-scale models (Byrne et al., 2021; Kimball et al., 2002). TISS uses conservative tracers (typically bromide or chloride) and synchronous (or synoptic) water sampling to measure the flow and pollutants concentrations. For example, the TISS method revealed the spatial profiles of dissolved, colloidal, and total Zn loads in Cement Creek, Colorado, USA (Fig. 9 in Kimball et al., 2002). Furthermore, a new paradigm called SEPSTAT has been proposed for effective heavy metal monitoring based on dry preservation: solid-phase extraction, preservation, storage, transport, and analysis of trace contaminants. It was designed to overcome the logistical challenge and could create the required large-scale data in resource-limited settings. (Hanhauser et al., 2020). In addition, hyperspectral remote sensing offers a non-destructive and real-time method for retrieving soil metal concentrations, which could facilitate the simulation of ubiquitous spatial heterogeneity in watershed-scale HM models (Nawar et al., 2020).

5 Conclusions and recommendations

This study provided an overview of the current generation of watershed-scale HM models in terms of their simplifications and assumptions, components and functions, strengths and weaknesses. The primary conclusions and recommendations, including model improvement, data acquisition, and their combined use, are as follows:

- **Model development in compliance with the intended use**

The future directions of model development were identified for four different aims. For Aim 1 (improving understanding), the metal attenuation and release processes in the hyporheic zone, as well as the dynamic K_d should be incorporated to understand the transport mechanisms in the river. SOM/DOM module and sub-daily schemes should be incorporated when the objective is to predict better metal toxicity and risk (Aim 2, risk assessment). For Aim 3 (identifying critical source areas), fully-distributed models would be suitable for small-to mesoscale watersheds, while semi-distributed models with the Markov chains theory could be applied on large scale watersheds. Aim 4 (scenario analysis) requires an improved representation of mitigation practices in existing models to inform effective management decisions.

- **Data acquisition through numerical and field experiments**

Watershed HM studies as a whole suffer from a lack of spatiotemporal measurements. Model developers and experimental researchers should work together to ensure that our models reflect the best available systems understanding and to ensure that monitoring programs provide the maximum information models require. Both virtual (e,g., OED technique) and actual (e.g., TISS method) experiments could be helpful to optimize experimental schemes and obtain better quality data.

- **'Benchmark' models/codes and data sets for model application**

The comparison and evaluation of available metal models using real data sets need to be done for developing benchmark models/data and pre-and post-processing tools to facilitate better visualization, accessibility, and commutations. The existing experimental watersheds with long-term and high-frequency data provide a valuable opportunity. Ultimately, the goal is to establish a flexible framework that combines hydrology, sediment, and chemical sub-models at various levels of complexity to match the available data and support the corresponding model purpose.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare no competing financial interest.

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