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1	Modeling transport and fate of heavy metals at the watershed
2	scale: state-of-the-art and future directions
3	
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17 Abstract

18 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 19 20 mitigating river pollution and developing effective river basin management strategies. 21 Developing such strategies requires adequate monitoring and comprehensive models 22 based on a solid scientific understanding of the watershed system. However, a 23 comprehensive review of existing studies on the watershed-scale HM fate and transport 24 modeling is lacking. In this review, we synthesize the recent developments in the 25 current generation of watershed-scale HM models, which cover a wide range of 26 functionalities, capabilities, and spatial and temporal scales (resolutions). Existing 27 models, constructed at various levels of complexity, have their strengths and 28 weaknesses in supporting diverse intended uses. Additionally, current challenges in the 29 application of watershed HM modeling are covered, including the representation of in-30 stream processes, organic matter/carbon dynamics and mitigation practices, the issues 31 of model calibration and uncertainty analysis, and the balance between model complexity and available data. Finally, we outline future research requirements 32 33 regarding modeling, strategic monitoring, and their combined use to enhance model 34 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 35 36 specific applications.

37 Keywords

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

40 **1 Introduction**

41 Elevated concentrations of heavy metals (HMs) are a global threat to aquatic 42 systems and human health owing to their potential accumulation, biomagnification, and 43 toxicity. The 'heavy metals' is a collective term used here to represent a group of metals 44 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. 45 46 Although there still exist debates concerning the imprecise use of the term 'heavy 47 metals' and its alternatives, including 'toxic metals', 'trace metals', 'trace elements', and 'potentially toxic trace elements' (Duffus, 2002), we used the term 'heavy metals' 48 49 consistently in this review for convenience. HMs are ubiquitous in the environment as 50 naturally occurring elements. For example, As pollution from geogenic sources is a 51 major problem in South Asia (e.g., Winkel et al., 2008). Meanwhile, HMs, such as Cd, 52 Hg, Cu, As, Cr, and Pb, have contaminated river systems in many parts of the world as 53 a by-product of industrialization (Johnson et al., 2018; Mason, 2013). For example, the 54 signature of Pb mining and smelting activities by ancient Greeks and Romans have been 55 documented in the Greenland ice cores (Hong et al., 1994). Moreover, over 100,000 abandoned or inactive mining sites are spread over 2,000 km² in the United States 56

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(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).

61 Knowledge of the HMs released from contaminated soils and sites in the upland 62 and their subsequent migration in river networks is critical for assessing environmental 63 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 64 65 various diffusion pathways, including surface runoff, subsurface flow, groundwater flow, and soil erosion. Meanwhile, many biogeochemical processes greatly influence 66 67 and regulate HM's mobility (Carrillo-González et al., 2006). These mechanisms 68 involve sorption, complexation, precipitation, redox reactions as well as weathering processes influenced by environmental factors such as pH, redox potential, and 69 70 temperature (Borch et al., 2010; Degryse et al., 2009). Extensive studies, including field 71 measurements, have been performed on the mechanisms of different soil 72 biogeochemical reactions at the plot and field scales (Selim and Kingery, 2003). 73 However, when it turns to the watershed scales, a quantitative and complete description 74 of metal migration may be hindered by the strong spatial heterogeneity and temporal 75 variability of HM production, transformation, and transport processes (Li, 2019). To 76 fully understand the complex mechanisms of HMs transport at a watershed scale, a 77 large amount of time- and resource-consuming fieldwork is needed. Watershed-scale 4

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).

85 Over the last few decades, water quality models concerning the quantification of 86 nutrients (e.g., nitrogen and phosphorus) dynamics at the watershed-scale have been 87 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). 88 89 Previous reviews have focused mainly on the spatiotemporal distribution of HMs in 90 soil and river systems, their transformation and partitioning at solid-liquid interfaces 91 (e.g., Degryse et al., 2009), and plot, field, and river-scale numerical transport models 92 (e.g., Carrillo-González et al., 2006; Garneau et al., 2017). To our knowledge, a holistic 93 description of watershed HM processes accounting for natural and anthropogenic inputs, 94 terrestrial delivers into streams, and in-stream dynamics is lacking. The last significant 95 and most relevant review came from a USEPA workshop in 2007 (Caruso et al., 2008), 96 which gathered experts from academia and the government to explore state-of-the-art 97 models for simulating metal fate and transport from different scales and application 98 domains, such as equilibrium, stream, and watershed models. Caruso et al. (2008) stated 5

99 that existing watershed models require further testing and evaluation using more field 100 data, and a truly calibrated watershed HM model did not exist. In the last 15 years, new 101 HM watershed models have been developed (Meng et al., 2018; Motovilov and 102 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 103 104 has been conducted till date. Therefore, we present a contemporary analysis of existing watershed pollution models by comparing the differences in functionality and 105 106 underlying assumptions to highlight the challenges and opportunities for future model 107 research and development.

108 Owing to the complexity of natural environmental systems, models are always necessarily simplified descriptions of reality. Moreover, models are often constructed 109 110 at different levels of complexity in terms of structure, function, and processes depending on scientific knowledge, purposes, and data availability. Therefore, we 111 112 evaluate models' strengths and weaknesses in this review according to their diverse 113 intended uses. The remainder of this review is organized as follows. Section 2 outlines 114 the primary sources, transformation mechanisms, and transport pathways of HMs in the natural environment. Section 3 reviews contemporary HM watershed models and 115 116 highlights their basic assumptions, simplifications, components, and distinctions. 117 Section 4 summarizes the research gaps and challenges in watershed HM modeling and 118 applications. Finally, Section 5 concludes with future research needs in HMs 119 monitoring, modeling, and their combined use.

6

120 **2** Fate and transport of HMs in the real world

121 **2.1** Sources of HMs in the environment

122 There are two main categories of HM sources: natural and anthropogenic. Natural sources mainly include bedrock weathering, volcanic eruptions, and atmospheric 123 124 deposition. Anthropogenic sources (e.g., industrial, agricultural, and municipal) have 125 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 126 often associated with metal mining and smelting, chemical production, dyeing and 127 printing, and burning fossil fuels (Rauch and Pacyna, 2009). In addition, applying 128 129 fertilizers, pesticides, manure, and wastewater irrigation has substantially increased 130 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 131 132 quantities of HMs to aquatic environments (Zhou et al., 2018). Vehicular exhaust and 133 wear and tear of tires are other important HM sources (Werkenthin et al., 2014). For 134 example, Zn isotopes in sediment cores of eight lakes across the United States indicated 135 that vehicle emissions are the most significant source of Zn (Thapalia et al., 2015). 136 Finally, it should be noted that human activities are deeply intertwined with natural 137 processes, sometimes blurring the boundaries. For example, HMs emitted from 138 industrial activities are transported through the atmosphere, deposited in the soil, and 139 then transported to water bodies via runoff and erosion (Andronikov et al., 2021).

140 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 141 142 pollution is discharged directly from a discernible source, such as a discharge pipe from 143 a factory or sewage plant. For example, the Seine (Chen et al., 2008) and Rhine 144 (Stigliani et al., 1993) river basins in Europe and Dongting Lake in China (Li et al., 145 2013) receive most of their HM pollution from point sources. Unlike point sources, 146 diffuse (nonpoint) sources do not originate from a specified location. Instead, they are characterized by intermittent occurrences and spatial heterogeneity, such as runoff from 147 148 agricultural land during rainfall, which makes them challenging to trace and control (Patterson et al., 2013). 149

150 **2.2**

2.2 Transformation mechanisms

151 HM's mobility and bioavailability in terrestrial and aquatic systems depends on 152 chemical speciation (van Leeuwen et al., 2005). In the most simple sense, chemical 153 speciation refers to whether a metal exists in a dissolved/solute form or a solid/particle-154 contained form (Fig. 1). In the natural environment, several reactions can change HM 155 speciation, (adsorption/desorption), complexation such sorption as (association/dissociation), precipitation/dissolution, diffusion into carbonates and 156 157 oxyhydroxides (Degryse et al., 2009). In the solid phase, HMs are present as labile (M_1) , 158 non-labile (M_n) , or inert metal (M_{inert}) species. Labile metal can exchange rapidly with 159 the solution phase. Furthermore, metals in the labile pool in the solid phase can slowly 160 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 161 162 unlikely to be released to a solution phase. In the solution phase, metals appear as free 163 ions (M^{n+}) , complexes with inorganic or organic ligands (ML), or associated with 164 mineral colloids (MLinert) (Honeyman and Santschi, 1988). Generally, the free ions in 165 the solution tend to react most actively with the solid phase. However, similar to inert 166 solid metals, some metals in solution, such as those in colloidal minerals, may also be 167 non-reactive. Metals complexes with inorganic or organic ligands could be divided into 168 labile and non-labile ML (ML_{labile} and ML_{non-labile}) according to the dissociation rate of 169 these complexes.

Soil HM's solubility and mobility are governed by soil properties such as soluble 170 171 ligands in soil pore water, soil matrix composition (e.g., oxides, clay, and organic 172 matter), pH, temperature, and redox potential (Young, 2013). In soil solutions, HM 173 species are significantly affected by the presence of different organic and inorganic 174 ligands. The soil solid phase consists of various constituents (clay minerals, organic 175 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 176 177 influencing metal speciation in soils, thus the master variable affecting metal behavior 178 in soil systems. In addition, the increase/decrease of soil redox potential (Eh) could 179 regulate a series of biogeochemical reactions. For example, some variable-valence HMs 180 such as Hg, As, Cr, and Fe could undergo valence changes within the range of redox 9

potentials (Carrillo - Gonz á lez et al., 2006). Biomethylation could occur under
anaerobic conditions, transforming the inorganic forms of Hg and As into methylated
forms.





184

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).

188 **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).

199 After water infiltrates the soil, it undergoes the processes of vertical leaching and 200 lateral flow, with the concomitant of dissolved metals. Soil leaching is the downward 201 movement of dissolved metals in the soil profile via percolating water. Subsurface 202 lateral flow refers to soil water processes where infiltrating water accumulates and 203 moves laterally downslope along the upper surface of a less permeable layer in the soil. 204 Subsurface lateral flow is abundant at the interface between the soil and bedrock, where 205 permeability changes dramatically. A range of terms are used to refer to subsurface lateral flow, including throughflow, subsurface runoff, and interflow. The relative 206 207 contribution of soil leaching or subsurface lateral flow to HM transport varies largely 208 depending on the soil attributes and topographic and meteorological conditions. Xia et 209 al. (2014) found that soil leaching is the dominant export pathway of soil HM in the 210 southern Song-nen Plain of Northeast China. The subsurface flow from acid mine 211 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 212 213 that soil leaching was the most important contributor of Cd (20%), Zn (40%), and Pb 214 (40%) to surface water (Bonten et al., 2008). Enhanced metal leaching is associated 215 with acidic drainage due to high metal solubility and sulfide weathering rates under 216 acidic conditions (RoyChowdhury et al., 2015).

217 Groundwater discharge is another possible input of HMs into surface waters. 218 Groundwater containing dissolved contaminants migrates from the soil into subjacent 219 aquifers and finally enters adjacent streams. Several hydrological and biochemical 220 factors determine the amount of metal transported from the groundwater to streams. 221 Generally, HM fluxes via groundwater discharge are significant in mountainous mining 222 areas. Polluted aquifers act as long-term pollution sources for the surrounding rivers, 223 even after mining activities have stopped (Wang et al., 2019). For example, the inputs 224 of Cd (43%) and Zn (28%) to the Riou Mort River in France are mainly through 225 groundwater discharge (Coynel et al. (2007). In contrast, fieldwork in the Gilt Edge 226 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 227 228 groundwater movement and HM attenuation in aquifers due to sorption could reduce 229 the metal loads to the streams. Thus, HM transport in subsurface environments can be 230 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 12

238	significant HM input to terrestrial environments (Lofts, 2007). For example, an
239	inventory study of HM inputs to agricultural soils in China showed that atmospheric
240	deposition accounted for 43-85 % of the total As, Cr, Hg, Ni, and Pb inputs (Luo et al.,
241	2009). Atmospheric deposition contributes more Zn, Ni, and Pb to European
242	agricultural soils than phosphate fertilizer application (Nziguheba and Smolders, 2008).
243	After HMs enter rivers, a number of physical (e.g., convection, diffusion, erosion
244	and deposition of sediments), chemical (e.g., sorption, complexation, precipitation),
245	and biological (e.g., bioturbation) processes could influence the fate of HMs in aquatic
246	systems to some degree (e.g., Mason, 2013). The scavenging of HMs in river water
247	depends largely on the solid-liquid distribution and the presence/properties of
248	suspended/riverbed sediments (Honeyman and Santschi, 1988). Most HMs entering the
249	rivers may be immobilized and stored by adsorption onto the riverbed sediments (Peng
250	et al., 2009). A portion of HMs that adsorbed on fine suspended solids (e.g., hydrous
251	oxides, clays) could transport downstream over long distances (Hochella et al., 2005).
252	In addition, "big events", such as large storms and floods, have been shown to
253	significantly affect HMs' remobilization and transportation (Ciszewski and Grygar,
254	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

258 **3.1 Existing representative models**

259 Nine representative models were selected based on a thorough literature evaluation: 260 L-THIA (Park et al., 2013), METALPOL (Vink and Peters, 2003), WARMF (Chen et 261 al., 2000), ECOMAG-HM (Motovilov and Fashchevskaya, 2019), SWAT-HM (Meng 262 et al., 2018), INCA-Metals (Whitehead et al., 2009), CTT&F (Johnson et al., 2011), 263 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 264 265 of all available watershed scale HM models. These representative models were selected 266 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 267

fate/transport description varies among the models, ranging from simple export 268 coefficient models (e.g., L-THIA and METALPOL) to more complex integrated 269 270 watershed models (e.g., SWAT-HM and TOPKAPI-ETH). It should also be noted that 271 urban watershed models, such as SWMM model, were not included in this review. 272 Urban models focus more on the buildup and washoff of pollutants from impervious 273 surfaces and subsequent transport and transformation processes in the urban water 274 infrastructure systems. Though urban area is usually a significant part of a watershed, 275 the prominent particularities of urban models render them incomparable with general 276 watershed models which mainly target the natural to less urbanized environments. 277 Useful reviews on urban water quantity and quality modeling can be found in Zoppou (2001). 278

279 As mentioned in Section 2, metal behavior in the natural environment is highly complex in terms of various pollution sources, transformation reactions, and transport 280 281 pathways. Therefore, models are always simplified descriptions of environmental 282 systems with different levels of complexity. Furthermore, models have evolved over 283 time, becoming increasingly detailed in terms of spatiotemporal resolution and the number of components and processes included. The selected models have been 284 285 developed for a range of different objectives. They reflect a broad spectrum of concepts 286 and assumptions, which can be categorized according to various criteria, including 287 representation of processes (e.g., empirical, conceptual, process-based, or physically-288 based), spatial scale (e.g., plot, field, or watershed), spatial discretization (e.g., lumped, 15

289 semi-distributed, and fully-distributed), and temporal scales (e.g., event-driven or long-290 term simulation). However, it is accepted that these categories are sometimes vague, 291 and in practice, many models include elements of different categories. Generally, two 292 main processes (contaminant partitioning and transformation and contaminant transport) 293 are considered in watershed-scale metal models. The contaminant transport component 294 commonly consists of three processes: (1) overland hydrological processes, (2) soil erosion and sediment transport, and (3) in-stream processes. The main features and 295 296 components of the reviewed models and associated references are summarized in Table 297 1, with additional comparisons in Sections 3.2 and 3.3.

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

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

							couple with other processes	
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	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)

300 **3.2 Representation of metal partitioning and transformation**

301 **3.2.1** Existing metal transformation schemes

302 Existing models generally have four levels of complexity for reaction mechanisms 303 (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 304 305 conceptually appealing, it requires extensive input information, often unavailable in 306 routine research. The level 3 scheme does not consider the differences between non-307 labile and inert metals in the solid and solution phases. However, it requires 308 simultaneous modeling or observation of dissolved organic matter (DOM) owing to its 309 explicit modeling of metal complexes. The level 2 scheme consists of three metal pools: 310 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 311 312 simplified level 1 scheme consists of two pools: M_d and particulate metal (M_p) , in which $M_{\rm l}$ and $M_{\rm n}$ are further regarded together as $M_{\rm p}$. 313

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.

327 Sorption

328 Sorption refers to the adsorption-desorption processes between the dissolved metal 329 in the solution phase and the labile metal in the solid phase. Several studies have 330 demonstrated that adsorption-desorption is the most important process affecting the mobility and bioavailability of metals (Degryse et al., 2009). Dissolved metals (solution 331 332 phase, $[M_d]$) are reversibly adsorbed onto solids and become labile adsorbed metals 333 (solid phase, M_1). The solid-solution partition coefficient (K_d) is defined as the ratio of 334 labile metal concentration in the solid phase to dissolved metal concentration in the 335 solution phase when equilibrium is attained:

$$K_{\rm d} = \frac{M_1}{\left[M_{\rm d}\right]} \tag{1}$$

where K_d is the solid-solution partition coefficient (L kg⁻¹), and M_1 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.

340 It should be noted that K_d is an apparent (lumped) partition coefficient for 341 describing the equilibrium speciation of metals between solid and solution phases, as it 342 describes both the sorption and complexation of free ions in solution rather than a single 343 mechanism. Moreover, because K_d is a strict equilibrium concept, equilibrium is 344 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 345 346 can be determined from an extensive literature search (e.g., Allison and Allison, 2005) 347 or estimated through laboratory adsorption/desorption batch tests. (2) Regression 348 models can be incorporated with the K_d concept to reflect the spatial variability of soil $K_{\rm d}$. For example, most regression models involve a multivariate linear relationship 349 350 between $\log K_d$ and the routinely measured soil properties (e.g., pH and soil organic 351 carbon) (De Groot et al., 1998).

352 Slow reaction

"Slow reaction" refers to all the slow chemical processes (between labile and nonlabile 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_1) and their non-labile counterparts (solid phase, M_n) with kinetic rates (k_1, k_{-1}).

358
$$\frac{dM_{i}}{dt} = -k_{1}M_{1} + k_{-1}M_{n}$$
$$\frac{dM_{n}}{dt} = k_{1}M_{1} - k_{-1}M_{n}$$
(2)

359 where k_1 and k_{-1} are the forward and backward rates of the slow reaction (d⁻¹). 360 Slow reaction is included in the SWAT-HM and TOPKAPI-ETH models because it 361 plays an important role in long-term simulations (Buckers et al., 2008; Crout et al., 362 2006). For example, using synthetic numerical experiments, Sui et al. (2022)
363 demonstrated the influence of slow reactions on the transport of dissolved Cd from
364 uplands to rivers over longer timescales (>5 years), highlighting the non-labile metal as
365 a long-lasting source of HM pollution.

366



367

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).

371 **3.2.2** Equilibrium approach versus kinetic approach

The equilibrium-based (K_d) approach is commonly used for watershed-scale water 372 quality models in Caruso et al. (2008) review. Recently developed models (e.g., SWAT-373 HM and TOPKAPI-ETH) have examined the equilibrium assumption adopted in the 374 375 previous models to propose a new scheme (i.e., kinetic approach) to enhance their 376 applicability. Specifically, the equilibrium assumption between the solution and solid 377 phases without considering the slow reaction (transformation between labile and non-378 labile pools) may not reflect reality, especially in long-term metal simulations (Sui et 379 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 380 381 have not yet been incorporated into the existing watershed HM models, although the development of reactive transport models (RTMs) in the subsurface geochemistry 382 383 community has advanced rapidly since the 1980s (Steefel et al., 2015). The reactions 384 in RTMs models include both kinetically controlled (e.g., microbe-mediated redox 385 reaction, mineral dissolution, and precipitation) and equilibrium-controlled ones (e.g., 386 ion exchange, surface complexation (sorption) and aqueous complexation) (Li, 2019). 387 A few attempts (e.g., Bao et al., 2017) have been made to bring the RTMs from the 388 "closed" groundwater systems into the "open" watersheds.

389 3.3 Representation of watershed-scale transport processes

390 **3.3.1** Spatial discretization and temporal scale

391 A spatially distributed representation of the hydrology and contamination transport

392 processes is necessary for watershed management. Thus, the watershed model 393 simulates water flow and contaminant dynamics across discretized landscape units. The models differ in how they account for heterogeneity within each sub-basin. In 394 395 watershed-scale models, spatial representation (discretization) is typically classified 396 into three types: (1) lumped, (2) semi-distributed, and (3) fully-distributed models (Fig. 397 4). The lumped spatial approach does not discretize the sub-basins and represents them 398 using average lumped parameters to represent the physical processes within each subbasin. The WARMF model follows this lumped approach (Chen et al., 2001). Semi-399 400 distributed approaches are based on properties of land use, soil type, and topography, 401 such as slope. Examples of such models are the SWAT model, which uses Hydrologic 402 Response Units (HRUs) (Arnold et al., 2010), and the 'landscape units' in INCA-Metals 403 (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-404 405 basin but are routed individually to the basin outlet. The fully-distributed approach 406 divides the watershed and sub-basins into hydraulically connected elements, such as 407 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 408 409 implemented in TREX (Velleux et al., 2008) and CTT&F (Johnson et al., 2011). A 410 principal advantage of a fully-distributed watershed model is the opportunity to identify 411 the critical source areas (Aim 3) within the watershed and sub-basin, such as waste piles 412 that contribute the most to HM transport. However, owing to the computational burden 413 and high demand for data, applying a fully-distributed model is limited to the small and 24

414 mesoscale scale. The decreased spatial resolution of the semi-distributed model allows 415 for a coarser calculation time step (e.g., daily), thus effectively reducing computational 416 resources. The decreased spatial resolution of semi-distributed models allows for a coarser calculation time step (e.g., daily), thus effectively reducing computational 417 resources. Semi-distributed models are still widely used for sub-basins prioritization 418 419 when accurate location is not demanding. For instance, Chen et al. (2014) developed a 420 framework integrating a watershed model with the Markov chain theory to pinpoint priority sub-basins. 421

422 For temporal scale, watershed-scale models can be divided into two categories: 423 event and continuous models. Event models simulate watershed responses to a single 424 rainfall event with a fine time resolution, like an hour or minutes, and are thus suit short-425 term simulating needs. In contrast, continuous models simulate the inter-rainfall 426 environmental processes in the watershed as well as the rainfall events *alone*; thus, they 427 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 428 429 capability. Other models, such as INCA-Metals and SWAT-HM, are able to analyze the 430 long-term effects of hydrological changes and water management practices. The daily 431 time step is likely one of the best temporal resolutions for the ease of computation and 432 availability of datasets while maintaining the capability to manifest temporal variation. 433 The daily time resolution is probably adequate for larger creeks or rivers that are not 434 "flashy" (i.e., the hydrograph peaks and falls back to normal flow quickly within 24 435 hours). However, the daily time step may not be adequate to determine pollutant loads 25 436 from flashy systems. Concerning toxicity modeling (Aim 2, , risk assessment), if acute 437 toxicity is of primary concern and the metal concentration dynamic fluctuates on an 438 hour- or minute-scale, event models become necessary to perform reliable risk 439 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 440 441 likely adequate. It should also be noted that although most applications of SWAT have 442 been on a daily time step, recent modifications make the sub-daily calculation 443 operational (Brighenti et al., 2019). These modifications include adding Green and Ampt infiltration equations using rainfall input at any time increment and channel 444 445 routing at an hourly time step.



447



448 Fig. 4 Spatial discretization of the watershed model: (a) lumped, (b) semi-distributed,

449 and (c)fully-distributed. HRUs are hydrological response units.

450 **3.3.2 Overland hydrological processes**

Modeling surface and subsurface hydrological processes is a prerequisite for 451 452 process-based metal transport models because runoff drives soil HM deliveries into 453 streams. Hydrological submodels in existing watershed-scale metal models can be 454 divided into physically-based and conceptual. Every hydrological model requires two 455 essential components: runoff generation and runoff routing. TREX and TOPKAPI are typical physically-based models that use the Green-Ampt equation to simulate 456 457 infiltration and surface runoff generation. In contrast, the SCS-CN (curve number) 458 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 459 460 equations. The former uses diffusive wave approximation to simulate two-dimensional overland flow (i.e., surface runoff), while the latter uses kinematic wave approximation. 461 462 They are both simpler forms of the St. Venant equations, also called dynamic wave 463 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– 471 diffusion-reaction equation (the conservation of solute mass) is the basic equation to 472 simulate the movement of HMs driven by the hydrological flow and biogeochemical 473 reactions (Steefel et al., 2005). Some simplifications are made in the reviewed HM 474 models. For example, the HM transport in grid-based TOPKAPI-ETH is approximated 475 as an advection process, neglecting the diffusion process. For semi-distributed models, 476 the HRU or 'landscape unit' is used as the basic calculation unit to calculate the mass 477 balance equations assuming spatial uniformity.

478 **3.3.3** Soil erosion and sediment transport

479 As a major part of soil HM is tightly adsorbed to mineral particles, bound with 480 organic matter, or present in parent minerals, soil erosion is the primary pathway of soil 481 HMs to water bodies and has been studied at various scales (plot, watershed, and 482 national scales) under natural or simulated conditions (Huang et al., 2019a; Quinton 483 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 484 485 (Liu et al., 2019). Moreover, erosion is a highly selective process that enriches the 486 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 487

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

489 where C_0 denotes the concentration in the original soil, and C_i represents the mean 490 concentration in the eroded sediment.

491 Several soil erosion and sediment yield models are available in the existing 28 492 watershed-scale metal models with different process complexity and data requirements. 493 The erosion and transport of particle HMs are directly coupled to corresponding fluxes 494 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 495 496 amount of soil transported to water bodies over a defined area in a given period. 497 Therefore, it is critical to account for all erosion and sediment transport processes 498 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 499 500 erosion. However, USLE series models do not consider sediment deposition or route 501 sediment in a spatial context; thus, they cannot be directly used to predict watershed 502 sediment yield.

503 In many cases, USLE/RUSLE is applied to simulate hillslope erosion, along with 504 sediment delivery ratios (SDRs), to determine the sediment delivered from the hillslope 505 to water bodies. For example, METALPOL employed a modified USLE with the SDR 506 to calculate the soil loss in river basins. The SWAT-HM uses the modified USLE 507 (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 508 509 yield prediction for a single storm event by considering the runoff characteristics. 510 Physically-based models (e.g., TREX and TOPKAPI-ETH) integrate a spatially 511 distributed soil erosion and suspended sediment transport module. This module 512 simultaneously accounts for 4 main sediment transport processes, advection, dispersion, 513 erosion and deposition on a two-dimensional overland plane; the latter two processes 29

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.

518

3.3.4 In-stream processes

Current watershed metal models employ significantly different levels of 519 complexity in modeling in-stream processes. Most models (e.g., TREX and TOPKAPI-520 521 ETH) assume a one-dimensional transport along a stream reach for simplicity. Models 522 such as SWAT-HM and WARMF assume a well-mixed water column for each channel. 523 Regarding channel flow, TREX and TOPKAPI-ETH use diffusive wave approximation 524 and kinematic wave approximation under the overland flow modeling. SWAT-HM 525 provides the variable storage and Muskingum methods for water routing in the channel 526 network. Physically-based models commonly consist of two sediment transport processes in rivers/streams: (1) advection and dispersion and (2) erosion and deposition. 527 528 A simplified stream power equation calculates the maximum sediment load in river 529 channels in SWAT-HM. Concerning the metal module, the CTT&F model includes a four-phase equilibrium partitioning (dissolved, precipitated, sorbed to sediment 530 531 particles, and complexed with the dissolved organic carbon (DOC)). In contrast, some 532 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 533 534 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 representthe inputs into a watershed.

537 **3.3.5** Point sources and atmospheric deposition

There are generally two methods for quantifying point source emissions: the 538 539 measurement method and the emission factor method when the source locations are identifiable and time series of effluent discharges and metal concentrations are available. 540 541 Representing the point sources in the model is relatively easy. However, detailed 542 observations are not available in most cases. Multiplying the estimated discharge 543 (inhabitants connected to the point source \times water volume used per person per day) by 544 the average HM concentration could be a reliable way to estimate the daily HM loads 545 (Liu et al., 2018). Notably, this approach cannot account for short-term fluctuations in 546 HM concentrations and loads. Moreover, detailed locations and point source emissions 547 are unavailable in some large-scale applications. Therefore, a bottom-up approach combining the activity levels of various industry sectors with HM-specific emission 548 549 factors have been preferred to evaluate the aqueous emissions of HMs (Huang et al., 550 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-551 552 distributed model from that in fully distributed models. Semi-distributed models add 553 point source loads to the inlets of the reaches receiving the discharge for the balance 554 calculation, whereas fully-distributed models have the sink/source term of the river 555 solute from the external point source appended to the transport continuity equation in a

31

556 river channel reach.

557 Atmosphere deposition is typically considered as the model input for watershedscale water quality models. That is to say, most watershed models do not simulate 558 559 atmospheric deposition processes, but instead use the measured fluxes of atmospheric deposition or simulated fluxes derived from air quality models. For example, modeling 560 561 studies have mapped the global atmospheric concentrations and regional atmospheric 562 deposition of priority heavy metals like Hg, Cd, and Pb under the United Nations' Convention on Long-Range Transboundary Air Pollution (Ilvin et al., 2022). Mosses 563 564 have been used successfully as biomonitors to map the spatial patterns of HM 565 deposition across Europe (e.g., Harmens et al., 2010).

566 4 Current challenges and research needs

567 4.1 Improving the model representation of real-world processes

568 4.1.1 Integrating with a carbon cycle module

569 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 570 571 decomposition of soil organic matter (SOM) and its associated processes directly influence soil carbon, oxygen, and nitrogen cycles, and indirectly regulate soil HM 572 573 cycles by modulating Eh and pH. SOM decomposition reactions have long been 574 recognized as complex and mostly microbe-mediated. Among the development and 575 applications of 9 reviewed models, only a few works has explicitly considered the 576 dynamic linking between SOM and HM (Du et al., 2019). In soil solutions, Metals such 577 as Cu and Pb may mostly be present as metal complexes, while Cd and Zn are usually 578 present as free ions or labile complexes (Nolan et al., 2003). From the perspective of 579 transport modeling, the total solution concentration, and not the metal speciation (e.g., 580 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 581 582 identify which metal species are taken up since bioavailability is influenced by the 583 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 584 585 despite its importance in metal risk and toxicity assessments (Caruso et al., 2008). 586 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 587 588 organic carbon. For example, Futter et al. (2007) presented a process-based model for 589 simulating DOC in soil and river water called the Integrated Catchments Model for 590 Carbon (INCA-C), and Zhang et al. (2013) developed the SWAT-C model to simulate 591 the mass balance of soil organic carbon. In addition, recent studies have enhanced the 592 SWAT model by introducing microbe-mediated SOM turnover processes based on Microbial Kinetics and Thermodynamics model using dual Michaelis-Menten kinetics 593 594 (Bhanja et al., 2019a; 2019b). Thus, SWAT-HM and INCA-metals are the most 595 prospective model among the 9 models due to their amenability to integrate the 596 SOM/DOM-HM interaction by taking the advantage of the existing carbon modules.

597 **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 598 599 of surface water and groundwater (Fig. 2). All of the nine models mentioned above 600 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 601 602 incorporated to understand the transport mechanisms in the river (Aim 1, improving understanding). Biogeochemical processes (both chemical and microbial) occurring 603 604 within the hyporheic zone can significantly influence the fate and transport of HMs 605 (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, 606 607 2000). In contrast, microorganisms' respiration may deplete the hyporheic zone's dissolved oxygen (Bourg and Bertin, 1993). The induced redox change could promote 608 609 the dissolution of iron and manganese oxides and the adsorbed metals, causing their 610 release into the solution and making the hyporheic zone a metal source (Coynel et al., 611 2007). Hyporheic zones are closely dependent on riverbed morphology and hence vary with higher spatial resolution. Meanwhile, the river morphology could affect the 612 613 physicochemical properties of river sediment and floodplain soil and thus contribute to 614 the further redistribution of HMs (Wei et al., 2022). Integrating hyporheic zones into 615 the watershed model may be cumbersome for semi-distributed models because of their 616 predefined flow direction and usually an inadequate resolution of the reach channel. On 617 the other hand, fully-distributed models with grid cell discretization have better

618 potential to model hyporheic exchange in detail. Integrating the transient storage reach-

619 scale models (e.g., OTIS) within the fully-distributed watershed framework could be a

620 solution. However, it is still challenging because of the high data requirements to reflect

- 621 the remarkable heterogeneity of hyporheic exchange across the river network.
- 622 **4.1.3** Re

.3 Refining the solid/liquid distribution (*K*_d) in rivers

In rivers, the fate of HMs depends on their solid/liquid distribution between water 623 624 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 625 626 fixed "K_d" using the recommended screening values or finite field measurements. 627 However, the K_d variability is in the order of magnitudes depending on several 628 environmental factors, such as SS, DOM/DOC content, and pH (Lu and Allen, 2006). 629 None of the existing HM models has the capability to reflect the dynamic changes in 630 $K_{\rm d}$ values under different hydrological conditions. Recently, Tomczak et al. (2019) compiled a database containing 8564 K_d values from 50 elements with their potential 631 632 explanatory factors and determined the K_d distributions for in situ water/SS conditions 633 as a function of SS, DOC, and pH. For example, assuming a log-normal distribution, 634 the changes of geometric mean (K_d) and geometric standard deviation (K_d) were 635 identified as power laws of m/V (ratio of solid mass to water volume) for Cd, Cu, Hg 636 and Pb (Fig. 4 in Tomczak et al. 2019). Adding such relations to existing models could reduce the global variability of K_d values. 637

638 **4.2** Gearing toward mitigation practices and climate change

Measuring pollution loads from all pathways within a watershed and evaluating the 639 640 effectiveness of mitigation practices through actual implementation in the field is time-641 consuming and resource intensive. Numerical models can be valuable tools for 642 developing targeted remediation strategies and assessing the impact of climate change 643 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 644 645 cleanup scenarios considering point source reductions to evaluate the effects of mine 646 restoration on water quality. Nonpoint source control measures should be evaluated in future watershed management plans because numerous studies suggest they play an 647 important role in metal transport at the watershed scale (Liu et al., 2019; Zhou et al., 648 2023). For example, soil conservation measures (e.g., terracing, contour farming, and 649 650 strip cropping) are common management operations for soil pollution control. 651 Additionally, the extensive use of nitrogen fertilizers has resulted in significant soil 652 acidification in several areas of China over the last three decades. This has contributed 653 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 654 grains, as it increases soil pH and reduces Cd's bioavailability (CaCl₂-extractable) in 655 656 the rhizosphere (Chen et al., 2018). Therefore, further investigations are required to 657 represent mitigation practices in watershed-scale HM models for effective management 658 decisions.

659 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 660 in the Rocky Mountains, USA, intensified generation of Acid Mine Drainage has been 661 linked to warmer summer air temperatures and earlier drying of shallow soils, which 662 expands weathering fronts and promotes oxidation (Rue and McKnight, 2021). In UK 663 664 watersheds where low river flows are expected to occur more frequently and severely 665 due to climate change, metal-rich groundwater may significantly influence stream metal concentrations (Byrne et al., 2020). Thus, assessing metal transport dynamics and 666 responses to climate change scenarios is essential to develop effective watershed 667 management strategies. 668

669 4.3 Reforming model calibration and uncertainty analysis

670 In the watershed-scale models, except for the physical parameters, some 671 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 672 673 conducted manually by trial and error or automatically through a computer-based 674 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, 675 676 focusing on the proportion of surface runoff and baseflow; 2) calibration of sediment 677 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 678 679 concentrations and loads (Meng et al., 2018; Sui et al., 2022).

680 Although numerous algorithms and tools exist for parameter calibration, the non-681 uniqueness feature (equifinality) in calibration makes the estimation of a unique or best parameter set meaningless (Abbaspour, 2022; Beven, 2006). Given the various types 682 and sources of uncertainty, no calibration problem in the hydrology and water quality 683 684 domain is uniquely solvable. In other words, if a single model (a best parameter set) fits 685 the measurements well, many models (multiple parameter sets) exist that can achieve 686 statistically similar model accuracy. For example, a model may exhibit satisfactory statistical agreement with measured streamflow data while misrepresenting flow 687 688 pathways (e.g., surface runoff, lateral flow, and baseflow).

689 Mitigation of the non-uniqueness problem may be partially achieved by: (1) 690 improving model representation and developing more robust models (discussed in 691 Section 4.1), (2) implementing thorough parameter sensitivity analyses prior to calibration, (3) collecting more and better quality data (e.g., incorporating soft data) 692 693 and extracting more information from the collected data, and (4) obtaining through multi-variable, multi-objective 694 unconditional parameters calibration 695 procedures. For example, sensitivity analysis can reduce the number of parameters for calibration by identifying the parameters with negligible influence on the output, 696 697 thereby reducing the combinations of parameter sets that produce similar results. Some 698 studies have separately calibrated surface runoff and baseflow (Zhang et al., 2011). 699 Calibrating metal parameters using both dissolved and total metal concentrations could 700 also improve parameter identifiability. For example, a long-term and high-frequency 701 estimation of metal concentrations and fluxes in rivers could be obtained by analyzing 38

the relationship between sporadic sampled (dissolved/particulate/total) metal
concentrations and continuously monitored proxy indicators (e.g.,
discharge/SS/turbidity) (Nasrabadi et al., 2016).

705 Moreover, tracer and isotope data may assist watershed-scale model calibration because they provide information on both hydrologic pathways and specific 706 707 contaminants (Jensen et al., 2018). Multi-objective (e.g., multi-criteria and multi-708 variable) calibration routines have been proposed to estimate model parameters using 709 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 710 711 improve the model's realism (Arnold et al., 2015). Typical soft data for metal modeling 712 could be long-term average sediment yield, event mean concentration, and source 713 apportionment using isotope analysis.

714 Recognizing and quantifying model uncertainties are vital for applying watershed 715 HM models. As mentioned above, the uncertainties could be introduced by model 716 validation data (e.g., limited data) and model structures (e.g., different representations 717 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 718 719 precision of the DEM is expected to affect the delineation of watersheds and the 720 calculation of terrain factors (e.g., slope, slope length), which will further influence 721 models' simulations of flow, sediment, and metal transport processes (Wechsler, 2007). 722 Most HM model studies have been calibrated against HM concentrations in river water 723 but occasionally report model uncertainty. Zhou et al. (2020) applied the SUFI-2 39 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.

730 **4.4 Balancing model complexity and data requirements**

731 In Section 3, the problems of model complexity and data requirements have been 732 raised. Well-informed modeling relies on a well-designed monitoring network. 733 However, an enormous amount of input and calibration data is required to build and 734 calibrate complex water quality models. Moreover, the data requirements of water 735 quality models vary with model complexity and purpose. Thus, in addition to collecting 736 more and better quality monitoring data, it is necessary to determine the amount of data 737 (Ledergerber et al., 2019) and the value of the data (Abbaspour et al., 1996) to be 738 collected. The optimal experimental design (OED) technique is a useful tool for 739 identifying data shortages and maximizing available information behind the 740 measurement data. For example, suppose a new dataset is to be collected; model-based 741 OED can evaluate the informational gain from the perspective of model calibration 742 from a bundle of proposed experiments and help reach a cost-effective experimental 743 design (Vanrolleghem et al., 1995).

744

Regarding better quality monitoring data, existing monitoring protocols by

745 environmental regulators often collect grab samples, which cannot detect dynamic 746 changes in HM concentrations, particularly during high-flow periods (Neal et al., 2012). 747 Future research should incorporate the new advancements in sampling and analytical technologies which enable more representative and efficient measurement of HMs in 748 soil and water. For instance, Frau et al. (2018) investigated the possibility of using novel 749 750 electromagnetic wave sensors for the real-time and continuous monitoring of HMs in 751 surface water. Moreover, several studies have applied the tracer injection and synoptic 752 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 753 754 watershed-scale models (Byrne et al., 2021; Kimball et al., 2002). TISS uses 755 conservative tracers (typically bromide or chloride) and synchronous (or synoptic) 756 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 757 758 Cement Creek, Colorado, USA (Fig. 9 in Kimball et al., 2002). Furthermore, a new 759 paradigm called SEPSTAT has been proposed for effective heavy metal monitoring 760 based on dry preservation: solid-phase extraction, preservation, storage, transport, and analysis of trace contaminants. It was designed to overcome the logistical challenge and 761 762 could create the required large-scale data in resource-limited settings. (Hanhauser et al., 763 2020). In addition, hyperspectral remote sensing offers a non-destructive and real-time 764 method for retrieving soil metal concentrations, which could facilitate the simulation of 765 ubiquitous spatial heterogeneity in watershed-scale HM models (Nawar et al., 2020).

766

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:

771

Model development in compliance with the intended use

The future directions of model development were identified for four different aims. 772 773 For Aim 1 (improving understanding), the metal attenuation and release processes in 774 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 775 776 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 777 778 would be suitable for small-to mesoscale watersheds, while semi-distributed models 779 with the Markov chains theory could be applied on large scale watersheds. Aim 4 780 (scenario analysis) requires an improved representation of mitigation practices in existing models to inform effective management decisions. 781

782

• 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.

789 'Benchmark' models/codes and data sets for model application 790 The comparison and evaluation of available metal models using real data sets need 791 to be done for developing benchmark models/data and pre-and post-processing tools to 792 facilitate better visualization, accessibility, and commutations. The existing 793 experimental watersheds with long-term and high-frequency data provide a valuable opportunity. Ultimately, the goal is to establish a flexible framework that combines 794 795 hydrology, sediment, and chemical sub-models at various levels of complexity to match 796 the available data and support the corresponding model purpose.

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798 Data availability

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

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801 Declaration of Competing Interest

802 The authors declare no competing financial interest.

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