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1 **Model-based evaluation of reduction strategies for point and**
2 **nonpoint source Cd pollution in a large river system**

3

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18

19 **Abstract**

20 Cadmium (Cd) is a toxic trace element that threatens ecosystem and human health worldwide.
21 Quantitative understanding of land-to-river Cd fluxes and riverine Cd loads in response to various
22 watershed management measures is essential for developing effective mitigation strategies for large
23 river systems. However, detailed analyses of watershed Cd dynamics under different management
24 scenarios are lacking. Here, we investigated the effects of four management scenarios by combining
25 point and nonpoint source control measures with a previously developed watershed Cd model that
26 was validated with site-specific measurements. The Soil and Water Assessment Tool-Heavy Metal
27 (SWAT-HM) model was applied to simulate the Xiang River Basin's (XRB, ~90,000 km²) baseline
28 hydrology, soil erosion, and Cd transport processes in China. Using scenario simulations, we found
29 that smelting emissions reduction was the most influential measure for controlling dissolved Cd
30 (DCd) and particulate Cd (PCd) loads at the basin scale. Elimination of 50% emissions from the
31 smelting sector could significantly ($p < 0.05$) decrease the monthly mean loads of DCd from 940 to
32 720 kg and of PCd from 2,150 to 1,760 kg at the XRB outlet. In contrast, reduction in mining
33 emissions had no influence on the Cd load at the XRB outlet because most mining Cd emissions
34 occurred upstream and midstream of the XRB, and the natural attenuation processes in the river
35 limit the transportation of Cd downstream. The effectiveness of management practices for reducing
36 total Cd (TCd) and DCd loads was not always mutually beneficial. For example, soil erosion control
37 may decrease the PCd flux *via* erosion but increase the subsurface DCd flux to rivers due to greater
38 lateral flow. In addition, increasing soil pH could be a practical and effective measure to reduce
39 nonpoint DCd and PCd fluxes. Such effects may be caused by the declined upward migration of Cd
40 through soil evaporation owing to the decreased Cd concentration in the soil pore water after pH

41 increases. In conclusion, effective watershed management of Cd pollution in large basins requires
42 an integrated plan that combines multiple mitigation measures; strategic modeling experiments
43 could provide valuable insights into the design of such plans.

44

45 **Keywords:** Cadmium loads; Watershed model; Scenario analysis; Nonpoint source pollution;

46 Industrial point emission; Watershed management

47

48 **1. Introduction**

49 Cadmium (Cd), classified as a group 1 human carcinogen (IARC, 2018), is a global threat to
50 terrestrial and aquatic ecosystems and human health (Kubier et al., 2019; Satarug et al., 2003;
51 Satarug et al., 2017; WHO, 2010). Industrial (e.g., mining and smelting) and agricultural (e.g.,
52 phosphate fertilizers) activities have discharged a large amount of Cd into soils and water worldwide,
53 including in Europe and China (Nziguheba and Smolders, 2008; Shi et al., 2019; Ulrich, 2019).
54 Human activities have increased soil Cd concentrations by approximately 0.1–0.3 mg Cd kg⁻¹ above
55 pre-industrial levels (Smolders and Mertens, 2013). The long-term dietary intake of Cd at elevated
56 levels can lead to serious health problems, such as the "Itai-itai" disease that occurred in Japan in
57 the 1950s (Aoshima, 2016). A 2014 national soil survey in China showed that Cd is the most serious
58 contaminant, accounting for 43% of all soil quality exceedances (MEPPRC and MLRPRC, 2014).
59 In addition, millions of hectares of agricultural land in China are now being removed from
60 production due to Cd pollution (Hou and Li, 2017). Moreover, soil Cd concentrations continue to
61 increase despite stricter environmental protection regulations (Hu et al., 2016).

62 According to a meta-analysis of the global evaluation of heavy metal pollution in surface water,
63 China reported the most pollution sites of heavy metals, followed by India and other developing
64 countries (Kumar et al., 2019). China's river basins have experienced extensive metal pollution over
65 the past decades, with the Xiang River Basin (~90,000 km²) being the most polluted. The issue of
66 Cd pollution in soil, water, sediment, and rice in the XRB has attracted substantial attention (Han et
67 al., 2014; Li et al., 2018; Williams et al., 2009; Zhang et al., 2008). In 2011, the Chinese central
68 government approved the Xiang River Basin Control Plan for Heavy Metal Pollution (hereafter
69 XRB Plan) to combat severe heavy metal pollution (<http://www.gov.cn/gzdt/2011->

70 07/23/content_1912271.htm). This ambitious XRB Plan (declared as the Chinese Rhine project)
71 invested up to 59.5 billion RMB (9.8 billion US Dollars) and focused mainly on the industrial sectors
72 to reach the 50% target of metal emission reduction by 2015 from the 2008 level (Hu et al., 2014).
73 However, river pollution mitigation requires holistic accounting for both point and nonpoint (diffuse)
74 sources. Point emissions, such as Zn–Cd smelters, have been stopped in numerous places; however,
75 residual soil Cd contamination remains (e.g., Y. Zhou et al., 2020). Recent studies in UK mined
76 watersheds have demonstrated that the remediation of point sources of metals could be less efficient
77 because of the greater importance of untreated diffuse sources under extremely low flows
78 (groundwater from underground mine workings, Byrne et al., 2020) and extremely high flows
79 (runoff from surface mine wastes, Jarvis et al., 2019). Elevated soil Cd concentrations have been
80 reported in many mining areas of the XRB (e.g., Lei et al., 2015). Moreover, it has long been
81 acknowledged that soil acidification can contribute to increased Cd mobility and loss in soil (e.g.,
82 Kicińska et al., 2022). Therefore, a quantitative understanding of land-to-river Cd fluxes and
83 riverine Cd loads in response to different watershed management measures is vital for developing
84 effective mitigation strategies in large-scale complex river networks, such as the Xiang River system.

85 Numerical models are valuable tools for developing remediation strategies (Nair et al., 2022;
86 Xie et al., 2015; Zhuang et al., 2016). Several watershed-scale heavy metal models with various
87 levels of complexity have been developed to address these challenges, including TREX (Velleux et
88 al., 2008), INCA-Metals (Whitehead et al., 2009), SWAT-HM (Meng et al., 2018), ECOMAG-HM
89 (Motovilov and Fashchevskaya, 2019), and TOPKAPI-ETH (Sui et al., 2022). Generally, two main
90 categories of processes (contaminant transformation and transport) are considered in the watershed-
91 scale metal fate and transport models. Contaminant transport commonly consists of three processes:

92 (1) overland hydrological processes, (2) soil erosion and sediment transport, and (3) in-stream
93 processes. According to the temporal scales, the models can be divided into event-driven and
94 continuous models. For example, TREX is mainly an event model that can simulate the fate and
95 transport of metals during a single rainfall event at the watershed scale (Velleux et al., 2008). The
96 ECOMAG-HM does not include a sediment component and is inapplicable to erosion-prone areas
97 (Motovilov and Fashchevskaya, 2019). The TOPKAPI-ETH is a fully distributed model that divides
98 the watershed and sub-basins into hydraulically connected grid cells to depict detailed cell-to-cell
99 transport (Sui et al., 2022). However, owing to the computational burden and high demand for data,
100 the application of TOPKAPI-ETH to large-scale basins such as the XRB is limited. In contrast,
101 models such as INCA-Metals and SWAT-HM are semi-distributed, continuous models with
102 reasonable model structural complexity, which enable them to analyze the long-term effects of
103 hydrological changes and water management practices. In this study, we chose SWAT-HM because
104 the SWAT component is a widely used nonpoint source hydrologic model with an open-source code,
105 making it amenable to coupling with other models and expanding the model representation of
106 different environmental management scenarios.

107 Watershed models have been widely used for scenario analyses to assess the best management
108 practices for sediment, nitrogen, and phosphorus load mitigation (Hunt et al., 2019; Kast et al., 2021;
109 Shen et al., 2015). Thus far, only a few watershed-scale HM models have been used to evaluate the
110 impacts of mitigation practices (Jiao et al., 2014). For example, Whitehead et al. (2009) examined
111 the effects of mine restoration on downstream metal loads, but were limited to point-source cleanup
112 scenarios. Nonpoint source control measures have rarely been considered in the evaluation of
113 watershed management plans, although many studies have suggested that nonpoint pathways play

114 an important role in watershed-scale metal transport. For instance, [Liu et al. \(2019\)](#) reported that
115 soil conservation projects have reduced the lateral transport of heavy metals by 56% in the Loess
116 Plateau over the past two decades. Moreover, field experiments have shown that liming can
117 effectively increase soil pH and reduce Cd mobility and bioavailability in agricultural lands
118 ([Holland et al., 2018](#)).

119 To the best of our knowledge, a detailed investigation of watershed Cd dynamics under
120 different management scenarios, particularly for large-scale river systems with various point and
121 nonpoint sources, is lacking. Thus, the overall aim of this study was to demonstrate how a
122 watershed-scale HM model can be used to assess the sensitivity of different management scenarios
123 to land-to-river Cd fluxes and riverine Cd loads at various spatiotemporal scales and to develop a
124 feasible and desirable watershed management plan for achieving water quality targets in the XRB.
125 The results of this study support the development of numerical models of Cd fate and transport in
126 large river basins and offer critical insights into the potential impacts of different Cd pollution
127 reduction strategies on water quality.

128

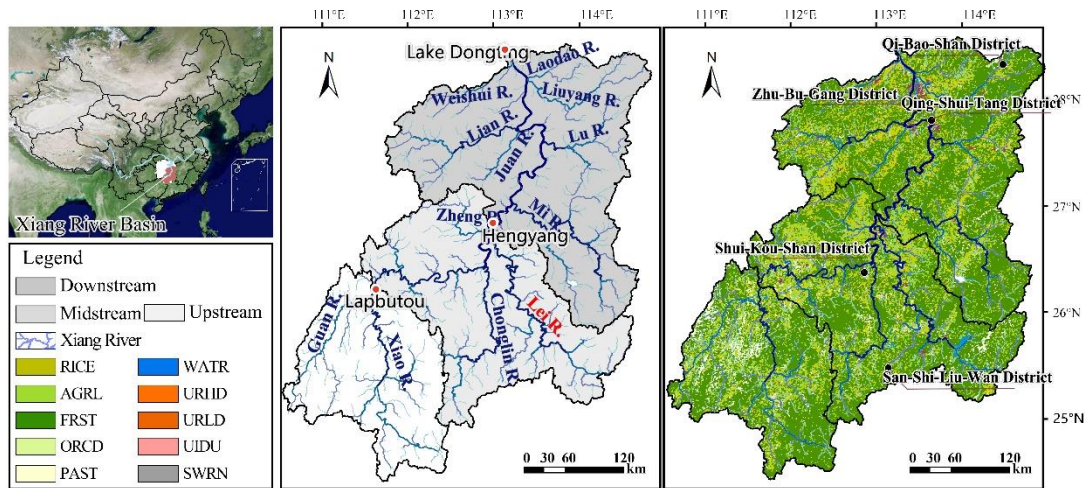
129 **2. Materials and Methods**

130 *2.1. Study area*

131 The Xiang River Basin (E:110°30'–114°15', N:24°38'–28°39') is one of the seven major
132 tributaries of the Yangtze River, located in South-Central China, spanning over 9,400 km² with a
133 length of 948 km ([Fig. 1a](#)). The main stream of the Xiang River flows from south to north and drains
134 into Dongting Lake of the Yangtze River system. The Xiang River can be divided into three main

135 sections: the upper section from the headstream to Lapbutou, the middle section from Lapbutou to
136 Hengyang, and the lower section from Hengyang to the outlet (Dongting Lake). The major
137 tributaries include the Guan, Chonglin, Zheng, Lei, Mi, Juan, Lu, Lian, Liuyang, Laodao, and Wei
138 Rivers (Fig. 1b). In the XRB, the elevation decreases from south to north, varying from 2,092 m to
139 7 m. The basin is of a subtropical humid monsoon climate with an annual precipitation of 1,400 mm
140 mainly concentrated between April–September (70%). The main landuses of XRB are forests (FRST,
141 62.1%), paddy fields (RICE, 20.8%), agricultural land (AGRL, 8.6%), pasture (PAST, 4.0%), and
142 urban areas (1.7%) (Fig. 1c). The river receives massive Cd loads from both point (e.g., industrial
143 emissions) and diffuse sources (e.g., land runoff and erosion). In a previous study (Zhou et al., 2023),
144 we estimated that intensive industrial activities discharged approximately 20,000 kg yr⁻¹ of Cd into
145 the Xiang River during 2000–2015. Among them, mining and processing of nonferrous metal ores
146 (hereafter referred to as mining) and smelting and pressing of nonferrous metals (hereafter referred
147 to as smelting) are two main polluters, accounting for 93% of the total industrial Cd emissions.
148 Additionally, many years of historical mining in the XRB have left abandoned mining waste that
149 contributes metal loads to the Xiang River via diffuse processes. Elevated Cd concentrations in soils
150 can also be transported to rivers through hydrological processes and soil erosion. In general, the
151 XRB is representative of many industrialized river basins around the world with point and diffuse
152 sources.

153



154

155 Fig. 1. Study area. (a) Location of the Xiang River Basin in China (b) the river network and up-,

156 mid-, and downstream of XRB (c) land uses in the watershed.

157

158 2.2. Watershed-scale Cd model

159 In our model development paper (Zhou et al., 2023), the SWAT-HM model for the XRB was

160 developed to quantify the flow, sediment, and dissolved Cd (DCd) and particulate Cd (PCd) fluxes

161 in both the land and river phases of the XRB between 2000 and 2015. As discussed in Zhou et al.

162 (2023) and illustrated in Fig. 2, The SWAT-HM, which combines a heavy metal transport and

163 transformation module with the well-established SWAT model (Arnold et al., 1998), is a semi-

164 distributed process-based model for simulating terrestrial metal delivery and riverine metal

165 dynamics. The SWAT model requires Digital Elevation Model (DEM), land use, soil types, and

166 observed meteorological and hydrological and sediment data to run. Point sources (e.g., industrial

167 and municipal metal loads) and nonpoint sources (e.g., soil metal concentrations) data are two main

168 inputs for the HM module. The original version of SWAT-HM was developed by Meng et al. (2018)

169 with a metal transformation module of three-phase (dissolved, labile, and non-labile metal species)

170 equilibrium partitioning and kinetic reactions. However, detailed observations of labile and non-

171 labile metal species in soils are usually not available, especially in large-scale applications such as
172 XRB. The current version was thus modified by simplifying the metal transformation scheme, in
173 which solid labile and non-labile metals are regarded together as particulate metals. This
174 modification maintains a reasonable model structural complexity while considerably minimizing
175 the data requirements. The data requirement of SWAT-HM was summarized in Table 1 of [Zhou et al. \(2023\)](#)
176 [al. \(2023\)](#) with a detailed description in [Zhou et al. \(2023\)](#) SI Text S1. The model was run for extra
177 two years (a warm-up period of 1998–1999) to equilibrate to steady-state conditions. To capture
178 more detailed Cd transport processes and facilitate management scenario analysis, the XRB was
179 divided into 1,118 sub-basins and 23,363 Hydrologic Response Units (HRUs) with the smallest
180 spatial discretization of zero thresholds for land use, soil, and slope in each sub-basin. Prior to this
181 work, parameters have been carefully constrained using multiple field measurements with a 2-
182 step procedure ([Zhou et al., 2023](#)). As a first step, SWAT-CUP was used to calibrate and validate
183 parameters related to hydrological and sediment processes ([Abbaspour, 2015](#)). To investigate the
184 intrinsic model performance and model defects, five parameters pertaining to metal dynamics were
185 deliberately not calibrated but were instead obtained from field measurements and the literature
186 ([Han et al., 2014](#); [Meng et al., 2018](#); [Qin et al., 2012](#); [L. Zhou et al., 2020](#)). The model was validated
187 against long-term historical observations of monthly streamflow and sediment load and Cd
188 concentrations at 42 (4380 data points), 11 (1183 data points), and 10 (600 data points) gauges,
189 respectively. As detailed in [Zhou et al. \(2023\)](#) sections 2.3 and 3.1, the model accuracy was
190 evaluated using both statistical (the coefficient of determination (R^2), Nash-Sutcliffe efficiency
191 (NSE), and percent bias ($PBIAS$)) and graphical (scatter plots) analyses. For streamflow, the mean
192 of R^2 and NSE were 0.84 and 0.75 with the $PBIAS$ ranging from –34.4% to 48.8%. For the sediment

193 load, the R^2 and NSE averaged 0.57 and 0.42, with a $PBIAS$ of -61.7% to 39.3% . Approximately
 194 92.0% of the simulated Cd values were within the 5-fold range of the measured concentrations,
 195 indicating that the SWAT-HM model was successfully applied to the XRB. The key components of
 196 the SWAT-HM are introduced below. For further information on model description and model
 197 development in the XRB, see (Meng et al., 2018; L. Zhou et al., 2020; Zhou et al., 2023).

198 In SWAT, surface runoff (SR) was estimated using the SCS curve number method (Eq. 1).

$$199 \quad SR = \frac{(R-I)^2}{(R-I+S)} \quad (1)$$

200 where R is the rainfall for the day; I is the initial abstraction, which includes surface storage,
 201 interception, and infiltration prior to runoff; and S is the retention parameter, which is a function of
 202 the curve number (CN) for the day (Eq. 2).

$$203 \quad S = 25.4 \left(\frac{1000}{CN} - 10 \right) \quad (2)$$

204 where CN is a function of the soil permeability, land use, and antecedent soil water conditions. CN_2
 205 was defined as the curve number for moisture condition II.

206 SWAT uses the Modified Universal Soil Loss Equation (MUSLE) to calculate the soil erosion
 207 and sediment yield (SY) for each HRU within the watershed (Eq. 3).

$$208 \quad SY = 11.8 \cdot (Qq_p A)^{0.56} C \cdot P \cdot K \cdot LS \cdot F \quad (3)$$

209 where Q is the daily runoff volume, q_p is the peak runoff discharge, and A is the HRU area. C , P ,
 210 and K are the HRU crop cover, soil protection, and soil erodibility factors, as defined in the original
 211 Universal Soil Loss Equation (USLE). LS is the USLE topography factor. F is a dimensionless factor
 212 that considers the soil stoniness.

213 In SWAT-HM, soil Cd exists as dissolved Cd ($[M_d]$, mg L^{-1}) in the pore water and particulate
 214 Cd (M_p , mg kg^{-1}) in the solid soil, controlled by the partition coefficient (K_{d_soil} , L kg^{-1}) defined in

215 Eq. 4, which is a function of the soil pH and soil organic carbon (SOC) (Degryse et al., 2009) (Eq.

216 5).

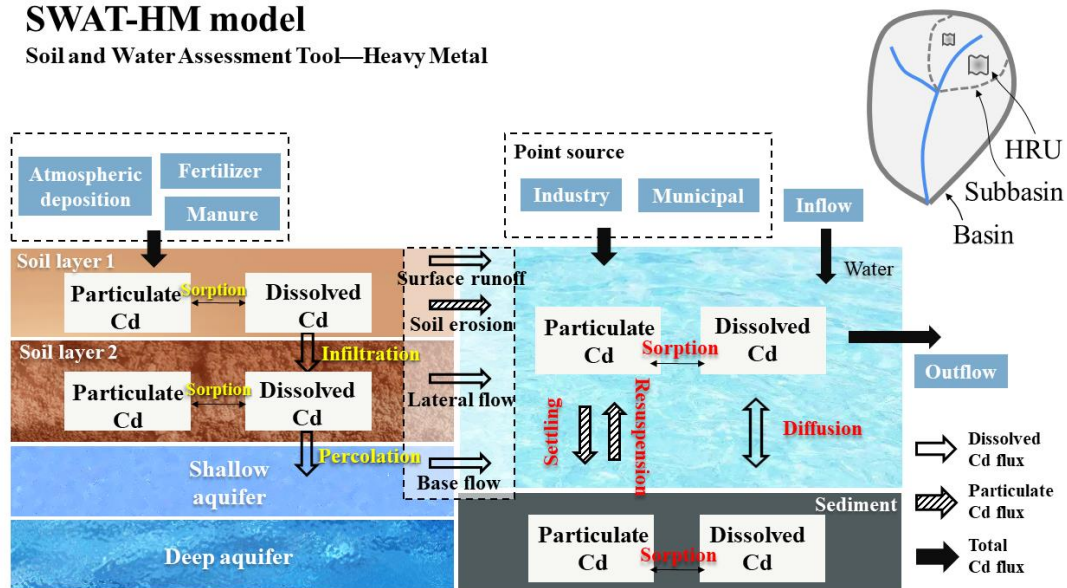
$$217 \quad K_{d_soil} = \frac{M_p}{[M_d]} \quad (4)$$

$$218 \quad K_{d_soil} = 0.55 \cdot pH + 0.70 \cdot \log(SOC) - 1.04 \quad (5)$$

219

SWAT-HM model

Soil and Water Assessment Tool—Heavy Metal



220

221 Fig. 2. A schematic diagram of the main processes in both overland and channel phases of the SWAT-

222 HM model.

223

224 2.3. Watershed management scenarios planning and analysis

225 In this study, four management plans that consider both point and nonpoint source pollution

226 control were proposed to mitigate Cd pollution (Table 1). As detailed below, management measures

227 are represented in model simulations by changing the corresponding model inputs or parameter

228 values to depict the changes in watershed processes and water quality responses.

229 Industrial point source control is the major management measure in the XRB, among which

230 the mining and smelting sectors are the two main polluters. Scenarios S1.1–S1.5 and S2.1–S2.5
231 represent the reduction of mining and smelting Cd emissions, respectively, by various percentages
232 (–10%, –20%, –30%, –40%, and –50%). Metal industrial emissions should be reduced by 50%,
233 according to the XRB Plan, which defined targets of 10, 20, 30, 40, and 50%. As an approximation
234 in the model, the same elimination rate is evenly applied to the enterprises in the study area, which
235 is deemed realistic because regulation driven by a regional environmental authority is usually
236 implemented by a uniform requirement for all enterprises. Nonetheless, a uniform elimination rate
237 across different enterprises will have different effects because of the location, and hence,
238 hydrological connectivity disparities.

239 Scenarios 3.1–3.5 consist of soil erosion control measures. In SWAT, terracing, contour
240 farming, and strip cropping are built-in management operations for soil conservation. For example,
241 the adoption of contour farming permits the reduction of surface runoff by impounding water in
242 small depressions and reduces soil erosion by reducing the erosive power of surface runoff (Arabi
243 et al., 2007). To represent contouring practice, the SCS curve number for moisture condition II (CN_2)
244 and USLE practice factor ($USLE_P$) were modified. In Scenario 3.1–3.5, the improvement in water
245 infiltration was represented by reducing the calibrated CN_2 value by 1, 2, 3, 4, and 5 units. In
246 addition, the $USLE_P$ factor, which represents the ratio of soil loss by a support practice to that of
247 straight-row farming up and down the slope, was reduced by 10%, 20%, 30%, 40%, and 50%. The
248 adjustment values for CN_2 and $USLE_P$ were within the ranges suggested by Tuppad et al. (2010).

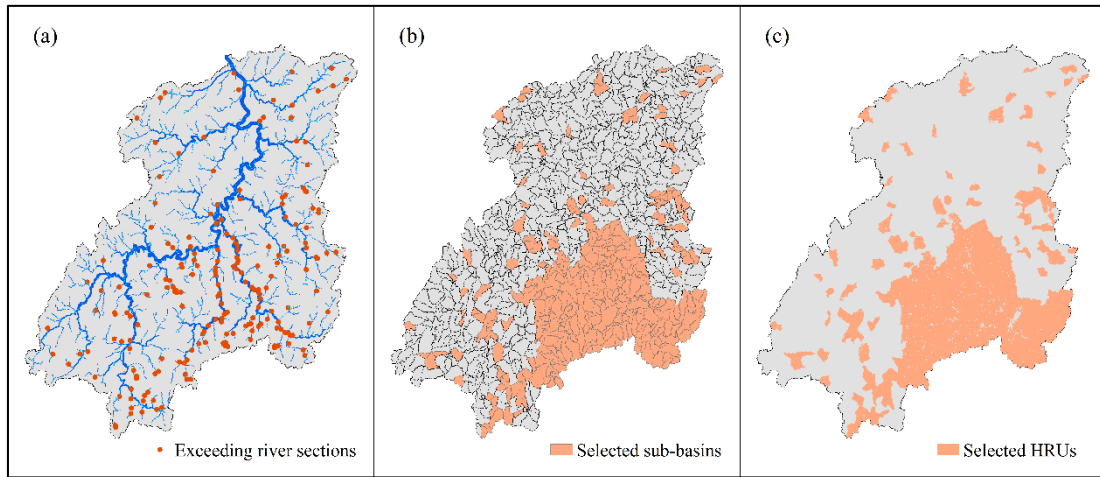
249 Scenarios 4.1–4.5 correspond to the implementation of soil remediation measures to increase
250 the soil pH. Soil pH is the most prominent factor affecting metal partitioning in acidic soil, to control
251 the mobility and bioavailability of metals (Eq. 5). To control soil pH, lime (CaO or $Ca(OH)_2$), soda

252 ash (sodium carbonate, Na_2CO_3), sodium hydroxide, and to a lesser extent, magnesium hydroxide
253 are most commonly used; liming to increase soil pH is an effective and economical option (Zhu et
254 al., 2016). Therefore, we derived Scenarios 4.1–4.5 by simply increasing soil pH by 0.1, 0.2, 0.3,
255 0.4, and 0.5 unit, respectively. The increase in cap (by 0.5) was deemed practically attainable. For
256 example, the application of $7.5 \text{ t ha}^{-1} \text{ CaCO}_3$ could increase soil pH from 5.5 to 6.5 at paddy sites
257 (Chen et al., 2018).

258 The baseline scenario (S0) represents the reference condition of watershed processes using
259 calibrated parameters and default inputs (Zhou et al., 2023). All scenarios, including the baseline
260 scenario, were simulated using 16-year historical climate records from 2000–2015.

261 Given the spatial variability of Cd loads, management practices were implemented at priority
262 sites within the watershed. Since the XRB Plan was approved in 2011 and started in 2012, we
263 identified 196 river sections (Fig. 3a) where the monthly TCd concentration in 2012–2015 exceeded
264 the Class III ($1.0 \mu\text{g L}^{-1}$) of the Environmental Quality Standard for Surface Water (GB 3838-2002).
265 Furthermore, 344 upstream sub-basins (Fig. 3b) of these polluted river sections were selected as
266 priority management areas. Finally, 6,955 HRUs (Fig. 3c) with 6 specific land uses (forests (FRST),
267 paddy fields (RICE), agricultural land (AGRL), orchard (ORCD), pasture (PAST), and barren land
268 (SWRN)) were selected as management areas for nonpoint source control (i.e., soil erosion control
269 (S3.1–3.5) and soil pH elevation (S4.1–4.5)).

270



271

272 Fig. 3. (a) The river sections exceeding the water quality standard ($1.0 \mu\text{g L}^{-1}$, GB 3838-2002) during

273 2012–2015, (b) selected sub-basins, and (c) HRUs for implementing point and nonpoint source

274 control measures in XRB.

Table 1. Management scenarios run through the XRB SWAT-HM model

	Scenario code	Specific settings: modified parameters and inputs in scenario simulations	Management description
Baseline	S0	Default	None
Industrial emissions for mining sector¹	S1.1	Mining * (1 – 10%)	The impact of different emission reduction levels of the mining sector on downstream Cd load is related to the industrial emission intensity and spatial layout.
	S1.2	Mining * (1 – 20%)	
	S1.3	Mining * (1 – 30%)	
	S1.4	Mining * (1 – 40%)	
	S1.5	Mining * (1 – 50%)	
Industrial emissions for smelting sector¹	S2.1	Smelting * (1 – 10%)	The impact of different emission reduction levels of the smelting sector on downstream Cd load is related to the industrial emission intensity and spatial layout.
	S2.2	Smelting * (1 – 20%)	
	S2.3	Smelting * (1 – 30%)	
	S2.4	Smelting * (1 – 40%)	
	S2.5	Smelting * (1 – 50%)	
Soil erosion control	S3.1	<i>USLE_P</i> * (1 – 10%); <i>CN₂</i> – 1	Implementing soil conservation measures by changing the parameter values of <i>CN₂</i> and <i>USLE_P</i> (Arabi et al., 2007)
	S3.2	<i>USLE_P</i> * (1 – 20%); <i>CN₂</i> – 2	
	S3.3	<i>USLE_P</i> * (1 – 30%); <i>CN₂</i> – 3	
	S3.4	<i>USLE_P</i> * (1 – 40%); <i>CN₂</i> – 4	
	S3.5	<i>USLE_P</i> * (1 – 50%); <i>CN₂</i> – 5	
Soil remediation (soil pH control)	S4.1	pH + 0.1	Liming to increase soil pH of top and second soil layers (Chen et al., 2018)
	S4.2	pH + 0.2	
	S4.3	pH + 0.3	
	S4.4	pH + 0.4	
	S4.5	pH + 0.5	

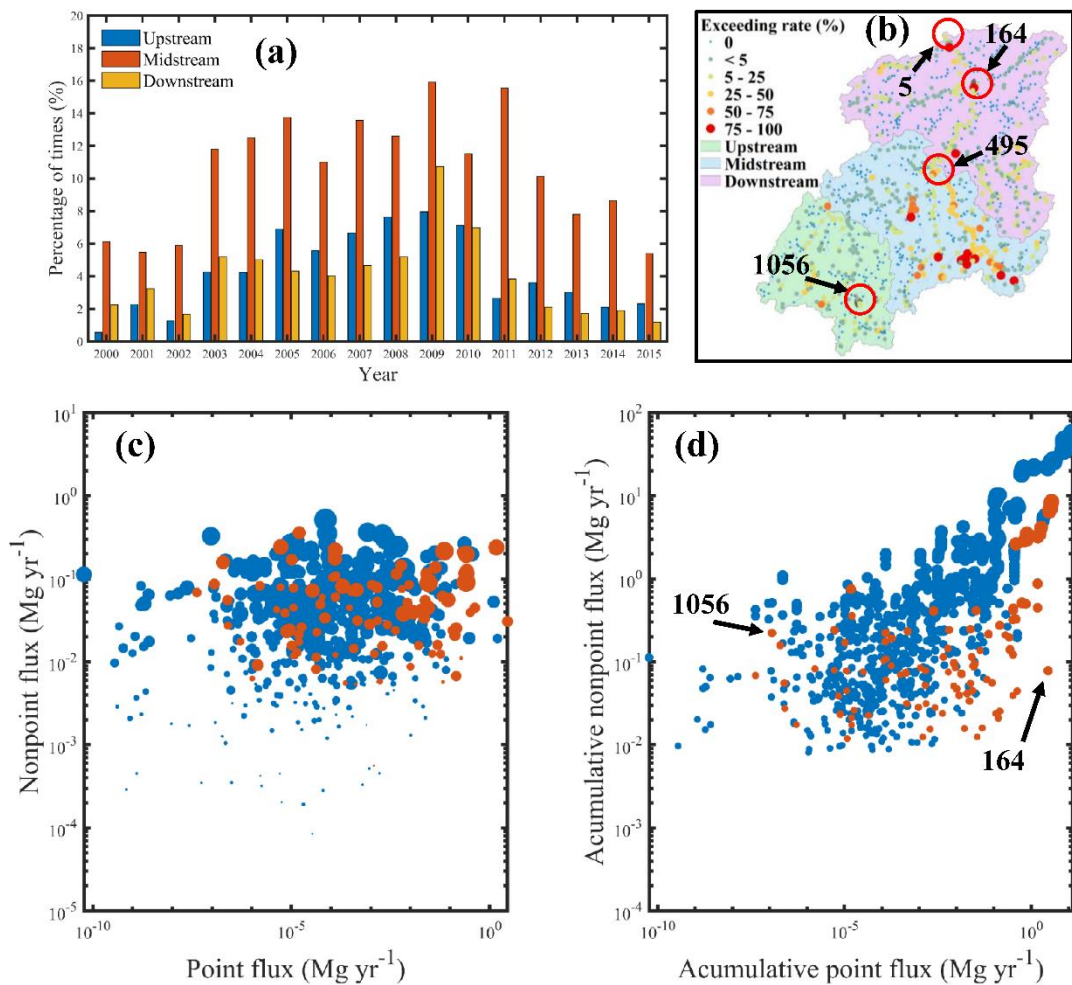
¹Mining is short for Mining and Processing of Nonferrous Metal Ores, Smelting is short for Smelting and Pressing of Nonferrous Metals.

277 **3. Results and Discussion**

278 ***3.1. River sections exceeding the water quality standards***

279 First, we investigated the spatiotemporal patterns of Cd concentrations in the Xiang River
280 system based on the baseline model validated with site-specific measurement. Fig. 4a displays the
281 river sections where the monthly mean concentrations of TCd exceeded the water quality standard
282 (GB3838-2002) of $1.0 \mu\text{g L}^{-1}$ for the up-, mid-, and downstream regions. In general, the exceedance
283 frequency increased first and then declined from 2000 to 2015. The midstream has the highest
284 exceeding rates, ranging from 5.4% to 15.9%, with upstream and downstream having a range of
285 0.6–7.9% and 1.2–10.7%, respectively. In Fig. 4b, a spatial analysis revealed that most river sections
286 with high exceeding frequency ($> 75\%$) were clustered in the southeast of the XRB (part of the
287 midstream region in Fig. 1) because of the high mining emissions and low dilution capacity.
288 Furthermore, we compared the point Cd fluxes (industrial emissions) and nonpoint Cd fluxes
289 (surface runoff+ lateral flow + soil erosion) between the non-exceeding and exceeding river sections.
290 The comparison was made at both the sub-basin and upstream basin level, since riverine Cd loads
291 originate from both upstream channels and sub-basins. At the sub-basin level, the exceeding river
292 sections (red dots in Fig. 4c) occurred under large ranges of point and nonpoint Cd fluxes, which
293 showed no obvious difference from the non-exceeding river sections (blue dots in Fig. 4c). In
294 contrast, the accumulative point and nonpoint Cd fluxes of the upstream sub-basins were also
295 compared. At the upstream basin level, the exceeding river sections (red dots in Fig. 4d) were
296 generally clustered in the region of large point/nonpoint ratios, indicating the dominant role of
297 industrial emissions on riverine Cd load (Fig. 4d). For example, sub-basin outlet 164 (Fig. 4b) is

298 located at the downstream of Qing-Shui-Tang industrial district, which is the largest industrial
 299 district in XRB and contributes 21.7% of the total industrial Cd emissions between 2000 and 2015
 300 (Zhou et al., 2023). However, there also exist some exceeding river sections with small point Cd
 301 input (e.g., sub-basin outlet 1056 in Fig. 4b) indicating that nonpoint source Cd input is more
 302 responsible for the exceedance.
 303



304
 305 Fig. 4. (a) Percentage of times that monthly mean TCd concentrations exceeded China surface water
 306 quality standard of Cd ($1.0 \mu\text{g L}^{-1}$) in the upstream, midstream, and downstream of XRB. (b)
 307 Percentage of times that monthly mean TCd concentrations exceeded the water quality standard of
 308 Cd ($1.0 \mu\text{g L}^{-1}$) for 1118 river sections over 16 years. (c) Comparison of point (industrial emissions)

309 and nonpoint source (surface runoff + lateral flow + soil erosion) Cd fluxes at the sub-basin level.
310 Blue dots represent the non-exceeding river sections, and red dots represent the exceeding river
311 sections. The point size indicates the sub-basin area. (d) Comparison of accumulative point and
312 nonpoint Cd fluxes at the upstream basin level. Blue dots represent the non-exceeding river sections
313 and red dots represent the exceeding river sections. The point size indicates the yearly mean
314 streamflow at the sub-basin outlet. Data presented are for the period 2000 to 2015.

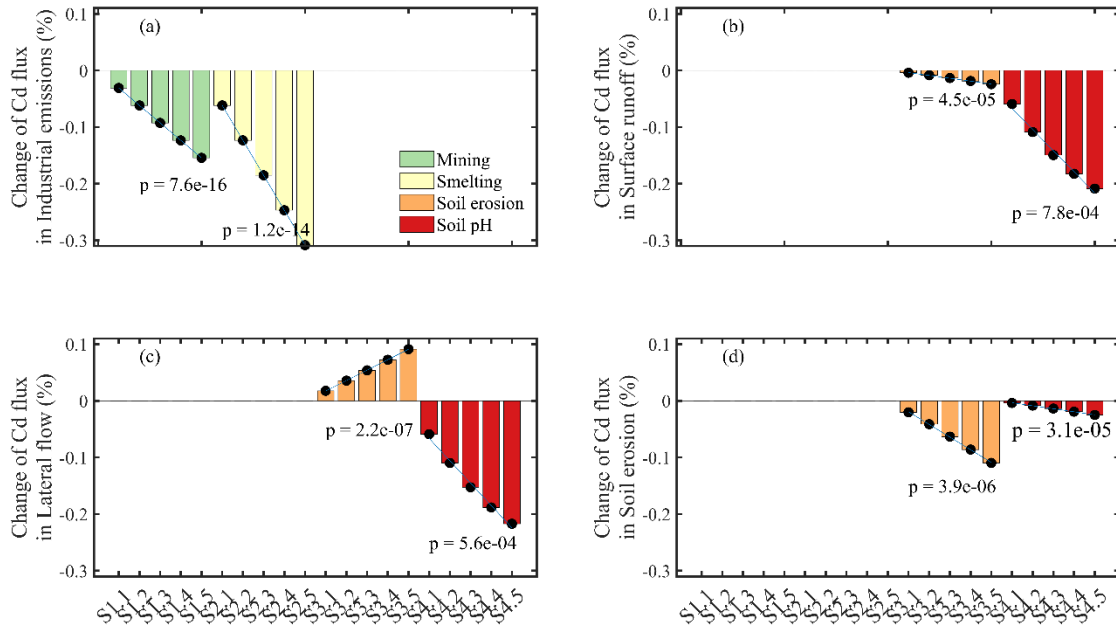
315

316 ***3.2. Changes in land-to-river Cd fluxes in different scenarios***

317 Four management scenarios were compared with the baseline condition to evaluate their
318 effectiveness on land-to-river fluxes in four main transport pathways: industrial emissions, surface
319 runoff, lateral flow, and soil erosion (Fig. 5). At the basin level, both the emission reductions of the
320 mining and smelting sectors could significantly ($p < 0.01$) reduce the industrial emissions with a
321 range of 3.1% to 30.8% (Fig. 5a). The elimination of 50% of the smelting sector resulted in the most
322 significant reduction (30.8%) in industrial Cd emissions, while a 50% cut in the mining sector could
323 reduce 15.4% of industrial Cd emissions. Clearly, soil conservation and soil remediation did not
324 affect industrial Cd emissions but significantly ($p < 0.01$) impacted other Cd pathways. Changing
325 the soil pH had a greater influence than soil erosion control on Cd fluxes in both surface runoff and
326 lateral flow (Fig. 5b-c). Increasing soil pH by 0.5 units could reduce surface runoff and lateral flow
327 of Cd fluxes by 20.9% and 21.7%. Interestingly, controlling soil erosion could increase the Cd flux
328 to the river through lateral flow (Fig. 5c). This is because infiltration and soil water increase when
329 surface runoff decreases, leading to higher Cd fluxes through lateral flow. Soil conservation, such
330 as terraces, has long been acknowledged as an effective way to control runoff and increase soil

331 moisture, leading to a greater lateral flow (Camera et al., 2012; Stanchi et al., 2012). In addition,
332 increasing the soil pH may reduce Cd fluxes through soil erosion owing to the decreased Cd
333 concentration in the top soil layer (Fig. 5d). Heavy metals in soil could move upward to the topsoil
334 through evaporation-induced capillary rise (Dold and Fontboté, 2001; Lima et al., 2014). However,
335 the decreased dissolved Cd concentration in soil pore water resulting from the pH-induced
336 equilibrium shift limits the upward movement of Cd to the topsoil. Such effects may be caused by
337 the declined upward migration of Cd through soil evaporation owing to the decreased Cd
338 concentration in the soil pore water after pH increases. Additionally, the impact of climate change
339 in this area is worth mentioning. For example, Du et al. (2013) combined the standardized
340 precipitation index and Mann–Kendall (MK) statistical test to investigate trends of dry and wet
341 conditions in the study area during 1951–2007. They found XRB becomes drier in spring and
342 autumn and wetter in summer and winter. Many studies have shown that the relative contribution
343 of different source waters varies greatly under dry and wet conditions (e.g., Li et al., 2017; Zhi et
344 al., 2019). Such a change in climate and hydrological regime may change the mechanism of metal
345 delivery from the upland to the river. Thus, the impacts of climate change should be evaluated to
346 address the challenges posed by climate change on water quality improvement.

347



348

349 Fig. 5. Percent change of simulated land-to-river Cd fluxes (industrial emission, surface runoff,
 350 lateral flow, and soil erosion) under four management scenarios. See Table 1 for scenario
 351 descriptions.

352

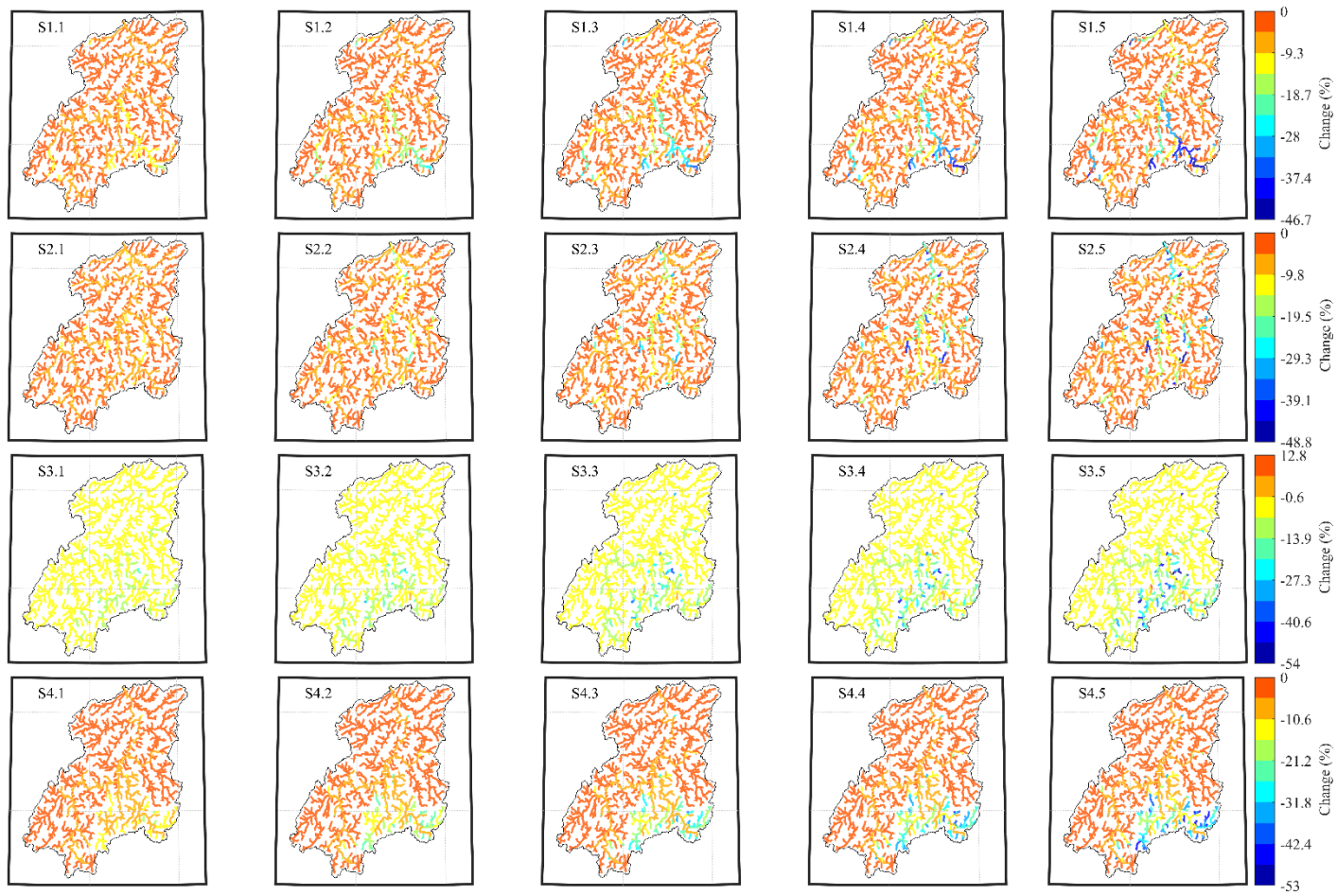
353 3.3. Changes of riverine Cd loads for different scenarios

354 In addition to the land-to-river Cd fluxes, we investigated riverine Cd loads under four
 355 management scenarios in the XRB. The reduction in TCd loads varied across the 1186 sub-basin
 356 outlets (Fig. 6). For mining control, the sub-basin outlets with high load reduction appear mainly in
 357 the upstream and midstream reaches, especially in the Southeast Lei River (Fig. 1). In contrast,
 358 smelting control mainly reduced TCd in the midstream and downstream areas. This is reasonable
 359 because most large-scale smelting activities occur in urban areas of the XRB midstream and
 360 downstream. Soil erosion control is the only management measure that could increase the TCd load
 361 as a result of the net increase in land-to-river Cd fluxes in some sub-basins. As a practical and
 362 effective measure, changing (increasing) the soil pH resulted in a reduction in TCd, ranging from

363 53.0% to 0% across the sub-basins. Soil acidification occurs widely in Chinese croplands owing to
364 excessive nitrogen fertilization and acid precipitation (Guo et al., 2010; Zhu et al., 2018). For
365 example, a 30-year field experiment in paddy soils of XRB found that mean topsoil pH declined by
366 0.94 units from the 1980s to 2014, at a mean rate of 0.031 units yr⁻¹ (Zhu et al., 2016). Acidification
367 can significantly alter the biogeochemistry of Cd in agroecosystems. A century-lasting experiment
368 at Rothamsted Experimental Station has revealed that soil acidification to pH 4 mobilized 60%–90%
369 of total soil Cd (Blake and Goulding, 2002). Therefore, agricultural land acidification should be
370 prevented to minimize Cd transport in the XRB. Liming to increase the soil pH, reducing the
371 application rate of chemical nitrogen fertilizers, and increasing organic fertilizers, such as manure,
372 could be preferentially implemented.

373 **Fig. 7** shows the boxplots of the monthly DCd and PCd loads at three representative outlets
374 (outlets 1056, 495, and 5). A paired-sample t-test was used to determine whether the management
375 scenario differed from the baseline scenario (S0); the upward-pointing triangle below each boxplot
376 indicated a significant difference at the level of 0.05. Outlet 1056 (**Fig. 4b**) is the exceeding river
377 section with a small proportion of upstream point source input. The upstream sub-basins of outlet
378 1056 cover approximately 213 km² with 96 percent of them designated as nonpoint source control
379 areas (details in **section 2.3**). As a nonpoint-dominated site, it benefited from soil erosion control
380 (S3.1–3.5) and soil pH elevation (S4.1–4.5), as evidenced by the significant reductions of both DCd
381 and PCd (**Fig. 7a-b**). The outlet of sub-basin 495 (**Fig. 4b**) is the outlet of the Lei River, one of the
382 major tributaries in Southeast XRB. For outlet 495 (**Fig. 7c-d**), mining control (Scenarios 1.1–1.5)
383 led to a decline in monthly mean DCd by 5.4–28.2% and in monthly mean PCd by 5.2–25.6%. The
384 simulation results for the entire XRB outlet (Outlet 5 in **Fig. 4b**) indicated that maximal

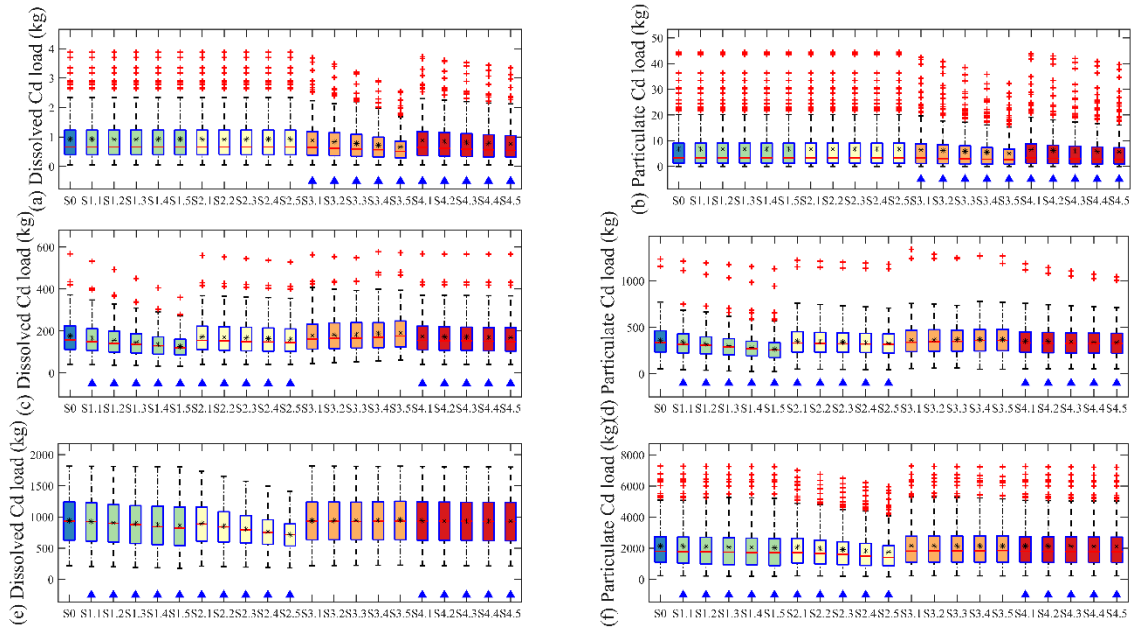
385 improvements were achieved when implementing emission control of smelting sectors (Scenarios
386 2.1–2.5 in Fig. 7e-f). For example, scenario 2.5 could significantly ($p < 0.05$) decrease the monthly
387 mean loads of DCd from 940 to 720 kg and of PCd from 2,150 to 1,760 kg. It should be noted that
388 soil conservation scenarios did not reduce the DCd and PCd at the entire XRB outlet (Fig. 7e-f).



389

390 Fig. 6. Percent change (%) of simulated TCd loads over 2000–2015 across the 1118 sub-basin outlets under four management scenarios. See Table 1 for scenario

391 descriptions.



392

393 Fig. 7. Boxplots of simulated monthly DCd and PCd loads at outlets 1056 (a, b), 495 (c, d), and 5

394 (e, f) under four management scenarios. Each boxplot represents 192 monthly Cd loads from 2000–

395 2015 for each scenario. Outliers are classified as all points outside 1.5 times the interquartile range

396 above the upper quartile and below the lower quartile, and the outliers are plotted individually using

397 the '+' marker symbol. Black asterisk points represent mean values. The upward-pointing triangle

398 below each boxplot indicated a significant difference between management scenario and baseline

399 scenario at the significance level of 0.05. See Table 1 for scenario descriptions.

400

401 3.4. Watershed-scale Cd budgets reveal the effectiveness of management measures

402 Owing to the unexpected results of the limited reduction of riverine Cd loads under soil

403 conservation scenarios, we further examined the complete watershed-average Cd fluxes in both land

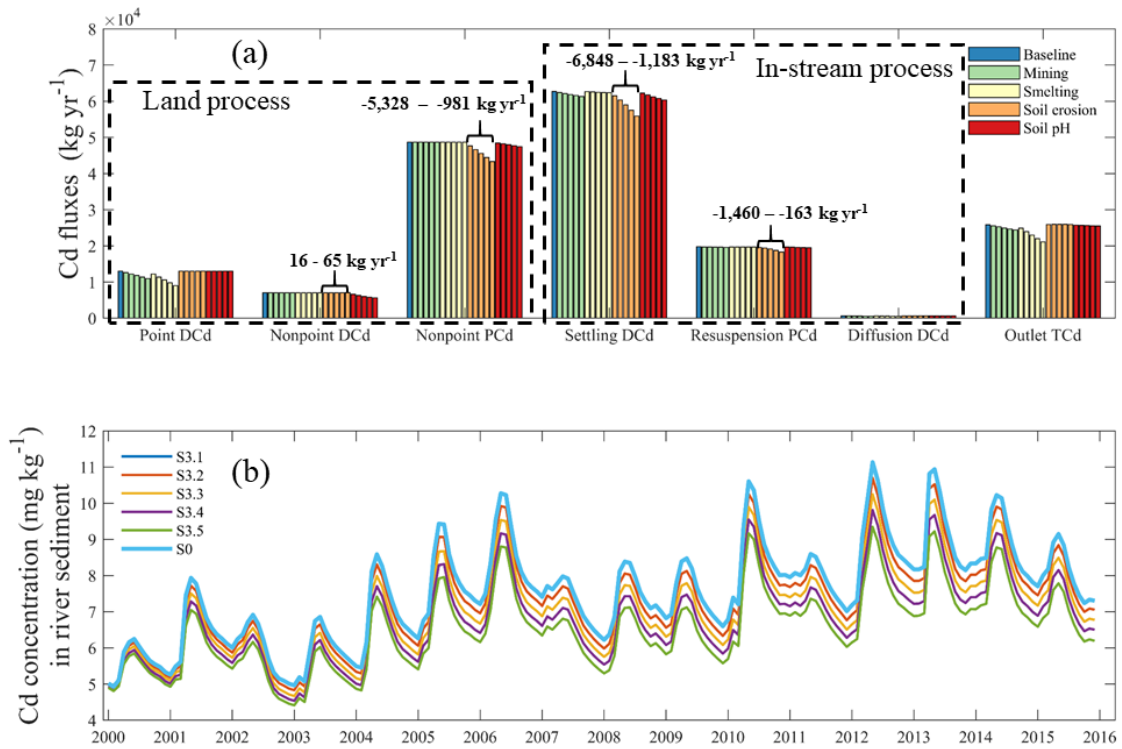
404 and in-stream phases. As shown in Fig. 8a, the implementation of soil erosion control (S3.1–3.5)

405 decreased the PCd flux (–5,328 to –981 kg yr⁻¹) in soil erosion and slightly increased the DCd fluxes

406 (15–65 kg yr⁻¹) through surface and subsurface flow. Overall, this resulted in a reduction in the total

407 Cd fluxes to the river. However, the riverine TCd load at the XRB outlet did not decrease as expected
408 but increased slightly. This is because the net retention (settling–resuspension) of Cd in the stream
409 also decreased. Moreover, the reduction in Cd retention was greater than that in the land-to-river Cd
410 load. Therefore, a quantitative understanding of the variable importance of point and nonpoint
411 sources of pollution, as well as the instream processes of metal attenuation and release, is crucial
412 for evaluating the effects of measures on downstream water quality. It should be noted that although
413 soil conservation measures do not benefit the riverine Cd load, they can curb the accumulation of
414 Cd in river sediments. For example, the time series of yearly mean Cd concentration in the sediment
415 of 196 polluted river sections showed that soil erosion control could reduce the Cd accumulation in
416 sediment at the end of 2015 by 0.1–15.2% under S3.1–S3.5 (Fig. 8b). A frequent occurrence of
417 heavy floods was witnessed across the XRB (Du et al., 2019), which may flush these sediment-
418 bound metals downstream during high-flow events. Recent studies have analyzed the simulated
419 climate extreme indices from 18 CMIP6 models and found that all regions of China witnessed an
420 increase in extreme precipitation (Zhu et al., 2021). For example, the areal-mean 95th percentile
421 precipitation would increase remarkably by 16.5%, 25.4%, and 46.5% for the 1.5, 2, and 3 °C global
422 warming levels, respectively, with respect to the reference period of 1985–2005. Therefore,
423 modified or new strategies may be required to minimize the potential negative impacts of climate
424 change, for example, on river sediment dynamics, to meet future water quality targets.

425



426

427 Fig. 8. (a) Simulated Cd fluxes (kg yr⁻¹) in land and in-stream phases of XRB. (b) The time series

428 (2000–2015) of monthly mean Cd concentrations (mg kg⁻¹) in the sediment of river sections where

429 river water TCd concentrations exceeded water quality standard of 1 μg L⁻¹. See Table 1 for scenario

430 descriptions.

431 **4. Conclusions**

432 In this study, we applied a process-based watershed-scale Cd model within a scenario analysis
433 framework to understand and evaluate the effects of different management practices on land-to-river
434 Cd fluxes and riverine Cd loads in an industrialized river basin with both point and nonpoint source
435 pollution. Based on our findings, we recommend several key management measures for achieving
436 water quality targets in river basins with Cd pollution.

437 (1) Effective remediation requires a comprehensive understanding of the relative contributions of
438 metals from all important sources in a basin, and that understanding must be based on spatially
439 detailed quantification of metal loads in different pathways. In addition, both loads from the
440 upstream channels and the corresponding sub-basin should be considered. Furthermore, it is
441 important to consider the dynamics of metals in the river network because in-stream processes
442 may significantly affect the riverine metal load at the downstream outlets. Numerical models
443 such as the SWAT-HM can be valuable tools to simulate metal fate and transport in both land
444 and river phases to develop remediation strategies.

445 (2) Different management measures will yield diverse outcomes. For example, reducing the
446 riverine Cd load at the XRB outlet could be achieved by cutting the point source Cd emissions
447 from the smelting sector rather than the mining sector, owing to their different spatial
448 distributions. Controlling soil erosion may decrease the PCd flux into rivers while increasing
449 the DCd flux, thereby affecting the riverine Cd load to a limited extent. However, controlling
450 soil erosion could be an effective way to restrain heavy metal accumulation in river sediments.
451 In addition, increasing the soil pH could be a practical and effective measure for reducing the
452 nonpoint Cd loads in nonpoint-dominated sub-basins.

453 (3) Targeted remedial strategies should be implemented for water quality management of large river
454 basins, such as the XRB. For example, a zoning control scheme can be proposed that includes
455 point source control areas, nonpoint source control areas, and mixed-source control areas. Given
456 that smelting and mining are the two major drivers of water quality deterioration in most parts
457 of the XRB, industrial emission reductions need to be maintained. In addition, soil remediation
458 could be implemented by increasing soil pH in nonpoint and mixed-source control areas.
459 Moreover, incorporating climate change considerations and assessing the proposed
460 management scenarios for their climate vulnerabilities will build more resilience in confronting
461 future conditions.

462

463 **Notes**

464 The authors declare no competing financial interest.

465

466 **Data availability**

467 The data will be made available upon reasonable request. The SWAT-HM model is available at
468 <https://github.com/LyntonZhou/SWAT-HM-pre-post-processing>.

469

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475

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