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Combine the soil water assessment tool (SWAT) with sediment geochemistry to evaluate diffuse heavy metal loadings at watershed scale

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HIGHLIGHTS

- Sediment core analysis provides valuable information for monitoring purpose.
- Particulate heavy metals were computed from simulated phosphorus by SWAT.
- Critical source areas were identified by interpolating estimated field loadings.
- Sediment yield played more importance in controlling diffuse heavy metal loadings.
- Combining SWAT with sediment geochemistry is helpful for watershed water management.

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ABSTRACT

Assessing the diffuse pollutant loadings at watershed scale has become increasingly important when formulating effective watershed water management strategies, but the process was seldom achieved for heavy metals. In this study, the overall temporal–spatial variability of particulate Pb, Cu, Cr and Ni losses within an agricultural watershed was quantitatively evaluated by combining SWAT with sediment geochemistry. Results showed that the watershed particulate heavy metal loadings displayed strong variability in the simulation period 1981–2010, with an obvious increasing trend in recent years. The simulated annual average loadings were 20.21 g/ha, 21.75 g/ha, 47.35 g/ha and 21.27 g/ha for Pb, Cu, Cr and Ni, respectively. By comparison, these annual average values generally matched the estimated particulate heavy metal loadings at field scale. With spatial interpolation of field loadings, it was found that the diffuse heavy metal pollution mainly came from the sub-basins dominated with cultivated lands, accounting for over 70% of total watershed loadings. The watershed distribution of particulate heavy metal losses was very similar to that of soil loss but contrary to that of heavy metal concentrations in soil, highlighting the important role of sediment yield in controlling the diffuse heavy metal loadings.

1. Introduction

Due to continuous industrial emissions control, the assessment of diffuse pollutant loadings at watershed scale is becoming more important when formulating effective watershed water management strategies [1,2]. In the past few decades, the watershed nutrient losses have been quantitatively assessed by applying various water quality models, which had important significance for eutrophication control [3,4]. However, this process was seldom achieved for hazardous materials such as heavy metals. Once heavy metals are introduced into the water environment, they may inhibit the normal aquatic activities and most importantly, pose serious threats to public health if the receiving body is used as a drinking water source or as a recreational site [5]. Therefore, special attention should be paid to the diffuse heavy metal pollution in watershed water management.

Agriculture is considered to be the predominant diffuse pressure in rural areas, although not invariably the most severe [6]. When compared to natural lands, the frequent tillage in agricultural lands can greatly disrupt the soil structure, causing more erosion and associated material losses [7]. As heavy metals in soil are tightly bound to soil colloids and organic matter [8], the diffuse heavy metal pollution occurs mainly in particulate form. Consequently, water erosion can act as an important vector for the movement of

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particulate heavy metals from soils to surface waters. To date, the role of soil erosion in detaching and transporting heavy metals has been well studied at the field scale, which improved our knowledge of diffuse pollution processes [9,10]. However, these studies are usually conducted in a given small plot and controlled under laboratory condition. Considering the fact that mechanisms involved in soil erosion vary over time and space, a long-term variability of particulate heavy metal losses at the watershed scale is beyond the result of field work and needs further analysis.

Watershed models provide an efficient tool for quantitatively evaluating diffuse pollutant losses over long timescales in large areas [11]. Since the end of 1970s numerous watershed models have been developed, but most of them focused only on regular contaminants such as nitrogen and phosphorus, as well as a variety of pesticides. Even so, the developments in distributed modeling have greatly enriched the availability of geospatial data analysis, which allow investigating multimedia environmental problems in a spatially distributed manner over a larger area [12,13]. More recently, Velleux et al. [14] developed a physically-based distributed model named two-dimensional, runoff, erosion, and export (TREX), which has been successfully applied for simulating metals transport and fate in the California Gulch watershed. However, the model is expensive to construct and difficult to calibrate because of its high data requirement. This fact reflects the difficulties in simulating diffuse heavy metal pollution when the required data are deficient in both quantity and quality, as is the case in most developing countries.

Sedimentation processes usually occur during the subsequent transport of heavy metals from various sources to the surface water [15]. During the past few decades, the analysis of river sediment has proven to be an excellent approach for assessing heavy metal pollution, providing insight into natural and anthropogenic impact at different spatial scales [16,17]. Also, the concentration distribution of heavy metals in river sediment core can be used to investigate long-term watershed pollution, as the makeup of the sediment core reflects the geochemical history of source region [18]. Thus, the experimental data obtained from sediment analysis are useful indicators for monitoring purpose, which may help to simulate diffuse heavy metal pollution in data-sparse or un-gauged watersheds.

Our previous study showed that long-term agricultural reclamation in Northeast China has caused Pb, Cu, Cr and Ni losses from the soils [19]. In this paper, the overall temporal–spatial variability of particulate Pb, Cu, Cr and Ni losses within an agricultural watershed was quantitatively evaluated through an innovative approach of combining SWAT with sediment geochemistry. The specific objectives of this study were: (1) to investigate the heavy metals accumulation in sediment core under long-term agricultural development; (2) to identify the impact of land use conversions on diffuse heavy metal pollution at watershed scale; and (3) to characterize the soil erosion process for effective diffuse heavy metal control.

2. Materials and methods

2.1. Study area description

The selected study area lies in the northeast corner of China, which is on the border with Russia and has a total area of 142.5 km^2 (Fig. 1). Historically, this watershed was covered mainly with natural forestland and wetland, but it has been undergoing an intensive agricultural reclamation since the 1980s. Consequently, the area of upland and paddy land expanded rapidly and had exceeded 50% of total watershed area according to the land use distribution in 2009. At present, the two main types of crops being grown are rice and soybean.

The climate is continental monsoon, with an average annual temperature of 2.94 °C. The average annual rainfall is 583.18 mm, most of which falls in the period between May and September. The main river flows eastward with the altitude dropping from 129 m to 38 m. According to the World Reference Base for Soil Resources [20], soils in this area are classified mainly as Albic Luvisols. This type of soil has a fertile but porous A horizon, it is therefore vulnerable to surface runoff and erosion, especially in the summer storm season.

2.2. Sampling and chemical analysis

With the 1.5 km grids, a total of 47 topsoil samples (0–20 cm in depth) were collected from the study area in April 2012, just after the freezing period and prior to the growing season [21]. Around the center of each grid, three sub-samples were collected from an area of approximately 100 m^2 and they were fully mixed to get a composite soil sample. Furthermore, one river sediment core of 30 cm in length was taken from the watershed outlet and sliced into thin sections at 1 cm intervals (Fig. 1). Immediately after collection, all samples were sealed in plastic bags and transported to the laboratory where they were air dried, slightly crushed and passed through a 100-mesh sieve. The dry samples were then digested with HNO_3–HF–$HClO_4$ mixture and analyzed for total phosphorus (TP), Pb, Cu, Cr and Ni concentrations by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

2.3. Estimating watershed sediment and associated phosphorus loadings by SWAT

The SWAT model was applied to simulate watershed sediment and particulate phosphorus loadings in the period 1981–2010. The details of SWAT applicability to this watershed can be obtained from our earlier paper [22]. To perform the SWAT model, the watershed topography data was downloaded from the database of Chinese Academy of Sciences [23]. According to the digital elevation map (DEM), this watershed was totally divided into 44 sub-basins. The soil property data was obtained by referring to the national database [24]. The monitoring weather data from 1981 to 2010 were directly collected from local weather gauges. The land use data of 2009 was applied through interpreting a Landsat image from the Chinese Academy of Sciences [23]. After field investigation, the agricultural practices of paddy rice and soybean were taken into account in the model [25].

For this study, an important aspect is related to the processes of sediment formation and transport. In SWAT, the sediment loading in each sub-basin is calculated by using the Modified Universal Soil Loss Equation (MUSLE). However, the sediment transport is considered under control of two simultaneous processes: deposition and degradation [26]. Based on local environmental features, three dominant parameters affecting these processes were selected and estimated. They are defined as a linear parameter for calculating the maximum amount of sediment that can be entrained during channel sediment routing (SPCON), an exponential parameter for calculating the channel sediment routing (SPEXP) and a MUSLE equation support practice factor (USLE_P), respectively [22].

2.4. Estimating particulate heavy metal loadings at field scale

The process of soil erosion tends to be selective toward fine particles [27]. As a result, the sediment being transported has a finer texture than the source soil material, which causes an increased chemical concentration due to larger surface area. Based on the concept of sediment enrichment ratio, the particulate heavy metal

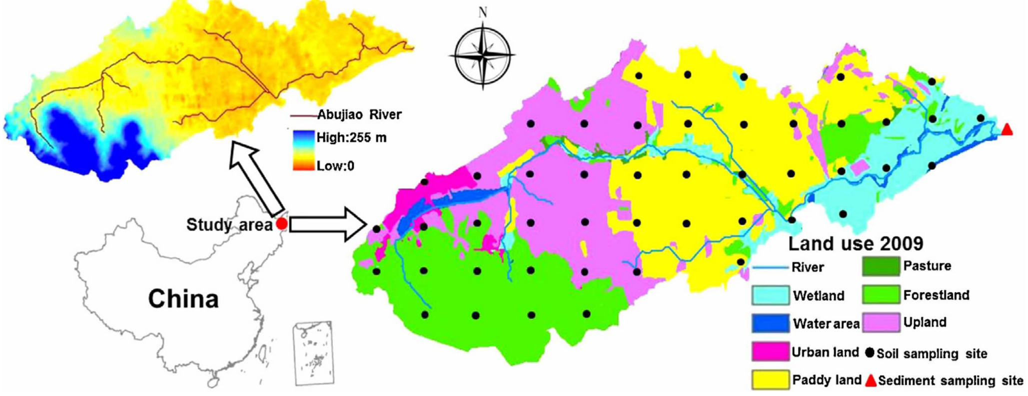

Fig. 1. Location, topography and land use distribution of study area.

loss at each sampling site can be calculated by using the equation as follows:

$$L = C \cdot \delta \cdot Q \tag{1}$$

where L is the particulate heavy metal loading (g/ha), C is the heavy metal concentration in soil (mg/kg), δ is the ratio of heavy metal concentration in transported sediment to the concentration in soil, and Q is the sediment loading (t/ha). In this paper the sediment enrichment ratios of Pb, Cu, Cr and Ni (3.27, 3.98, 2.1 and 3.01, respectively) were referenced from a 6-year field study [10], and the sediment loading at each site was assumed as the simulated value of sub-basin by SWAT.

2.5. Statistical and spatial analysis

After analyzing the soil samples at 1.5 km-grid, the heavy metal concentrations from different land uses were compared using one-way analysis of variance (ANOVA) followed by post hoc least significant difference (LSD) test. With simple linear regression, the long-term relationships between total phosphorus and heavy metal concentrations in the river sediment core were assessed. In order to identify areas of significant soil erosion, the simulated sediment loadings in years 1981–2010 were averaged within each sub-basin by SWAT. Based on the results of 46 sampling sites, the ordinary kriging integrated in Geographical Information Systems (GIS) was used to achieve spatial interpolation of particulate Pb, Cu, Cr and Ni loadings in the whole watershed. To perform the kriging and the SWAT model, all GIS data were projected into the Universal Transverse Mercator coordinate system.

3. Results

3.1. Heavy metal concentrations in soil with different land uses

As this watershed consists mainly of wetland, forestland, paddy land and upland, the Pb, Cu, Cr and Ni concentrations in the four land uses were presented in Table 1. The analytical data quality was assessed by using simultaneously the reference material GBW-07402. Good agreements were obtained between the measured and the certified values, with the average recoveries ranging from 96.34% for Pb to 101.47% for Cr. When compared with regional background values, the Pb, Cu and Cr concentrations in soil were all elevated after about 30 years of agricultural development, with the averages of 20.40 mg/kg, 24.60 mg/kg and 52.52 mg/kg, respectively. However, they did not exceed the guideline values of Chinese Environmental Quality Standard for Soils [28]. In general, these heavy metals varied significantly among different land uses, but they were all higher in natural lands than in paddy land and upland. The lower heavy metal concentrations in cultivated areas indicated that frequent tillage has caused large heavy metal losses from the soils. By comparison, the Cu, Cr and Ni concentrations in paddy land were significantly larger than those in upland. However, Pb had a higher concentration in upland than in paddy land, which was considerably different from other three metals.

3.2. Vertical distribution of heavy metal concentrations in river sediment core

Fig. 2 illustrates the concentration distribution of Pb, Cu, Cr and Ni with depth in the river sediment core from watershed out. Reference material GBW-07401 was used to assess the data quality, and the average recoveries varied between 98.56% for Pb and 102.78% for Ni. These heavy metals generally fluctuated with increasing depth, but they were all lowest at the bottom of the core and highest at the surface. The Pb concentration decreased rapidly from 26.85 mg/kg to 22.97 mg/kg at depths of 0–3 cm, and then fluctuated slightly at subsequent depths. The average concentrations of Cu, Cr and Ni in the sediment core were 26.58 mg/kg, 63.62 mg/kg and 28.30 mg/kg, respectively, with obvious decreasing trends at depths of 0–3 cm and 19–23 cm. In general, the makeup of sediment core reflected the impact of long-term agricultural development in this watershed. It was also observed that the concentration distributions of Pb, Cu, Cr and Ni were very similar to that of TP in the sediment core. The similar distribution trends implied that they may have a similar inputting history and therefore, the relationships between them were further analyzed in Section 3.3.

3.3. Relationships between heavy metals and TP in river sediment core

The simple linear regression models were employed to express relationships between TP and heavy metal concentrations in the river sediment core from watershed core (Fig. 3). It was found that TP generally correlated well with Pb, Cu, Cr and Ni in the sediment core, with the R^2 values of 0.451, 0.792, 0.732 and 0.843, respectively. Based on these relationships, the long-term particulate Pb, Cu, Cr and Ni loadings could be computed from simulated phosphorus data by SWAT. As the fitting line of Cr had a lower slope than those of other heavy metals, the simulated Cr loading would be much more sensitive to phosphorus loss.

3.4. Simulation of long-term particulate heavy metal loadings

According to the above empirical relationships, the watershed particulate Pb, Cu, Cr and Ni loadings were computed from simulated phosphorus loading for the period 1981–2010. As shown

Table 1
Heavy metal concentrations in soil with different land uses.

Land uses	Heavy metals (mg/kg)			
	Pb	Cu	Cr	Ni
Wetland	23.66 ± 1.11a	31.42 ± 1.02a	60.70 ± 1.39a	26.17 ± 0.68a
Forestland	21.27 ± 1.56b	26.70 ± 1.82b	55.13 ± 1.66b	24.21 ± 0.62b
Paddy land	17.58 ± 1.78c	22.55 ± 1.61c	50.11 ± 1.95c	20.40 ± 1.05c
Upland	20.59 ± 1.33b	20.15 ± 1.60d	47.07 ± 1.09d	18.52 ± 0.53d
Background value[a]	17.79	22.60	28.20	27.10
Guideline value[b]	250	50	150	40

Means in a column followed by the same letter were not significantly different.

[a] Soil background values.

[b] Chinese Environmental Quality Standard for Soils [28].

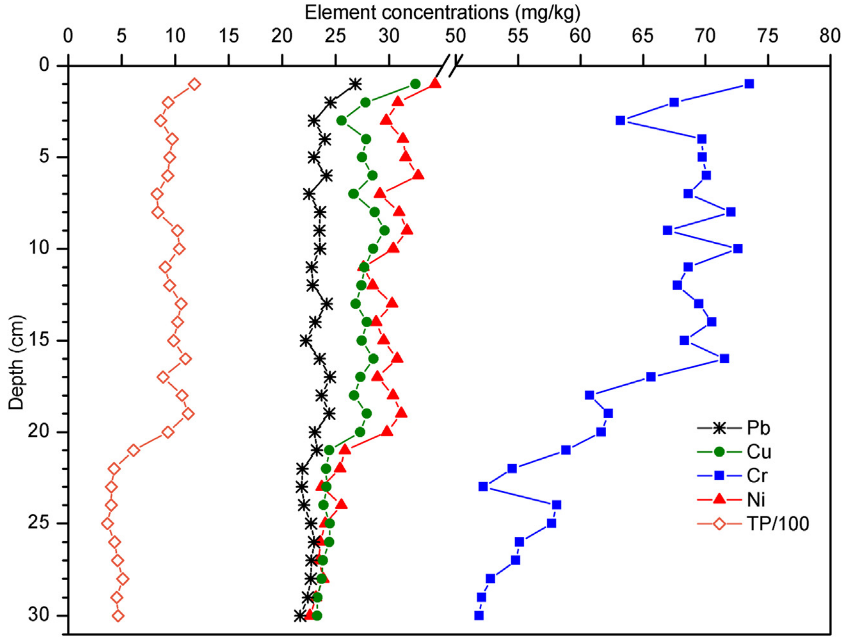

Fig. 2. Vertical distribution of heavy metal concentrations in the sediment core of watershed outlet.

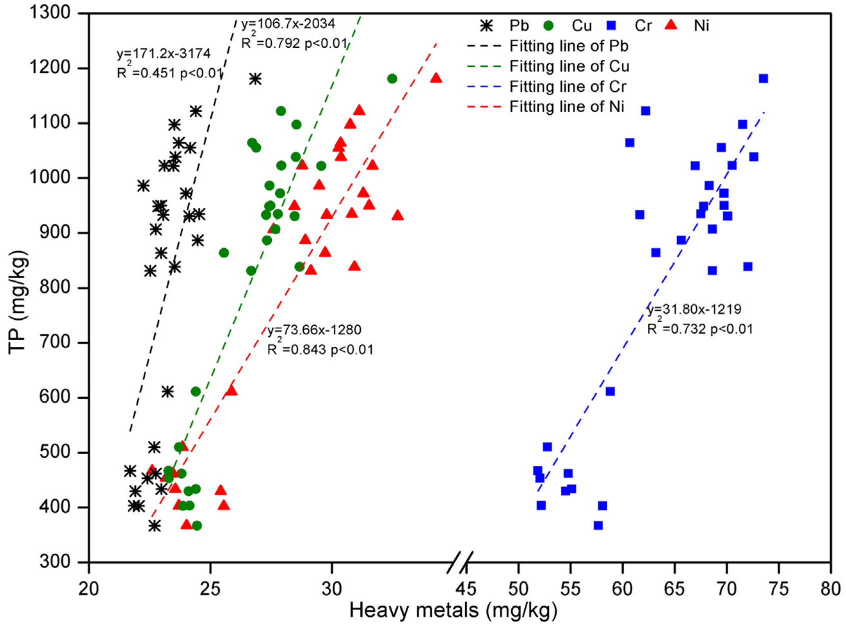

Fig. 3. Relationships between heavy metals and TP in the sediment core of watershed outlet.

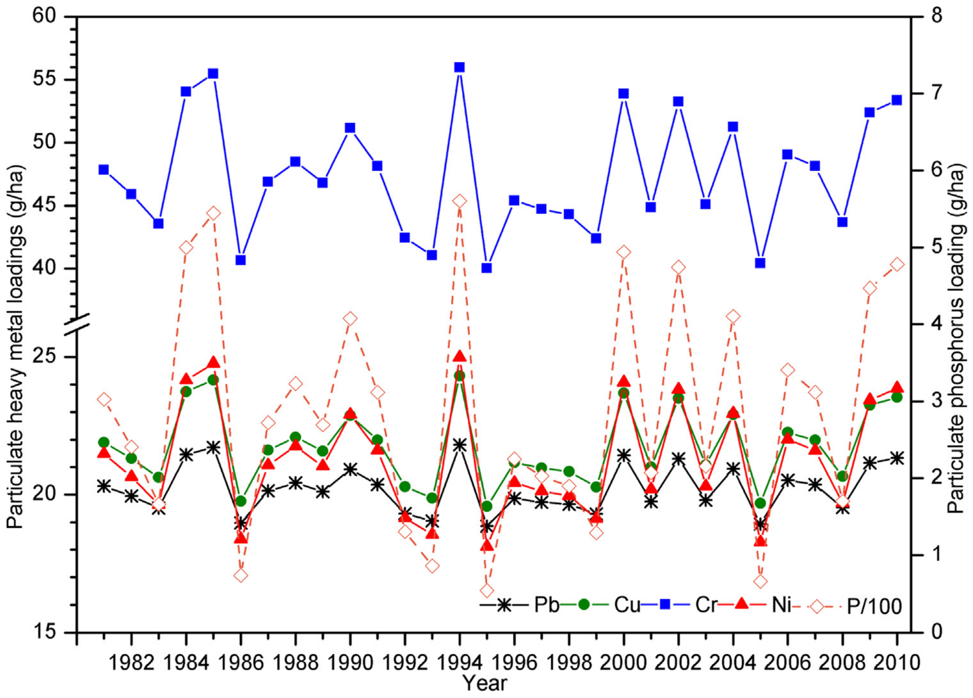

Fig. 4. Simulated particulate heavy metal loadings in the period 1981–2010.

in Fig. 4, the particulate heavy metal loadings generally displayed strong variability in the total simulation period: Pb ranged from 18.85 g/ha to 21.81 g/ha, with the annual average of 20.21 g/ha; Cu ranged from 19.57 g/ha to 24.32 g/ha, with the annual average of 21.75 g/ha; Cr ranged from 40.03 g/ha to 55.96 g/ha, with the annual average of 47.35 g/ha; and Ni ranged from 18.11 g/ha to 24.99 g/ha, with the annual average of 21.27 g/ha. Consequently, Cr was identified as the main diffuse pollutant due to its high loss loading in this watershed. Because we have no long-term observed data, the simulation results at watershed scale were assessed by comparing with the estimated particulate heavy metal loadings at field scale. Based on Eq. (1) the average particulate Pb, Cu and Ni loadings of all sampling sites were 17.17 g/ha, 24.03 g/ha and 16.73 g/ha, respectively, which matched the simulated annual average values satisfactorily. As Cr has a low sediment enrichment ratio, the estimated field loading of 27.90 g/ha was much lower than the simulated value, but they were still in the same order of magnitude.

3.5. *Identification of critical source areas of diffuse heavy metal pollution*

In order to identify areas of significant soil erosion, the simulated sediment loadings in years 1981–2010 were averaged within each sub-basin (Fig. 5). During the sediment simulation by SWAT, SPEXP, SPCON and USLE_P were selected as the most sensitive parameters, which had the values of 1.16, 0.05 and 0.14, respectively. As a whole, the soil loss in this watershed was quite varied spatially, with the average sediment loading of 0.31 t/ha. Among the 44 sub-basins numbers 21, 23, 25, 27, 28, 33, 34 and 35 were identified as areas with high soil loss (up to 0.35 t/ha). Based on the results at field scale, the spatial interpolation of particulate Pb, Cu, Cr and Ni loadings was presented in Fig. 6. By comparison, we found that the spatial trend of particulate heavy metal losses was very similar to that of soil loss. However, the particulate heavy metal loadings generally showed a reverse spatial trend compared with the heavy metal concentrations in soil. When overlaying land use

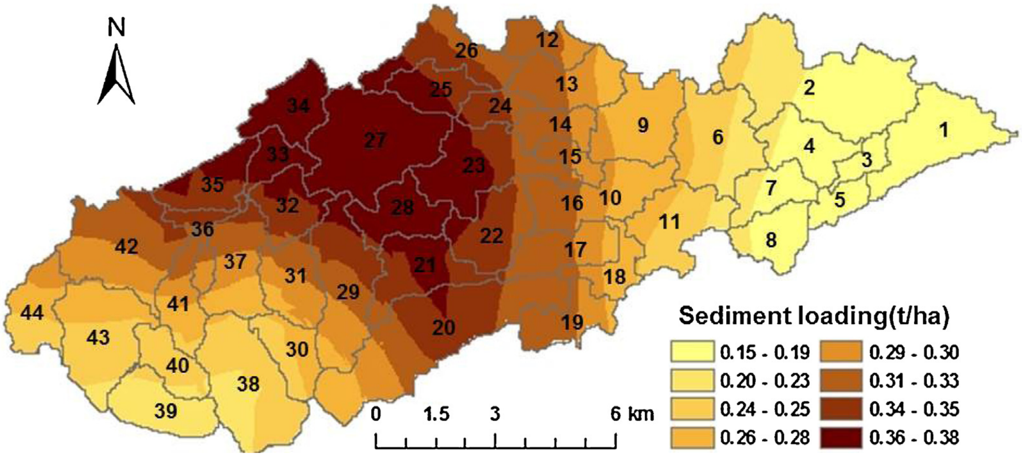

Fig. 5. Spatial distribution of soil loss.

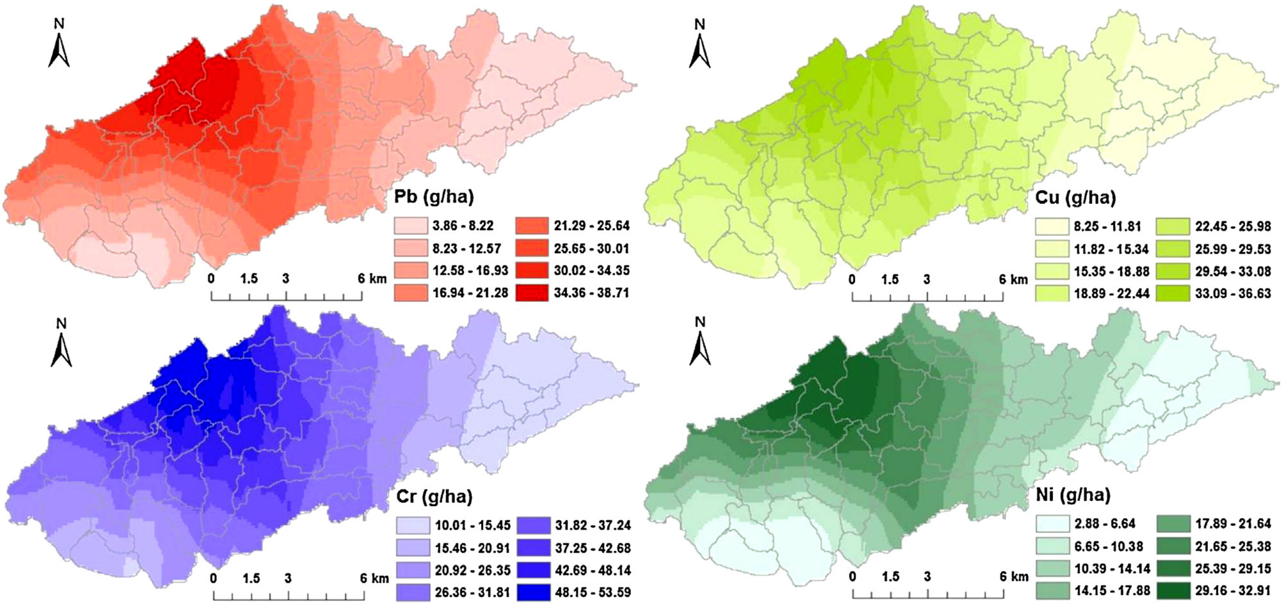

Fig. 6. Spatial distribution of particulate heavy metal losses.

distribution, it was observed that the diffuse heavy metal pollution mainly came from the sub-basins dominated with paddy land and upland, accounting for over 70% of total watershed loadings. Due to serious soil erosion, the upland was identified as the land use type with highest particulate heavy metal losses.

4. Discussion

4.1. Heavy metals accumulation in sediments under long-term agricultural development

Intensive agriculture has caused environmental degradation through soil erosion and nutrient losses in many watersheds of the world [29,30]. In this study, the impact of long-term agricultural development on watershed heavy metal losses was adequately evaluated by taking one river sediment core from watershed out. It was found that the Pb, Cu, Cr and Ni concentrations generally fluctuated in the sediment core, with their highest values at the surface and lowest at the bottom. Similar distribution was also observed for an agricultural watershed with high-yield grain production in the Yangtze-Huaihe region of China [31]. The higher heavy metal concentrations at surface sediment indicated that an increased watershed loading has occurred in recent years. This conclusion can be well supported by our simulation results. In 2008 the watershed particulate Pb, Cu, Cr and Ni loadings were 19.53 g/ha, 20.66 g/ha, 43.68 g/ha and 19.69 g/ha, respectively. However, they had been rising rapidly in the later several years, reaching as high as 21.33 g/ha, 23.54 g/ha, 53.36 g/ha and 23.87 g/ha in 2010, respectively. In general, the particulate heavy metal loadings showed great variability in the total simulation period. This variability was mainly attributed to the hydrological fluctuations from year to year, because they can strongly affect sediment formation and transport [32]. A direct evidence for this is that the simulated average annual sediment loading of 0.31 t/ha in this watershed was much lower than the 4.14 t/ha reported for an Isábena watershed (Southern Central Pyrenees, France), where the soils experience frequent floods [33].

It should be noted that the Cr concentration was much higher and displayed larger variability than other metal concentrations in the sediment core. These findings suggested that more anthropogenic Cr was introduced into the watershed water environment during long-term agricultural development. Chromium is a common pollutant in phosphate fertilizer. With rapid agricultural development, the amount of phosphate fertilizer usage has increased significantly in this area, reaching 87 kg P/ha by 2010. However, researchers have pointed out that only 10–15% of applied phosphate fertilizer is absorbed by crops, while the rest is lost [34]. According to the sediment quality guidelines developed by US EPA [35], the Cr concentration at surface sediment has been close to the heavy pollution level of 75 mg/kg. This is especially serious if we consider the fact that sediments can act not only as a sink for a wide variety of pollutants, but also as a potential secondary source [36].

4.2. Impact of land use conversions on diffuse heavy metal pollution at watershed scale

Different land uses have special hydrological, biological and physicochemical characteristics that alter the occurrence of diffuse pollution events [25]. Therefore, the long-term agricultural reclamation and land use conversions can greatly affect the diffuse heavy metal pollution in this watershed. According to the land use distribution in 2009, the sub-basins of paddy land and upland in the central area were identified as contributing to major diffuse heavy metal pollution. This result was consistent with our previous report for phosphorus [22] and suggested that the conversions of natural lands into agricultural lands have lead to large heavy metal losses from the soils. With the analysis of relationships between heavy metals and soil properties in different land uses, Jiao et al. [19] concluded that the heavy metal losses after long-term land reclamation in Northeast China was closely related to the reduction of soil organic matter and clay contents.

By comparison, the upland displayed higher loss loadings than paddy land. However, topography is predominately responsible for the difference in diffuse heavy metal pollution in both land uses. To some extent, the low-lying topography of paddy fields can reduce water erosion potential and enhance heavy metals accumulation in soil [37]. Consequently, the Cu, Cr and Ni concentrations were observed higher in paddy land than in upland. However, Pb had the reverse concentration distribution. This was very likely associated with the strong reduction of Fe–Mn oxides in paddy soil, which can serve as important scavengers of Pb [38]. With increasing food demand, a large area of upland in Northeast China has been converted into paddy land for achieving higher grain output. As rice cultivation requires moderate flooding, most heavy metals in the paddy soil can be gradually transformed from stronger bound fractions to weaker bound fractions, leading to a release of dissolved heavy metals [39]. Although the diffuse heavy metal pollution occurs mainly in particulate form, the water-soluble heavy metals are considered to have a higher bioavailability, which can greatly threaten human health through water supply and food chain.

4.3. *Implications for diffuse heavy metal control*

The control of diffuse pollution is more difficult than for point source pollution since it involves fundamental land use changes [40]. Furthermore, as soil erosion can be a highly selective process, it needs deep analysis at different erosion intensities. More intense erosion events generally mobilize a broad range of particle sizes, while lower intensity events transport only the smaller size but more metal-rich materials [10]. In this study, the particulate heavy metal loadings generally showed a reverse spatial distribution compared with the heavy metal concentrations in soil. However, the spatial trend of particulate heavy metal losses was very similar to that of soil loss. These findings indicated that when compared to heavy metal concentration in soil and its enrichment in sediment, sediment yield played more importance in controlling the diffuse heavy metal loadings. Therefore, much more attention should be paid to the large-intensity erosion events in future mitigation strategy, although they usually have a low frequency. This conclusion was also well supported by Gozzard et al. [41], who examined both low and high flow regimes to assess diffuse Zn pollution in the River West Allen watershed and concluded that the contribution from diffuse sources would greatly elevate riverine Zn loading only in high-intensity rainfalls.

Quantifying diffuse pollution can allow better decisions on pollution control and watershed management [42]. However, field measurements and collection of data are generally difficult tasks, rarely achieved over long timescales in large areas. By using emission factors and regional statistics, Vink and Peters [43] simulated diffuse heavy metal emissions in the Elbe watershed, which has a total area of 148,268 km^2. Although they considered multiple diffuse sources, the simulated average annual Pb and Cu loadings (11.40 g/ha and 15.35 g/ha, respectively) were still much lower than our results in this watershed. One proper explanation is that the Elbe watershed is too bigger when compared with our study area, even if it has a high pollution flux. In this research, the long-term particulate heavy metal loadings were estimated from simulated phosphorus by SWAT, after obtaining their relationships through sediment analysis. However, the approach indeed gives us an overestimated pollution level. This is because SWAT allows all soil eroded by runoff to reach the river directly, without considering sediment deposition remaining on surface watershed areas [26]. In addition, the sediment enrichment ratios were referenced from a previous study conducted in other area, which affected the calculation accuracy at field scale. However, the findings were generally acceptable based on the temporal-spatial analysis and provided valuable information for formulating effective watershed management strategies, especially in data-sparse or un-gauged regions.

5. Conclusions

This study revealed that combining model simulation with sediment analysis is a practical way to evaluate the diffuse heavy metal loadings at watershed scale. By analyzing Pb, Cu, Cr and Ni concentrations in the river sediment core, it was found that these heavy metals generally fluctuated with increasing depth, but they were all lowest at the bottom and highest at the surface. The higher heavy metal concentrations at surface sediment indicated that an increased watershed loading has occurred in recent years. According to the sediment quality guidelines developed by US EPA [35], the Cr concentration at surface sediment has been close to the heavy pollution level of 75 mg/kg. It was also observed that the concentration distributions of Pb, Cu, Cr and Ni were very similar to that of TP in the sediment core. The similar distribution trends implied that they may have a similar inputting history and therefore, the relationships between them were further defined by using simple linear regression. Based on these empirical relationships, the long-term particulate Pb, Cu, Cr and Ni loadings were computed from simulated phosphorus data by SWAT.

Simulation results showed that the watershed particulate heavy metal loadings displayed strong variability in the period 1981–2010, with an obvious increasing trend during 2008–2010. Due to the lacking of long-term observed data, the simulation results at watershed scale were assessed by comparing with the estimated particulate heavy metal loadings at field scale. With spatial interpolation of field loadings, it was found that the diffuse heavy metal pollution mainly came from the sub-basins dominated with cultivated lands, especially the upland. When compared with heavy metal concentrations in soil, the particulate heavy metal loadings generally had the reverse spatial distribution. However, the spatial trend of particulate heavy metal losses was very similar to that of soil loss, indicating that sediment yield played more importance in controlling the diffuse heavy metal loadings. Therefore, much more attention should be paid to the large-intensity erosion events in future mitigation strategy. Although there were certain limitations in this research and more data can improve the overall quality, the particulate Pb, Cu, Cr and Ni loadings were adequately evaluated based on the temporal–spatial analysis, which provided valuable information for formulating effective watershed management strategies.

Acknowledgements

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