Contamination and Potential Ecology Risk of Heavy Metals in the Sediment of Cau River, Vietnam

ABSTRACT

Five sediment cores collected at Cau river section flowing through Thai Nguyen were analyzed to evaluated the vertical profile, enrichments, and contamination of six heavy metals including Cu, Pb, Zn, Cr, As, Cd. The impacts of investigated metals on ecology were estimated by the toxic unit and the potential ecological risk index. The obtained mean heavy metal concentration in the five sediment cores for investigated metals was: Cd (0.56 - 1.74 mg kg^{-1}) < As (10.2 - 32.3 mg kg^{-1}) < Cr (12.1 - 36.2 mg kg^{-1}) < Cu (16.0 - 51.2 mg kg^{-1}) < Pb (24.5 - 85.5 mg kg^{-1}) < Zn (48.2 - 151 mg kg^{-1}). The spatial distribution and vertical patterns of heavy metal concentration in the sediment cores differed substantially among the investigated sites. Among the six investigated heavy metals, Cr was of natural origin while the remaining 5 metals (Cu, Pb, Zn, As, Cd) came primarily from human activities. Based on the classification using EF, I_{geo}, and PLI, sediment at S3, where there was a concentration of discharge from main activities of the area, were strongly contaminated with heavy metals. The other sites (S1, S2, S4, S5) were in the condition of slightly contaminated with heavy metals. As and Cd were mostly associated to overall pollution load index of heavy metals in sediment of Cau river. The highest ΣTU and considerable risk from heavy metals were observed at S3. Sediment at S1, S2, S4, and S5 posed moderate ecological risk.

Keywords: heavy metals, sediment core, contamination, ecological risk, Cau river

1. INTRODUCTION

Heavy metal pollution in aquatic environment has become a major concern due its threats to aquatic ecosystems, and adverse effects on human health through the water and food supply chains [1, 2]. When metals enter the environment, they will distribute between the aqueous phase and the suspended sediments during their transport [3, 4]. Metals tend to be assimilated in sediment. Hence the river sediment serves as the sink and the source of heavy metals in the water environment [5] Heavy metals bound to sediments are characterized by their long residual time and high toxicity [6, 7]. An excessive accumulation of heavy metals in sediments can result adverse effects to the water environment and the ecology [8]. Therefore, the level of heavy metals in sediment can serve as a good indicator of regional pollution conditions and the information of heavy metals in the sediment core can record the changes in anthropogenic and natural sources in catchment basin [9]

As a developing country, Vietnam is now facing the rapid industrialization and urbanization. Consequently, environmental pollution has become more severe. Cau river one of the major river of Hong Delta, the

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second-largest delta in Vietnam with the catchment area of 6,030 km² and the length of 290km [10]. The river basin includes Thai Nguyen province and parts of other six provinces. Cau river receives discharge from domestic waste water, industrial wastewater from mining and mineral processing, metallurgy, chemical production, and wastewater from agriculture and activities of the nearby villages. Our previous study found the contamination of heavy metals in water and surficial sediment of Cau river however, the information of the vertical profiles of metals in sediment are scare. The objectives of this study are (1) to examine the spatial variation and the vertical profile of 06 heavy metals (Cu, Pb, Zn, Cr, As) in the sediment of Cau river; (2) to assess the metal contamination using the geo-accumulation index (I_{geo}), the enrichment factor (EF), and the pollution index (PLI); and (3) to estimate the potential ecological risk of the presence of heavy metals in sediment.

2. MATERIAL AND METHODS

2.1. Sample collection and analysis

Five sediment cores (length of 30cm) were collected along the section of Cau river flowing through Thai Nguyen city in October 2019 using gravity corer. The sampling sites were shown in Fig. 1. The collected sediment core in cylindrical acrylic tubes were cautiously sliced into 5 cm segments by using an acrylic slicer, transferred into zipped polypropylene bags, kept in cool condition and transported to the laboratory with 24 hours. At the laboratory, sediment samples were stored at -30°C for further treatment and analysis.

Heavy metals (Fe, Cu, Pb, Zn, Cr, As, Cd) in the sediment were extracted by microwave-assisted extraction procedure following EPA 3051A method and the concentration of heavy metals in filtrates were analyzed using an ICP-MS (7500c, Agilent Technologies, Santa Clara, CA) according to SMEWW 3125B:2012.

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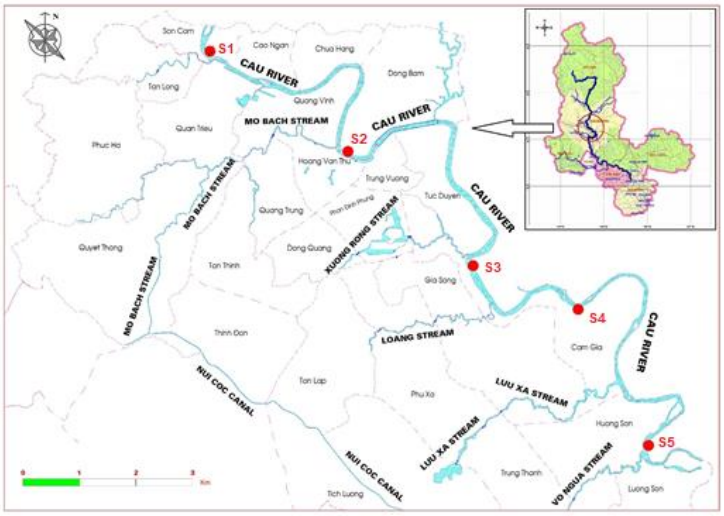

Figure 1. Map of sampling sites in Cau river

2.2. Sediment pollution assessment

Heavy metal contamination in the sediment cores were evaluated using the enrichment factor (EF), the geo-accumulation index (I_{geo}), and the pollution index (PLI).

Enrichment Factor (EF)

EF was used to determine whether metals in sediment were of anthropogenic origin [11]. To identify the contamination level, the observed metal concentration should be normalized using conservative elements, such as Al, Fe, and Si. In this study, iron was used as the conservative tracer to differentiate natural from anthropogenic components. The EF was calculated according to the following equation:

$$EF = \frac{\left({}^{C_m}/_{C_{Fe}}\right)}{\left({}^{B_m}/_{B_{Fe}}\right)} \qquad (1)$$

where (C_m/C_{Fe}) is the ratio between the concentration of heavy metals and Fe concentrations in sediment cores and and (B_m/B_{Fe}) is the ratio between the background concentration of heavy metals and Fe, respectively.

As the background value of the metals in the current study site are not available, the earth crust values [12] were adopted.

Geo-accumulation index (Igeo)

I_{geo} was proposed by Muller [13] to assess heavy metal contamination. The associated equation is

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$$I_{geo} = log_2(\frac{C_m}{1.5B_m}) \quad (2)$$

where C_m is the heavy metal concentration in the sediment; *Bm* is the background concentration of the corresponding heavy metal. The coefficient value of 1.5 is the correction factor of the background matrix, which primarily aims at adjusting the lithogenic influences.

Pollution Loading Index (PLI)

PLI provides a comprehensive assessment of heavy metal contamination in sediment [14]. PLI can be calculated according to the following equation:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n} \quad (3)$$

where CF is the contamination factor, CF= C_m/B_m; and n is the number of the investigated heavy metal.

2.3. Ecological Risk Assessment

Toxic unit

Toxic unit was defined as the ratio of the observed concentration of metal in sediment to the probable effect level (PEL) value of such metal. Potential acute toxicity of heavy metals in sediment can be assessed by the sum of toxic units (ΣTU) of all investigated heavy metals [15]. The formula for computation of ΣTU is:

$$\Sigma TU = \sum(\frac{C_i}{PEL_i}) \quad (4)$$

where PEL_i is the probable effect level (PEL) value of each heavy metal; in particular, Cu = 108 mg kg^{-1}, Pb = 112 mg kg^{-1}, Zn = 271 mg kg^{-1}, Cr = 160 mg kg^{-1}, As = 41.6 mg kg^{-1}, and Cd = 4.21 mg kg^{-1} [16].

Potential ecological risk index (RI)

RI was used to assess the comprehensive potential ecological risk of heavy metals in sediment and was initially introduced by Hakanson [17]. RI was defined as ecological risk associated with a single metal (Er_i) and the overall potential risks of investigated metals and was calculated as:

$$RI = \sum Er_i = \sum PI \times T_i = \sum(\frac{C_i}{B_i}) \times T_i \quad (5)$$

where Er_i is the potential ecological risk factor of a single species of heavy metal; PI is the pollution index; and T_i is the biological toxicity factor (i.e., Hg = 40, Cd = 30, Cr = 2, Cu = 5, Pb = 5, and Zn = 1) [17].

3. RESULTS AND DISCUSSION

3.1. Heavy metal concentration in sediment

Heavy metal concentrations in the sediment of investigated sites were summarized in table 1. The mean heavy metal contents in sediment cores in Cau river are as follows: Cd (0.56-1.74 mg kg^{-1}); As (10.2 - 32.3 mg kg^{-1}); Cr (12.1 - 36.2 mg kg^{-1}); Cu (16.0 - 51.2 mg kg^{-1}); Pb (24.5 - 85.5 mg kg^{-1}), and Zn (48.2 - 151 mg kg^{-1}). The mean heavy metal contents in the sediment core at S3 were considerably higher than

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those from the other cores. S3 site located at the ending flow out of Thai Nguyen city which received tributes containing wastewater from industrial and domestic activities of the city. Heavy metals in domestic and industrial waste water might contribute to the accumulation of heavy metals in sediment corers.

Table 1. Heavy metal concentration [mg/L] in sediment cores in Cau River

Site	Fe[a]	Cu	Pb	Zn	Cr	As	Cd
S1	10,032±3,028[b]	18.7±7.85	25.4±7.93	48.2±10.2	18.2±4.80	11.2±7.56	0.56±0.64
S2	9,368±2,652	18.0±7.02	54.7±39.3	80.4±76.6	12.1±3.89	14.3±11.4	1.42±0.47
S3	22,701±2,660	51.2±8.55	85.5±44.3	150±32.9	36.2±9.49	32.3±7.93	1.74±0.37
S4	8,878±1,810	16.0±3.67	34.8±8.54	52.4±13.3	13.6±2.51	10.16±1.14	1.05±0.44
S5	8,920±4,077	16.0±7.90	32.1±11.8	58.6±26.6	12.4±6.63	10.4±4.42	1.29±0.41

[a] all the values of item are basis on dry weight of sediment

[b] mean ± standard deviation

Fig. 2 showed the distribution of heavy metals in the sediment core. At S1 site, except for Cd, the distribution of the other 5 metals was quite similar where their concentration increased from the first layer (0-5cm) to the second layer (5-10cm) and then gradually decreased then increased again at the 20-25cm deep layer. At S2, Cu, Zn, and Cr revealed similar trend: highest at the upper layer (0-5cm) then decreased with increasing depth. For Pb, As, Cd the highest level found at 5-10cm layer, the 25-30 cm layer and the 10-15cm layer, respectively. Similar variation pattern of heavy metals was found at S3 and S4, where concentration of metals increased from upper layer (0-5cm) to the second layer (5-10cm), then decreased increasing the sediment depth except for Cd. At S5, Cu, Cr, and As were fairly consistent, in which the concentration sharply decreased from layer at the 0-5cm to the 5-10 cm layer then gradually decreased.

The spatial and vertical distributions of heavy metal concentrations in the five sediment cores varied substantially, probably because of the different hydrodynamic mechanisms, discharge source and characteristics of sediment cores.

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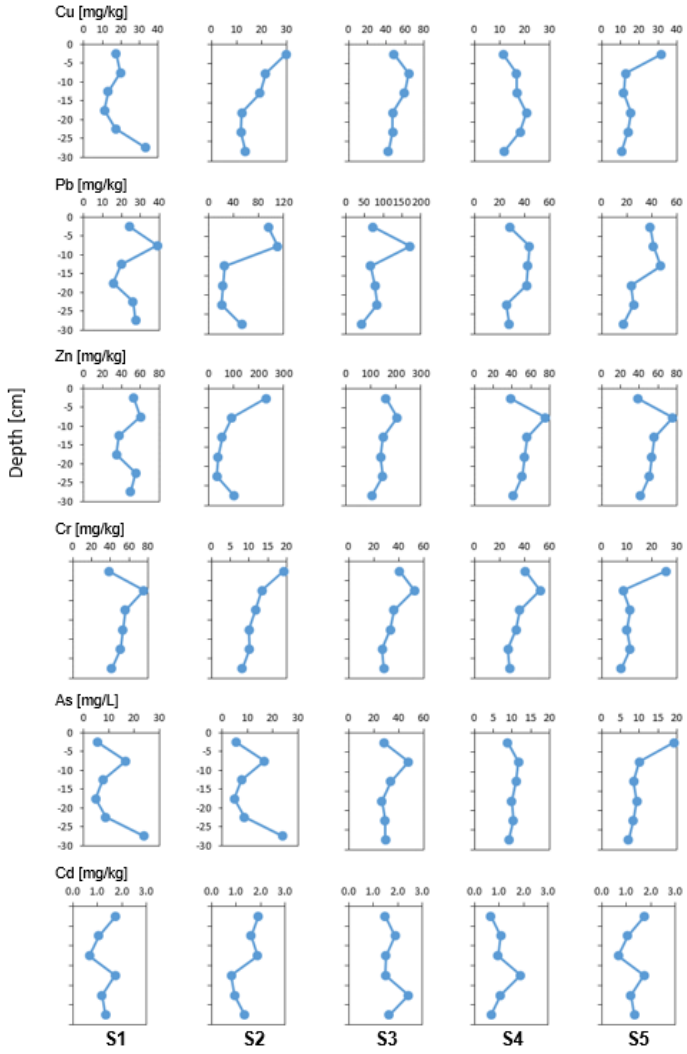

Figure 2. Heavy metal concentration at different sediment depth in Cau River

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3.2. Contamination of heavy metals in sediment cores

In this study, the level of heavy metal contamination was assessed using three types of indices namely, EF, *I*geo, and PLI. An EF value can be used to distinguish whether the heavy metals come from anthropogenic activities (EF>1) or from nature (EF≤1) [18, 19]. Furthermore, EF < 1 indicates no enrichment, 1 - 3 is minor enrichment, 3 - 5 is moderate enrichment, 5 - 10 is moderately severe enrichment,

10 - 25 is severe enrichment, 25 - 50 is very severe enrichment, and > 50 is extremely severe enrichment [20]. In Cau river sediment, the calculated EF of 5 investigated metals were larger than 1 except for Cr (Fig.3) which revealed that Cr was of natural origin while the remaining 5 metals (Cu, Pb, Zn, As, Cd) were derived primarily from human activities. From Fig. 3 the enrichment of heavy metals in the sediment cores of Cau river could be divided into three groups. Cr and Cu was classified the levels were approximately at natural background values meaning no or minor enrichment, Zn was in the range of moderate enrichment, Pb fell into the severe enrichment category and notably, As and Cd were categorized as very severe enrichment. There was no significantly difference in the metal enrichment level among the sediment cores along the investigated section of the river. As mentioned in the previous section, Cau river basin includes the whole Thai Nguyen province which is a densely populated area and is the center of industrial activities in the Northern of Vietnam. Therefore, the observed contamination might be primarily derived from industrial activity.

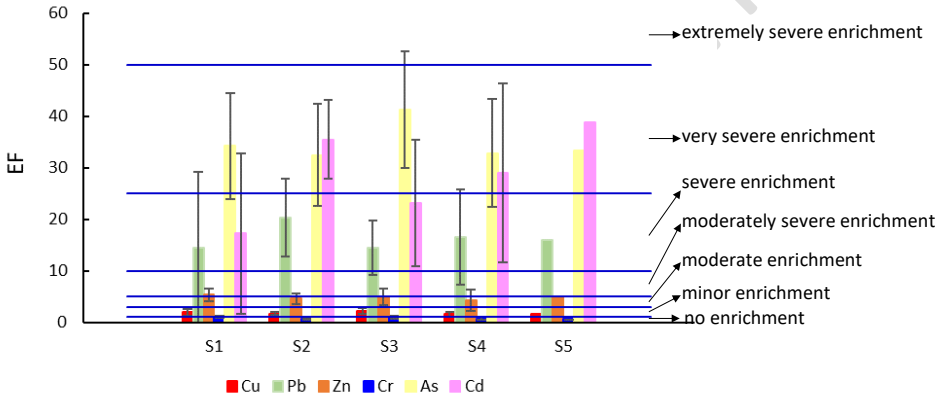

Figure 3. Enrichment factor (EF) of heavy metals in sediment core of Cau river

I_{geo}, a quantitative index to assess heavy metal contamination and can be classified as: $I_{geo} \leq 0$: practically uncontaminated; $0 < I_{geo} \leq 1$: uncontaminated to moderately contaminated; $1 < I_{geo} \leq 2$: moderately contaminated; $2 < I_{geo} \leq 3$: moderately to heavily contaminated; $3 < I_{geo} \leq 4$: heavily contaminated; $4 < I_{geo} \leq 5$: heavily to extremely contaminated; and $I_{geo} > 5$: extremely contaminated [13]. Fig.4 showed the results of calculated I_{geo} for sediment cores collected in Cau river. The degree of heavy metal contamination in the sediment of S3 core was higher than those of the other 4 sampling sites. In S3 core, As was at the strongly contaminated, Cd was at moderately to strongly contaminated level, and Pb was at moderately contaminated level. Recorded levels of contamination were consistent with the discharge to the river. S3 sampling location was at the downstream of Thai Nguyen city where there was a concentration of discharge from domestic and industrial wastewater. Consequently, there might be an accumulation of heavy metal in the river sediment. Among investigated metals, observed Cr, Cu and mostly of Zn exhibited uncontaminated

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level while As and Cd was in the condition of moderately to strongly contaminated. Pb mainly found uncontaminated to moderately contaminated.

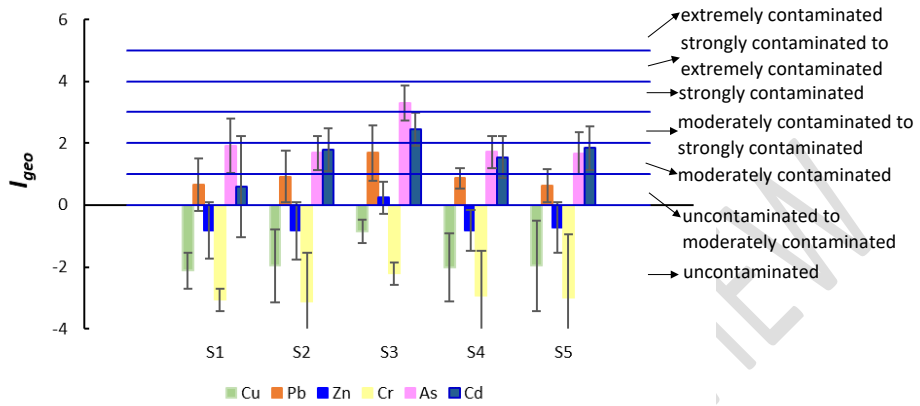

Figure 4. Geo-accumulation index (I_{geo}) of heavy metals in sediment core of Cau river

PLI provides a comprehensive assessment of heavy metal contamination in sediment [14] PLI ≥1 indicates that the sediment contaminated by heavy metal while PLI<1 indicates an uncontaminated condition. Fig. 5 shows the PLI values corresponding to the depth of sediment cores and the contribution the investigated metals to PLI. S3 core revealed the most contaminated level with the PLI varied in the range of 2.3-4.3. At the other four cores, the observed PLI were from 0.6 to 2.5. At cores S2, S3, S5, PLI presented a slightly decreasing trend from the upper to the lower layers of sediment, in which highest PLI was observed at the 0-5cm depth for S2 and S5, and at the depth of 5-10cm for S3. For core S4, PLI slightly fluctuated through the sediment depth and was from 0.9 to 1.4. Generally, the contribution of investigated heavy metals to the PLI was in the order of As>Cd>Pb>>Zn>Cu>Cr. As and Cd contributed to 58-86% in PLI while the three metals including Cu, Zn, Cr contributed to 5-17% in PLI.

Thus, the three indices EF, I_{geo}, and PLI led to similar conclusions regarding the contamination of investigated heavy metals in sediment core in Cau river. Except for S3 site, the sediments in Cau river were slightly contaminated with heavy metals. At S3 where discharge from main activities of the area, the sediment was found to be strongly contaminated with heavy metals.

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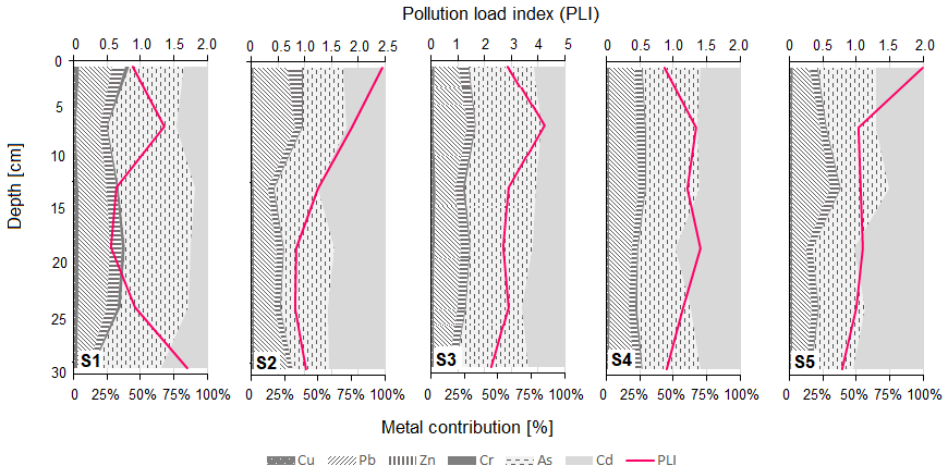

Figure 5. Pollution load indices (PLI) for six heavy metals and their contributions in sediment cores of Cau river

3.3. Potential ecological risk of heavy metals in sediment

Fig. 6 presented the distribution of the mean ΣTU and RI calculated from investigated heavy metals in the studied sites. The sum of toxic units (ΣTU) is an index to evaluate the potential acute toxicity of heavy metals in sediment [15]. Similar to RI, S3 exhibited the highest ΣTU. The distribution of ΣTU of sediment cores was in the order S3>S2>S5>S4>S1. Pb, Zn, As, Cd acted as major contributors to the ΣTU.

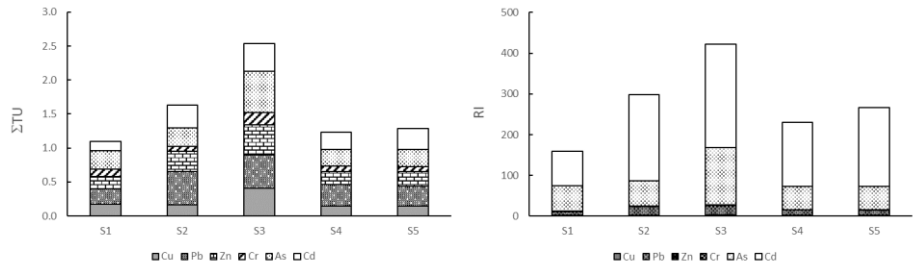

Figure 6. Distribution of the total toxic unit (ΣTU), and potential ecological risk index (RI) values in sediment cores of Cau river

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The estimation of RI was used to comprehensively assess the ecological risks caused by heavy metals [17]. Potential ecological risk is classified into the 4 categories according to the estimated RI value: low ecological risk (RI < 150), moderate ecological risk (RI: 150 – 300), considerable ecological risk (RI: 300 – 600), and very high ecological risk (RI ≥ 600). The mean RI values of the five sediment cores varied from

160 to 423 with the highest value observed at S3 (423). In general, sediments at S1, S2, S4, and S5 were of moderate ecological risk, while considerable risk was observed at S3. Contribution of individual heavy metals to the RI was mainly associated to Cd and As with the percentage of 52.9-72.5% and 21.7-39.0%, respectively.

CONCLUSIONS

In this study, the vertical distribution, contamination and ecological risk of heavy metals in the sediment cores of Cau River section flowing through Thai Nguyen were investigated. Based on the observed monitoring data, the main findings were as follows:

The mean concentration of investigated heavy metal varied in the range of 0.56-1.74 mg kg^{-1} for Cd; 10.2–32.3 mg kg^{-1} for As; 12.1-36.2 mg kg^{-1} for Cr; 16.0–51.2 mg kg^{-1} for Cu; 24.5-85.5 mg kg^{-1} for Pb, and 48.2–151 mg kg^{-1} for Zn. S3 was the site of the highest observed level of metals. The vertical patterns of the investigated heavy metals in investigated sediment cores were stable,

The calculated indices EF, I_{geo}, and PLI revealed consistent results on heavy metal contamination. Among the six investigated heavy metals, Cr was of natural origin while the remaining 5 metals (Cu, Pb, Zn, As, Cd) were derived primarily from human activities. Among the 5 investigated cores, core S3 exhibited severe enrichment and strong contamination of heavy metals as a results of discharge from main activities of the area, the sediment. At the other 4 cores (S1, S2, S4, S5) the sediments were slightly contaminated with heavy metals. As and Cd were the two metals that had high enrichment and were the main contributing component to the pollution load index of heavy metals in the sediment of Cau river.

The potential risk assessment showed that the highest contaminated site S3 was classified as considerable risk while the other sites of S1, S2, S4, and S5 posed moderate ecological risk.

The obtained results provided detailed information regarding the heavy contamination in Cau river sediment and raised the necessity of a proper management measure for controlling heavy metals discharge into Cau river in general and at site 3 specifically.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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