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ASSESSMENT OF HEAVY METAL POLLUTION IN THE SURFACE WATER OF THE DOI CANAL, THE CHO DEM AND BEN LUC RIVERS, VIETNAM

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ABSTRACT

The Doi Canal and the Cho Dem and Ben Luc Rivers play the key roles in irrigation, navigation and ecological restoration. It is important to clearly identify the pollution, influencing factors, ecological risks and possible sources of heavy metals in the surface water of this river system. The surface water of 7 sampling sites was collected over 7 consecutive periods from April 2019 to October 2021. Each surface water sample was analyzed for 9 heavy metals including Fe, Mn, Cr, Zn, Cu, Pb, Cd, Ni, As. Sampling and sample handling techniques were performed based on the Standard Methods for the Examination of Water and Wastewater. Among all nine heavy metals examined in the study area, the concentrations of Fe (1.00 ÷ 5.06 mg/L) and Mn (0.14 ÷ 0.28 mg/L) were the highest and the concentrations of Cr, Cd and As were below the lower limit of detection. The results showed that the average Fe and Mn contents both exceeded the permissible thresholds of the National technical regulation on surface water quality (QCVN 08-MT: 2015/BTNMT). Additionally, the content of Fe, Mn, Zn, Cu, Pb, Ni did not meet the water quality standards for aquatic life (United State Environmental Protection Agency).

Keywords: Distribution; Heavy metal pollution; River; Surface water; Water quality protection.

1 INTRODUCTION

The Doi Canal and the Cho Dem and Ben Luc Rivers has a length of about 30 km, a width of 30 ÷ 70 m, a depth of 3 ÷ 7 m. This river system is one of the important inland waterways connecting Ho Chi Minh City with Long An province (Mekong Delta). This river system plays an important role in irrigation, transportation and ecological restoration. Among the inorganic pollutants of river water, heavy metals have drawn significant attention on their non-biodegradable nature and often accumulate at tropical areas causing harmful biological effects [1]. Heavy metal pollution levels in aquatic ecosystems are of urgent concern because of their persistence, environmental toxicity, and bioaccumulation. The aquatic environment receives heavy metals in untreated or inadequately treated wastewater from domestic, industrial, agricultural and navigation sources [2]. Man-made activities such as mining, final disposal of treated and untreated wastes containing toxic metals as well as metal chelates [3] from industries such as steel mills, battery industry, thermal power plants, etc. and also the indiscriminate use of fertilizers and pesticides containing heavy metals in agriculture led to the deterioration of water quality causing serious environmental problems threatening human health [4] and aquatic ecosystem [5, 6].

Sankar et al. [7] stated that the concentrations of different metals, such as Chromium (Cr), Manganese (Mn), Cobalt (Co), Nickel (Ni), Cooper (Cu), Zinc (Zn), Lead (Pb), Cadmium (Cd). Mercury (Hg) and Arsenic (As) increased sharply in coastal areas due to agricultural and domestic waste; guidelines for waste treatment from industries such as metal plating; penetration of organic and inorganic chemicals; metal leaching from solid waste; and the use of metals and metal components. Concentrations of heavy metals in water and fish from the Yamuna River at

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Allahabad have found that Pb and Cu are above the WHO allowable limits, indicating a hazardous risk to human health, while Arsenic was detected below the allowable limit [7]. In Vietnam, temperature, pH, dissolved oxygen (DO), conductivity, salinity, chlorophyll-a, phaeopigments, concentration of suspended particulate matter (SPM), particle size distribution, nutrients, carbon and dissolved and granular organic phosphorus, and trace metal concentrations (Cr, Ni, Cu, Zn, As, Cd, Pb, Hg and MMHg) were measured at 17 sites along the Saigon River in the country (filtered and suspended matter) and sediment. This study showed that the water quality of the Saigon River was moderately polluted, in which the discharge sources containing significant heavy metal concentrations have been identified [8].

The Doi Canal and the Cho Dem and Ben Luc Rivers received heavy metals in untreated or inadequately treated wastewater from domestic, industrial, agricultural and waterway sources. It was very important to monitor and assess the current pollution status, influencing factors, ecological risks and possible sources of heavy metals in surface water of this river system. This topic was very important to determine the level of heavy metal pollution in this river system. The results contributed to providing information and data for local authorities on heavy metal parameters as well as pollution levels of the Doi Canal and the Cho Dem and Ben Luc Rivers.

2 MATERIALS AND METHODS

2.1. Study area

Data from about 70 km^2 with length of 30 km were used as representative samples for the study areas. Water samples for heavy metal analysis (Iron, Manganese, Chrome, Zinc, Copper, Lead, Cadmium, Nickel and Arsenic) at 7 sites were taken in 7 periods in April and October (2019, 2020); April, June and October (2021) (see Fig. 1; Tab. 1).

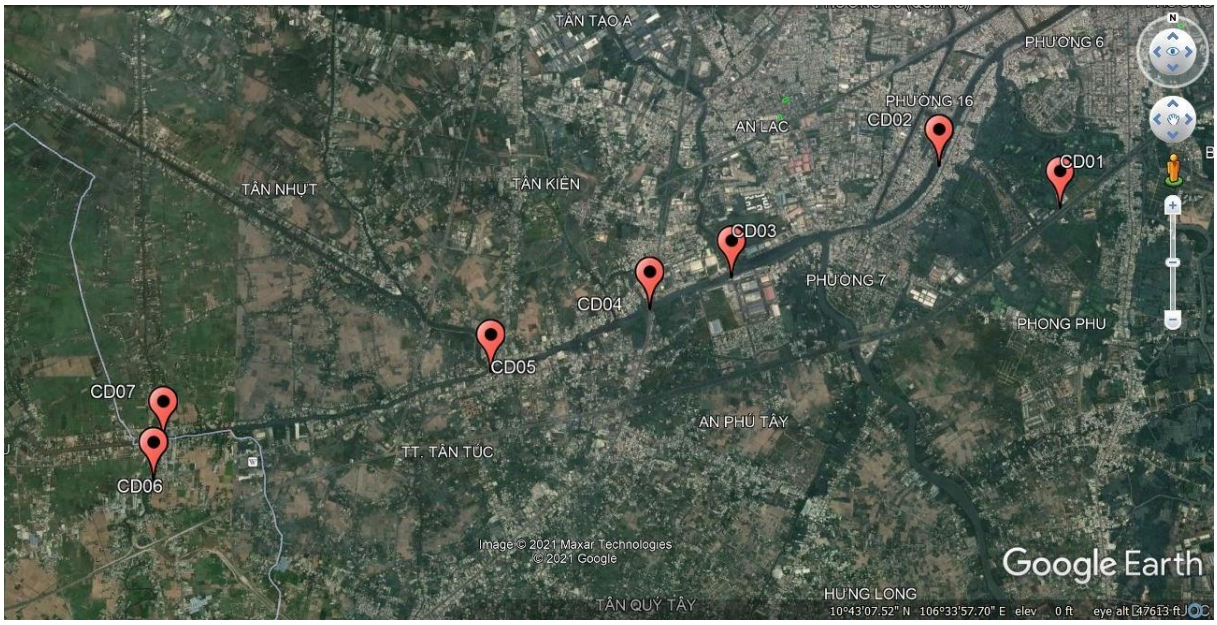

Figure 1. *Study area of heavy metal concentrations with 7 sampling sites*

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Table 1. *Coordinates and locations of the sampling sites in study area*

Sites	Local Names	Longitude (N)	Latitude (S)
CD01	Ba Lon Creek flows into Doi Canal (near Residential Area 13C)	10°42'48.05" N	106°38'49.51" E
CD02	Doi Canal at 16 Ward, District 8 (near River Wharf)	10°43'06.17" N	106°37'57.22" E
CD03	Binh Dien River (near Binh Dien Market)	10°42'18.03" N	106°36'25.97" E
CD04	Binh Dien River (near Binh Dien Bridge)	10°42'04.67" N	106°35'50.39" E
CD05	Binh Dien River (near Cai Tam Bridge)	10°41'37.99" N	106°34'41.70" E
CD06	My Nhan Creek flow into Ben Luc River (near Tan Bua Ferry Station)	10°40'52.58" N	106°32'17.54" E
CD07	Ben Luc River (near Tan Bua Ferry Station)	10°41'09.70" N	106°32'21.22" E

2.2. Sample collection

Water samples for on-site particulate metal analysis were taken in accordance with the standards of TCVN 6663 – 1:2011 (ISO 5667 – 1:2006) *Water quality – Sampling – Part 1: Guidance on the design of sampling programmes and sampling techniques*; and, TCVN 6663 – 3:2008 (ISO 5667 – 3:2003) *Water quality – Sampling – Part 3: Instructions for sample storage and handling* [9, 10]. All samples were collected in clean, 2.0-litre polyethylene bottles, pre-washed with 10% nitric acid and deionized water. Prior to sampling, the bottles were rinsed at least three times with water from the sampling site. Sample locations at each point were taken in the middle of the river with a surface water depth of 30 ÷ 40 cm [10-12]. All water samples were immediately brought to the laboratory.

2.3. Analytical methods

The standard methods of heavy metals and their analytical methods were presented briefly in Tab. 2.

Table 2. *Parameters and methods of water quality analysis*

No.	Parameters	Unit	Methods	QCVN 08-MT: 2015/BTNT	
				A1	B1
1	Fe	mg/L	TCVN 6177:1996	0.5	1.5
2	Mn	mg/L	SMEWW 3111B:2017	0.1	0.5
3	Cr	mg/L	TCVN 6222:2008	0.05	0.5
4	Zn	mg/L	TCVN 6193:1996	0.5	1.5
5	Cu	mg/L	SMEWW 3111B:2017	0.1	0.5
6	Pb	mg/L	SMEWW 3111B:2017	0.02	0.05
7	Cd	mg/L	SMEWW 3111B:2017	0.005	0.01
8	Ni	mg/L	SMEWW 3111B:2017	0.1	0.1
9	As	mg/L	US EPA Method 2008	0.01	0.05

Notes: A1 Level (water quality for domestic water supply and aquatic life conservation); B1 (water quality for irrigation and drainage purposes)

Samples were acidified with 2 mL of concentrated Nitric acid to prevent precipitation of metals, reduce adsorption of analyst to vessel walls and to avoid microbial activity, then aqueous samples were preserved at 2°C until analysis. Surface water samples were filtered through a milipore filter using 0.45 µm Whatman filter paper. If the concentration exceeded the calibration curve, the samples were appropriately diluted and acid was added to measure the sample. Samples for heavy metal analysis were measured in the Inductively Coupled Plasma Optimal Emission Spectrometer [13].

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2.4. Data analysis

The obtained data were subjected to a statistical analysis to check the analysis of variance (ANOVA) and the correlation between all parameters using R statistical software. Map of the study area and Sampling locations were applied using Google Earth.

3 RESULTS AND DISCUSSIONS

3.1. Heavy metal concentrations in river water

Fe, Mn, Cu, Ni, Zn, Pb, Cr, Cd and As concentrations have been detected in the surface water at seven different locations of seven periods on the Doi Canal and the Cho Dem and Ben Luc Rivers during 2019, 2020 and 2021 were detected and recorded in Tab. 3.

Table 3. *Heavy metal concentrations in the surface water of the study area*

Parameters	**Sampling Sites**						
(mg/L)	**CD01**	**CD02**	**CD03**	**CD04**	**CD05**	**CD06**	**CD07**
Fe (mg/L)							
Range	1.01÷1.16	2.38÷3.63	2.72÷5.04	1.65÷2.11	1.21÷2.85	1.05÷1.84	1.06÷2.04
Mean	1.06	3.25	3.59	1.91	1.78	1.36	1.68
Mn (mg/L)							
Range	0.14÷0.19	0.24÷0.27	0.22÷0.28	0.16÷0.23	0.16÷0.22	0.16÷0.19	0.16÷0.18
Mean	0.16	0.25	0.24	0.20	0.19	0.17	0.17
Cu (mg/L)							
Range	0.029÷00.34	0.057÷0.078	0.038÷0.081	0.032÷0.065	0.026÷0.070	0.051÷0.062	0.040÷0.058
Mean	0.031	0.062	0.053	0.045	0.047	0.056	0.049
Ni (mg/L)							
Range	0.029÷0.037	0.043÷0.057	0.034÷0.053	0.031÷0.043	0.025÷0.038	0.026÷0.033	0.025÷0.030
Mean	0.033	0.049	0.44	0.037	0.031	0.029	0.028
Zn (mg/L)							
Range	0.026÷0.034	0.048÷0.056	0.045÷0.068	0.030÷0.041	0.026÷0.030	0.026÷0.032	0.026÷0.034
Mean	0.029	0.052	0.054	0.036	0.028	0.030	0.029
Pb (mg/L)							
Range	0.008÷0.010	0.010÷0.012	0.008÷0.012	0.008÷0.010	0.008÷0.010	0.008÷0.012	0.08÷0.010
Mean	0.009	0.011	0.011	0.009	0.010	0.010	0.010
Cr (mg/L)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Cd (mg/L)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
As (mg/L)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005

Tab. 3 showed that the average concentrations of most heavy metals were observed in descending order Fe > Mn > Cu > Ni > Zn > Pb > Cr, Cd, As compared with the concentrations of heavy metals (Mn > Cu > Ni > Zn > Pb) were within the allowable limit of the National technical regulation on surface water quality for QCVN 08-MT: 2015/BTNMT at the B1 Level [14]. In particular, the concentration of heavy metals such as chromium, cadmium and arsenic has not been detected in water samples at this system. While the average iron (Fe) content exceeded the allowable threshold of the National technical regulation on surface water quality for QCVN 08-MT: 2015/BTNMT at the B1 Level. In addition, the average concentrations of Fe, Mn, Cu, Ni, Zn and Pb were all higher than the values above the allowable limits of the National technical regulation on surface water quality for QCVN 08-MT: 2015/BTNMT at the A1 Level [15]. Human activities could be the main source of heavy metals in surface water of the Doi Canal and the Cho Dem and Ben Luc Rivers.

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3.2. Spatial distribution of heavy metal concentrations in river water

The concentration of different metals in river water orders as follows: Fe > Mn > Cu > Zn > Ni > Pb (Fig. 2). The results showed that the heavy metals iron and zinc had the highest concentrations at the CD2 and CD3 sites. The next concentration is shown at the CD4 position and the lowest concentration at the CD1 site. The results showed that the iron and zinc had the highest concentrations at the CD2 and CD3 sites. The next concentration indicated in the site CD4, and the lowest concentrations in site CD1. The results of concentrations of lead and nickel fluctuated similar to the concentrations of in manganese and copper. While the concentrations of chromium, cadmium and arsenic were lower than the lower the limit of detection (Fig. 2). These results were quite similar to the heavy metal pollution study in the Lake Manzal, Egypt [16] which showed that the concentrations of different metals in water, plankton and fish tissue follow the same order: Zn > Cu > Pb> Cd. The average concentrations of metals in water were as follows: Cu, 0.055; Zn, 0.311; Cd, 0.020; and Pb, 0.022 mg/L.

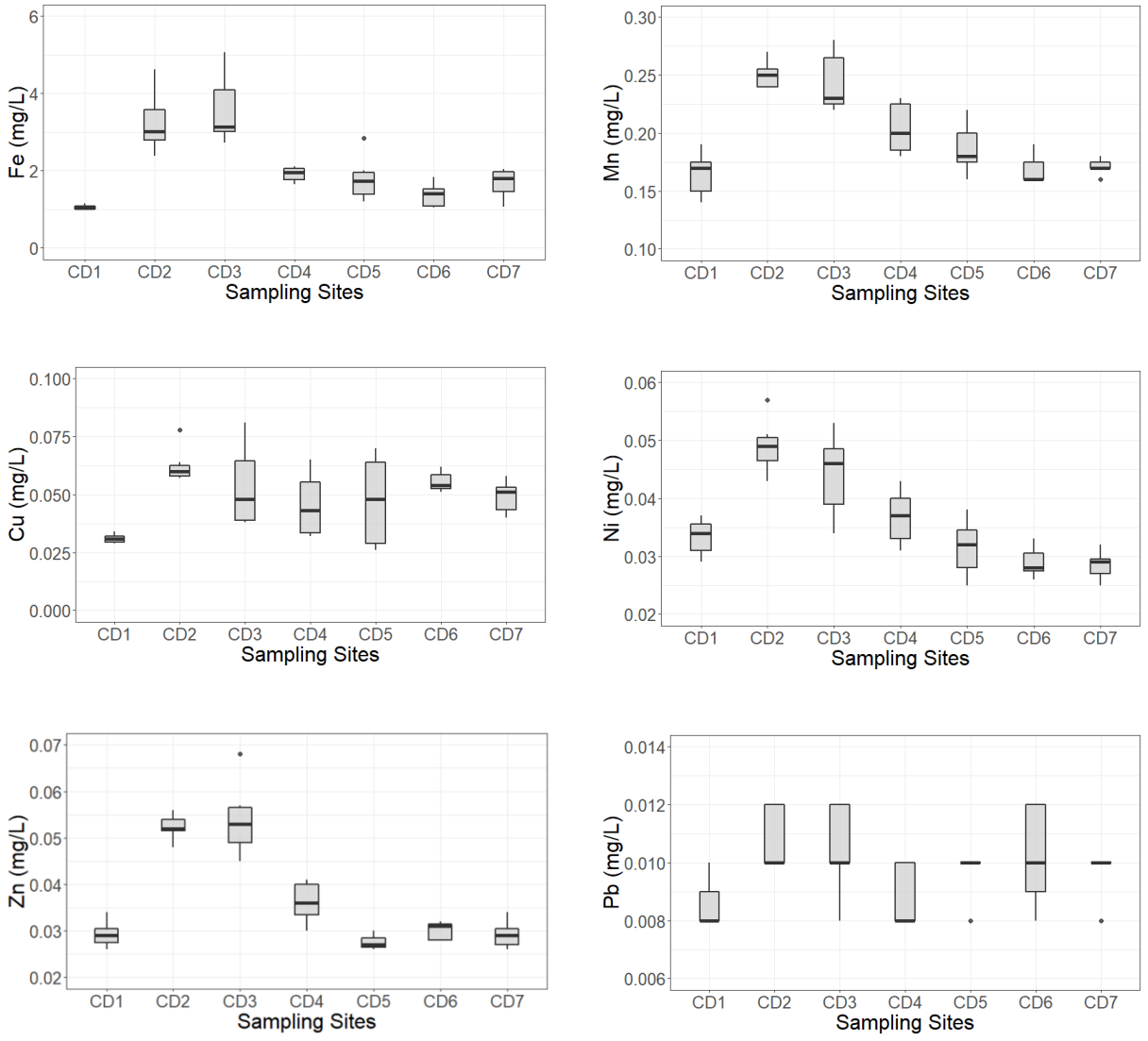

Figure 2. *Heavy metals measured in the 7 sampling sites at the study area*

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Among the six heavy metals identified above, the seasonal variation was not significant. This needed to be observed further to provide a clear understanding of the characteristics of seasonal variations in heavy metal concentrations. Tran et al. (2020) suggested that the total metal concentration in the sea water of the Saigon – Dong Nai estuaries in the rainy season was higher than in the dry season [17]. The increase in rainfall over the Saigon – Dongnai River Basin during the transition period mobilized both dissolved and granular metals (Fe, Cr, Ni, and Pb) from terrestrial to aquatic environments [18]. In addition, Raji et al. (2016) indicated that the concentrations of heavy metals monitored in the Sokoto River in Northwestern Nigeria were generally higher in the dry season than during the wet season [19]. The distribution of heavy metals could also be affected by the properties of the heavy metals and by fluctuations in the water flow.

3.3. Correlation analysis

Pearson's correlation was performed on the data set summarizing the average values of surface water of the study area based on significant levels (p=0.05). Correlation analysis was performed for the association between metals and intrametals to understand the significance of the association between metals and samples. Surface water has a positive correlation between Fe-Mn (0.79), Fe-Zn (0.82), Fe-Cu (0.42), Fe-Pb (0.46), Fe-Ni (0.64); Mn-Zn (0.81), Mn-Cu (0.41), Mn-Pb (0.40), Mn-Ni (0.76); Zn-Cu (0.48), Zn-Pb (0.35), Zn-Ni (0.87); Cu-Pb (0.39), Cu-Ni (0.51); and Pb-Ni (0.25). (Fig. 3). This would help to understand the nature of these metals and their species characteristics in aquatic environments.

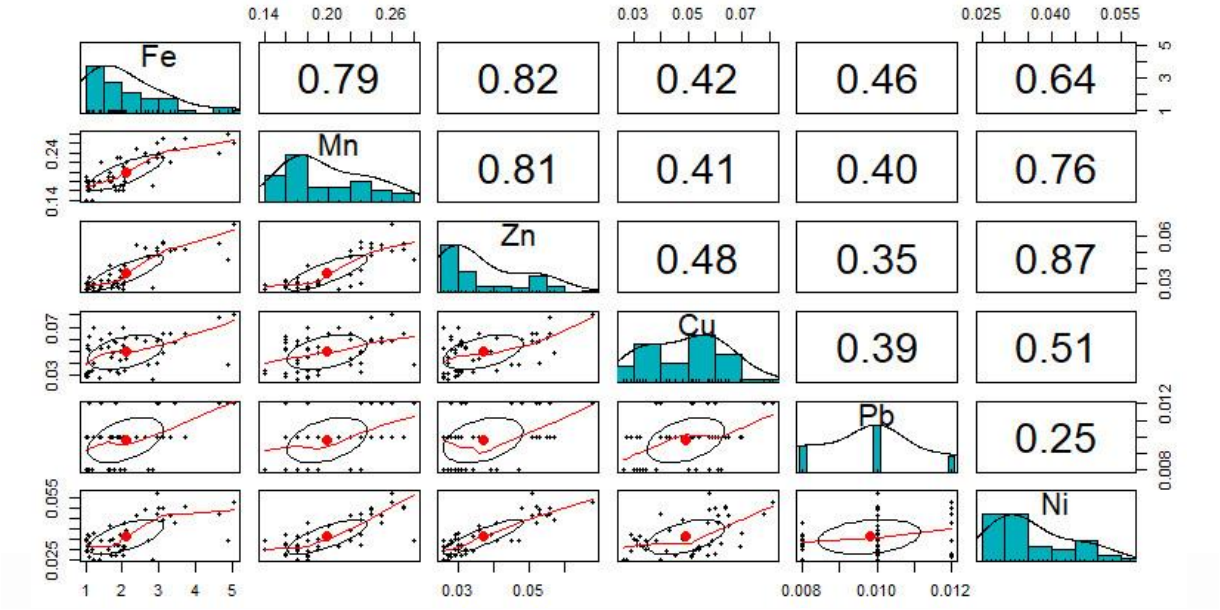

Figure 3. *Relationship among heavy metal concentrations in the study area*

Among the nine heavy metals, there are six parameters that were evaluated according to the results of correlation analysis, including Fe, Mn, Zn, Cu, Pb, Ni (Fig. 3). Among heavy metals, a significant positive correlation was observed between Fe, Mn, Zn and Ni (0.64 ÷ 0.87), while Cu exhibited a significant positive correlation with Ni (0.51). Cu and Pb showed a not too strong correlation with Fe, Mn, Zn and Ni (0.25 ÷ 0.48) (Fig. 3). This could help to understand the nature of these metals and their species characteristics in aquatic environments. Similar to the study of Kar et al (2008), it could be concluded that such river water was not suitable for drinking purpose due to the inappropriate concentrations of Fe, Mn, Zn, Cu and Ni and it could not be suitable for irrigation due to the excess concentration of Fe and Mn [1]. Different from the results of Strady et al., (2017), this study did not show a correlation between Fe and As as well as Fe and Ni [8].

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4 CONCLUSIONS

The results showed the spatial homogeneity of heavy metals in surface water of studied rivers. Among all nine heavy metals examined in the study area, the concentrations of Fe (1.00 ÷ 5.06 mg/L) and Mn (0.14 ÷ 0.28 mg/L) were the highest, and the lowest concentrations of Cr, Cd and As (under the limit of detection). The results showed that the average Fe and Mn contents both exceeded the permissible thresholds of the National technical regulation on surface water quality (QCVN 08-MT: 2015/BTNMT). While the concentrations of Fe, Mn, Zn, Cu, Pb, Ni did not meet the water quality criteria for aquatic life (United State Environmental Protection Agency).

Among the six heavy metals identified above, the seasonal variation was not significant. This needs to be observed further to provide a clear understanding of the characteristics of seasonal variations in heavy metal concentrations. Among the heavy metals, a significant positive correlation was observed between Fe, Mn, Zn and Ni Fe, Mn, Zn and Ni (0.64 ÷ 0.87), while Cu exhibited a significant positive correlation with Ni (0.51). Additionally, Cu and Pb showed a not too strong correlation with Fe, Mn, Zn and Ni (0.25 ÷ 0.48). This could help to understand the nature of these metals and their species characteristics in aquatic environments.

Although some heavy metals have been found to be beneficial to humans and organisms to a certain extent, it could be harmful to a certain extent. Therefore, the appropriate water treatment measures need to be taken immediately to remove heavy metal loads from industrial wastewater and renovate wastewater treatment plants as well as monitor water quality for the human health protection.

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