Assessment of Heavy Metal Pollution in the Surface Water of the Doi-Cho Dem-Ben Luc Rivers, Vietnam

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Abstract

Heavy metals are a pressing concern in terms of their pollution in aquatic ecosystems because of their persistence, environmental toxicity, bioaccumulation. Aquatic environments receive heavy metals in untreated or inadequately treated wastewater from domestic, industrial, agricultural, and navigation sources. The Doi-Cho Dem-Ben Luc Rivers play the key roles of irrigation, navigation and ecological restoration. It is crucial to ascertain the pollution status, influencing factors, ecological risks, and possible sources of heavy metals in the surface water of the Doi-Cho Dem-Ben Luc Rivers. In this study, surface water from 7 sampling sites over was collected from the Doi-Cho Dem-Ben Luc Rivers, over 7 consecutive periods from April 2019 to October 2021. Each surface sample was analyzed for 9 heavy metals including Fe, Mn, Cr, Zn, Cu, Pb, Cd, Ni, As. The sampling technique and sample treatment were done based on the Standard Methods for the Examination of Water and Wastewater. The time and space variation of heavy metal concentrations were examined to test the analysis of variance (ANOVA) and correlation among all the parameters using R statistical software.

The results suggest a spatial homogeneity of heavy metals in the surface water the studied rivers. Among all nine examined heavy metals in the studied area, the concentrations of Fe (1.00 ÷ 5.06 mg/L) and Mn (0.14 ÷ 0.28 mg/L) are the highest, and the concentrations of Cr, Cd and As are the lowest that lower limit of detection. The results suggested that the mean concentrations of Fe and Mn were above the acceptable limits of the National technical regulation on surface water quality (QCVN 08-MT: 2015/BTNMT). While the concentrations of Fe, Mn, Zn, Cu, Pb, Ni do not meet the Water quality criteria for aquatic life (United State Environmental Protection Agency). Anthropogenic activities can be the main source of heavy metals in in the surface water of the Doi-Cho Dem-Ben Luc Rivers. Among the heavy metals, a significant positive correlation was observed between Fe, Mn, Zn and Ni (0.64 ÷ 0.87), whereas Cu exhibited a significant positive correlation with Ni (0.51). While Cu and Pb showed a not too strong correlation with Fe, Mn, Zn and Ni (0.25 ÷ 0.48). The distribution of heavy metals may also be influenced by properties of heavy metals and fluctuations in water flows. The results provide guidance for controlling heavry metal pollution and protectting water sources in the Doi-Cho Dem-Ben Luc Rivers.

Keywords: *heavy metal pollution, surface water, distribution, river, Doi-Cho Dem-Ben Luc, water quality protection*

1. Introduction

The Doi-Cho Dem-Ben Luc Rivers has a length of about 30 km with a width of from 30 to 70 m and a depth of 3 ÷ 7 m. It's one of an important inland waterway that connects HCMC with Long An Province (Mekong Delta). The Doi-Cho Dem-Ben Luc rivers play an important role in irrigation, transportation and ecological restoration. Among the inorganic pollutants of river water, heavy metals are gaining importance because of their non-biodegradable nature and often accumulate at tropical levels causing harmful biological effects [1]. Heavy metals are a pressing concern in terms of their pollution in aquatic ecosystems because of their persistence, environmental toxicity, bioaccumulation [2]. Anthropogenic activities like mining, ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates [3] from different industries steel plants, battery industries, thermal power plants etc. and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing threat on human beings [4] and sustaining aquatic biodiversity [5, 6].

Sankar et al (2018) claimed that The concentrations of different metals, like Chromium (Cr), Manganese (Mn), Cobalt (Co), Nickel (Ni), Cooper (Cu), Zink (Zn), Lead (Pb), Cadmium (Cd), Mercury (Hg) and Arsenic (As) were highly increasing in coastal areas due to the discharge of agricultural and domestic wastes; intrusion of wastes from industries like metal plating; entry of organic and inorganic chemicals; leaching of metals from solid waste; and use of metal and metal components [7]. Heavy metal concentrations in water and fish from River Yamuna, at Allahabad were found that Pb and Cu were higher than the permissible limits of WHO, that gives an indication of hazardous risk to human health. Whereas Arsenic was detected lower than the permissible limit (Kumar et al., 2014). In Vietnam, the temperature, pH, dissolved oxygen (DO), conductivity, salinity, chlorophyll-a, phaeopigments, suspended particulate matter (SPM) concentrations, grain size distributions, nutrients, dissolved and particulate organic carbon and phosphorus, and trace metal(oid) (Cr, Ni, Cu, Zn, As, Cd, Pb, Hg, and MMHg) concentrations were measured at 17 sites along the Saigon River in water (filtered and suspended matter) and sediment. This research showed that the Saigon River remains moderately contaminated albeit the city was proved to be the major contributor of metal(oid)s [8].

The Doi-Cho Dem-Ben Luc Rivers receive heavy metals in untreated or inadequately treated wastewater from domestic, industrial, agricultural, and navigation sources. It is very important to monitor and evaluate the pollution status,

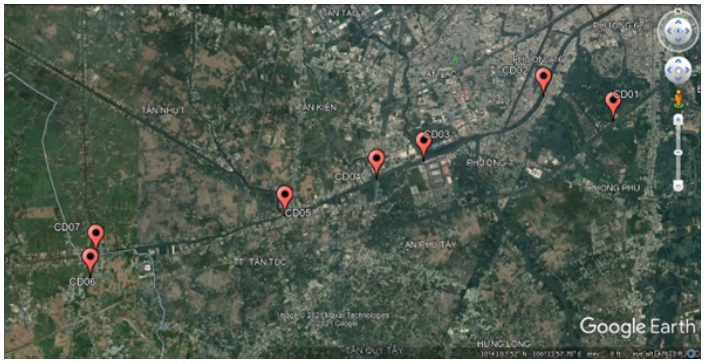

Fig. 1. Study area of heavy metal concentrations with 7 sampling sites (B1-B10)
Rys. 1. Obszar badań koncentracji metali ciężkich z 7 punktami poboru próbek (B1-B10)

Tab. 1. Coordinates and locations of the sampling sites in study area
Tab. 1. Współrzędne i położenie punktów poboru próbek na obszarze badań

Sites	Local Names	Longitude (N)	Latitude (S)
CD01	Ba Lon Creek flows into Doi Canal (near Residental 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

influencing factors, ecological risks, and possible sources of heavy metals in the surface water of the Doi-Cho Dem-Ben Luc Rivers. This topic is crucial identify the levels of heavy metal pollution in the Doi-Cho Dem-Ben Luc Rivers. The results contribute to providing information and data for local authorities on heavy metal parameters as well as pollution levels of this system.

2. Materials and Methods

2.1. Study Area

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

2.2. Sample Collection

The water samples for havey metal analyses in the field were collected according to 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 2.0 litre, clean polyethylene bottles, which were prewashed with 10% nitric acid and de-ionized water. Before sampling, the bottles were rinsed at least three times with water from the sampling site. Sample locations at each site were taken in the middle of the river with a depth layer of surface water of 30–40 cm [10-12]. All water samples were immediately brought to the laboratory.

2.3. Analytical Methods

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

The samples were acidified with 2 mL concentrated Nitric acid to prevent precipitation of metals, reduce adsorption of the analytes onto the walls of containers and to avoid microbial activity, then water samples were stored at 2°C until the analyses. Surface water samples were filtered through milipor filtering unit using 0.45 µm Whatman filter paper. If the concentrations exceeding the calibration curve, the samples were appropriately diluted, and acid was added to measure samples. The samples for heavy metal analysis were measured in the Inductively Coupled Plasma Optimal Emission Spectrometer [13].

2.4. Data Analysis

The obtained data were subject to statistical analysis to test the analysis of variance (ANOVA) and correlation among all the parameters using R statistical software. The maps of the study area and sampling sites were applied using Google Earth.

3. Results and Discussions

3.1. Concentrations of heavy metals in river water

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

Tab. 3 showed that the mean concentrations of almost heavy metals were observed in decreasing order of Fe > Mn > Cu > Ni > Zn > Pb > Cr, Cd, As whereas the concentrations of heavy metals (Mn > Cu > Ni > Zn > Pb) were within the acceptable limits of the National technical regulation on surface

Tab. 2. Parameters and methods of water quality analysis

Tab. 2. Parametry jakości wody i metody oznacznia

No.	Parameters	Unit	Methods
1	Fe	mg/L	TCVN 6177:1996
2	Mn	mg/L	SMEWW 3111B:2017
3	Cr	mg/L	TCVN 6222:2008
4	Zn	mg/L	TCVN 6193:1996
5	Cu	mg/L	SMEWW 3111B:2017
6	Pb	mg/L	SMEWW 3111B:2017
7	Cd	mg/L	SMEWW 3111B:2017
8	Ni	mg/L	SMEWW 3111B:2017
9	As	mg/L	US EPA Method 2008

Tab. 3. Concentrations of heavy metals in the surface water of the study area. Notes: ND is non detect

Tab. 3. Zawartość metali ciężkich w wodach powierzchniowych na badanym terenie. Uwaga: ND nie wykryte

Parameters (mg/L)	Sampling Sites						
	CD01	CD02	CD03	CD04	CD05	CD06	CD07
Fe (mg l^{-1})							
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^{-1})							
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^{-1})							
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^{-1})							
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^{-1})							
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^{-1})							
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^{-1})	ND	ND	ND	ND	ND	ND	ND
Cd (mg l^{-1})	ND	ND	ND	ND	ND	ND	ND
As (mg l^{-1})	ND	ND	ND	ND	ND	ND	ND

water quality for QCVN 08-MT: 2015/BTNMT at the B1 Level (water quality for irrigation and drainage purposes or other uses with similar water quality requirements) [14]. Especially, the concentrations of heavy metals such as chromium, cadmium and arsenic have not been detected in water samples in this system. While the mean concentrations of iron (Fe) were above the permissible limits of the National technical regulation on surface water quality for QCVN 08-MT: 2015/BTNMT at the B1 Level. Moreover the mean concentrations of Fe, Mn, Cu, Ni, Zn and Pb were above concentration of the values than the permissible limits set by the water quality criteria for aquatic life [15].

3.2. Spatial in heavy metal concentrations of river water

The concentration of different metals in river water order as follow: Fe > Mn > Cu > Zn > Ni > Pb (Fig. 2). The results showed that heavy metals of iron and zinc had the highest concentrations in the sites CD2 and CD3. The next concentration indicated in the site CD4, and the lowest concentration in site CD1. The results showed that heavy metals of iron and zinc had the highest concentrations in the sites CD2 and CD3. The next concentration indicated in the site CD4, and the lowest concentration 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 the lowest that lowered the limit of detection (Fig. 2). These results were quite similar to the research of heavy metal pollution in the Lake Manzal, Egypt [16] that showed the concentration of different metals in water, plankton, and fish tissues followed the same order: Zn > Cu > Pb> Cd. The mean concentrations of metals in the water were as follow: Cu, 0.055; Zn, 0.311; Cd, 0.020; and Pb, 0.022 mg/L.

Among the six heavy metals identified above, the seasonal change was not significant. This needs to be further observed to provide a clear understanding of the characteristics of seasonal variations in heavy metal concentrations. While Tran et al. (2020) claimed that the total metal concentrations in the seawater of the Saigon – Dongnai Estuaries were higher during the rainy season than those during the dry season [17]. The increase of rainfall in the Saigon – Dongnai River Basin in the transition time mobilized both dissolved and particulate metals (Fe, Cr, Ni, and Pb) from the terrestrial environment to the aquatic environment [18]. Additionally, Raji et al. (2016) indicated that the concentrations of heavy metals that monitored at the Sokoto River in North-western Nigeria were generally higher in dry season than in the rainy season [19].

3.3. Correlation analysis

Pearson's correlation was performed on the combined data set of average values of the surface water of the studied area based on the significant levels (p=0.05). Correlation analysis was carried out for inter-metallic and intra-metallic association to understand the significance of association among the metals and the samples. The surface water exhibited 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

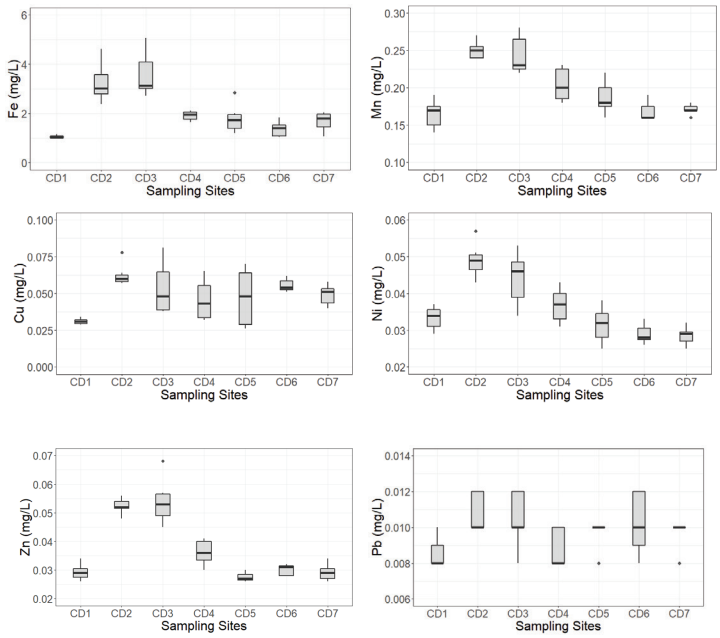

Fig. 2. Heavy metals measured in the 7 sampling sites at the study area
Rys. 2. Zmierzone zawartości metali ciężkich na badanym terenie

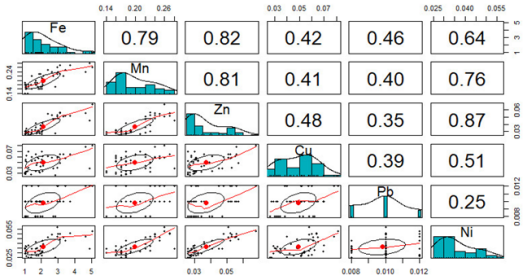

Fig. 3. Relationship among heavy metal concentrations in the study area
Rys. 3. Zależności pomiędzy zawartościami metali ciężkich w badanym terenie

(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 speciation in the aquatic environment.

Among the nine heavy metals, there were six parameters evaluated results to calculate the correlation analysis with each other including Fe, Mn, Zn, Cu, Pb, and Ni (Figure 4). Among the heavy metals, a significant positive correlation was observed between Fe, Mn, Zn and Ni (0.64 ÷ 0.87), whereas Cu exhibited a significant positive correlation with Ni (0.51). While Cu and Pb showed a not too strong correlation with Fe, Mn, Zn and Ni (0.25 ÷ 0.48). This will help to understand the nature of these metals and their species speciation in the aquatic environment (Fig. 4). Similar to the study of Kar et al (2008), it may be concluded that the river water as such is not suitable for drinking purpose due to the inappropriate concentrations of Fe, Mn, Zn, Cu and Ni and it may not be suitable for irrigation due to the excess concentration of Fe and Mn [1]. There was a difference with the results of Strady et al., (2017), this study had not shown the correlation between Fe and As as well as Fe and Ni [8].

4. Conclusions

The results suggested a spatial homogeneity of heavy metals in the surface water the studied rivers. Among all nine examined heavy metals in the studied 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 the lowest that lowered the limit of detection. The results suggested that the mean concentrations of Fe and Mn were above the acceptable limits 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)

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Although some heavy metals have been found to be beneficial to humans and creatures to a certain extent, it can be harmful beyond that. Therefore, the appropriate treatment measures needed be taken to remove heavy metal loads from industrial wastewater and renovate wastewater treatment plants as well as monitor water quality to improve river's water quality and save people's health protection. This helped to understand the nature of these metals and their species speciation in the aquatic environment.

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Ocena zanieczyszczenia metalami ciężkimi wód powierzchniowych rzek Doi-Cho Dem-Ben Luc w Wietnamie

Metale ciężkie stanowią palący problem zanieczyszczenia w ekosystemach wodnych ze względu na ich trwałość, toksyczność dla środowiska i bioakumulację. Środowiska wodne sa zasilane w metale ciężkie z nieoczyszczonych lub nieodpowiednio oczyszczonych ścieków ze źródeł domowych, przemysłowych, rolniczych i żeglugowych. Rzeki Doi-Cho Dem-Ben Luc odgrywają kluczową rolę w nawadnianiu terenów, transporcie odnym i odbudowie ekologicznej. Kluczowe znaczenie ma ustalenie stanu zanieczyszczenia, czynników wpływających, zagrożeń ekologicznych i możliwych źródeł metali ciężkich w wodach powierzchniowych rzek Doi-Cho Dem-Ben Luc. W artykule przedstawiono wyniki badania wód powierzchniowych, próbki pobrano z 7 punktów pomiarowych z rzek Doi-Cho Dem-Ben Luc przez 7 kolejnych okresów od kwietnia 2019 r. do października 2021 r. Każda próbka została przeanalizowana pod kątem zawartości 9 metali ciężkich: Fe, Mn, Cr , Zn, Cu, Pb, Cd, Ni, As. Metodyka pobierania próbek i obróbki próbek zostały opracowane w oparciu o Standardowe Metody Badania Wód i Ścieków. Zbadano zmienność w czasie i przestrzeni stężeń metali ciężkich, do analizyy wyników wykorzystano analizę wariancji (ANOVA) i korelacji między wszystkimi parametrami przy użyciu oprogramowania statystycznego. Wyniki sugerują przestrzenną jednorodność zawartości metali ciężkich w wodach powierzchniowych badanych rzek. Spośród wszystkich dziewięciu badanych metali ciężkich w badanym terenie najwyższe są stężenia Fe (1,00 ÷ 5,06 mg/L) i Mn (0,14 ÷ 0,28 mg/L), a najniższe Cr, Cd i As (wartości odpowiadające dolnej granicy wykrywalności). Wyniki wskazują, że średnie stężenia Fe i Mn były powyżej dopuszczalnych limitów, opisanych w krajowych normach dotyczących jakości wód powierzchniowych (QCVN 08-MT: 2015/BTNMT). Natomiast stężenia Fe, Mn, Zn, Cu, Pb, Ni nie spełniają kryteriów jakości wody dla organizmów wodnych (Agencja Ochrony Środowiska Stanów Zjednoczonych). Działalność antropogeniczna może być głównym źródłem metali ciężkich w wodach powierzchniowych rzek Doi-Cho Dem-Ben Luc. Wśród metali ciężkich zaobserwowano istotną dodatnią korelację między zawartością Fe, Mn, Zn i Ni (0,64 ÷ 0,87), natomiast Cu wykazywała istotną dodatnią korelację z Ni (0,51). Zawartości Cu i Pb wykazywały niezbyt silną korelację z Fe, Mn, Zn i Ni (0,25 ÷ 0,48). Na rozmieszczenie metali ciężkich mogą mieć również wpływ właściwości metali ciężkich oraz wahania przepływów wody. Wyniki dostarczają wskazówek dotyczących kontrolowania zanieczyszczenia metalami ciężkimi i ochrony źródeł wody w rzekach Doi-Cho Dem-Ben Luc.

Słowa kluczowe: *zanieczyszczenie metalami ciężkimi, wody powierzchniowe, dystrybucja, rzeka, Doi-Cho Dem-Ben Luc, ochrona jakości wody*