Correlation of Water Quality and Heavy Metal Concentration in Chao Phraya River Basin: An Effect on Human Health

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Abstract

Heavy metal contamination in river was concerned as the national problem in Thailand because the contaminant may be accumulated in sediment, aquatic organisms, entered food chain and affected to human health. This study reported the correlation between heavy metal concentration and water parameters with stepwise multiple linear regression by using observed data over a 10-year period (2009-2018) of Chao Phraya River Basin. The results indicated that the concentration of As, Cd, Cr, Cu, Pb, Hg, Mn, Fe, Ni and Zn were closely related to pH, turbidity, NH_3, Total Phosphorus (TP), and Dissolved Oxygen (DO). The stepwise multiple regression showed that 70% of the equation had r2 values greater than 0.842. The model in this study will be applied to predict the heavy metal contamination in surface water. The Hazard Quotient (HQ), Hazard Index (HI) and Carcinogenic Risk (CR) of adult and children were also calculated. The human health assessment information will be applied coupled with multiple linear regression model for effective management of heavy metal pollution in Chao Phraya River.

Keyword: Water Quality, Heavy Metal Concentration, Chao Phraya River Basin, Hazard Quotient

INTRODUCTION

Chao Phraya River basin is the largest basin in Thailand (20,523.42 km2) which located in the center of the country. The main river is Chao Phraya River (Hydro-Informatic Institute, 2012). With 372 kilometer-long, the Chao Phraya River supports 13 million people and is used in a variety of ways, including drinking water and irrigation. The principal tributaries of the Chao Phraya River are the Ping River, the Wang River, the Yom River and the Nan River.

The Pollution Control Department (PCD) had carried out regular water quality monitoring for the Chao Phraya River. Since 1994, the overall water quality of the rivers was found to be polluted or degrading, particularly near urban centers. Significant sources of water pollution were identified as urban development, domestic wastewater discharge coupled with effluent discharges from commercial establishments (UN-WWAP, 2006). Moreover, there were more than 30,000 industrial factories located in the Chao Phraya River basin (Mingkhwan and Worakhunpiset, 2018). They released toxic substances including heavy metals, solvents, and persistence organic compounds from industrial effluents to the river.

For better understanding of the concentration, distribution, and assessment of heavy metals in the Chao Phraya River basin, systematic work was urgently needed. Therefore, the objective of this research was to evaluate the correlation of water quality and heavy metal concentration during 10-years. The health risk assessment of heavy metal contaminated in Chao Phraya River Basin was also calculated and reported.

MATERIALS AND METHODS

1. The study area

The observed data of water quality and heavy metal concentration over a 10-year period (2009-2018)

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from the Pollution Control Department, Ministry of Natural Resource and Environment were used in this study. Each year contained 4 quarter data (January, May, July, and November) of 5 rivers (Ping, Wang, Yom, Nan, Chao Phraya River) from 65 stations (Chao Phraya 18 stations, Nan 14 stations, Ping 14 stations, Yom 13 stations, Wang 6 stations) (Figure 1). All of data was verified for the accuracy before the application in next step.

2. Data analysis

In first step, Pearson correlation analysis (SPSS software for window Version 22) was used to determine correlation among each water quality parameter (pH, turbidity, conductivity, salinity, Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), Total Phosphorus (TP), ammonia-nitrogen (NH_3-N), Suspended Solids (SS), Total Dissolve Solid (TDS) and heavy metal species (Fe, Cd, Cr, Mn, Ni, Pb, Zn, Cu, Hg, and As). Then, the stepwise multiple linear regression was applied to select the best fit model that can be described the relationship between water quality and heavy metal concentration.

3. Human health risk assessment

Ingestion and dermal exposure were important pathways in water health risk assessments and the heavy metals both carcinogen and non-carcinogen causing the impacts for human health. The Environmental Protection Agency (EPA) of the United States assess these heavy metals toxicity effects by calculated these elements concentrations with various variables such as duration of exposure, body weight and exposure frequency. The average daily dose (ADD) was calculated in the Eq.1 and 2. The $ADD_{ingestion}$ represent the direct intake exposure dose and ADD_{dermal} represent the exposure dose that absorbed into the body through the skin (Adeyemi and Ojekunle, 2021; Wu et al., 2021).

$$ADD_{ingestion} = (Cw \times IR \times EF \times ED)/ (BW \times AT) \quad (1)$$

$$ADD_{dermal} = (Cw \times SA \times Kp \times EF \times ED \times 10^{-3})/ (BW \times AT) \quad (2)$$

The Hazard Quotient (HQ) and Hazard Index (HI) estimated by each pathway were calculated in Eq. 3 and 4 (Wu et al., 2021).

$$HQ = ADD/RfD \quad (3)$$

$$HI = \sum HQs \quad (4)$$

Which, HQ value higher than 1 can be described that there is probability of non-carcinogen heavy metal impacts on human health while HQ value under 1 showed that the heavy metals intake would not possibly have effect on human health.

For carcinogenic heavy metal risk was evaluated using Eq. 5 Wu et al. (2021)

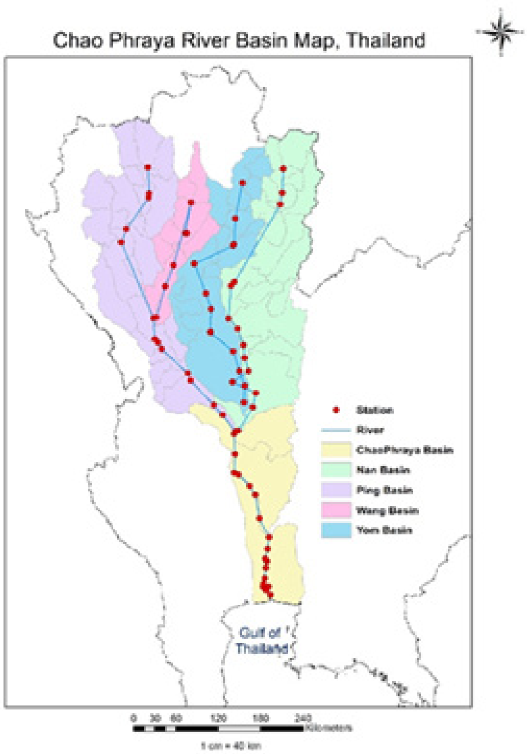

Figure 1. The sampling stations at Chao Phraya River Basin

$$CR = ADD \times Sf \quad (5)$$

The parameters used in the equations were shown in Table 1 and 2.

RESULTS AND DISCUSSION

1. Correlation of heavy metal concentration and water parameters

Changes in environmental conditions such as pH and DO can affect the enrichment and migration of metals (Butler, 2009). Li et al (2020) reported that Cd and Zn had positive correlation with total nitrogen (TN) and TP ($p < 0.05$) by Pearson correlation analysis. Generally, when the pH in water decreased, heavy metal solubility increased. However, some of heavy metals may be adsorbed in bottom sediments, where they remained for many years. In this study, Pearson correlation analysis showed that Hg and As had negative correlation with pH and also as Cd, Hg and As had negative correlation with DO ($p < 0.01$) (Table 2). It can be implied that at low pH, the concentration of Hg and As

Table 1 Distributions of parameters for the health risk assessment of heavy metal

Parameter	Units	Distribution	
		Adult	Child
Average concentration of heavy metal in water (Cw)	μg/L		
Intake rate (IR)	L/day	2	0.64
Exposure frequency (EF)	days/year	350	350
Duration of exposure (ED)	years	30	6
Exposed area of skin (SA)	cm^2	18000	6600
Exposure time (ET)	h/day	1	0.58
Body weight (BW)	kg	70	15
Average time (AT)	days	25550	2190

Table 2 Reference dose (RfD), dermal permeability coefficient in samples (Kp) and slope factor (SF) for health risk assessment of heavy metals

	Kp (cm/h)	$SF_{ingestion}$ $(mg/kg/d)^{-1}$	SF_{dermal} $(mg/kg/d)^{-1}$	$RfD_{ingestion}$ (μg/kg/day)	RfD_{dermal} (μg/kg/day)
Fe	1×10^{-3}			0.7	1.1×10^{-4}
Cd	1×10^{-3}	6.1	0.38	0.5	0.025
Cr	1×10^{-3}	0.5	20	3	0.075
Mn	1×10^{-3}			24	0.96
Ni	2×10^{-4}	1.7	42.5	20	0.8
Pb	1×10^{-4}	8.5×10^{-3}	0.073	1.4	0.42
Zn	6×10^{-4}			300	60
As	1×10^{-3}	1.5	1.5	0.3	0.285
Hg	1×10^{-3}			3×10^{-4}	0.0285
Cu	1×10^{-3}			40	8

in water will be high. Wu et al. (2021) reported that high concentrations of As appeared in the agricultural land in the upper areas of the Beiyun River basin, indicating that agricultural activities may be the main source of As pollution in river.

The results indicated that Fe had high positive correlation (r=0.893) with turbidity ($p < 0.01$). Dhirachaikulpanich (2001) reported that the Lower Central Plain or Chao Phraya Plain was a fault-bounded basin developed in the Plio- Pleistocene epoch. The Pleistocene deposits represented a complex interplay of alluvial, fluvial and deltaic environments of the Chao Phraya River and its tributaries. The upper layer of sediment found reddish-brown dots of iron-oxide. Therefore, during the rainy season, when soil erosion occurred, the turbidity of water was high. Adsorbed-Fe may be also released from the sediment.

In this study, Fe, Cd, Cr and Pb had positive correlation with TP ($p < 0.01$). The excessive use of fertilizers and pesticides in agricultural areas near the Chao Phraya River can lead to the accumulation of these heavy metals in the water. In case of Beiyun River, Cr contamination may come from automobile exhaust, coal combustion, and industrial drainage from electroplating plants (Xiao et al., 2019).

The stepwise multiple linear regression was applied to create best fit model for each heavy metal by using 10-years observed data. The results showed that As, Cd, Fe, Pb, Zn, Cu and Hg had high correlation with water parameters ($r2 > 0.842$) (Table 3). However, Mn and Ni indicated low correlation with water quality ($r2 = 0.593$ and $r2 = 0.532$), respectively. The models showed that heavy metal concentrations were related with the water quality including pH, turbidity, TP, DO and NH_3. These models with high r2 will be applied to predict the heavy metal concentration in Chao Phraya River.

2. Human health risk assessment of heavy metals in water

The human health risks of residents living near Chao Phraya River were estimated by calculating HQ and HI of heavy metals between different age groups (adult and children) (Table 5). The results showed that

Table 3 Pearson correlation analysis of heavy metal and water quality

	pH	tur	Conduct	Sal	DO	BOD	TP	NH3	SS	TDS	Fe	Cd	Cr	Mn	Ni	Pb	Zn	Cu	Hg	As
pH	1	0.38	-.671**	-.501**	.819**	-.530**	.123	-.660**	.175	-.563**	0.42	-0.36	.227	-.082	.001	.215	-0.46	0.254	-.572**	-.641**
tur		1	-.157	-.108	0.292	.066	.503**	-.170	.824**	-.158	.893**	.160	0.41	0.463	0.286	0.45	-.547**	-.071	-0.32	-.045
Conduct			1	.911**	-.686**	.692**	.061	.885**	.040	.888**	-.230	.590**	.033	.304*	-.065	-.095	0.482	.080	.220	.551**
Salinity				1	-.543**	.516**	.096	.724**	.097	.914**	-.169	.617**	.081	0.371	-.026	-.020	0.434	.173	.084	0.451
DO					1	-.708**	-.157	-.669**	.230	-.615**	0.29	-.539**	.009	-.037	-.105	.012	-0.45	.091	-.553**	-.814**
BOD						1	0.471	.791**	.120	.534**	.109	.611**	.200	.213	.077	.166	.040	-.051	.160	.547**
TP							1	.050	0.465	.027	.714**	.604**	.589**	0.257	.312*	.784**	-.565**	.273*	-0.32	0.297
NH3								1	-.019	.741**	-.214	0.48	.045	.187	-.049	-.136	0.387	-.048	0.284	.514**
SS									1	.044	.728**	.279*	0.35	.534**	.179	0.404	-0.47	-.063	-0.29	.003
TDS										1	-.229	.598**	.064	0.336	-.058	-.091	0.468	.107	.183	.508**
Fe											1	0.32	.562**	0.344	0.286	.664**	-.750**	.046	-0.42	-.033
Cd												1	.590**	0.255	.154	.564**	-.174	.194	-.018	.618**
Cr													1	.105	.219	.695**	-.518**	0.347	-0.34	.200
Mn														1	-.010	.094	.005	.093	-.236	.130
Ni															1	0.321	-.186	-.143	.190	.167
Pb																1	-.539**	0.368	-0.3	0.269
Zn																	1	.084	0.441	0.309
Cu																		1	-.623**	.001
Hg																			1	.575**
As																				1
**	positively significance at P<0.01																			
**	negatively significance at P<0.01																			

Table 4 Multiple linear regression model described the relationship of water quality and each kind of heavy metal

Equation	r^2
As = (0.418Cd)-(0.035Ni)+(0.037Cu)+(0.516Hg)-(0.002pH)+(1.006×10^{-5} turbidity)+(0.004TP)+0.015	0.940
Cd = (0.068Pb)-(0.005Zn)+(0.367As)-(1.007×10^{-5}turbidity) -2.91×10^{-4}	0.918
Cr = (0.006pH)+(0.011NH_3)-(0.023Zn) -0.034	0.753
Fe = (0.017turbidity)+(2.923TP) -1.146	0.950
Mn = -(0.121pH)+0.772	0.593
Pb = (2.089Cd)+(0.020TP)+ 0.017	0.842
Zn = (1.208Cu) +(0.120pH)-(0.040DO)-(0.247TP)-(26.751Cd)-(7.013Cr) -0.412	0.917
Ni = (35.220Hg)+(0.999TP)-(0.066Fe) -2.622	0.532
Cu = -(9.022Hg)-(1.62×10^{-4}turbidity)+(0.075Zn)+(10.267As) -0.197	0.897
Hg = -(0.003pH)+(1.237As)+(0.058Ni)-(0.078Cu)-0.017	0.944

Table 5 Hazard Quotient (HQ) and Hazard Index (HI) of adult and children

	$HQ_{ingestion}$		HQ_{dermal}		$HI_{ingestion}$		HI_{dermal}	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Fe	21.6202	75.3347	1238.252	2867.425	111.5359	388.6419	1238.298	2867.533
Cd	0.0466	0.1624	0.0083	0.0194				
Cr	0.0277	0.0965	0.0099	0.0231				
Mn	0.0732	0.2552	0.0164	0.0381				
Ni	0.0043	0.0150	0.0002	0.0005				
Pb	0.0822	0.2865	0.0003	0.0006				
Zn	0.0099	0.0347	0.0003	0.0006				
Cu	0.0116	0.0405	0.0005	0.0012				
Hg	89.4539	311.6973	0.0084	0.0196				
As	0.2063	0.7191	0.0020	0.0045				

the highest Hazard Index (HI) value caused by dermal pathway at 2867.533 for children and 1238.298 for adult which 99% of this value mainly from Fe-HQ_{dermal} value (2867.425 for children and 1238.252 for adult). According to the concentration of Fe in Chao Phraya River, was highest compared to other metals, Fe had the potential to effect human health by absorbed through the skin. Some activities of local residents such as swimming, application water from river for washing and taking a bath caused Fe absorption by dermal. Accordingly, the highest value of $HI_{ingestion}$ were 388.6419 for children and 111.5359 for adult which 80% of $HI_{ingestion}$ from Hg-$HQ_{ingestion}$ (311.6973 for children and 89.4539 for adult). The 19% of $HI_{ingestion}$ was Fe-$HQ_{ingestion}$ (75.3347 for children and 21.6202 for adult), respectively. The results indicated that both Hg and Fe had the potential to pose significant harm to residents by dermal and/or ingestion.

In this study, the value of $HQ_{ingestion}$ and HQ_{dermal} for Cd, Cr, Mn, Ni, Pb, Zn, Cu, and As were lower than 1 indicating the ingestion and dermal routes did not pose significant harm to local people. Wu et al., (2021) also reported that the value of $HQ_{ingestion}$ and HQ_{dermal} calculating by using Mn, Ni, Pb, Zn, As, Cr, Cd and Cu in the Beiyun River were less than 1. However, Adesiyan et al. (2018) reported that the value of $HQ_{ingestion}$ of Cd and As in rivers in southwest Nigeria were greater than 1 and also as $HI_{ingestion}$. The value of HI_{dermal} in this study was higher than Houjing River at Taiwan (Hoang et al., 2021), groundwater at Nigeria (Ayantobo et al., 2014; Adeyemi and Ojekunle, 2021). The value of $HI_{ingestion}$ in groundwater in east India was 0.5-888 (Mukherjee et al., 2020). In this study, the results showed that the value of $HI_{ingestion}$ and HI_{dermal} were greater than 1 because $HQ_{ingestion}$ and HQ_{dermal} of Fe and Hg were extremely high.

The carcinogenic Risk (CR) value was calculated for carcinogenic heavy metals (Cd, Cr, Ni, Pb and As) at both pathways (ingestion and dermal) (Table 6). The results revealed that for Cd, Cr, Ni, Pb and As, the value of $CR_{ingestion}$ was high ($>10^{-3}$) both in children and adult indicating extremely high risk. In case of Cr and Ni, the value of CR_{dermal} for children were between 5×10^{-5} to 10^{-4} indicating as medium risk. For Cr, the value of CR_{dermal} for adult was between 10^{-6} to 5×10^{-5} indicating low-medium risk. In case of Ni, the value of CR_{dermal} for adult was between 10^{-6} to 10^{-5} indicating low risk. In this study, the value of $CR_{ingestion}$ was higher than CR_{dermal} for Cd, Cr, Ni, Pb and As. It could be implied that the carcinogenic risk mostly occurred by ingestion including consumption aquatic flora and fauna grown in Chao Phraya River, which is contaminated by heavy metal. Moreover, the value of $CR_{ingestion}$ and CR_{dermal} for children were greater than adult. Most of CR was higher than the standard range (10^{-6} to 10^{-4}) which signifies a possibly to have carcinogenic adverse effect (Adeyemi and Ojekunle, 2021).

Table 6 Carcinogenic Risk (CR) of adult and children

	$CR_{ingestion}$		CR_{dermal}	
	Adult	Children	Adult	Children
Cd	0.0038	0.0133	0.0006	0.0013
Cr	0.1662	0.5793	3.74×10^{-5}	8.7×10^{-5}
Ni	0.0509	0.17747	3.66×10^{-6}	8.5×10^{-5}
Pb	13.5467	47.2031	0.0014	0.0032
As	0.0412	0.1438	0.0004	0.0009

CONCLUSION

In this study, the multiple linear regression model indicated that heavy metal concentrations were significantly related with the water quality including pH, turbidity, TP, DO and NH_3. The level of As, Cd, Fe, Pb, Zn, Cu and Hg in water had high correlation with water parameters, while Mn and Ni showed low correlation with water quality.

The value of $HI_{ingestion}$ was > 1 because $HQ_{ingestion}$ of Hg was extremely high. $HQ_{ingestion}$ of Hg in children was 3.48 times greater than in adult. The value of HI_{dermal} was > 1 because HQ_{dermal} of Fe was high. HQ_{dermal} of Fe in children was 2.31 times greater than in adult. The value of $CR_{ingestion}$ was higher than CR_{dermal} for Cd, Cr, Ni, Pb and As. For further study, the consumption of aquatic plants and animals grown in contaminated water of local residents should be more investigated for sustainable management to reduce human health risk of heavy metal.

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