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Spatial and Temporal Variation of Dissolved Heavy Metals in the Mun River, Northeast Thailand

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Abstract: River water samples between August 2017 (wet season) and March 2018 (dry season) from the Mun River Basin in northeast Thailand were collected and their dissolved heavy metals concentrations (Al, Mn, Fe, Cu, Zn, and Ba) were measured. Compared with international drinking water guidelines, Mn was the dominant pollutant in the dry season. The correlation analysis (CA) suggested that similar sources were shown in each element pair of Al-Fe, Mn-Zn, and Fe-Ba in both seasons. The principal component analysis (PCA) results showed that the dominant source of dissolved heavy metals was sedimentary inputs or colloid destabilization in the wet season, while anthropogenic inputs were the main sources in the dry season, such as agricultural runoff, industrial effluents, and domestic discharge. On the basis of water quality index (WQI), water at most sites in the wet and dry seasons can be categorized as excellent water, except for a few sites with substandard values. The river water posed no significant health risks according to the health risk assessment, but Mn, Fe, and Ba needed to be paid more attention due to the relatively high values. Al, Fe, and Ba were the main dissolved heavy metals flowing into the Mekong River, and Cu contributed to the background value in the Mekong river.

Keywords: dissolved heavy metals; correlation analysis; principal component analysis; water quality index; health risk assessment; the Mun River

1. Introduction

Heavy metals are a global concern due to their effects on ecological risks to human health [1–4]. Moreover, heavy metals are difficult to be degraded or relieved of harmfulness through physical, chemical, or biological purification in natural environments [5], and can cause severe diseases, such as nervous disorders, visceral dysfunction, and cancers, through food chains [6,7]. Heavy metals in the dissolved phase are one of the most harmful substances that can directly affect the water quality of drinking water and irrigation water [8–11], and they are of greater toxicity than those in suspended and sedimentary phases [12–14]. In order to control water pollution and protect local water resources, it is of great significance to understand the spatial distribution, temporal variation, and sources of dissolved heavy metals, as well as the water quality and health risk level of water.

The Mun river, a large drainage basin in northeastern Thailand, receives large amounts of heavy metal pollutants from different sources every year. Sources of dissolved heavy metals in the river may include emissions by industrial activities [7,15], urban construction [9,16], vehicle exhaust [17], etc. Many heavy metal elements used to be detected in industrial and domestic sewage without treatment, such as Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Sb, Ba, Pb, etc. [3,8]. In addition, agriculture lands occupy the main area of the drainage basin [18], where the emission sources of agricultural activities have to be taken into consideration, such as commercial fertilizers, pesticides, and sewage sludge containing a variety of heavy metals [19–21], which may divert the sources of dissolved heavy metals. Moreover, the factors of heavy metal enrichment may change with the seasons.

To identify the possible pollution sources of dissolved heavy metals in the Mun River, 104 water samples were collected from 57 sampling sites in the Mun River, northeast Thailand, during the wet season (August 2017) and dry season (March 2018). Multivariate statistical methods were applied to six dissolved heavy metals (Al, Mn, Fe, Cu, Zn, and Ba), including correlation analysis (CA) and principal component analysis (PCA). Water quality index (WQI) was performed to evaluate the water quality, and hazard quotient (HQ) and hazard index (HI) were calculated to assess the risk to human health. The purpose of this article is to help develop local water management for preventing hazardous contamination of dissolved heavy metals.

2. Materials and Methods

2.1. Study Area

The Mun River is the largest river in the northeastern part of Thailand (Figure 1) and is also a right bank tributary of the Mekong River. It lies in the drainage basin approximately between latitudes of $14^{\circ}00' N$ – $16^{\circ}00' N$ and longitudes $101^{\circ}30' E$ – $105^{\circ}30' E$ (Figure 1). The whole drainage basin has an approximate area of $82,000 \text{ km}^2$ [22], where plateaus and mountains are located in the southwestern area, and plains are situated in the central and eastern areas [23]. The Mun River originates from Nakhon Ratchasima and flows towards the east for 673 km until it joins the Mekong River in the Ubon Ratchathani province (Figure 2) [19]. The average runoff rate of the Mun River is about $959 \text{ m}^3/\text{s}$ during the wet season and $367 \text{ m}^3/\text{s}$ during the dry season [24], and the annual contribution to the Mekong River is about $2.5 \times 10^{10} \text{ m}^3$ [25]. The Mun River is divided into three main reaches: upper Mun ($101^{\circ}30' E$ – $102^{\circ}30' E$), middle Mun ($102^{\circ}30' E$ – $104^{\circ}30' E$), and lower Mun ($104^{\circ}30' E$ – $105^{\circ}30' E$) (Figure 2) [19].

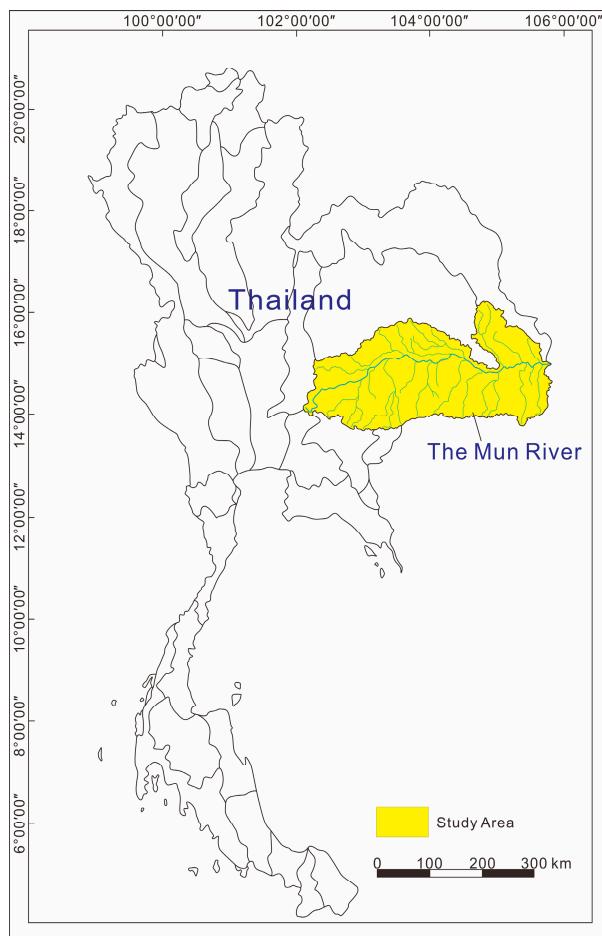


Figure 1. Location of the Mun River Basin.

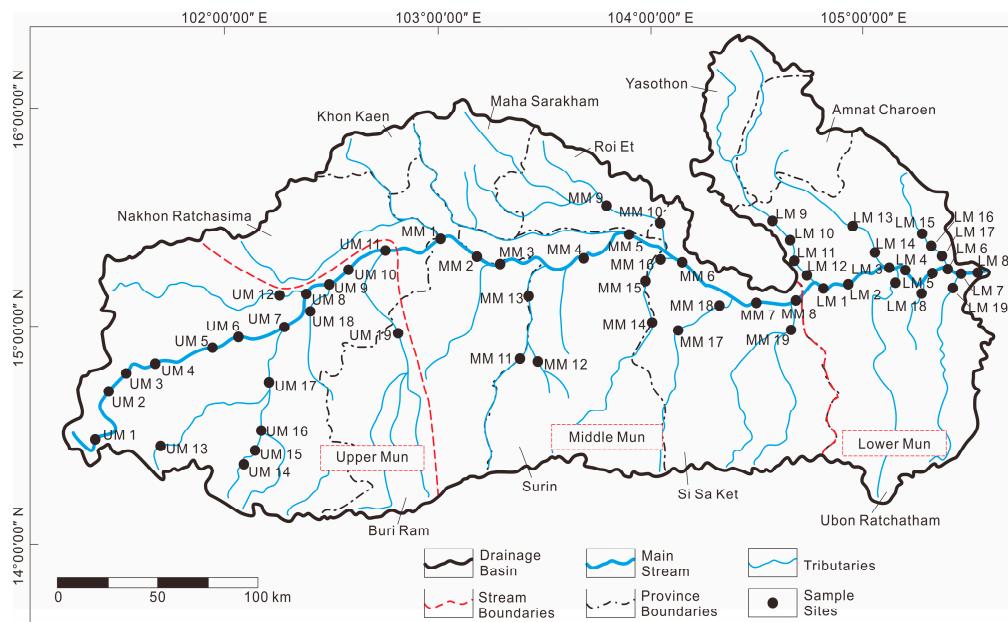


Figure 2. Sample distribution in the Mun River.

Thailand is among the top ten largest rice-producing countries in the world [18]. The industry area is sporadically distributed in the basin, and the agriculture is well-developed in the Mun River Basin [20], where the main types of agriculture are rice, forest, perennial plants, vegetables, and other

plants (Figure 3). The duration of rice cultivation includes the vegetative stage (July–September), reproductive stage (October), and ripening stage (November) [26]. The drainage basin is situated in a savannah climate zone [27], and the main mechanism for the rainfall pattern is the southeastern monsoon. The annual precipitation is within 955–1711 mm, and the precipitation in the wet season and the dry season are 880–1617 mm and 42–120 mm, respectively [22]. The mean annual precipitation is 1131 mm for the whole basin, whereas it is 1082 mm in the upper Mun, 1197 mm in the middle Mun, and 1436 mm in the lower Mun [19].

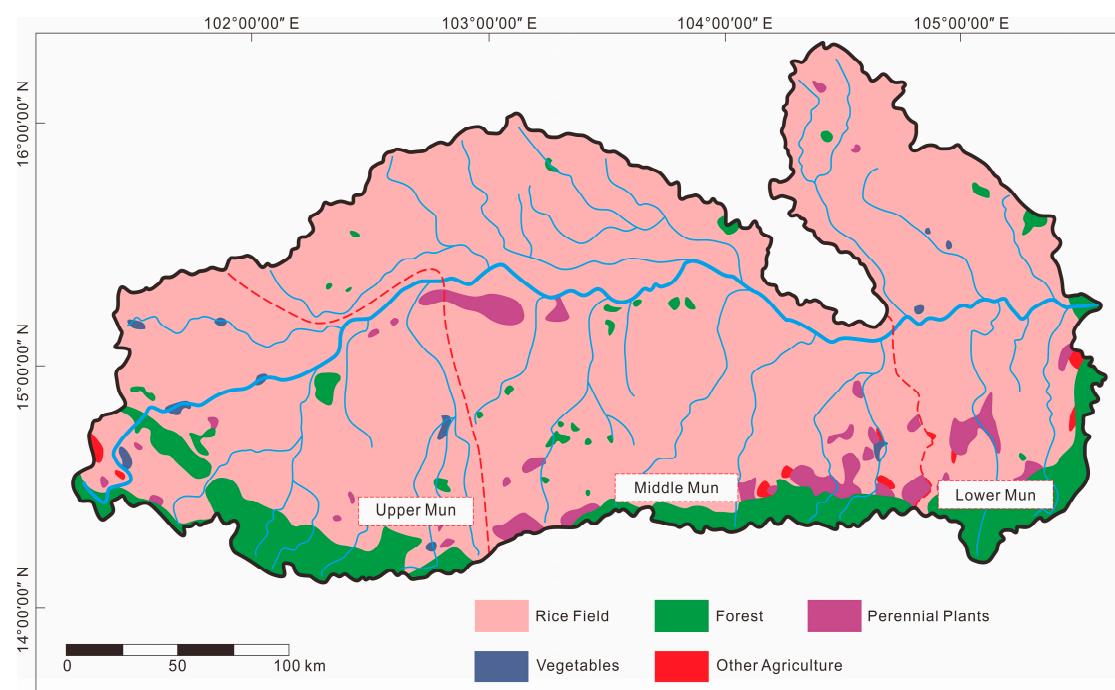


Figure 3. Agricultural land use map of the Mun River Basin (land use data from Akter and Babel [19]).

2.2. Sample Collection and Storage

Sampling surveys were conducted in August 2017 (wet season) and March 2018 (dry season). A total of 104 water samples were collected from 57 sampling sites in the upper Mun River, middle Mun River, and lower Mun River, and labelled with UM 1–19, MM 1–19, and LM 1–19, respectively (Figure 2). Samples UM 1–11, MM 1–8, and LM 1–9 were collected from the mainstream, and other samples are collected from tributaries. Before sample collection, all sampling instruments were rinsed with river water three times, to avoid contamination of dissolved heavy metals. Samples were collected using a water sampler and stored in pre-cleaned high-density polyethylene (HDPE) plastic bottles [28]. Water samples were filtered through a 0.22- μm filter membrane for the determination of dissolved heavy metals. The filtrate was acidified to $\text{pH} \leq 2$ using ultra-pure concentrated nitric acid (HNO_3). All water samples were stored in the dark before subsequent measurement and determination.

2.3. Physicochemical Measurement and Elemental Determination

The physicochemical parameters were monitored on-site using a YSI water quality monitoring instrument (Xylem Inc., Yellow Springs, OH, USA). Dissolved heavy metals were measured using an inductively coupled plasma mass spectrometer (ICP-MS, Elan 9000, Perkin Elmer Optima, Waltham, MA, USA) at Institute of Geology and Geophysics, Chinese Academy of Sciences, China. The standard reference used for quality control was GSB 04-1767-2004, and the uncertainty was below 0.7%. The percentage recoveries varied from 97.21% to 109.80%, showing a good agreement between the determined elements and standard reference material. Procedural blanks were determined between every 10 samples. Method precision was controlled by determining replicate samples between each

batch of 10 water samples, and the relative standard deviations (RSD) of the randomly selected replicate samples were 0.01%–6.08%.

2.4. Multivariate Statistics

For comparison of the distribution and to search for the possible sources of dissolved heavy metals in the Mun River, all of the data were processed using Microsoft Office 2019 (Microsoft Corporation, Redmond, WA, USA) and SPSS 25.0 (IBM Corporation, Armonk, NY, USA). One-way analysis of variance (ANOVA) was performed in this study ($p < 0.05$; least-significance difference, LSD) to test the spatial and temporal variation between physicochemical variables and dissolved heavy metals of the Mun River. Pearson correlation matrixes were used to investigate the relations and interactions of dissolved heavy metals in the Mun River. The principal component analysis (PCA) was used to explore the possible sources of trace metals by converting a large number of potentially related variables into a set of linearly unrelated variables using a dimensionality reduction technique. In PCA, the Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity test were used to examine the adequacy and suitability of the dataset. Before performing the PCA, the dataset was standardized by z-scale transformation to avoid numerical ranges of the original variables [29].

2.5. Water Quality and Health Risk Assessment

2.5.1. Water Quality Index

The WQI is introduced as a mathematical tool to convert the water quality dataset into a single number at each sampling site, where the results are eliminating subjective assessments of water quality and biases of individual water quality experts [30,31]. To assess the WQI, the impacts caused by different water quality variables were calculated with the following equation:

$$WQI = \sum [W_i \times (C_i/S_i)] \times 100, \quad (1)$$

where W_i represents the weight of each parameter and is calculated on the basis of the eigenvalues for each principal component (PC) and factor loading for each parameter from the PCA results; C_i represents the concentration of each dissolved heavy metal; and S_i is the guideline values for each element, and obtained from Nabizadeh et al. [30]. Based on WQI values, the water quality is interpreted as: (1) excellent water quality ($0 \leq WQI < 50$); (2) good water quality ($50 \leq WQI < 100$); (3) poor water quality ($100 \leq WQI < 200$); (4) very poor water quality ($200 \leq WQI < 300$); and (5) water unsuitable for drinking ($WQI \geq 300$) [30].

2.5.2. Health Risk Assessment

The HQ and HI are calculated to assess the toxicity of heavy metals in aqueous systems [7]. HQ is the ratio between exposure through individual pathways and the reference dose. HI is the sum of the HQs from both the applicable pathways, which is aimed to identify the potential non-carcinogenic risk. Non-carcinogenic risk or adverse effects on human health exist when HQ or HI is ≥ 1 , and no deleterious effects exist when HQ or HI is < 1 [32]. The values of HQ and HI are calculated by equations as follows:

$$ADD_{\text{ingestion}} = (C_w \times IR \times EF \times ED) / (BW \times AT), \quad (2)$$

$$ADD_{\text{dermal}} = (C_w \times SA \times K_p \times ET \times EF \times ED \times 10^{-3}) / (BW \times AT), \quad (3)$$

$$HQ = ADD/RfD, \quad (4)$$

$$RfD_{\text{dermal}} = RfD \times ABS_{GI}, \quad (5)$$

$$HI = \sum HQs, \quad (6)$$

where the ADD_{ingestion} and ADD_{dermal} represents the average daily dose from ingestion and dermal absorption, respectively ($\mu\text{g}/\text{kg}/\text{day}$); C_w represents the average concentration of each element in water ($\mu\text{g}/\text{L}$); BW is the average body weight (70 kg for adults and 15 kg for children); IR is the ingestion rate (2 L/day for adults and 0.64 L/day for children); EF is the exposure frequency (350 days/year); ED is the exposure duration (30 years for adults and 6 years for children); AT is the average time ($=\text{ED} \times 365 \text{ days/year}$); SA represents the exposed skin area (18,000 cm^2 for adults and 6600 cm^2 for children); ET is the exposure time (0.58 h/day for adults and 1 h/day for children); K_p represents the dermal permeability coefficient in water (cm/h); RfD is the reference dose ($\mu\text{g}/\text{kg}/\text{day}$); ABS_{GI} is the gastrointestinal absorption factor. The reference values were obtained from the United States Environmental Protection Agency [33].

2.6. Fluxes of Dissolved Heavy Metals

The Mun river is a large tributary that eventually flows into the Mekong river. The effects of dissolved heavy metals on the Mekong River can be estimated by calculating the fluxes on the basis of the discharge data and weighted volume concentrations in the wet season and dry season of the Mun River. The flux of each dissolved heavy metals was calculated using the following equation:

$$\text{flux (tons/month)} = Q_A \times C_A, \quad (7)$$

where Q_A is the average water discharge in the wet season ($959 \text{ m}^3/\text{s}$) and dry season ($367 \text{ m}^3/\text{s}$) [24]; C_A is the average concentration of dissolved heavy metals near the estuary, which are collected from sites LM5–9, LM15–17, and LM19.

3. Results and Discussion

3.1. Dissolved Heavy Metals in the River Water

The results of physicochemical parameters and concentrations of dissolved heavy metals are listed in Table 1. The Kolmogorov-Smirnov (K-S) statistics were processed to test the normal distribution of the data [7], which indicated that only temperature is normally distributed with bilateral significance >0.100 . The K-S test results and large standard deviation values of Al (75.17), Fe (60.61), and Ba (31.10) suggested that the mean values reflected the reliability of the data, due to the presence of outliers with extremely high or low values. In this study, the median values were used for calculation; however, the mean values were used for comparisons with the guideline values given as arithmetic means.

The water temperature is relatively high with little variation throughout the year, ranging from 20.30°C to 31.10°C in the wet season and 24.00°C to 33.00°C in the dry season (Figure 4a). In the wet season, the water pH values in the upper Mun River exhibit an alkaline condition ranging from 7.06 to 8.42; the pH of samples from middle Mun River were of low values, ranging from 6.36 to 6.90; and the pH values of the lower Mun River water change between weak acidic and weak alkaline, ranging from 6.45 to 7.36 (Figure 4b); the pH values of samples in the dry season were significantly higher than that in the wet season (Figure 4b). Statistically, there are many wet season samples in the middle Mun River that are not within approved limits (6.50–8.50) [34], which may be harmful to human health and should be paid more attention.

Table 1. Physicochemical parameters and concentrations of dissolved heavy metals in the Mun River.

	Min	Max	Mean	Median	SD ¹	K-S Test ²
Wet Season						
T (°C)	20.30	31.10	28.47	28.70	1.89	0.181
pH	6.36	8.42	7.01	6.89	0.49	0.014
Al (µg/L)	nd ³	517.96	34.76	12.01	75.17	0.000
Mn (µg/L)	0.03	4.35	0.39	0.22	0.61	0.000
Fe (µg/L)	8.04	378.90	57.94	41.48	60.61	0.000
Cu (µg/L)	nd	2.51	0.47	0.41	0.37	0.000
Zn (µg/L)	nd	4.82	1.07	0.81	1.13	0.000
Ba (µg/L)	6.24	155.75	38.99	26.66	31.10	0.000
Dry Season						
T (°C)	24.00	33.00	28.58	28.70	1.79	0.198
pH	6.11	8.51	7.41	7.50	0.49	0.086
Al (µg/L)	0.27	167.42	12.99	2.32	33.00	0.000
Mn (µg/L)	0.09	527.00	72.17	20.70	104.94	0.000
Fe (µg/L)	21.49	536.05	114.64	103.07	80.91	0.000
Cu (µg/L)	0.17	1.51	0.60	0.58	0.27	0.001
Zn (µg/L)	0.15	6.24	2.38	2.03	1.41	0.019
Ba (µg/L)	11.96	115.89	55.18	58.41	22.37	0.063

¹ SD: standard deviation; ² K-S test: Kolmogorov-Smirnov test; nd: no data.

The one-way ANOVA results are shown in Supplementary Materials (Table S1). The results suggested that Mn, Fe, and Cu in both seasons showed some significant spatial patterns ($p < 0.05$), while dissolved Zn and Ba in the wet season exhibited a greater level of significance with $p < 0.01$, indicating that the river water had a strong mixing ability. However, Al showed no significant variation among the sampling sites.

The total concentrations of dissolved heavy metals in the wet and dry season are displayed in Table 1. Based on the mean concentrations, the dissolved heavy metals were classified into two categories: (1) Mn, Cu, and Zn (<10 µg/L); (2) Al, Fe, and Ba (>10 µg/L). The concentrations of Mn, Fe, Cu, Zn, and Ba in the dry season are basically higher than those in the wet season, while the concentration of Al in the middle Mun and lower Mun are higher in the wet season (Figure 4). Based on the guideline values for drinking water reported by the World Health Organization [34], the United States Environmental Protection Agency [35], and China GB 5749-2006 [36] (Table 2), contamination of dissolved heavy metals was evaluated by comparing their concentrations of each element. The maximum concentrations of Cu, Zn, and Ba were lower than all the guidelines listed in Table 2. The peak values of Al, Mn, and Fe were higher than the World Health Organization (WHO) drinking water guideline values (200 µg/L, 400 µg/L, and 300 µg/L, respectively). However, Mn concentrations in 15 water samples in the dry season were out of limits of the Chinese standard (100 µg/L). Excessive intake of Mn can cause severe diseases, such as hyperthyroidism and damage vital organs [37]. Therefore, local management should pay more attention to the concentration of Mn.

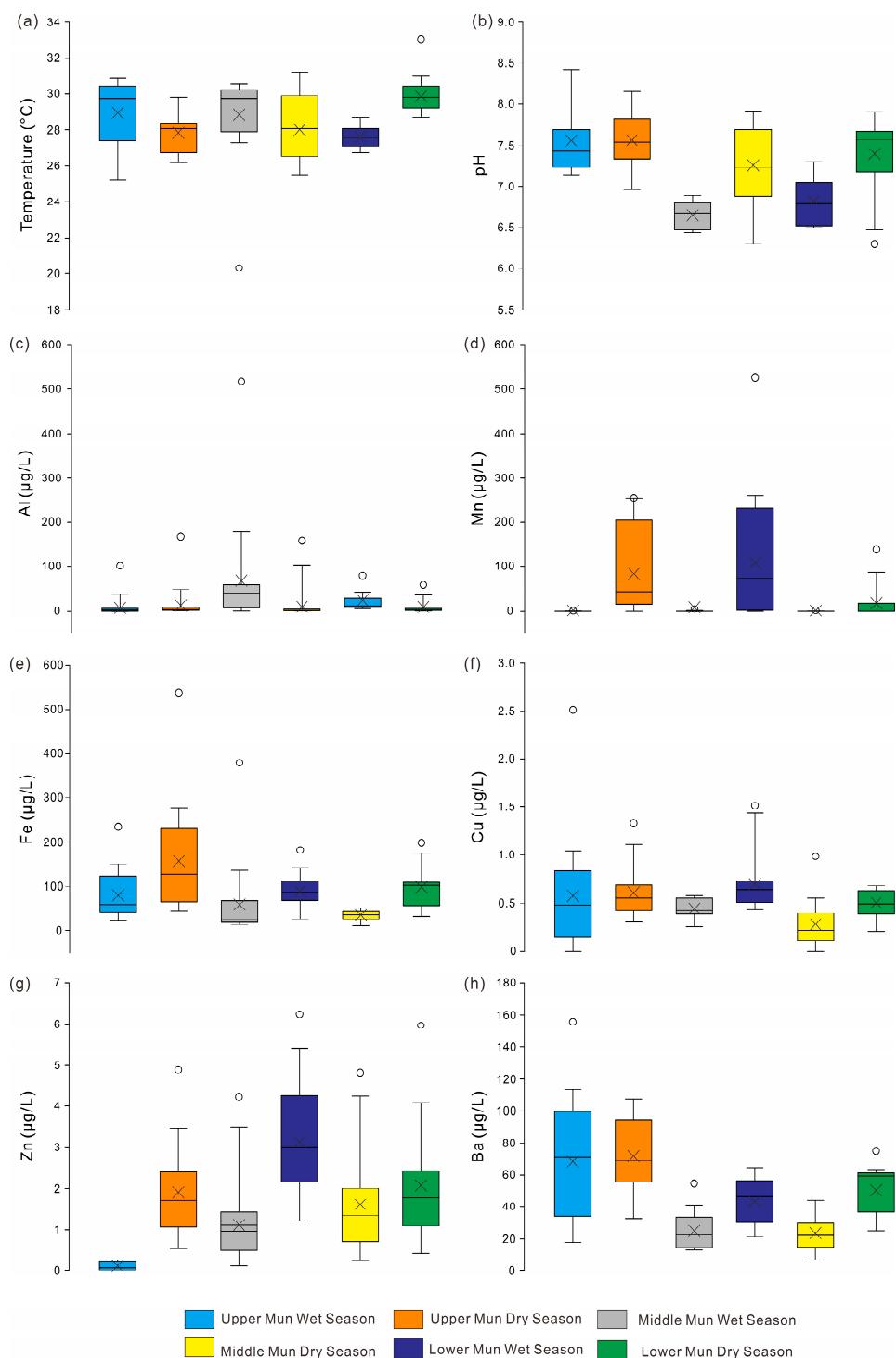


Figure 4. Box plots of (a) temperature, (b) pH value, and the concentration of (c) Al, (d) Mn, (e) Fe, (f) Cu, (g) Zn, and (h) Ba in the Mun River (o donates respective outliers, and \times represents mean values).

Table 2. Guideline values for heavy metals in drinking water.

Elements	WHO ¹	US EPA ²	China ³
Al ($\mu\text{g/L}$)	200	/	200
Mn ($\mu\text{g/L}$)	400	/	100
Fe ($\mu\text{g/L}$)	300	/	300
Cu ($\mu\text{g/L}$)	2000	1300	1000
Zn ($\mu\text{g/L}$)	/	/	1000
Ba ($\mu\text{g/L}$)	1300	2000	700

¹ World Health Organization [34]; ² United States Environmental Protection Agency [35]; ³ China GB 5749-2006 [36].

Based on previously published results, low concentrations of dissolved heavy metals in rivers might result from natural sources and be characterized by slow accumulation [15], while concentrations of some elements can be largely increased through anthropogenic activities [8]. The world average concentrations of Al, Mn, Fe, Cu, Zn, and Ba are 32 $\mu\text{g/L}$, 34 $\mu\text{g/L}$, 66 $\mu\text{g/L}$, 1.5 $\mu\text{g/L}$, 0.6 $\mu\text{g/L}$, and 23 $\mu\text{g/L}$, respectively (Table 3). Among the wet season samples, the concentration of Al, Fe, Cu, and Zn are close to the world average values; Cu and Zn in dry season water were close to the world average values, while other elements differ significantly from the world average. The concentration of Al is higher than that of Tonle Sap-Bassac Rivers. The concentrations of Mn in the dry season, as well as Ba, are lower than that in Citarum River. The concentrations of Fe are far below the values in Citarum River and Saigon River. Cu and Zn are not abundant relative to the values in the Mahanadi River during the wet season and dry season, as well as the metal concentrations in the other four rivers.

Table 3. The concentrations of dissolved heavy metals ($\mu\text{g/L}$) in southeast Asian rivers.

Element	World Average ¹	Tonle Sap-Bassac Rivers, Cambodia ¹	Citarum River, Indonesia ¹	Lower Chao Phraya River, Thailand ¹	Saigon River, Vietnam ¹	Mahanadi River, India (Wet Season) ²	Mahanadi River, India (Dry Season) ²
Al	32	11	130	100	245	/	/
Mn	34	1	260	210	90	22.04	17.51
Fe	66	10	230	100	370	222.3	113.5
Cu	1.5	1	3	4	5	9.53	9.86
Zn	0.6	/	12	53	75	18.76	23.21
Ba	23	7	30	175	19	/	/

Data are from ¹ Chanpiwat and Sthiannopkao [38]; ² Kumar et al. [39].

3.2. Source Identification

3.2.1. Correlation Matrix

The interrelationships between pairs of dissolved heavy metals were investigated using correlation matrixes (Table 4). Among the wet season water samples, dissolved Mn had significant positive correlation with Al (0.414), Fe (0.319), and Zn (0.425) ($p < 0.01$), Al and Fe were strongly correlated with each other (0.736) ($p < 0.01$), Fe and Cu also exhibited a strong positive correlation (0.470) ($p < 0.01$), Ba had a strong positive correlation with Fe (0.522) and Cu (0.703), and a strong negative correlation with Zn (-0.411) ($p < 0.01$). Among the dry season water samples, Fe had a strong correlation with Al (0.344) and Ba (0.500) ($p < 0.01$), and Mn was strongly correlated with Cu (0.366) ($p < 0.01$) and Zn (0.292) ($p < 0.05$). Three different sources in the dry season were marked by the element pairs of Al-Fe, Mn-Cu-Zn, and Fe-Ba. Overall, Al-Fe, Mn-Zn, and Fe-Ba exhibited strong interrelationships in both seasons, and similar sources were identified in each pair of Al-Fe, Mn-Zn, and Fe-Ba.

Table 4. Pearson correlation matrix of dissolved heavy metals in the Mun River.

	Al	Mn	Fe	Cu	Zn	Ba
Wet Season						
Al	1					
Mn	0.414 ¹	1				
Fe	0.736 ¹	0.391 ¹	1			
Cu	0.025	0.237	0.470 ¹	1		
Zn	0.042	0.425 ¹	-0.131	0.001	1	
Ba	-0.113	0.031	0.522 ¹	0.703 ¹	-0.411 ¹	1
Dry Season						
Al	1					
Mn	0.041	1				
Fe	0.344 ¹	-0.118	1			
Cu	0.129	0.366 ¹	-0.048	1		
Zn	0.148	0.292 ²	0.005	0.217	1	
Ba	-0.078	0.053	0.500 ¹	0.006	-0.106	1

¹ Correlation is significant at the 0.01 level (2-tailed); ² Correlation is significant at the 0.05 level (2-tailed).

3.2.2. Principal Component Analysis

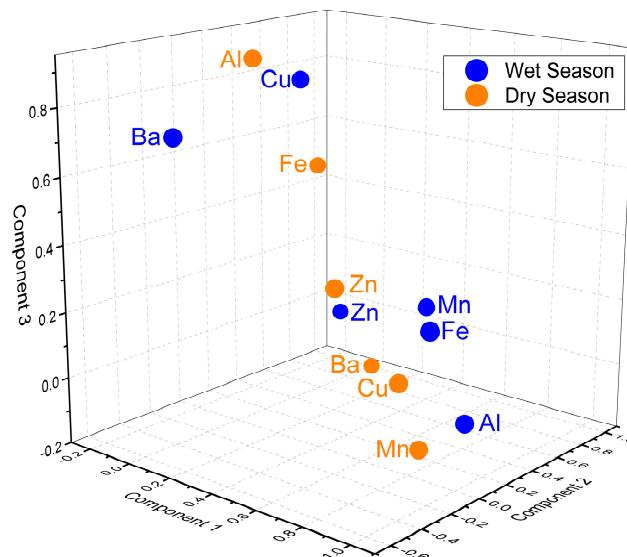
The PCA was processed to explore the origins of dissolved heavy metals by reducing the dataset to several influencing factors. The factor contribution or variables with minor significance obtained by PCA were further reduced using a varimax rotation method. The data was standardized by z-scale transformation to avoid numerical ranges of the original variables. The suitability of the data was tested by the Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity test, and the reliability for PCA was under 0.001.

The results of PCA, including the eigenvalues, variance, and communalities, are listed in Table 5, and the factor scores for each dissolved heavy metal are plotted in Figure 5. Three PCs with eigenvalues were extracting accounting for 83.82% in the wet season water. The loadings of PCs were classified into three categories: strong loading, moderate loading, and weak loading, on the basis of the loading values of >0.75, 0.75–0.50, and 0.50–0.30, respectively. PC 1 had strong positive loadings of Al (0.96) and Fe (0.94), and a weak loading of Mn (0.46), with a variance of 38.61%. Al and Fe are major components of crustal materials [7,8,17], and Fe and Mn are affected by the adsorption or desorption of iron and manganese oxyhydroxides in rivers [40]. Rocks and sediments were largely exposed in the upper and middle Mun River [41]. Thus, PC 1 might represent the sedimentary inputs or colloid destabilization. PC 2 had a strong loading of Zn (0.90), a moderate loading of Mn (0.68), and a weak loading of Cu (0.31). Mn, Cu, and Zn are the nutrient elements affected by anthropogenic sources [42–44], and their concentrations may be mainly related to the irregular utilization of pesticides and fertilizers by the residents in the Mun River Basin [22]. Moreover, the middle Mun River had more human interference than in the upper Mun River and lower Mun River [23], which might also contribute to the concentrations of Mn, Cu, and Zn. PC 3 explained 17.78% of the total variance, which had strong loadings of Cu (0.83) and Ba (0.74). Ba is a product of natural weathering [7], and PC 3 indicated that the concentrations of Cu and Ba were attributed to a mixed agricultural and natural source. Comparatively, there were also three PCs accounting for 71.73% of the total variances among the dry season samples, with the percentage of 27.46%, 26.16%, and 18.11% for PC 1, PC 2, and PC 3, respectively. PC 1 was strongly correlated with Mn (0.82), Cu (0.74), and Zn (0.58), similar to PC 2 in the wet season, which was probably affected by anthropogenic sources, such as agricultural runoff, industrial effluents, and domestic discharge [7,45]. PC 2 had strong loading of Fe (0.77) and Ba (0.92), reflecting a natural source from the input of sediments and weathering of rocks [43]. PC 3 was strongly correlated with Al (0.91), and weakly correlated with Fe (0.49) and Zn (0.34), which might be dominated by the inputs of crustal materials, as well as a small proportion of anthropogenic inputs.

Table 5. Varimax rotated component matrix for the dissolved heavy metals in the Mun River.

Variable	PC 1	PC 2	PC 3	Communalities
Wet Season				
Al	0.96	0.14	-0.04	0.94
Mn	0.46	0.68	0.13	0.70
Fe	0.94	-0.09	0.27	0.96
Cu	0.10	0.31	0.83	0.80
Zn	-0.09	0.90	-0.01	0.81
Ba	0.10	-0.51	0.74	0.82
Eigenvalues (%)	2.32	1.65	1.07	
Variance (%)	38.61	27.43	17.78	
Cumulative (%)	38.61	66.04	83.82	
Dry Season				
Al	0.08	0.03	0.91	0.84
Mn	0.82	0.04	-0.13	0.69
Fe	-0.12	0.77	0.49	0.85
Cu	0.74	0.02	0.06	0.55
Zn	0.58	-0.17	0.34	0.48
Ba	0.05	0.92	-0.18	0.89
Eigenvalues (%)	1.65	1.57	1.09	
Variance (%)	27.46	26.16	18.11	
Cumulative (%)	27.46	53.62	71.73	

Significance of Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity test is <0.001. Extraction method: Principal component analysis. Rotation method: Varimax with Kaiser normalization. Rotation converges after 4 iterations.

**Figure 5.** Loading plot of dissolved heavy metals in the Mun River.

3.3. Water Quality and Health Risk Assessment

3.3.1. Water Quality Index

The recommended limit of pH for drinking water varies from 6.5 to 8.5 [34], and 91.23% and 87.72% of samples in the wet season and in the dry season reach the pH standard. The weights of each parameter (W_i) obtained on the basis of the PCA results are provided in Supplementary Materials (Table S2). Based on the WQI values (Figure 6), the average water quality in the wet season ($WQI_{wet} = 10.23$) is better than that in the dry season ($WQI_{dry} = 22.93$). Water at site UM2, UM13, and MM9 in the dry season are of good water quality. The water quality in the wet season is categorized as excellent water, except for the poor water quality at MM15.

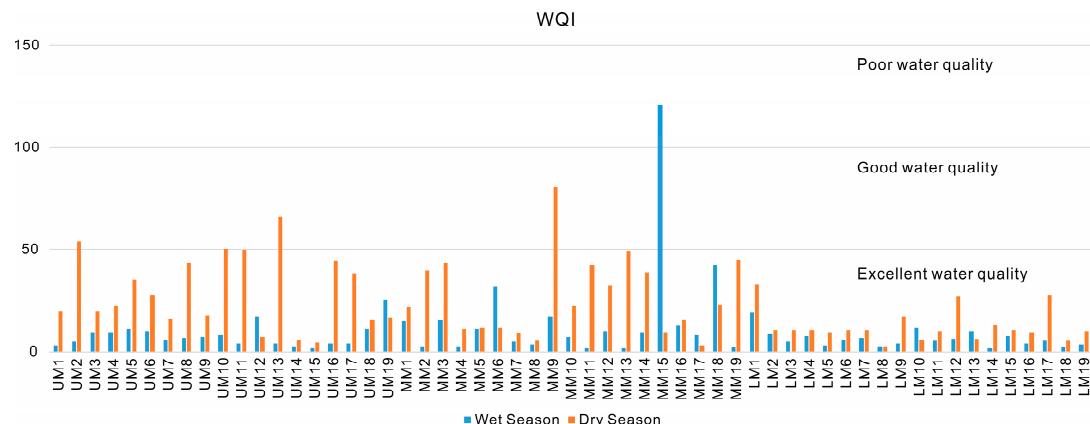


Figure 6. Water quality index (WQI) values of water in the Mun River.

3.3.2. Hazard Quotient and Hazard Index

The HI values ($=\Sigma HQs$) for dissolved heavy metals are listed in Table 6. The HQ for each element by ingestion and dermal pathways for adults and children are presented in Supplementary Materials (Table S3). Compared to adults, the higher $HQ_{ingestion}$ and HQ_{dermal} values for children suggested that children are more sensitive when exposed to dissolved heavy metals in water. For both adults and children, the $HQ_{ingestion}$ and HQ_{dermal} values for Al, Mn, Fe, Cu, Zn, and Ba in both seasons were smaller than 1, indicating no health effects on the human body and potential carcinogenic concern via daily intake and dermal absorption. The HI results showed that all the elements posed non-carcinogenic risks to human health in both seasons. Although Al, Cu, and Zn are low in concentrations and pose little health risk, Mn, Fe, and Ba in the dry season might be potentially harmful, with relatively high concentrations. The discharge of Mn, Fe, and Ba should be paid more attention in case of unnecessary health threats.

Table 6. Hazard index (HI) values for dissolved heavy metals in the Mun River.

	Wet Season		Dry Season	
	Adults	Children	Adults	Children
Al	3.38×10^{-4}	5.17×10^{-4}	6.52×10^{-5}	9.97×10^{-5}
Mn	3.35×10^{-4}	5.57×10^{-4}	3.21×10^{-2}	5.33×10^{-2}
Fe	3.92×10^{-3}	6.05×10^{-3}	9.74×10^{-3}	1.50×10^{-2}
Cu	2.89×10^{-4}	4.42×10^{-4}	4.10×10^{-4}	6.27×10^{-4}
Zn	7.54×10^{-5}	1.14×10^{-4}	1.88×10^{-4}	2.85×10^{-4}
Ba	1.07×10^{-2}	1.64×10^{-2}	2.35×10^{-2}	3.59×10^{-2}

3.4. Fluxes of Dissolved Heavy Metals

The monthly fluxes of dissolved heavy metals from the Mun River to the Mekong River in the wet season and dry season are estimated from the water discharge and the weighted volume concentrations (Figure 7). On the basis of the water fluxes, Fe and Ba were the dominant elements discharging into the Mekong River during both seasons. Although Mn was abundant in the whole drainage basin, its fluxes into the Mekong River were small. The elemental fluxes of Cu and Zn are negligible, but Cu might have a significant impact on the dissolved heavy metals in the Mekong River, the background values of which are $0.96 \mu\text{g/L}$ – $3.96 \mu\text{g/L}$ in the wet season and $0.63 \mu\text{g/L}$ – $1.41 \mu\text{g/L}$ in the dry season [46,47]. The estimated values suggested that the Mun River might be an important input of dissolved heavy metals in the Mekong, but it still needed further investigation.

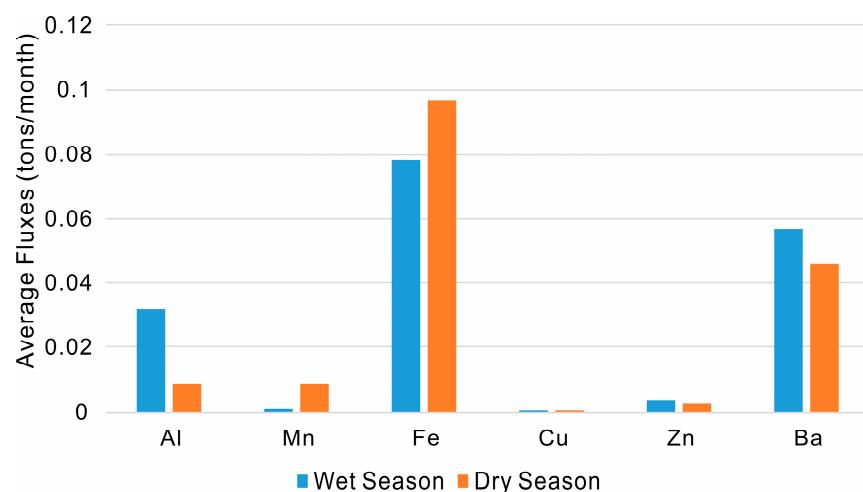


Figure 7. Estimated fluxes of dissolved heavy metals to the Mekong River.

4. Conclusions

This study reports the dissolved heavy metals compositions of river water in the Mun River, northeast Thailand. Based on the multivariate statistical methods, WQI values, and health risk assessment for the dissolved heavy metals in the Mun River, the results showed:

(1) The concentrations of Mn, Fe, Cu, Zn, and Ba in the dry season were higher than those in the wet season, while the concentration of Al in the middle and lower Mun River were higher in the wet season. Compared with the international guidelines for drinking water, Mn was the dominant pollutant in the dry season.

(2) The CA results suggested that similar sources were found in each pair of Al-Fe, Mn-Zn, and Fe-Ba in the wet and dry season. The PCA results showed that the dominant source of dissolved heavy metals was sedimentary inputs or colloid destabilization in the wet season, and anthropogenic inputs in the dry season are affected by agricultural runoff, industrial effluents, and domestic discharge.

(3) The WQI values showed that water at most sites in both seasons is categorized as excellent water, except for a few sites (UM2, UM13, and MM9 in the dry season, and MM15 in the wet season) with substandard values. The river water posed no significant health risks according to the health risk assessment, but Mn, Fe, and Ba needed to be paid more attention due to the relatively high values. Al, Fe, and Ba were the main elements flowing into the Mekong River, and Cu contributed the background value in the Mekong river.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/11/2/380/s1>. Table S1: One-way ANOVA for dissolved heavy metals in the Mun River. Table S2: Weights for the variables in the water samples. Table S3: Hazard quotient and hazard index for dissolved heavy metals in the Mun River.

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