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RESEARCH ARTICLE

Heavy Metals Pollution in Surface Water of Mahrut River, Diyala, Iraq

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Abstract

Surface water samples from Mahrut River in Diyala city of Iraq were collected for two seasons, summer and winter of 2010-2011, to examine the concentration of eight heavy metals, namely: Cadmium, Chromium, Copper, Iron, Lead, Manganese, Nickel and Zinc. The observed values of Cd, Cr, and Pb are well above the recommended value for rivers maintaining system and general water from pollution, while Cd, Cr, Cu and Pb exhibit higher values than the guidelines values for protection of aquatic life. The results of cluster analysis and the pollution load index suggest that the heavy metal pollution of Mahrut river water is mainly influenced by anthropogenic activates rather than natural activities.
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1. Introduction

Surface waters are most exposable to pollution due to their easy accessibility for disposal of wastewaters (Samarghandi*et* al., 2007). Pollution is continuously becoming a serious problem, mainly caused by the disposal of untreated sewage and industrial waste, nitrates from animal waste and chemical fertilizers. It is important to report that the continuous increase the demographic and the urbanized expansion and the increased weight for inhabitants of the cities. However, rivers in urban areas play a major role in carrying of industrial and municipal wastewater, manure discharges and runoff from agricultural fields and streets, which are responsible for river pollution (Al Obaidy et al., 2010; Al Obaidy & Al-Khateeb, 2013, Al-Ani, et al., 2014).

Heavy metals are inorganic elements essential for plant growth in traces or very minute quantities. They are toxic and poisonous in relatively higher concentrations (Kar et al., 2008). Nevertheless, the most important anthropogenic sources of heavy metals in the urban areas that negatively influence the nearby environment are mining and related operations (Vanek et al., 2005).

There are two factors contribute to the harmful effects of heavy metals as environmental pollutants. They cannot be destroyed by biological degradation, and they are easily assimilated and can be bio-accumulated in the aquatic organisms (Egborge, 1994).

Huge amount of heavy metals inter the aquatic ecosystem from natural processes and anthropogenic activities. It can be transported as dissolved species in water or as an integral part of suspended sediments. These potentially toxic pollutants can cause danger to human health by being integrated in the food chain (Wogu & Okaka, 2011).

Mahrut River is a canal which serves as a main conduit for irrigation and passed through Muqdadiyah which is a city in the Diyala Governorate of Iraq. However, this study aims to investigate the current status of heavy metals concentration in the surface water of Mahrut River.

2. Materials and Methods

Six sites were selected along Mahrut River within Muqdadiyah city (**Figure 1**). Water samples were collected during summer and winter of 2010-2011. The samples were collected from a depth of 50 cm below the surface and kept in acid washed polyethylene containers. The containers were rinsed thoroughly with deionised water after being washed in dilute nitric acid (HNO_3). In the field the containers were rinsed several times with the river water and one liter sample was then collected at about 50cm below the water surface. Water samples were filtered using Whatman filter paper (0.45 µm pore size) for estimation of dissolved metal. These water samples were preserved with 1 ml nitric acid to prevent the precipitation of metals.

Samples were analyzed eight heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) using Atomic Absorption Spectrophotometry (AAS-6300, Shimadzu, Japan) according to (APHA, 2005).

The mean value from the sixth sampling sites was recorded for each metal. A comparison of the mean and range values of heavy metals concentration (mg/L) in Mahrut River with some standard guidelines values for Protection of Aquatic Life (CCME, 2007) and Maintenance Rivers from pollution (Law 25, 1967). The obtained data were subject to statistical analysis to test the analysis of cluster and correlation among all the parameters using SPSS statistical package.

3. Results and Discussion

3.1 General

The results are demonstrated by the mean values of pH and heavy metals concentration of Mahrut River water as compared to the rivers maintaining system and general water from pollution (Law 25, 1967) and guidelines values for protection of aquatic life (CCME, 2007) are presented in **Table 1**. An explanation of the observed characteristics follows in the following sections.

pH is a significant variable which can be used in evaluating the acid-base balance of water (WHO, 2004). The values of pH vary from 6.77 to 7.33 with a mean value of 7.03 and from 7.07 to 7.33 with a mean value of 7.2 in the winter and summer season respectively representing that the river water is almost neutral to sub-alkaline in nature. The observed values suggest that all water samples are within the recommended value for rivers maintaining system and general water from pollution (Law 25, 1967) and guidelines values for protection of aquatic life (CCME, 2007).

The heavy metals concentrations in the surface water samples from Mahrut River were decreased in the sequence: Cr>Pb>Fe>Ni>Mn>Cu>Cd>Zn for summer season and Cr>Fe>Ni>Mn>Cu>Pb>Cd>Zn for winter season. Cr has emerged as the dominant metal while Zn has the lowest concentration. A brief discussion about individual metals follows:

Cadmium: Human activity has significantly increased Cd concentration in the aquatic ecosystem. It can move for a long distances from the source of emission by atmospheric transport (WHO, 2010). The Cd concentration in the Mahrut river water varies from 8.0 to 12.0 µg/L in the summer season and from 13.9 to 23.5 µg/L in the winter season. However, the results indicated that the mean concentration of dissolved cadmium in the present study well above the recommended value for rivers maintaining system pollution (Law 25, 1967) and the acceptable guidelines values for protection of aquatic life (CCME, 2007). The reason of increasing Cd concentration in these study sites may be related to the sewage, industrial and the agricultural activities (Manahan, 1993).

Chromium: Concentrations over the maximum acceptable level for rivers maintaining system (Law 25, 1967) and the acceptable values for protection of aquatic life guideline (CCME, 2007), were found in Mahrut river water. It reported that industrial activities e.g. metal plating, dyes, pigments, ceramic; glues, tanning, wood preserving are reported to contribute Cr (Alloway, 1995).

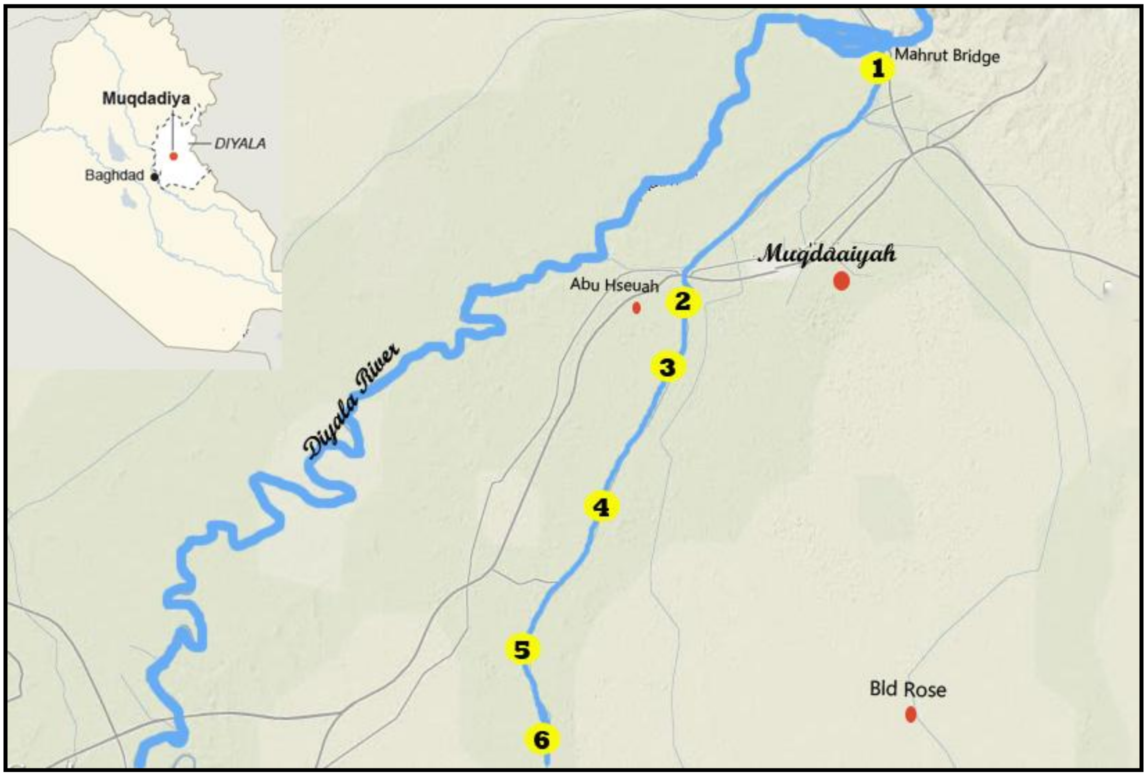


Table 1: Statistical summary of pH and heavy metals in surface water of study area

Parameters	Summer				Winter				Law 25, 1967	CCME, 2007
	Min	Max	Mean	SD	Min	Max	Mean	SD		
pH	6.77	7.33	7.03	±0.25	7.07	7.33	7.20	±0.11	6.5-8.5	6.5-9.0
Cd (µg/L)	8.00	12.00	9.87	±199.27	13.90	23.50	18.52	±3.71	5	0.017
Cr (µg/L)	496.00	1083.0	770.17	±0.05	853.00	1021.00	952.83	±56.15	50	1
Cu (µg/L)	ND	62.00	18.77	±27.48	29.90	47.20	40.25	±6.43	50	4
Fe (µg/L)	127.00	218.00	181.28	±34.92	131.00	189.00	162.17	±21.33	300	300
Pb (µg/L)	218.00	330.00	284.33	±38.77	10.00	79.00	37.83	±28.83	50	7
Mn (µg/L)	33.70	53.00	40.97	±7.09	68.30	95.90	84.77	±10.45	100	-----
Ni (µg/L)	86.00	108.00	99.67	±8.21	121.00	173.30	145.88	±20.88	100	150
Zn (µg/L)	2.80	9.00	6.33	±0.003	ND	8.00	3.77	±3.32	500	30

Copper: The Cu concentration ND to 62.0 µg/L and from 29.9 to 47.2 µg/L in the summer and winter season respectively. The observed mean values of Cu in this study have been within the recommended value for rivers maintaining system (Law 25, 1967) and well above the acceptable guidelines values for protection of aquatic life (CCME, 2007).

Iron: The Fe concentration in the Mahrut river water varies from 127.0 to 218.0 µg/L and from 131.0 to 189.0 µg/L in the summer and winter season respectively. The observed values of Fe in the study sites have been within the recommended values for rivers maintaining system (Law 25, 1967) and the acceptable guidelines values for protection of aquatic life (CCME, 2007).

Lead: Pb value varied from 218.0 to 330.0 µg/L and from 10.0 to 79.0 µg/L in the summer and winter season respectively. However, almost all the surface water sources have higher Pb content in the dry season than in the wet season. Furthermore, the observed vales was found well above the recommended values for rivers maintaining system (Law 25, 1967) and the acceptable guidelines values for protection of aquatic life (CCME, 2007). The high concentration of Pb in the river water can be related to the anthropogenic activities such as vehicular emissions.

Manganese: The Mn concentration in the Mahrut river water varies from 33.7 to 53.0 µg/L and from 68.3 to 95.90 µg/L in the summer and winter season respectively. The observed values of Mn in the study sites have been within the recommended value for rivers maintaining system and general water from pollution (Law 25, 1967).

Nickel: The Ni concentration in the Mahrut river water varies from 86.0 to 108.0 µg/L and from 121.0 to 173.3 µg/L in the summer and winter season respectively. The observed values of Ni in the winter season have been above the recommended value for rivers maintaining system and general water from pollution (Law 25, 1967) but within the acceptable guidelines values for protection of aquatic life (CCME, 2007). Sources of Ni in water include contamination from municipal sewage sludge and wastewater. Anthropogenic sources include combustion of fuel or waste released from industries (Bhagure & Mirgane, 2010).

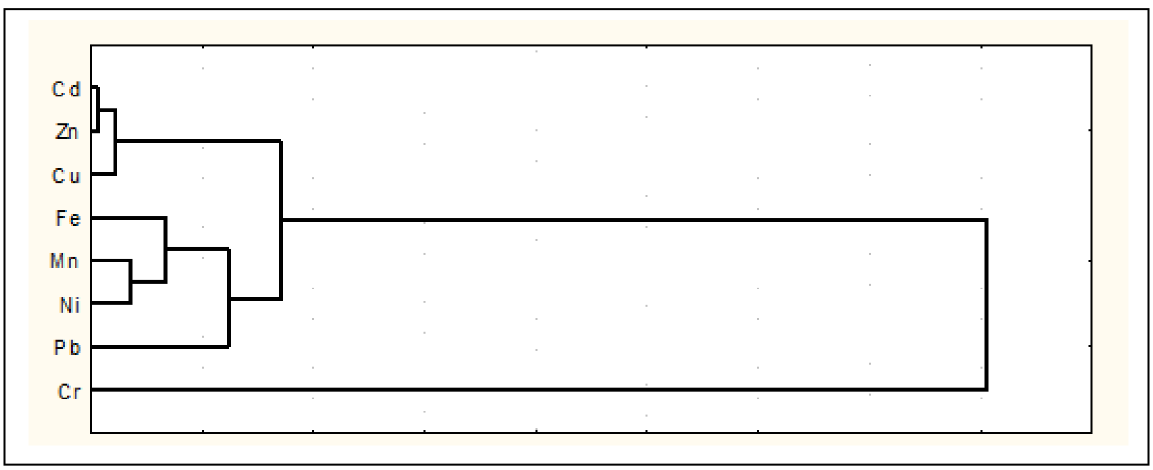
Zinc: The Mn concentration in the Mahrut river water varies from 2.8 to 9.0 µg/L and from ND to 8.0 µg/L in the summer and winter season respectively. The observed values of Zn in this study have been within the recommended values for rivers maintaining system (Law 25, 1967) and the acceptable guidelines values for protection of aquatic life (CCME, 2007).

3.2 Cluster Analysis

Cluster analysis is one of the methods used to find different groups within the investigated data. Various techniques for data transformation, standardization, distance coefficients and clustering methods are available. Cluster analysis was carried out applying Ward's method, using Squared Euclidean Distance as a measure of similarity. Ward's method was chosen for this purpose as it aims to minimize the loss of information at each step in the clustering process (Ward, 1963).

Cluster analysis was applied on the heavy metals data of all sites of the Mahrut River to identify interrelationships and discover different sub clusters within the water quality that might help us to allow us to determine the associations among different elements and their input source.

The results of cluster analysis for the heavy metals data are illustrated with a tree dendrogram (**Figure 2**). The dendrogram shows that the heavy metals could be mainly grouped into three main clusters. Cluster I consists of Cd, Zn and Cu indicating that combustion of lubricating oils (Makepeace et al., 1995) and operation and maintenance of vehicles are the main sources, while cluster II consists of Fe, Mn, Ni and Pb which also suggest their common sources. Cr appears in one cluster.



3.3 Correlation Matrix

Correlation coefficients indicate the strength of a relationship between variables. The emphasis is on the degree to which two sets of values vary together around their respective means and on the direction of co-variation of the variables. The correlation matrices obtained for all heavy metals data is presented in **Table 2**.

Cd display strong correlation coefficient with Pb, Mn and Ni (0.79, 0.77 and 0.75 respectively) which indicates a strong linear correlation at the 0.05 significance level and a common origin of these metals. Cr exhibited positive correlations with both Pb (0.59) and Mn (0.66). Cu display positive correlation with both Fe (0.74) and Zn (0.58), suggesting they probably originated from some common sources. Pb is also strongly correlated with Mn (0.89) and Ni (0.74) indicates that its occurrence in the surface water was mainly due to natural or anthropogenic sources. The lack of significant linear correlation between Fe and the other heavy metals suggests that its sources were quite different from those of the others.

Table 2: Correlation coefficient matrix of all heavy metals data

	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Cd	1							
Cr	0.50	1						
Cu	0.39	0.48	1					
Fe	0.21	0.28	**0.74**	1				
Pb	**0.79**	**0.59**	0.61	0.54	1			
Mn	**0.77**	**0.66**	0.51	0.18	**0.89**	1		
Ni	**0.75**	0.43	0.43	0.10	**0.74**	**0.87**	1	
Zn	0.30	0.09	**0.58**	0.29	0.45	0.16	0.19	1

3.4 Pollution Load Index

Pollution load index (PLI), has been evaluated following the method proposed by Tomilson et al. (1980). This parameter is expressed as:

$$PLI = (CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x } \ldots\ldots\ldots\ldots \text{ x } CF_n)^{1/n}$$

Where, n is the number of metals and CF is the contamination factor. The contamination factor can be calculated from the following relation:

$$CF = \frac{C_{sample}}{C_{background}}$$

Where, C_{sample} and $C_{background}$ refer the recommended value for rivers maintaining system (Law 25, 1967) and the acceptable guidelines values for protection of aquatic life (CCME, 2007).

The PLI<1 denote perfection; PLI=1 present that only baseline levels of pollutants are present and PLI>1 would indicate deterioration of water quality (Thomilson et al., 1980).

The results of the pollution load index (**Table 3**) indicate that the pollution load index in all cases is higher than one and suggests that the heavy metal pollution of Mahrut river water is mainly influenced by anthropogenic activates rather than natural activities.

Table 3: Calculated pollution load index values

Season	PLI values	
	Refer to recommended value for rivers maintaining system (Law 25, 1967)	Refer to guidelines values for protection of aquatic life (CCME, 2007)
Summer	5.57	17.68
Winter	4.68	15.40

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