Evaluation of Surface Water Quality Indices for Heavy Metals of Diyala River-Iraq

Enaam J. Abdullah
Geology department, College of science, Baghdad University, PO box 47066, Al-Jadria Str., Iraq
E-mail: dr.enaam2010@yahoo.com

Abstract
The present study aimed to envisage the water quality status of Diyala River (Iraq) with respect to its heavy metal concentrations by preparing the most recent heavy metal pollution index, metal index and to evolve the sources of heavy metals. Ten locations were selected along of the Diyala River, from Kalar district to the confluence with Tigris River. Six heavy metals viz. Zinc (Zn), Nickel (Ni), Cadmium (Cd), Copper (Cu), Lead (Pb) and Chromium (Cr) were analyzed using Atomic Absorption Spectroscopy (AAS). The mean HPI 2097 far above the critical value of 100, indicates that Diyala River is critically polluted with respect to heavy metals. MI revealed low quality water with MI value 71.63, suggests that the river is seriously affected with respect to heavy metal. The study revealed the impact of anthropogenic sources on the pollution load of the river water.

Keywords: Diyala River, Heavy metal pollution index, metal index, Water contamination.

1. Introduction
Rapid urbanization and industrial development during last decade have provoked some serious concerns for the environment. Heavy metals contamination in river is one of the major quality issues in many fast growing cities, because maintenance of water quality and sanitation infrastructure did not increase along with population and urbanization growth especially for the developing countries (Sundaray et al., 2006; Akoto et al., 2008; Ahmad et al., 2010). Heavy metals are among the most common environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources. The main natural sources of metals in waters are chemical weathering of minerals and soil leaching. The anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm, water runoff, landfill leachate, mining of coal and ore, atmospheric sources and inputs rural areas (Zarazua et al., 2006). Rivers in urban areas have also been associated with water quality problems because of the practice of discharging of untreated domestic and small scale industries into the water bodies which leads to the increase in the level of metals concentration in river water (Sekabira et al., 2010). Trace metal contaminations are important due to their potential toxicity for the environment and human beings (Lee et al., 2007; Adams et al., 2008). Some of the metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for the life processes in animals and plants while many other metals such as Cd, Cr, Pb and Co have no known physiological activities (Kar et al., 2008; Suthar and Singh, 2008; Akhtar et al., 2010). Metals are non-degradable and can accumulate in the human body system, causing damage to nervous system and internal organs (Lee et al., 2007; Lohani et al., 2008). However, the rivers play a major role in assimilation or transporting municipal and industrial wastewater and runoff from agricultural and mining land (Singh et al., 2004). The spatial study of heavy metals by producing heavy metal pollution index can be helpful in identifying and quantifying trends in water quality (Prasad & Kumari, 2008; Reza & Singh, 2010) and can provide the accumulated information and assessments in a form that resource management and regulatory agencies can use to evaluate alternatives and make necessary decisions (Nair et al., 2010).

The present study aimed to envisage the water quality status of Diyala River with respect to its heavy metal concentrations by preparing the most recent heavy metal pollution index and metal index and to evolve the sources of heavy metals.

2. Materials and Methods
2.1 Study area:
Diyala River basin is located between Latitude (33° 13´00" N- 35° 50´00" N) and Longitude (44° 30´00" E- 44° 50´00" E), and passes the river in Diyala province northeast of Baghdad, Figure (1). Diyala River is one of the main water resources of Iraq and one of the most important tributaries of Tigris River in Iraq. For this reason many cities are situated on its banks, as well as, wastes fluids of agricultural and industrial activities in these cities are also concentrated directly to this river. It drains an area of about 32600 km² lying across Iraqi-Iranian frontiers. The river basin is widely varied through the entire catchments area from semi-arid plain north of Baghdad to mountainous area of western Iran (Al- Ansari and Al-Jabbari, 1987). The river catchments were divided into four parts; above Derbendikhan, Upper Diyala, Middle Diyala and Lower Diyala, each of these have
different characteristics and different contribution to the main river flow. From geological view point, river catchments have different geological units; above Derbendikhan the catchments lies within thrust zone and the exposed rocks are of Jurassic age, whereas the Upper and Middle Diyala lie within the folded zone in which the cretaceous strata are exposed, as well as Mukdadiya, Fatha formations and Quaternary terraces are dispersed. Lower Diyala is covered mainly by recent alluvium and lies within the unfolded zone. The Climatic conditions vary so much in the river catchments in which the rainy season starting from November to April, the annual amount of precipitation varies from 800 mm near the northern parts to 250 mm near southern limits of the basin. The annual evaporation rate may reach as high as 2000 mm/year (Al-Jiboury, 1991). These conditions have clear effects on alteration of wet and dry years and then on the variation of river water quality. However, the catchments area of Diyala river are lies within highly cultivated regions and have many canals and drainage channels, which contributing and affects river hydrochemistry. The Diyala River basin is one of these basins, which cover the important parts of Iraq and its impact in the quality of the waters of the Tigris, which meets the latter south of Baghdad (Al-Timemi, 2007).

2.2 Field sampling and laboratory methods

For this study numerous stations had been sampled. Ten water samples were collected from the study area during November 2011. The samples covered the study area from Kalar district to the confluence with Tigris River, Figure 1. The samples were collected at 10-15 cm depth in separate pre-conditioned and acid rinsed clean polypropylene bottles. The collected samples were filtered (Whatman no. 42) and acidified with concentrated nitric acid to a pH below 2.0 to minimize precipitation and adsorption on container walls. For the determination of total heavy metals in the samples extraction procedures as described in APHA, 2005 were followed. Heavy metals concentrations (Zn, Ni, Cd, Cu, Pb, Cr) were determined in acidified filtrates water samples by atomic absorption spectroscopy in the laboratories of college of sciences, Baghdad University.

2.3 Heavy metal Pollution index

Heavy metal pollution index (HPI) is a technique of rating that provides the composite influence of individual heavy metal on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance of individual quality considerations and inversely proportional to the recommended standard (Si) for each parameter (Reza & Singh, 2010; Prasad and Mondal, 2008; Prasad & Kumari, 2008). The calculation of HPI involves the following steps:

First, the calculation of weightage of ith parameter

Second, the calculation of the quality rating for each of the heavy metal

Third, the summation of these sub-indices in the overall index

The weightage of ith parameter

\[ W_i = \frac{k}{S_i} \]  

(1)

Where \( W_i \) is the unit weightage and \( S_i \) the recommended standard for ith parameter, while \( k \) is the constant of proportionality.

Individual quality rating is given by the expression

\[ Q_i = \frac{100 \cdot V_i}{S_i} \]  

(2)

where \( Q_i \) is the sub-index of ith parameter, \( V_i \) is the monitored value of the ith parameter and \( S_i \) the standard or permissible limit for the ith parameter.

The Heavy Metal Index (HPI) is then calculated as follows

\[ \text{HPI} = \sum_{i=1}^{n} \left( Q_i \cdot W_i \right) / \sum_{i=1}^{n} W_i \]  

(3)

where \( Q_i \) is the sub-index of ith parameter. \( W_i \) is the unit weightage for ith parameter, \( n \) is the number of parameters considered. The critical pollution index value is 100. For the present study the \( S_i \) value was taken from the Iraqi drinking water specifications standard, 2009, No.417.

2.4 Metal Index

Another index used is the general metal index (MI) for drinking water (Bakan et al., 2010) which takes into account possible additive effect of heavy metals on the human health that help to quickly evaluate the overall quality of drinking waters. Metal pollution Index is given by the expression proposed by (Caeiro et al., 2005).

\[ MI = \sum \left[ C_i / (MAC) i \right] \]

Where MAC is maximum allowable concentration and \( C_i \) is mean concentration of each metal. The higher the concentration of a metal compared to its respective MAC value the worse the quality of water. MI value > 1 is a threshold of warning (Bakan et al., 2010). Water quality and its suitability for drinking purpose can be examined by determining its metal pollution index (Mohan et al., 1996; Prasad & Kumari, 2008).
3. Results and Discussion:

Concentrations of the six studied heavy metals have been shown in Table 1. The metal concentrations were significantly different between sampling locations. However, the concentrations of Ni, Cd, Pb and Cr were found to be above the highest permissible value of Iraqi standards for drinking water, 2009, No.417. While the concentrations of Zn and Cu were found to be below the highest permissible value of the mentioned guide line. Based on the concentration ranges and abundance heavy metals are ranked as Cr > Pb > Ni > Cd > Zn > Cu (Table 1).

Heavy metal pollution index is an effective tool to characterize the surface water pollution (Prasad & Kumari, 2008; Reza & Singh, 2010) as it combines several parameters to arrive at a particular value which can be compared with the critical value to assess the level of pollution load.

In order to calculate the HPI of the water, the mean concentration value of the selected metals (Zn, Ni, Cd, Cu, Pb, Cr) have been taken into account. Table 2 details the calculations of HPI with unit weightage (Wi) and standard permissible value (Si) as obtained in the presented study. The mean of heavy metal pollution index value was found to be 2097 far above the critical value of 100. Though HPI value indicates that Diyala River is critically polluted with respect to heavy metals.

HPI was also calculated separately for each sampling location to compare the pollution load and assess the water quality of the selected locations Table 3, Figure 2. The highest value of HPI was found in location 1, as Zn, Ni, Cd, Cu, Pb and Cr were found to have anthropogenic origin and mainly came from industrial activities, though municipal sewage, domestic wastes, traffic sources and atmospheric depositions, chemical weathering of minerals, and industrial discharges increase their concentration in water (Manoj et al., 2012). While the lower HPI value was found in location 5, this may indicate the dilution affect due to seepage or percolation of rain water (Reza et al., 2011).

MI for Diyala River revealed low quality water with MI value 71.63 table 4, suggests that the river is seriously affected with respect to heavy metal pollution according to Lyulko et al., 2001; Caerio et al., 2005, Table 5.

No work has been done on HPI and MI related to Iraqi Rivers, Prasad and Jaiprakash (1999) studied the mining area filled with fly ash and reported 11.25 HPI value, while Prasad and Sangita (2008) reported 36.67 which is below critical index, Nalawade et al., 2012 reported 5.5 index value near fly ash dumping sites, Manoj et al., 2012 reported 49.12 HPI value of the Subarnarekha River (India), Reza and Singh, 2010 found The mean values of HPI were 36.19 in summer and 32.37 for winter seasons of river water Angul-Talcher region india. Amadi et al., 2012 found that the MI indicates that the River Chanchaga, Minna, North-central Nigeria is slightly affected with respect to heavy metal pollution. Ameh and Akpah.,2011 reported MI index the River PovPov in Itakpe Nigeria status was 403 and 87.12 respectively, clearly indicating low-quality water.

4. Conclusion

Heavy metal pollution index is very useful tool in evaluating overall pollution of water bodies with respect to heavy metals. Overall HPI calculated based on the mean concentration of the heavy metals was found to be 2097 which is more than the critical pollution index value of 100, indicates that the selected water samples from the river are critically contaminated with respect to heavy metals. The result of the MI was found to be 71.63 suggests that the selected river is seriously affected with respect to heavy metal pollution. The study revealed the impact of anthropogenic sources on the pollution load of the river water.

Acknowledgement

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References

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Figure 1: Map of Study area along with sampling locations.
### Table 1: Heavy metal concentrations at different locations of Diyala River

<table>
<thead>
<tr>
<th>Sampling locations</th>
<th>Zn mg/l</th>
<th>Ni mg/l</th>
<th>Cd mg/l</th>
<th>Cu mg/l</th>
<th>Pb mg/l</th>
<th>Cr mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.105</td>
<td>N.D</td>
<td>0.267</td>
<td>0.193</td>
<td>0.402</td>
<td>1.626</td>
</tr>
<tr>
<td>2</td>
<td>0.176</td>
<td>0.184</td>
<td>0.086</td>
<td>0.097</td>
<td>0.087</td>
<td>1.973</td>
</tr>
<tr>
<td>3</td>
<td>0.123</td>
<td>0.259</td>
<td>0.108</td>
<td>0.096</td>
<td>0.258</td>
<td>2.445</td>
</tr>
<tr>
<td>4</td>
<td>N.D</td>
<td>0.098</td>
<td>N.D</td>
<td>0.098</td>
<td>0.151</td>
<td>N.D</td>
</tr>
<tr>
<td>5</td>
<td>0.032</td>
<td>0.064</td>
<td>N.D</td>
<td>N.D</td>
<td>0.036</td>
<td>N.D</td>
</tr>
<tr>
<td>6</td>
<td>0.072</td>
<td>0.108</td>
<td>N.D</td>
<td>0.074</td>
<td>0.151</td>
<td>N.D</td>
</tr>
<tr>
<td>7</td>
<td>0.368</td>
<td>0.063</td>
<td>0.034</td>
<td>N.D</td>
<td>0.708</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>0.073</td>
<td>0.106</td>
<td>0.051</td>
<td>0.09</td>
<td>0.228</td>
<td>1.027</td>
</tr>
<tr>
<td>9</td>
<td>0.066</td>
<td>0.159</td>
<td>0.047</td>
<td>N.D</td>
<td>0.11</td>
<td>0.413</td>
</tr>
<tr>
<td>10</td>
<td>0.089</td>
<td>0.078</td>
<td>0.079</td>
<td>0.018</td>
<td>0.326</td>
<td>N.D</td>
</tr>
</tbody>
</table>

N.D: not detected

### Table 2: Mean HPI of Diyala River

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Mean Concentrations mg/l (Vi)</th>
<th>Highest permitted value mg/l (Si)*</th>
<th>Unit weightage (Wi)</th>
<th>Subindex Qi</th>
<th>Wi x Qi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.1104</td>
<td>3</td>
<td>0.333</td>
<td>3.68</td>
<td>1.2254</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1119</td>
<td>0.02</td>
<td>50</td>
<td>559.5</td>
<td>27975</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0672</td>
<td>0.003</td>
<td>333.33</td>
<td>2240</td>
<td>746659</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0666</td>
<td>1</td>
<td>1</td>
<td>6.66</td>
<td>6.66</td>
</tr>
<tr>
<td>Pb</td>
<td>0.2457</td>
<td>0.01</td>
<td>100</td>
<td>2457</td>
<td>245700</td>
</tr>
<tr>
<td>Cr</td>
<td>0.9484</td>
<td>0.05</td>
<td>20</td>
<td>1897</td>
<td>37940</td>
</tr>
</tbody>
</table>

\[\sum Wi = 504.663\]
\[\sum Wi x Qi = 1058281.8\]

HPI = 2097


### Table 3: HPI recorded at different sampling locations

<table>
<thead>
<tr>
<th>Sampling locations</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPI</td>
<td>6803</td>
<td>2311</td>
<td>3210</td>
<td>347.7</td>
<td>103</td>
<td>352.7</td>
<td>2341</td>
<td>1708</td>
<td>1362.7</td>
<td>2421.9</td>
</tr>
</tbody>
</table>

\[\sum \text{HPI} = 2096\]
Figure 2: HPI values at various sampling points.

Table 4: Mean MI of Diyala River

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Mean Concentrations mg/l (Ci)</th>
<th>Highest permitted value mg/l (MAC)i</th>
<th>MI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.1104</td>
<td>3</td>
<td>0.0368</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1119</td>
<td>0.02</td>
<td>5.595</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0672</td>
<td>0.003</td>
<td>22.4</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0666</td>
<td>1</td>
<td>0.0666</td>
</tr>
<tr>
<td>Pb</td>
<td>0.2457</td>
<td>0.01</td>
<td>24.57</td>
</tr>
<tr>
<td>Cr</td>
<td>0.9484</td>
<td>0.05</td>
<td>18.968</td>
</tr>
</tbody>
</table>

\[ \sum \text{MI} = 71.636 \]

Table 5: Water Quality Classification using MI (Lyalko et al., 2001; Caerio et al., 2005)

<table>
<thead>
<tr>
<th>MI</th>
<th>Characteristics</th>
<th>Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.3</td>
<td>Very pure</td>
<td>I</td>
</tr>
<tr>
<td>0.3-1.0</td>
<td>Pure</td>
<td>II</td>
</tr>
<tr>
<td>1.0-2.0</td>
<td>Slightly affected</td>
<td>III</td>
</tr>
<tr>
<td>2.0-4.0</td>
<td>Moderately affected</td>
<td>IV</td>
</tr>
<tr>
<td>4.0-6.0</td>
<td>Strongly affected</td>
<td>V</td>
</tr>
<tr>
<td>&gt;6.0</td>
<td>Seriously affected</td>
<td>VI</td>
</tr>
</tbody>
</table>
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