J. Ecophysiol. Occup. Hlth. 12 (2012) 13-19

Heavy Metals Assessment in Sediment of Ramgarh Lake, UP, India.

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Abstract: *During this century, many lakes in India have received elevated inputs of heavy metals as a result of an increase in industrial, urban discharge and atmospheric deposition. The toxic heavy metals entering the ecosystem may lead to geo-accumulation, bioaccumulation and biomagnification. Heavy metals are important environmental pollutants threatening the health of human populations and natural ecosystems. In the present investigation, heavy metals concentration of Pb, Cd, As, Cu and Zn, were studied in Ramgarh Lake water and sediment in the month of December 2009. A method based on toxic-response factor was applied to assess the potential ecological risk of these heavy metals to the sediment of water body. The results indicated that the accumulating coefficient (C^i_f) sequence of the metals was Zn > Cu > Cd > Pb > As, while the sequence of the potential ecological risk coefficient (E^i_r)posed by the metals was Cd > As > Cu > Pb > Zn). The average indexes of potential ecological risk factors (Ri) for metals were 76.53, which shows low ecological risk for the Ramgarh Lake. The calculated potential ecological risk indices show that heavy metals in sediment were within the permissible limits except Cd, which indicates moderate pollution index. Lake Ramgarh was classified between moderate to good quality and found to have low metal concentrations in water and sediment, which indicates no significant anthropogenic metals input to the lake.*

Key words: Geo-accumulation, Heavy metals, Potential ecological risk, Ramgarh Lake.

Introduction

Lakes and surface water reservoirs are the planet's most important freshwater resources that provide innumerable benefits. They are source of water for domestic use, irrigation and renewable energy in the form of hydropower and are essential resources for industry. Lakes provide ecosystems for fish, thereby functioning as a source of essential protein, and for significant elements of the world's biological diversity (Rajashekhar and Vijaykumar, 2009). Heavy metals are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities to human. They include essential elements like iron as well as toxic metals like cadmium and mercury. Most of them show significant affinity to sulfur and disrupt enzyme function by forming bonds with sulfur groups in enzymes. Cadmium, copper, lead and mercury ions bind to the cell membranes hindering transport processes through the cell wall. Some of the metalloids, elements on the borderline between metals and nonmetals are significant water pollutants (Boran and Altınok, 2010). Some heavy metals are essential elements at low levels (Borovik, 1990; Hossain and Khan, 2001), others can exert toxic effects at concentrations encountered in polluted environments. Some of them persist in the environment and can become concentrated up the food chain (Benson and Ebong, 2005; Udosen *et al.*, 2006). Prapurna and Shashikanth (2002) carried out the analysis of heavy metal ions present in the water of Hussain Sagar Lake and found that the presence of various heavy metal ions in their dissolved state, that are hindering the beneficial uses of the lake waters. Sediment have always been considered as an indicator for aquatic ecosystems pollution. With the aim of achieving a broader assessment of lake heavy-metal pollution, in terms of ecological risks, a

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quantitative approach is needed (Huang *et al.,* 2009). Information on the total concentrations of metals alone is not sufficient to assess the environmental impact of polluted sediment because heavy metals are present as easily exchangeable metal carbonates, oxides, sulfides, organometallic compounds, ions in the crystal lattice of minerals etc. which determine their mobilization capacity and bioavailability (Gupta and Chen, 1975; Soto-Jimenez *et al.,* 2003). It is necessary to identify and quantify the forms in which a metal is present in sediment to gain a more precise understanding of the potential and actual impacts of elevated concentrations, and to evaluate processes of downstream transport, deposition and release under changing environmental conditions (Li *et al.*, 2000). The main objectives of this research was to quantify the total pollution of lead, cadmium, arsenic, copper and zinc in water and sediment from Ramgarh Lake, and to study the potential ecological risk of selected heavy metals to the water body with the method developed by Häkanson (1980) and results will be indicators of the metals pollution status of Ramgarh Lake.

Materials and Methods

Study Area

District Gorakhpur is situated in the north-east “Tarai” region of U.P. (India) and lies between 26.5º-27.9º N and 83.4º- 84.26º E at an altitude of 95 metre above sea level. There are many temporary and residential water bodies of varying size in this region. The Ramgarh Lake is a shallow, perennial eutrophic lake situated at 26º 44' 9" N, and 83º 24' 16" E eastern side of the Gorakhpur town close to the University campus. For the determination of heavy metals in lake water and sediment, five sampling site (Site-1 Paidleganj, Site-2 Boat Club, Site-3 Sahara Estate, Site-4 RKBK Mohaddipur, Site-5 Singhadia Canal Pump) were selected .

Sampling and pre-treatment

Lake water samples were collected (in triplicate) in the month of December 2009, by rowing boat by submerging pre-cleaned PE (Polyethylene) 10-12 feet deep from the bank and approximately 50 cm beneath the water surface of the lake by holding the bottles upward. Suspended particulate matter was separated by filtering water samples through 0.45-µm Whatman GF/C filters. Lake water was acidified to 0.5 % (V/V) separately by using concentrated nitric acid as for the precipitation of samples. The sediment samples were put in glass bottles (1000 cm^3 volume) that had been cleaned with 5% HCl (V/V) and 5% HNO_3 (V/V), and transported to the laboratory. In the laboratory, all the sediment samples were centrifuged and the supernatant was discarded. The samples of

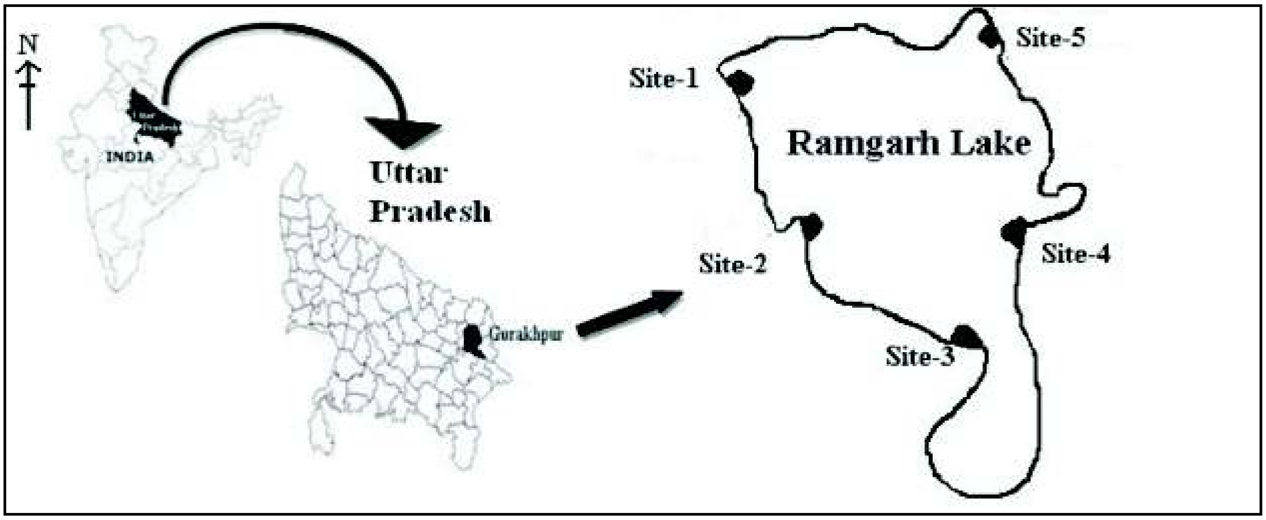

Fig. 1. Sampling sites for the collection of water and sediment samples of Ramgarh Lake, Gorakhpur.

the sediment were oven-dried at 105^{0}C and ground into powders for examination of heavy metals.

Sample analysis

For analyzing heavy metal content of water, 100 ml of water samples were taken and digested using HNO_3 and $HClO_4$ in a 5:1 ratio until a white fume was appeared, the water digests were filtered and diluted to 10 ml with 0.1N HNO_3 solution (APHA, 2005). Analysis of heavy metals in sediment samples were analyzed by method developed by Huang *et al.,* (2009). The prepared solutions of water and sediment were assayed by AAS (Elico SL-194) for Pb, Cd, As, Cu and Zn. The AAS value of blank (without sample) of each metal was deducted from the sample value for final calculations (Singh *et al.,* 2010, 2011).

Quality assurance and quality control

Appropriate quality assurance procedures and precautions were carried out to ensure reliability of the results. Double distilled water was used throughout the study. Glassware was properly cleaned, and the reagents were of analytical grade. Reagents blank determinations were used to correct the instrument readings.

Accumulating status of heavy metals

In this study, the accumulating coefficient was computed and applied to indicate the accumulating status of heavy metal in the sediment of Ramgarh Lake. The computing equation for accumulating coefficient (C^i_f) is as follows:

$$C^i_f = C^i_m/C^i_n$$

In this equation, C^i_m is the value of heavy-metal concentration in the sediment sample, and C^i_n is the reference. In the present study the references value of heavy metals based on background values in soil of Ramgarh Lake area (Pb=15.0 mg/kg, Cd=0.5 mg/kg, As=10.0 mg/kg, Cu=20.0 mg/kg and Zn=100.0 mg/kg), were applied for the calculations of C^i_f (Singh *et al.,* 2011).

Heavy-metal potential ecological risk

The potential ecological risk index method developed by Häkanson (1980) was applied in this study. According to this method, the potential ecological risk coefficient (E^i_r) of single element and the potential ecological risk index (R_i) of multi-element can be computed via the following equations:

$$E^i_r = T^i_f \times C^i_f$$

$$R_i = \Sigma E^i_r = \Sigma T^i_f \times C^i_f$$

Where T^i_f = the toxic-response factor for a given substance; C^i_f = the contamination factor or accumulation coefficient (the ratio between sediment and background value of metals in soil of Ramgarh Lake area). The toxic-response factors for common heavy metals Pb, Cd, As, Cu and Zn were 5, 30, 10, 5 and 1, respectively (Huang *et al.,* 2009).

Results and Discussion

Metal Concentration in water

The mean value of different sampling sites indicates a uniformly low degree of metal contamination in the lake. The concentration of various toxic heavy metals like Pb, Cd, As, Cu and Zn was elevated and are below the level of a

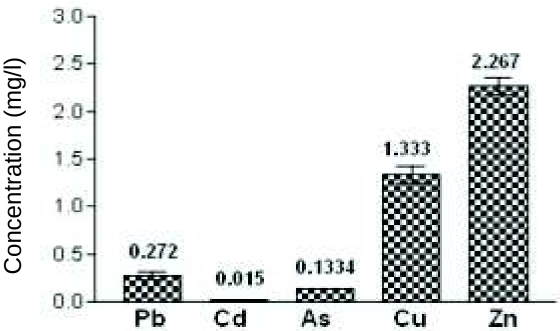

Fig. 2. Metal concentration in water of Ramgarh Lake.

polluted system. From the results, it is found that all five metals were present in lake water. In lake water the average total concentration (mg/l) of Pb(0.217) is two-fold higher to the limit (total heavy metal concentration < 0.1 mg/l for Pb in surface water), while other metals were within the limit of CPCB (2000) standards. It is observed that the average values of metal concentration (mg/l) in lake water was, 0.014(Cd), 0.207(Pb), 1.343(Cu), 0.139(As) and 1.992(Zn). This indicates that the heavy metal concentration in lake water is due to the discharge of waste water from industrial, municipal and domestic activities in the neighborhood. Singh and Upadhyay (2012) have found that Cu, Cr, Pb, Cd, and Mn are present in relatively higher concentrations as compared to their permissible limits whereas As, Zn and Ni concentration is below the permissible limit prescribed by WHO (2004) and USEPA (2002) for drinking water. When compared to the standards of CPCB (2000) for surface water it shows that all the heavy metals in Ramgarh Lake water were within the safe limits except for Pb that was beyond the limits. Heavy metal pollution is mainly the result of human activities such as agriculture, mining, construction and industrial processes (Chiras 2001; Singh et al. 2004). Pesticides and fertilizers are known to be the main sources of heavy metal pollution in lake water nearby agricultural areas (Kabata-Pendias and Pendias 2001; Whitney 1998).

Metal concentration in sediment

Although, metals in sediment vary between sampling stations, the mean concentration of anthropogenic metals (combination of three fractions) obtained from 5 stations (Fig. 3) were found to be low even lower than EPA guideline (Ahmad and Shuhaimi-Othman, 2010) concentrations in unpolluted area (Table 1). The trend of occurrence of heavy metals in sediment of Ramgarh Lake revealed; Zn(188.83) > Cu(32.47) > Pb(22.07) > As(13.17) > Cd(0.77). None of studied metals found exceed the maximum recommended concentration in sediment from unpolluted sediment. This indicates that Lake Ramgarh is considered as unpolluted from those metals. This study reveals that Lake Ramgarh is located near the developed area and anthropogenic sources, some metals namely Zn and Cu were found high and potential to contaminate the lake in the future. Improper agriculture and untreated discharge of domestic wastes and land clearance could lead to contamination in future (Singh *et al.,* 2011). Similar study was done by Yin *et al.,* (2011) in surface sediment of Lake Taihu, China and found that unfortunately,

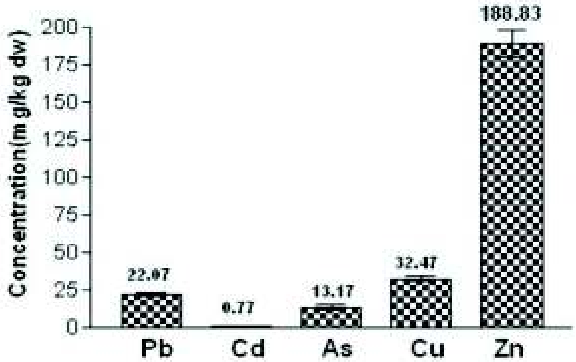

Fig. 3. Metal concentration in sediment of Ramgarh Lake.

Table 1. Sediment criteria according to EPA region V[a] (Ahmad, and Shuhaimi-Othman, 2010)

Heavy Metals	Unpolluted	Slightly polluted	Seriously polluted	Average concentration in Earth's crust
Pb	<40	40-60	>60	16
Cd	-	-	>6	0.2
As	-	-	-	-
Cu	<25	25-50	>50	70
Zn	<90	90-200	>200	80
Fe	<17000	17000-25000	>25000	50000

[a]Concentration in mg/kg dry wt.

overpopulation, rapid urbanization, improper management of water resources, and point and nonpoint pollution in the watershed have all greatly affected the water quality of Lake Taihu. Many of the domestic and industrial wastes were potential sources of heavy metal contamination that have the potential to threaten public health and impact the balance of the lake ecosystem (Fan *et al.,* 2004).

Accumulating coefficient (C^i_f)), potential ecological risk coefficient (E^i_r) and potential ecological risk index (R_i)

The mean result of Accumulating coefficient (C^i_f), potential ecological risk coefficient (E^i_r) and potential ecological risk index (R_i) of heavy metals obtained from 5 stations are presented in Table 2 The accumulating coefficient (C^i_f) in sediment of lake was found in the descending order of Zn(1.89) > Cu(1.63) > Cd(1.53) > Pb(1.47) > As(1.37) and potential ecological risk coefficient (E^i_r) descended in order of of Cd(45.99) > As(13.17) > Cu(8.12) > Pb(7.36) > Zn(1.89). According to the calculated accumulating coefficients, Zn was the most serious polluting element and As gave the lowest values among these heavy metals under study in this investigation. The study reveals that Zn gave the lowest and Cd gave the highest value to potential ecological risk coefficient on an average among the heavy metals under study in this investigation. The values of R_i (76.53) in Ramgarh Lake was lower than 150, indicating a low ecological risk for the water body. It is noted that the values of E^i_r for cadmium was higher than 40, where as all the other elements studied in this investigation were lower than 40, suggesting a low ecological risk for the Ramgarh Lake. Results shows that, only cadmium under this investigation in sediment exerted a moderate ecological risk to the water body. It is well known that acidic rain has been a serious problem in all over the world due to the combustion of a large amount of coal containing high concentrations of sulphur, arsenic, fluorine and other hazardous elements. On the one

Table 2. Accumulation coefficients, potential ecological risk coefficient and ecological risk index of heavy-metal in sediment of Ramgarh Lake.

S.No.	Chemicals	Accumulation coefficients(C^i_f)*	Potential ecological risk coefficient (E^i_r)	Ecological risk index (R_i)
1	Pb	1.48	7.36	
2	Cd	1.54	45.99	
3	As	1.32	13.17	76.53
4	Cu	1.63	8.12	
5	Zn	1.89	1.89	

*Based on the references of heavy-metal background values in soil of Ramgarh Lake Area (Singh et al. 2011; Singh and Upadhyay, 2012).

Table 3. Criteria for degrees of the ecological risk of heavy-metal in sediment (Huang et al. 2009).

E^i_r or R_i	Ecological pollution degree
$E^i_r < 40$ or $R_i < 150$	Low ecological risk for the water body
$40 = E^i_r < 80$ or $150 = R_i < 300$	Moderate ecological risk for the water body
$80 = E^i_r < 160$ or $300 = R_i < 600$	Considerable ecological risk for the water body
$160 = E^i_r < 320$ or $R_i < 600$	Very high ecological risk for the water body

hand, this can surely increase the arsenic baseline value in local soil; On the other hand, it may decrease the zinc baseline value because a more acidic environment can decrease the pH value in local soil, thus increased absorption of zinc by vegetation can consequently bring down the zinc level in soil. In the case of Ramgarh Lake, in addition to the above-mentioned sources, agricultural and urban sewage should be major sources of heavy-metal pollution. In addition, problems still exist for treatment of urban sewage from Gorakhpur city (with a population of approximately 7,00,000). These problems need to be properly addressed; otherwise concentrations of heavy metals will likely still rise in the lake in the future. The present study shows that cadmium was the main contributor to the pollution of sediment from Ramgarh Lake to which the population around Gorakhpur City can be exposed through drinking water or by consuming fish from the lake. Heavy metals have been a major concern in this regard because of the toxic effect of high metal concentrations on plants and because certain metals can be translocated into vegetable products and subsequently consumed by humans or grazing animals. Therefore, it is crucial to have a detailed investigation and assessment of ecological risks of heavy metals in Lake Ramgarh and the lake was classified between moderate to good quality and found to have low metal concentrations in water and sediment. but there is need for immediate action against illegal and untreated discharge of waste water in the lake and a regular bio-monitoring to evaluate water quality of lake.

Acknowledgement

The study was supported by Council of Science and Technology (CST), Uttar Pradesh, India (grant no. CST-1760).

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