Evaluation of heavy metals in sediment, water and Macrophyte (Eicchornea crassipes) of Yamuna River at Delhi

Sumit Kumar and Amita Saxena

DOI: https://doi.org/10.22271/chemi.2021.v9.i1ax.11784

Abstract
To examine the degree of contamination in Yamuna River at Delhi, eight heavy metal (Pb, Cd, Hg, Cu, Cr and Zn) were assessed in soil, water and macrophyte (Eicchornea Crassipes). Heavy metals are one among the toxic chemicals and accumulation in sediments and plants has been posing serious health impacts. The occurrence heavy metals in water were found in the order: Cr > Zn > Pb > Cu > Cd > Hg. In sediment order was: Cr > Zn > Pb > Cu > Cd > Hg and in macrophyte (Eicchornea Crassipes) in order: Zn > Pb > Cr > Cu > Cd > Hg. The analyses of macrophytes and sediment samples help in evaluating pollution status in aquatic environment. Heavy metals in water was found above the recommended level set by WHO for drinking.

Keywords: Heavy metals, water, sediment, Eicchornea Crassipes, Yamuna River

1. Introduction
The toxicity of trace metal contamination is a serious environmental problem that not only threatens aquatic ecosystems, but also causes serious health hazards through food-chain magnification. The elements with atomic number greater than 20 with higher density (>5 g/cm3) and metallic properties are chemically stable. These have long biological half-life compared to other xenobiotics and are non-biodegradable, toxic and persistent with serious ecological ramifications in ecosystems (Chopra et al., 2009) [2]. Trace metals are released into the environment by a wide range of natural and anthropogenic sources including industrial, agricultural, and domestic waste (Upadhyay et al., 2014) [3]. Some trace metals are persistent in nature and can reside in polluted environments for a longer period, which causes deleterious health effects to humans and aquatic organisms (Rai et al., 2015) [4]. Metal enrichment in river sediments reflects the upstream contamination sources and pollution over time, even when the levels in water are extremely low and metal concentrations undetectable with existing methods of analysis. Aquatic plants have not only high assimilation potential but also possess the ability to accumulate biogenic elements and toxic substances, including heavy metals. The contamination of the aquatic systems with toxic heavy metal ions is a problem of global concern. In addition to their toxic effects even at low concentrations, heavy metals can accumulate along the food chain which leads to serious ecological and health hazards as a result of their solubility and mobility (Yan et al., 2010) [5]. Sediments are important sinks for various pollutants like pesticides and play a significant role in the remobilization of contaminants in aquatic systems under favourable conditions with interactions between water and sediment (Ikem et al., 2003) [6]. The release of trace metals from sediments into water body depends on speciation of metals (precipitation, adsorption, and solubilisation) and other factors such as sediment pH and also the physical and chemical characteristics of aquatic system (Morgan and Stumm, 1991) [7]. Zhang (2004) [8] has said that chemical analysis of the environment matrix such as water, sediment is the most direct approach to reveal the heavy metal pollution status in the environment, while it cannot afford the powerful evidence on the integrated influence and possible toxicity of such pollution on the organisms and ecosystem. Yamuna, the life line of Delhi is the most polluted river in the country. Yamuna has witnessed maximum obstructions due to construction of barrages and weirs, abstraction by a number of canals and addition of pollution load including industrial effluents and sewage from the cities.
along the basin make the river an extreme example of over-exploitation for human use. Out of the total river length, about a 580 km stretch between Wazirabad barrage and Etawah is highly polluted and has resulted in a drastic decline in the fishery, both in respect to quality and quantity. The river condition is revived downstream to Etawah after receiving considerable flow from Chambal. The major sources contributing to the pollution of Yamuna are: untreated sewage, industrial effluents, the dumping of garbage and dead bodies, immersion of idols and pollution due to in-stream uses of water (CPCB, 2006) [5]. The capital of the nation, Delhi is the major contributor of pollution in the Yamuna River, followed by Agra and Mathura (Misra, 2010). The present study was, therefore, undertaken to examine the concentrations of six heavy metals Pb, Cd, Hg, Cu, Cr and Zn in order to understand the effects of human action on the quality of water, sediments and macrophytes growing in the water of river Yamuna. Interrelationships of these heavy metal concentrations in different components as well as with some other important water properties were also studied.

2. Material and Methods

2.1 Sampling
The 1000-km-long Yamuna River originates in the Himalayan mountains as a main tributary of the Ganges (Ganga) River. After descending through the Himalaya, the river passes through the capital city of India, Delhi, meanders through Agra and joins the Ganges River at Allahabad. The present investigation was carried out along the capital of India i.e. Delhi. Monthly samples of water, soil and macrophytes were collected from March 2019 to February 2020 for the present study.

River water samples were collected in pre cleaned polyethylene bottles and acidified with concentrated nitric acid (1.5 ml concentrated nitric acid per litre of sample). The bottles were stored in a refrigerator at approximately 4°C to prevent change in volume due to evaporation. Soil samples were collected using stainless steel scoops, and put into pre-cleaned plastic bags, which were sealed and delivered to the laboratory for analysis. The Macrophyte (Eichhornia crassipes) were collected and washed several times with the river water in order to remove the adhered invertebrates and large particles of mud. These were brought to the laboratory in the polyethylene bags where each sample was rinsed thoroughly with distilled water.

2.2 Heavy metal analysis
For the heavy metal analysis of water, 100 ml of well-mixed, acid-preserved sample was taken in an acid-washed beaker and 5 ml of concentrated nitric acid was added to it. The mixture was then digested at 80°C on a hot plate to the lowest volume possible (about 10–20 ml) before precipitation occurred. Heating and addition of concentrated nitric acid was continued until the digestion was complete (as indicated by a light-colored clear solution). After cooling, the digested samples were filtered using Whatman no. 42 filter paper, and the filtrate was diluted to 50 ml using de-ionized water.

The sediment samples were sieved through a 2 mm plastic sieve to obtain fine particles. 1g of the oven dried sample was placed in a 250 ml beaker to which 15 ml of aquarea (35% HCL and 70% high purity HNO₃ in 3:1 ratio) was added. Then the mixture was digested at 70 °C till the solution became transparent. The solution was filtered through Whatman filter paper no. 42 and diluted to 50 ml volumetric flask using deionized water.

The macrophyte samples were washed with deionized water, air-dried and then placed in a oven at 70 °C for 48 hours. 0.5 g of dried powdered sample will be moistened with 1-2 ml of deionized water & then 10 ml of concentrated HNO₃ will be added slowly and left overnight. The mixture was heated on a hot plate until complete leaching/digestion of the tissue. After then cooled to an ambient temperature & filtered through Whatman no. 40 filter paper. Filtrate was made to 50 ml with deionized water.

All the digested filtrates (river water, soil and macrophyte samples) were analyzed to quantify the amount of Pb, Cd, Hg, Cu, Cr and Zn using flame atomic adsorption spectrometer (Avanta Σ).

2.3 Bio-concentration Factor
Bio-concentration or bioaccumulation factor is the ratio of heavy metal concentration in the plant to that in the sediment. Higher values indicate of easy assimilation by plants from the sediment and also possibility of redistribution for the heavy metal (Zhang et al., 2009). Bioaccumulation factor for the concentration of heavy metals in macrophyte was calculated using equation

\[
\text{Bio-concentration Factor (BF)} = \frac{\text{Heavy metal content in macrophyte}}{\text{Heavy metal content in sediment}}
\]

Results were reported as average values of triplicate measurements. After examination of every 10 samples, blank and control standards were analysed to examine the instrument and minimize errors. One way ANOVA was applied to analyze the significant differences among sampling stations for different metal levels. Data was analyzed using IBM SPSS Statistics 26 software.

3. Results and Discussion
Average concentration of heavy metals in water of Yamuna river are presented in Figure 1. The range of heavy metals Pb, Cd, Hg, Cu, Cr & Zn were 0.768-2.78 mg/l, 0.025-0.089 mg/l, 0.002-0.007 mg/l, 0.689-1.68 mg/l, 8.12-20.11 mg/l & 4.12-8.84 mg/l respectively which are presented in Table 1. The mean concentration in water were Pb 1.97 mg/l, Cd 0.06 mg/l, Hg 0.004 mg/l, Cu 1.30 mg/l, Cr 14.98 mg/l & Zn 6.40 mg/l. The occurrence heavy metals in Yamuna river water were found in the order: Cr> Zn> Pb> Cu> Cd> Hg. In this study the high concentration levels of Pb, Cd, Hg, Cu, Cr & Zn in water samples at selected stations of Yamuna river which can be attributed to the enormous discharge of effluents from industries, factories and agricultural runoff directly into the water body without proper treatment. The lower concentration of heavy metals during monsoon might be due to the dilution effect of water (Mohiuddin et al., 2011; Islam et al., 2015; Adamu et al., 2015) [10, 11, 1]. High level of Cr in the industrial effluents has already been reported by Rawat et al., (2003). Pb in water could be conceived to mainly originate from industrial and domestic discharge of wastes in the river and is non-essential for plants and animals and is toxic by ingestion-being a cumulative poison, producing damaging effects on the kidney, liver, tissues, blood vessels, nervous system and depresses sperm count (Tijani et al., 2004). The level of Pb, Cd, Cr & Zn at site in Yamuna river was found above maximum permissible limit recommended by WHO (1996).
Table 1: Monthly variation in heavy metals concentration (mg/l) detected in water sample of Yamuna River at Delhi

| Months | Pb    | Cd    | Hg    | Cu    | Cr    | Zn    |
|--------|-------|-------|-------|-------|-------|-------|
| March  | 1.68  | 0.057 | 0.005 | 1.123 | 14.85 | 5.821 |
| April  | 2.137 | 0.062 | 0.006 | 1.201 | 13.42 | 6.433 |
| May    | 2.431 | 0.066 | 0.005 | 1.248 | 15.62 | 6.662 |
| June   | 2.517 | 0.079 | 0.005 | 1.415 | 17.74 | 8.841 |
| July   | 2.581 | 0.077 | 0.004 | 1.418 | 17.54 | 8.801 |
| August | 1.908 | 0.023 | 0.003 | 0.887 | 11.98 | 5.127 |
| September | 0.768 | 0.025 | 0.002 | 0.689 | 8.27  | 4.123 |
| October | 0.914 | 0.034 | 0.002 | 0.749 | 8.12  | 4.813 |
| November | 1.382 | 0.049 | 0.004 | 1.918 | 12.93 | 5.947 |
| December | 2.643 | 0.082 | 0.006 | 1.628 | 19.93 | 6.663 |
| January | 2.78  | 0.109 | 0.007 | 1.648 | 20.11 | 6.841 |
| February | 2.71  | 0.084 | 0.006 | 1.687 | 19.28 | 6.782 |
| Mean    | 0.97008 | 0.01083 | 0.00458 | 0.30917 | 14.9825 | 6.4045 |
| SD±    | 0.757972 | 0.0225 | 0.00162 | 0.390696 | 17.3802 | 4.16353 |

Average concentration of heavy metals in sediment of Yamuna river are presented in Table 2. The range of heavy metals Pb, Cd, Hg, Cu, Cr & Zn were 58.93-79.23 mg/l, 17.57-24.13 mg/kg, 12.60-41 mg/kg, 20.96-28.65 mg/kg, 1241.23-1562.01 mg/kg & 653.66-785.54 mg/kg respectively which are presented in Table 3. The mean concentration in soil were Pb 72.03 mg/kg, Cd 20.94 mg/kg, Hg 4.84 mg/kg, Cu 25.53 mg/kg, Cr 1424.70 mg/kg & Zn 730.67 mg/kg. The order of occurrence of heavy metal in soil of Yamuna river was found in order: Cr > Zn > Pb > Cu > Cd > Hg. Suspended sediments adsorb pollutants from the water, thus lowering their concentration in the water. Khan et al., (1998) [13] reported the Pb concentration ranged from 2.25 to 2.086 mg/kg in sediment in Ganges-Brahmputra-Meghna Estuary. Highest concentration of Cr in Yamuna river may be due to discharge of huge tannery waste, less rain water and agricultural run-off are the main reasons. The results showed variation in heavy metals with seasonal difference in the river and similar results were also reported by Brown et al., (2000) [14] and Marchand et al., (2010) [15]. In summer high temperature causes warming of soil and water, augmented decomposition of organic matter, reduction in cation exchange capacity, which increases nutrient and trace elements retention in wastewater and soil (Antoniadis and Alloway, 2001; Sardans et al. 2008; Van Gestel, 2008) [16, 17, 18].

Average concentration of heavy metals in macrophyte (Eichhornia crassipes) of Yamuna River are presented in Figure 3. The range of heavy metals Pb, Cd, Hg, Cu, Cr & Zn were 22.81-24.88 mg/kg, 7.60-8.88 mg/kg, 3.01-4.04 mg/kg, 9.42-10.81 mg/kg, 21.23-23.85 mg/kg & 31.82-34.23 mg/kg respectively which are presented in Table 4. The mean concentration in macrophyte were Pb 23.95 mg/kg, Cd 8.22 mg/kg, Hg 3.54 mg/kg, Cu 10.18 mg/kg, Cr 23.03 mg/kg & Zn 33.09 mg/kg. The order of occurrence of heavy metal in macrophyte of Yamuna river was found in order: Zn > Pb > Cr > Cu > Cd > Hg. The successful presence of aquatic macrophytes in polluted waters is usually due to the increases of aquatic macrophytes. Ramachandra et al., (2018) [21] reported concentration of different metals in the macrophyte samples were ranked as: Cr > Cu > Zn > Pb > Ni > Cd. The concentration of these metals is low when compared to values reported in other studies (Woitke et al., 2003; Kaushik et al., 2008) [22, 23].

Table 3: Monthly variation in heavy metals concentration (mg/l) detected in soil sample at of Yamuna River at Delhi

| Months | Pb | Cd | Hg | Cu | Cr | Zn |
|--------|----|----|----|----|----|----|
| March  | 689 | 19.19 | 5.314 | 24.72 | 1442.5 | 719.43 |
| April  | 74.92 | 19.92 | 5.217 | 25.62 | 1389.55 | 721.55 |
| May    | 75.64 | 21.96 | 5.847 | 25.19 | 1474.64 | 734.64 |
| June   | 77.92 | 24.13 | 6.215 | 26.86 | 1562.01 | 774.62 |
| July   | 77.16 | 20.19 | 6.342 | 27.14 | 1435.21 | 768.72 |
| August | 58.93 | 18.86 | 3.129 | 21.42 | 1268.96 | 672.42 |
| September | 59.06 | 17.57 | 1.208 | 20.96 | 1314.34 | 653.66 |
| October | 60.44 | 18.01 | 1.429 | 22.46 | 1241.23 | 706.71 |
| November | 75.22 | 21.16 | 4.892 | 26.91 | 1375.66 | 701.13 |
| December | 78.39 | 22.91 | 5.892 | 28.13 | 1521.26 | 745.42 |
| January | 79.23 | 23.84 | 6.41 | 28.34 | 1534.21 | 784.26 |
| February | 78.84 | 23.63 | 6.28 | 28.65 | 1536.85 | 785.54 |
| Mean   | 72.039717 | 20.9475 | 1.849717 | 25.5333 | 1424.702 | 730.675 |
| SD±    | 0.06986 | 2.330135 | 0.881212 | 12.673735 | 108.46254 | 83.14367 |

Table 2: Maximum permissible limit (MPL) of heavy metals in water (mg/L)

| Source | Pb    | Cd    | Hg    | Cu    | Cr    | Zn    |
|--------|-------|-------|-------|-------|-------|-------|
| WHO (2006) | 0.01 | 0.003 | 0.006 | 2 | 0.05 | 3 |

Fig 1: Mean concentration of heavy metals (mg/l) in water
The bio-concentration factor was found less than 1 for all the metals in macrophyte (Eichhornia crassipes). BCF less than 1 indicates that the plant is an accumulator and BCF value above one indicates an excluder plant. The accumulation pattern observed in the order Hg>Cd>Cu>Pb>Zn>Fe. Similar metal accumulation patterns have been reported in Myriophyllum spicatum growing in contaminated water sources in Egypt Galal et al., (2014) [25] and in E. crassipes, Ceratophyllum demersum, Typha domengensis growing naturally in the waters of river Nile Fawzy et al., (2012) [26].

The results of this finding indicates that it can be used for phytoremediation of heavy metals in polluted waters. Metal accumulating plant species (Typha angustifolia and Echhornia crassipes) concentrate toxic and heavy metals such as Mn, Cu, Zn, Pb, Ni and Fe up to 100–1000 times, compared to excluder plants Salt et al., (1995) [24]. Phytoremediation is highly recommended for removal of toxic heavy metals from water bodies and soil so that they do not enter the food chain and result in disease in humans and animals.

Table 5: Bio-concentration factor in Macrophyte (Eichhornia crassipes)

| Pb  | Cd  | Hg   | Cu  | Cr  | Zn  |
|-----|-----|------|-----|-----|-----|
| 0.32| 0.39| 0.73 | 0.39| 0.016| 0.045|

The above study concludes that these heavy metals in water body have exceeded their limit from drinking and other domestic uses. Regular use can cause carcinogenic effect on body. Heavy metals are becoming accumulated in sediment in high concentration. Eichhornia crassipes has shown good bioaccumulation of heavy metal that means it can be used in phytoremediation of polluted water body. The overall impact of heavy metal can cause degradation of riverine ecosystem.

4. Acknowledgement
Authors are grateful to Advisor Dr. Amita Saxena for their guidance during the study and authorities of G. B. Pant University of Agriculture and Technology, Pantnagar for providing facilities at College of Fisheries, Pantnagar to pursue the present study.

5. References
1. Adamu CI, Nganje TN, Edet A. Heavy metal contamination and healthrisk assessment associated with abandoned barite mines in Cross River State: Southeastern Nigeria. Environ. Nanotechnol. Monit. Manag 2015;3:10–21.
2. Chopra AK, Pathak C, Prasad G. Scenario of heavy metal contamination in agricultural soil and its management. Journal of Applied and Natural Science 2009;1(1):99-108.
3. Upadhyay AK, Singh NK, Rai UN. Comparative metal accumulation potential of Potamogeton pectinatus L. and Potamogeton crispus L. Role of enzymatic and non-enzymatic antioxidants in tolerance and detoxification of metals. Aquatic botany 2014;117:27-32.
4. Rai UN, Upadhyay AK, Singh NK, Dwivedi S, Tripathi RD. Seasonal applicability of horizontal sub-surface flow constructed wetland for trace elements and nutrient removal from urban wastes to conserve Ganga River water quality at Haridwar, India. Ecological engineering 2015;81:115-122.
5. Yan L, Wang J, Han X, Ren Y, Liu Q, Li F. Enhanced microwave absorption of Fe nanoflakes after coating with SiO2 nano shell. Nanotechnology 2010;21(9):
6. Ikem A, Egiebor NO, Nyavor K. Trace elements in water, fish and sediment from Tuskegee Lake, Southeastern USA. Water, Air, and Soil Pollution 2003;149(1):51-75.
7. Morgan JJ, Stumm W. Chemical processes in the environment, relevance of chemical speciation 1991.
8. Zhang MK, Ke ZX. Heavy metals, phosphorus and some other elements in urban soils of Hangzhou City, China. Pedosphere 2004;14(2):177-185.
9. CPCB. Water quality status of River Yamuna (1999–2005), Assessment and development study of river basin series (ADSORBS). ADSORB/41. Central Pollution Control Board, Delhi, India 2006
10. Mohiuddin KM, Ogawa YZHM, Zakir HM, Otomo K, Shikazono N. Heavy metals contamination in water and sediments of an urban river in a developing country. International journal of environmental science & technology 2011;8(4):723-736.
11. Islam MS, Ahmed MK, Habibullah-Al-Mamun M, Hoque MF. Preliminary assessment of heavy metal contamination in surface sediments from a river in Bangladesh. Environmental earth sciences 2015;73(4):1837-1848.
12. Yi Y, Yang Z, Zhang S. Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin, Environ. Pollut 2011;159;2575-2585.
13. Khan YSA, Hossain MS, Hossain SMGA, Halimuzzaman AHM. An environment of trace metals in the GBM Estuary. J Remote sensing. Environ 1998;2:103-113.

14. Brown PA, Gill SA, Allen SJ. Review paper: metal removal from wastewater using peat. Water Res 2000;34:3907–3916.

15. Marchand L, Mench M, Jacob DL, Otte ML. Metal and metalloid removal in constructed wetlands, with emphasis on the importance of plants and standardized measurements: a review. Environ. Pollut 2010;158:3447–3461.

16. Antoniadis V, Alloway BJ. Availability of Cd: Ni and Zn to Ryegrass in sewage sludge treated soil at different temperatures. Water Air Soil Pollut 2001;132:201–214.

17. Sardans J, Penuelas J, Prieto P, Estiarte M. Changes in Ca, Fe, Mg, Mo, Na, and S content in a Mediterranean shrubland under warming and drought. J. Geophys. Res 2008;13:1–11.

18. Van Gestel CAM. Physico-chemical and biological parameters determine metal bioavailability in soils. Sci. Total Environ 2008;406:385–395.

19. Miretzky P, Saralegui A, Fernandez Cirelli A. Aquatic macrophytes poten- tial for the simultaneous removal of heavy metals (Buenos Aires, Argentina). Chemosphere 2004;57:997–1005.

20. ATSDR. Agency for Toxic Substances and Disease Registry. Toxicological profile for Cadmium, US Department of Health and Human Services, Public Health Service 2012, 205-93-0606.

21. Ramachandra TV, Sudarshan PB, Mahesh MK, Vinay S. Spatial patterns of heavy metal accumulation in sediments and macrophytes of Bellandur wetland, Bangalore. Journal of environmental management 2018;206:1204-1210.

22. Woitke P, Wellmitz J, Helm D, Kube P, Lepom P, Litheraty P. Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. Chemosphere 2003;51:633–642.

23. Kaushik A, Kansal A, Santosh, Meena, Kumari S, Kaushik CP. Heavy metal contamination of river Yamuna, Haryana, India: assessment by metal enrichment factor of the sediments. J Hazard. Mater 2008;164:265–270.

24. Salt DE, Blaylock M, Kumar NP, Dushenkov V, Ensley BD, Chet I et al. Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. Biotechnol 1995;13(5):468–74.

25. Galal TM, Shehata HS. Evaluation of the invasive macrophyte Myriophyllum spicatum L. as a bioaccumulator for heavy metals in some water courses of Egypt. Ecol. Indicator 2014;41:209–214.

26. Fawzy MA, Badr NE, El-Khatib A, and El-Kaseem, A. A... Heavy metal biomonitoring and phytoremediation potentialities of aquatic macrophytes in River Nile. Environ. Monit. Assess, 2012,184, 1753–1771.

~ 3556 ~