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Estimation of Elemental Pollution in Freshwater Sediment Of Lerma River Using EDS and FRX Techniques (Assessment of Lerma River Bed Sediments Using EDS and FRX Techniques)

Dhananjay Tripathi[1,2], Kamal Uddin Ahamad[2], Diego Ríos-Pérez[3], D. K. Tiwari[4], Ana V. Coria Téllez[3*]

[1]Division of CBRN Defense, Institute of Nuclear Medicine and Allied Sciences, DRDO, Delhi, India
[2]Department of Civil Engineering, Tezpur University, Tezpur, Assam, India
[3]Laboratorio de Análisis y Diagnóstico del Patrimonio, El Colegio de Michoacán, Michoacán, México
[4]Consejo Nacional de Ciencia y Tecnología, Michoacán, México
*Corresponding Author: anac@colmich.edu.mx

INTRODUCTION

The Lerma River has been considered as one of the most polluted inland river of Mexico. Several studies (spatial and temporal) mention the presence of contaminants including heavy metals, pesticides, complex organic contaminants etc. above the maximum permissible limits (MPL) [1]. In recent times, heavy metal contamination has become the major issue worldwide due to their potential toxic effects and ability to bioaccumulate. In aquatic system, they are more prevalent in sediments from where they may enter into food chain. Therefore, study of aquatic system sediments is important as it provides information about metal contamination and its sources, its bioavailibity and toxicity. The present study aims to determine the concentration of various mineral elements and heavy metals in the river sediments using nondestructive techniques [2].

MATERIALS AND METHODS

The study area is part of the Lerma River, which has a wide curvature known as the "Meander of the Lerma River". It is located between the municipality of La Piedad, northeast of Michoacán, and the Santa Ana Pacueco belonging to Pénjamo municipality. For analysis, sediment samples were collected from seven different locations along the stretch of the river between 20°21'11.8” N, 102°00'26.8” W and 20°22'04” N, 102°01'09” W coordinates. From each sampling point, three sediment samples were obtained; two from each bank and one from the center of the river at a depth of 20 cm and mixed to form composite sample for each location.
Sediment mineral elemental analysis was carried out using energy dispersive spectroscopy (EDS, OXFORD INCA, LK-IE250) coupled to scanning electron microscope (SEM), (JEOL, model JSM-6390LV); in which 20 g air dried sediment sample was diluted with 40 ml of deionized water, homogenized for 30 min and allowed to settle for 24 hours. The solution was filtered and dried at 60°C for 48 hours. The mean of measurements has been reported (Table 1).

Heavy metal analysis in the river sediments was done using X- ray fluorescence Spectroscopy ((XRF, Thermo Scientific Niton XL 3t). The sediment samples collected were dried, homogenized and grounded into fine-powder. The prepared samples were then subjected to analysis and the results are presented in Table 2.

RESULTS

EDS Analysis: The mineral elements present in river sediment samples were analyzed and are presented in Table 1. The mean distribution of the mineral elements in the river sediment samples from different sites are in order O > C > Na > S > Ca > Si > Cl > K > Mg > Al > N > Fe > P > Mn. The maximum variation of sediment mineral elements was observed at site 4 and 6 where the highest (Al, Si, Fe at site 4 and O, Mg, Ca at site 6) and lowest (Mg, Ca, S at site 4 and Al, Si, Na, K at site 6) values are detected. Moreover, the percentage mineral elemental composition at different location for a particular element was more or less same. The comparison among the sites shows that the higher amount of mineral elements are in the sediment from the urban agglomeration.

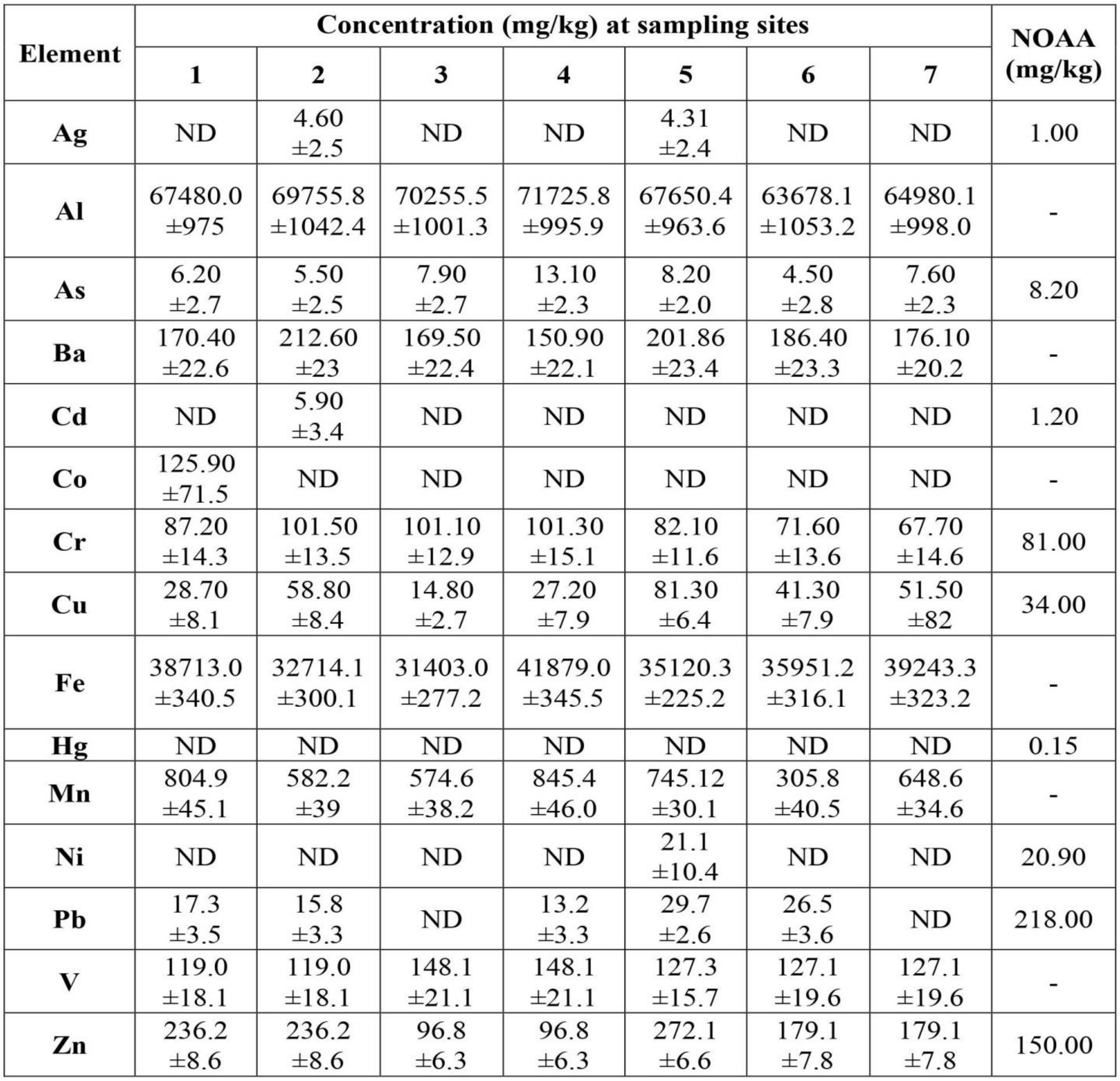
Table 1: Mineral elements concentration in Lerma River sediments

Element	Sampling sites (% Element)							Mean
	1	2	3	4	5	6	7	
C	18.89 ±3.73	15.15 ±2.44	14.65 ±2.41	14.15 ±1.59	18.45 ±1.27	15.18 ±1.41	13.25 ±1.11	15.67 ±2.25
N	1.06 ±0.92	1.33 ±0.89	1.00 ±0.92	0.40 ±0.57	0.56 ±0.78	0.90 ±0.76	0.18 ±0.50	0.78 ±0.41
O	14.38 ±1.01	45.87 ±1.01	44.00 ±1.17	46.83 ±1.10	46.06 ±0.45	48.21 ±0.52	46.85 ±0.98	46.03 ±1.46
Na	9.92 ±0.15	8.02 ±0.83	9.82 ±0.75	8.49 ±0.56	10.65 ±0.72	6.45 ±0.19	9.32 ±0.20	8.95 ±1.42
Mg	1.29 ±0.19	2.14 ±0.13	1.64 ±0.11	1.10 ±0.07	1.35 ±0.11	2.51 ±0.10	1.63 ±0.10	1.67 ±0.50
Al	1.12 ±0.85	0.22 ±0.05	0.72 ±0.17	3.53 ±0.60	0.29 ±0.06	0.06 ±0.07	0.53 ±0.04	0.92 ±1.20
Si	5.48 ±2.11	1.75 ±0.19	6.10 ±0.90	10.08 ±1.02	3.48 ±0.10	1.25 ±0.12	4.86 ±0.11	4.71 ±2.99
P	0.30 ±0.13	ND	0.46 ±0.10	0.04 ±0.08	0.06 ±0.07	0.02 ±0.05	0.33 ±0.06	0.17 ±0.19
S	6.76 ±0.63	12.45 ±0.22	7.65 ±0.33	5.01 ±0.43	7.59 ±0.30	11.03 ±0.25	9.30 ±0.20	8.54 ±2.56
Cl	4.39 ±0.24	3.69 ±0.28	5.88 ±0.21	3.65 ±0.33	2.29 ±0.11	2.91 ±0.18	3.74 ±0.19	3.79 ±1.14
K	2.06 ±0.32	2.71 ±0.10	2.77 ±0.14	2.18 ±0.13	2.74 ±0.23	1.59 ±0.06	2.94 ±0.12	2.43 ±0.49
Ca	3.84 ±0.79	6.65 ±0.18	5.04 ±0.16	2.89 ±0.06	6.34 ±0.49	9.86 ±0.45	6.74 ±0.20	5.91 ±2.28
Fe	0.50 ±0.44	0.02 ±0.06	0.29 ±0.19	1.65 ±0.25	0.13 ±0.16	ND	0.34 ±0.09	0.42 ±0.57
Mn	ND	ND	ND	ND	ND	0.04 ±0.01	ND	0.01 ±0.02

ND: Not Detected

XRF analysis: The finding in this study reveals that the concentration of Ag, As, Cd, Ni, Cr, Cu, and Zn in river sediment were above the permissible limit set by National Oceanic and Atmospheric Administration (NOAA) [3]. Generally, essential heavy metals that consist of Cu, Cr, Co, Fe, Mn and Zn are required by human body at concentration which could be beneficial to the body metabolites. On contrary, non-essential heavy metals (As, Cd, Pb, Ni and Hg) that are commonly found in environment have adverse health effects when found above MPL. The samples analyzed from site 5 have more incidences where heavy metal concentration exceeded that of MPL followed by site 2, which may be due to discharge of industrial effluents from various sources including untreated sewage, municipal waste and agrochemical runoff. Further, these sites are located near the urban settlement which can be one of the reasons for high metal contamination.

Table 2: Concentration of heavy metals in Lerma River sediments

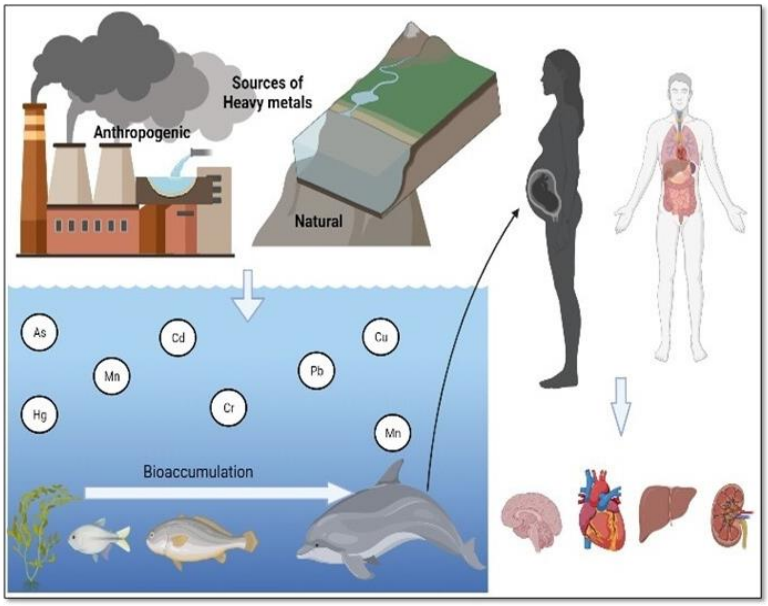


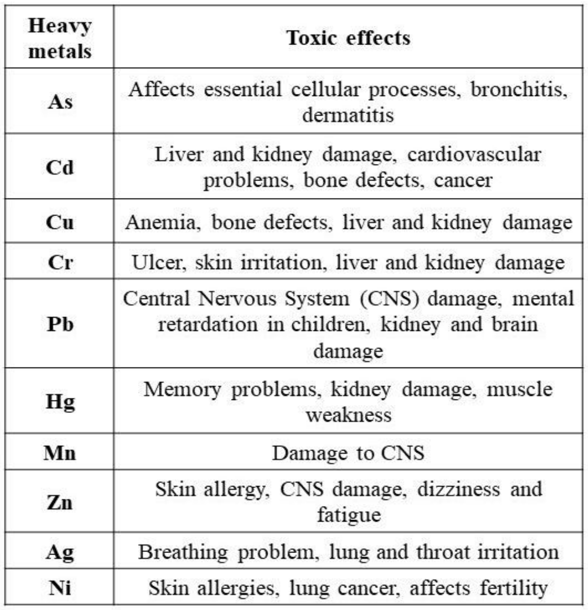
Element	Concentration (mg/kg) at sampling sites							NOAA (mg/kg)
	1	2	3	4	5	6	7	
Ag	ND	4.60 ±2.5	ND	ND	4.31 ±2.4	ND	ND	1.00
Al	67480.0 ±975	69755.8 ±1042.4	70255.5 ±1001.3	71725.8 ±995.9	67650.4 ±963.6	63678.1 ±1053.2	64980.1 ±998.0	-
As	6.20 ±2.7	5.50 ±2.5	7.90 ±2.7	13.10 ±2.3	8.20 ±2.0	4.50 ±2.8	7.60 ±2.3	8.20
Ba	170.40 ±22.6	212.60 ±23	169.50 ±22.4	150.90 ±22.1	201.86 ±23.4	186.40 ±23.3	176.10 ±20.2	-
Cd	ND	5.90 ±3.4	ND	ND	ND	ND	ND	1.20
Co	125.90 ±71.5	ND	ND	ND	ND	ND	ND	-
Cr	87.20 ±14.3	101.50 ±13.5	101.10 ±12.9	101.30 ±15.1	82.10 ±11.6	71.60 ±13.6	67.70 ±14.6	81.00
Cu	28.70 ±8.1	58.80 ±8.4	14.80 ±2.7	27.20 ±7.9	81.30 ±6.4	41.30 ±7.9	51.50 ±82	34.00
Fe	38713.0 ±340.5	32714.1 ±300.1	31403.0 ±277.2	41879.0 ±345.5	35120.3 ±225.2	35951.2 ±316.1	39243.3 ±323.2	-
Hg	ND	ND	ND	ND	ND	ND	ND	0.15
Mn	804.9 ±45.1	582.2 ±39	574.6 ±38.2	845.4 ±46.0	745.12 ±30.1	305.8 ±40.5	648.6 ±34.6	-
Ni	ND	ND	ND	ND	21.1 ±10.4	ND	ND	20.90
Pb	17.3 ±3.5	15.8 ±3.3	ND	13.2 ±3.3	29.7 ±2.6	26.5 ±3.6	ND	218.00
V	119.0 ±18.1	119.0 ±18.1	148.1 ±21.1	148.1 ±21.1	127.3 ±15.7	127.1 ±19.6	127.1 ±19.6	-
Zn	236.2 ±8.6	236.2 ±8.6	96.8 ±6.3	96.8 ±6.3	272.1 ±6.6	179.1 ±7.8	179.1 ±7.8	150.00

ND: Not Detected

The concentration of As ranged between 4.5 and 13.1 mg/kg. The maximum concentration of As was recorded (13.1 mg/kg) above the MPL. The concentration of Cd detected at site 2 found to be in higher concentration (5.9 mg/kg) of MPL. The non-detectable concentrations of Hg were observed in all the sediment samples collected from different locations. Also, Pb was found within MPL. Moreover, Ni was detected at site 5 (21.1 mg/kg) that exceeded allowable limits but do not seem to represent a major risk at other sites. The sources of these metals can be of natural or anthropogenic origin and are toxic to living organisms.

Cu and Zn concentration was measured between 14.8- 81.3 mg/kg and 96.8- 272 mg/kg respectively. The maximum level for these elements was reported at site 5 (81.3 mg/kg and 272 mg/kg respectively) where both exceeded MPL. The Cu and Zn are favorable to human health but excess level may cause severe health problems (Figure 1a & 1b). In addition to this, Cr, Co, Fe and Mn were also detected in the samples out of which Cr exceeded MPL at 3 sites. This is probably due to natural (concentration in sediments and soils bearing pyroxenes and silicate minerals) and/or anthropogenic (industrial activities including tanneries, textile etc.) sources. Mn occurs naturally but human activities are also responsible for excess level in environment. The concentration of Ag in sediment samples at site 2 (4.6 mg/kg) and 5 (4.3 mg/kg) were observed higher than the recommended permissible limits (1 mg/kg). The occurrence of Ag can be attributed to the Guanjuato Ag deposits and the mining industries along the stretch of the river.





Heavy metals	Toxic effects
As	Affects essential cellular processes, bronchitis, dermatitis
Cd	Liver and kidney damage, cardiovascular problems, bone defects, cancer
Cu	Anemia, bone defects, liver and kidney damage
Cr	Ulcer, skin irritation, liver and kidney damage
Pb	Central Nervous System (CNS) damage, mental retardation in children, kidney and brain damage
Hg	Memory problems, kidney damage, muscle weakness
Mn	Damage to CNS
Zn	Skin allergy, CNS damage, dizziness and fatigue
Ag	Breathing problem, lung and throat irritation
Ni	Skin allergies, lung cancer, affects fertility

Figure 1: a) Heavy metals and environmental interaction **b)** Toxic effects on human health [4]

CONCLUSION AND FUTURE PROSPECTS

It can be inferred from the results that river sediments are contaminated by one or more heavy metals especially near the urban settlement which is also responsible for ecological decline of the river. Hence, it indicates that the samples were greatly altered by the anthropogenic activities but the contribution of natural sources cannot be ruled out. Hence, there is need of continuous monitoring of heavy metals that exceeded MPL and have high risk of future contamination. In order to assess the risk in the ecological system, there is need to monitor sediment samples along with water samples that may be used to identify major pollution sources, their environmental fate and will help in establishing the pollution load of the river. Also, these studies will play an important role in designing the management and conservation policies of the Lerma River.

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