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HEAVY METAL ANALYSIS ON ROAD SIDE SEDIMENTS USING ATOMIC ABSORPTION SPECTROSCOPY (AAS) TECHNIQUE

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Abstract: **In this study road side sediment samples were collected in Chennai-Bangalore National Highway (Tamilnadu, India) for a stretch starting from Sunguvarchatram and ending at Maduravoyal and subjected for heavy metal (Cd, Pb, Zn, Cr) analysis through Atomic Absorption Spectroscopy (AAS) Technique. Totally 30 sites were selected for sediment sample collection and sediment samples were collected as per standard methods. The concentration of heavy metals present in the road side sediments from the study area was determined by flame absorption Atomic Absorption Spectrophotometer AA7000. Toxicity factors such as Contamination Factor(CF) and Geo-accumulation Index (*Igeo*) were calculated using average continental crustal values for heavy metals[1, 2]. From the toxicity parameter results, it is observed that the contamination of the road side sediments in the study area by the metals Cd, Pb and Zn is mainly due to the anthropogenic activities (man-made activities) like industrial effluents, vehicular emission and wastages supplied to environment on the travel and uncontrolled input of sewage, garbage into the road side environment.**
Key words: ***Road side sediments; Heavy metals; AAS***

I. INTRODUCTION

The evolution of magma by volcanic eruptions through weak crust areas of the Earth surface result in the formation of rocks on its crust. The rocks are subjected to wind, water streams, water condensations, chemical reactions, trees and plant growth and animal interventions and broken in to pieces and to finally particles. This process is called weathering and the weathered particles combine with organic material to form the soil. Since the earth's crust and molten core (magma) consists of metals and minerals, the weathered sediments are composed of various metals and minerals. Among the minerals and metals, some of the minerals and metals are industrially and economically important. At the same time some of the minerals and metals impose hazardous health effect to all living things. The mineralogical exploration of the sediments is very vital in view of country's economic growth. The metal and mineral contents of the sediments can be classified as radioactive minerals, industrially and commercially important metals and minerals and toxic elements.

The sediment which is deposited along the sides of a road is called as road side sediment. The road side sediments are the same as the normal sediments with its mineral and metal contents in major, but contaminated with hazardous impurities due to road side industrial and vehicular and related activities.

Heavy metal is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm ^{3}, or 5 times or more, greater than water[3,4,5,6,7,8,9]. Most of the heavy metals such as Cd, Cr, Ni, As, Mn and Pb has no nutritional value, rather they are carcinogenic and bio accumulate into toxic level to damage essential human and animal organs.

The road side sediment may contain different concentrations of heavy metals, which may cause detrimental and toxicological effects to both environment and to the mankind [5, 10, 11]. Heavy metals in the road side sediments are due to the various sources, including industrial and residential emissions, corrosion of building materials, and vehicular traffic emissions including particulates from wear and tear of tires, automobile bodies and brake lining [11]. These metal impurities are raised in the atmosphere and deposit on the roads as sediments.

The absorption of these metals by plants and lower food-chain organisms in roadside corridors is a potential concern. The road side sediments are mobilized by runoff waters[12,13]. The principal source of heavy metals are the motor vehicles[14,15] , engine , brake pad wear, (e.g. Cd, Cu and Ni)[14], lubricants (e.g. Cd, Cu and Zn)[16], exhaust emissions, (e.g. Pb) [17,18,19] and tyre abrasion (e.g. Zn)[20]. Moreover urban sediments are part of a complex system in which particulates accumulate potentially toxic pollutants, ultimately posing a threat to urban water-bodies and public health[21].

II. SCOPE OF THE STUDY

The main objectives of the study:

1. To analyze the heavy metal composition of road side sediments collected from 30 selected locations over a stretch from Sunguvarchatram to Maduravoyal in National Highway road (Tamilnadu, India).

2. To calculate some important toxicity parameters to know contamination level of the road side sediments.

To achieve the objectives, Atomic Absorption Spectroscopy (AAS) was employed to characterize the sediment samples. The sediment samples were digested by CEM microwave digester using MARSX press (self-regulating microwave vessel).

III. MATERIALS AND METHODS

Heavy metals are natural constituents of the Earth's crust, but indiscriminate human activities have drastically altered their geochemical cycles and biochemical balance. Prolonged exposure to heavy metals such as cadmium, copper, lead, nickel, and zinc can cause deleterious health effects in humans. These metals are a cause of environmental pollution from sources such as leaded petrol, industrial effluents, garbage, wastages, and leaching of metal ions in addition to natural origin from earth crust. They exist in the road side sediment as a result of weathering, intrusion of contamination through the above said sources and subsequent deposition along the road sides from the water streams.

Any metal (heavy or trace metals) species may be considered a "contaminant" if it occurs where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect. Some of the metallic contaminants include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), selenium (Se), nickel (Ni), silver (Ag), and zinc (Zn). Other lesser common metallic contaminants include aluminium (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U)[22].

A. Study Area

The study area is a National Highway road and it was chosen from Sunguvarchatram to Maduravoyal in Chennai – Bangalore Highway in Tamilnadu, India. The highway road is one the of the busiest highway line with high density of moving vehicles. Further there are lots of industries in the highway road from Sunguvarchatram to Maduravoyal. Sunguvarchatram is a place situated near Kancheepuram at a distance of 24 km distance. Due to heavy traffic and more industries along the above segment of the highway it was chosen for heavy metal studies.

B. Sample Collection

The present study area covers a total length of about 40 km from which 30 successive locations were selected and road side sediment samples were collected and numbered as S1 to S30. The site number and the corresponding location are given in table I. Each location is separated by a distance of 1-1.5 km approximately. The samples from all the sites were collected manually from the top surface (0-5 cm depth) using plastic spade and packed in polyethylene bags during the month of February 2013. Stones and other impurities were removed and the collected samples were air dried at room temperature in open air.

C. Sample preparation

The collected samples were dried at 110 C using hot oven and stones and other impurities were removed. The dried samples were sieved using a sieve shaker to 250 µm grain size and the samples are packed for acid digestion and subsequent elemental analysis using Atomic Absorption spectrophotometer.

Table I. Sampling locations along Sunguvarchatram – Maduravoyal National Highway

D. Atomic Absorption Spectroscopy Technique (AAS)

Atomic absorption spectroscopy (AAS) is a spectro-analytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. The technique is used for determining the concentration of a particular element in a sample to be analyzed. Atomic Absorption (AA) occurs when a ground state atom absorbs energy in the form of light of a specific wavelength and is elevated to an excited state. The relationship between the amount of light absorbed and the concentration of analytes present in known standards can be used to determine unknown sample concentrations by measuring the amount of light they absorb.

Site No	Road Side Sampling Location
S1	Sunguvarchatram (Nearby Industry)
S 2	Sunguvarchatram
S 3	Near Petrol Bank (Sunguvarchatram)
S 4	Mambakkam Village (Construction Industry)
S 5	Between Sunguvarchatram and Sriperumbudur
S 6	3 km from Sriperumbudur
S 7	2 km from Sriperumbudur (Industrial Zone)
S 8	VRP Chatram Village (Industrial Zone)
S 9	Govt. School, Sriperumbudur
S 10	St. Mary's Matric School, Sriperumbudur
S 11	Nearby bank area , Sriperumbudur
S 12	Panjalapattu (Sriperumbudur Arch)
S 13	Near Tollgate, Sriperumbudur
S 14	Near Engineering Institution, Sriperumbudur
S 15	Near Irungattukottai, Opp. To weighing Bridge Co.
S 16	Irungattukottai
S 17	Irungattukottai Industrial Area
S 18	Educational Institution area, Irungattukottai
S 19	Mevalurkuppam, Back of industrial area
S 20	Opp.to Sembarambakkam lake, Near Sembarambakkam
S 21	2 km from previous site, Near Sembarambakkam
S22	Near empty field , Sembarambakkam
S 23	Opp. to recreational centre, Near Sembarambakkam
S 24	Opp. to Indian oil petrol bunk, Near Sembarambakkam
S 25	Sembarambakkam Village
S 26	Kattupakkam (Hotel Industry)
S 27	Thirumazhisai
S 28	Poonamallee
S 29	1 km from Poonamallee
S 30	Govt. Hr. Sec. School, Poonamallee

IV RESULTS

A. Distribution of Heavy Metals

The heavy metal (Cd, Pb, Zn, Cr) concentrations obtained by AAS technique in the randomly selected 10 sampling sites is tabulated in the table II.

Table II. Heavy metal concentration of observed metals in the road side sediments under study

Site No.	Heavy Metal Concentration (ppm)*			
	Cd	*Pb*	*Zn*	*Cr*
S1	1.140	121.5	59.66	25.02
S3	0.466	136.2	83.54	30.38
S4	1.024	118.1	88.14	39.32
S7	0.790	5.680	129.9	316.3
S8	0.906	20.44	129.3	103.6
S17	0.558	15.90	84.00	41.10
S19	0.604	128.3	59.20	26.80
S24	0.302	18.18	88.74	50.04
S25	ND	13.62	177.2	66.14
S27	ND	132.8	53.06	76.86
Avg.	*0.579*	*71.09*	*95.29*	*77.56*
Max.	*1.140*	*136.2*	*177.2*	*316.3*
Min.	*0.300*	*5.680*	*53.06*	*25.02*

ND – Not Detectable *ppm – parts per million (mg/L)

The minimum, maximum and average values of the elemental concentration are compared with the crustal average as shown in the table III.

Table III Statistical summary of measured heavy metals

Site No.	Heavy Metal Concentration (ppm)			
	Cd	*Pb*	*Zn*	*Cr*
Avg.	*0.579*	*71.09*	*95.29*	*77.56*
Max.	*1.140*	*136.2*	*177.2*	*316.3*
Min.	*0.300*	*5.680*	*53.06*	*25.02*
Crustal Average[a]	*0.200*	*12.50*	*70.00*	*100.0*
Upper Continental Crust[b]	*0.102*	*17.00*	*52.00*	*35.00*

[a] – Crustal Averge[1] (CA)[1], [b] – Upper Continental Crust (UCC)[23]

From the above table, the average concentration of heavy metals are in the order Zn > Cr > Pb > Cd. From the above values, toxicity parameters such as Contamination Factor (CF) and Geo Accumulation Index (Igeo) are calculated and the results are discussed.

B. Estimating the Level of Toxicity

Contamination factor (CF)

The sediments in a area are the indicators of the lithogenic and anthropogenic changes and their composition is controlled by the nature of substrate, conditions controlling the dissolution and precipitation of metals, pollution sites etc. Sediments have the capability to record the history and indicate the degree of pollution[24, 25].

CF is the ratio between the sediment metal concentration at a given site and the background value of the metal [24, 1]. Contamination Factor CF is an effective tool in monitoring the pollution over a period of time.

Contamination Factor (CF) = Measured concentration of the metal / Background value of the metal

Table IV Contamination Factor values of observed metals in the road side sediments of the study areas.

Site No.	Contamination Factor			
	Cd	*Pb*	*Zn*	*Cr*
S1	11.400	0.821	0.115	0.071
S3	4.660	0.921	0.161	0.087
S4	10.240	0.798	0.170	0.112
S7	7.900	0.038	0.250	0.904
S8	9.060	0.138	0.249	0.296
S17	5.580	0.107	0.162	0.117
S19	6.040	0.867	0.114	0.077
S24	3.020	0.123	0.171	0.143
S25	0.000	0.092	0.341	0.189
S27	0.000	0.898	0.102	0.220
Avg.	*5.790*	*0.480*	*0.183*	*0.222*
Max.	*11.400*	*0.921*	*0.341*	*0.904*
Min.	*0.000*	*0.038*	*0.102*	*0.071*

Geo-accumulation index (Igeo)

The geo-accumulation index (Igeo) defined by Muller[26] is also a measure of the metal pollution in aquatic sediments[24]. The geo accumulation index is given by

$$Igeo = \log_2 (Cn/1.5Bn)$$

Where Cn is the measured elemental concentration and Bn is the background value of the same element[2].

The factor 1.5 is used because of possible variations in background values for a given metal in the environment[24]. In the present study, Igeo was used to understand the heavy metals concentration in the road side sediments in the selected locations along the Sunguvarchatram –Maduravoyil National highway road under study. The world average concentrations of these elements[2] were taken as the background values.

The calculated geo-accumulation index (*Igeo)* values for the observed metals in the road side sediments along the selected sites of the national high way road under study are calculated and tabulated in table V

Table V Geo accumulation index values of observed metals in the road side sediments of the study areas.

Site No.	Geo accumulation Index (I geo)			
	Cd	*Pb*	*Zn*	*Cr*
S1	2.925	2.453	-0.387	-1.069
S3	1.635	2.618	0.099	-0.789
S4	2.771	2.412	0.176	-0.417
S7	2.397	-1.967	0.737	2.591
S8	2.595	-0.119	0.730	0.981
S17	1.895	-0.482	0.107	-0.353
S19	2.010	2.531	-0.398	-0.970
S24	1.010	-0.288	0.186	-0.069
S25	ND	-0.705	1.184	0.333
S27	ND	2.581	-0.556	0.550
Avg.	*2.155*	*0.903*	*0.188*	*0.079*
Max.	*2.925*	*2.618*	*1.184*	*2.591*
Min.	*1.010*	*-1.967*	*-0.556*	*-1.069*

V. DISCUSSION

A. Contamination Factor (CF)

According to Pekey[27] and Jayaprakash [28], if the CF ≥1, it shows a low contamination factor. The value limit 1 ≤ CF < 3 shows moderate contamination factor. The CF value limit 3 ≤ CF < 6 shows considerable contamination factor. If the CF is greater than or equal to 6 it shows very high contamination factor.

The average contamination factor values given in the table IV exhibits the CF of the observed metals in the road sediments are found to be in the order: Cd > Pb > Cr > Zn. Since the average CF value observed for Cd lies between 3 and 6 and for Pb is more than zero, it may be concluded that the road side sediments in the study area along Sunguvarchatram-Maduravoyal National Highway is moderately contaminated by the metal Cd and very less contamination due to Pb. This is due to the fact that the study area is contaminated by the industrial effluents from the nearby industries and vehicular emissions. Further the sediments are very feebly contaminated by Zn and Cr. The above contamination may be due anthropogenic activities like releasing of industrial wastage and sewage to the environment. These moderate and feeble contaminations due to Cd and Pb may impose hazardous health effects to human beings as discussed earlier.

B. Geo accumulation Index (Igeo)

In this study, *I*geo was calculated using background values for world crustal average metal concentrations[2].

The value of geo-accumulation index explains the heavy metal enrichment with respect to the background values as given below:

Igeo	*Nature of Contamination*
<0	Unpolluted
0–1	From unpolluted to moderately polluted
1–2	Moderately polluted
2–3	From moderately polluted to strongly polluted
3–4	Strongly polluted
4–5	From strongly polluted to extremely polluted
>5	Extremely polluted[28, 26]

The average values of *Igeo* given in table V exhibit the strong pollution of road side sediments in the study area by the metal Cd and Pb. The Igeo values for Zn and Cr lie between 0 and 1 and this shows the moderate pollution of the sediments by the respective elements. Negative *Igeo* values exhibit unpolluted condition of the road side sediments by the concern metal.

The negative *I*geo values represent relatively the lithogenic contamination. However, for Cd, Pb and Zn, the values are much higher than the average continental crust in the study area and attribute for the enhanced results for enrichment and contamination factors.

VI. CONCLUSION

The heavy metal concentration in the road side sediments of Sunguvarchatram – Maduravoyal National Highway road study area was determined by flame absorption Atomic Absorption Spectrophotometer AA7000. Toxicity factors such as Contamination Factor (CF) and Geo-accumulation Index (*Igeo*) were calculated using average continental crustal values for heavy metals[1,2]. From the toxicity parameter results, it is observed that the contamination of the road side sediments in the study area by the metals Cd and Pb with Zn is mainly due to the anthropogenic activities (man-made activities) like industrial effluents, vehicular emission and wastages on the travel and uncontrolled input of sewage, garbage into the to the road side environment.

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