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Heavy Metals and its Fractions in Soils of Koratty Region, Kerala

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Abstract

Heavy metal pollution of the environment is a universal problem and the soil often forms a repository of these elements. The developmental activities especially industrialization and high input agriculture contribute to accumulation of heavy metals to toxic levels in the soils. An attempt has been made to estimate the accumulation of heavy metals like iron, zinc, copper, cadmium, lead, nickel and manganese in the soil of Koratty region in central Kerala which has a history of industrialization. The various fractions of these heavy metals namely, exchangeable, reducible, oxidizable and residual fractions were determined to reveal the fate of these metals in soil. The fractionation was done following the BCR process suggested by European Community Bureau of Reference. Iron seemed to be the easily mobilized element, while cadmium and copper were least mobile. The order of mobility in the exchangeable fractions was Fe>Mn>Pb>Ni>Zn>Cu=Cd. The degree of contamination, enrichment factor, and index of geoaccumulation revealed that cadmium, nickel and lead are pollutants in Koratty region of Kerala.

Keywords: Heavy metal fractions, soil, environment, Koratty.

Introduction

Heavy metals in the environment has increased beyond acceptable levels due to human intervention through developmental activities including industries and agriculture. These heavy metals become toxic and they accumulate in soft tissues of animals when they enter body through food, water, air or the skin[1-4]. Heavy metal toxicity can cause several diseases affecting almost all the vital organs and functions[5-9]. Unlike organic pollutants, heavy metals do not decay and hence persist in the environment. They have the potential of bioaccumulation and biomagnification also[10]. Soil often forms a repository of these elements because soil particles such as clay and humus have charges that help the metal cations to bind themselves with the soil, and thus prevent their release, though temporarily. The soluble forms of heavy metals are more dangerous because they are readily available to plants and animals[11].

Sequential extraction of different forms of heavy metals helps in quantifying the fractions in different phases. The commonly used procedure is the BCR [Community Bureau of Reference of the European Commission] now referred as standards, measuring and testing programme. Different fractions determined following this procedure are exchangeable, reducible, oxidisable and residual fractions. The BCR procedure has been tested for sediments[12] and soils[13]. Pollution of the environment, particularly the soil is ascertained by calculating the enrichment factor, the contamination factor and the degree of contamination[14,15]**.** Index of geoaccumulation (Igeo) is also widely used in the assessment of contamination by heavy metals in terrestrial, aquatic and marine environment[16,17]**.**

Koratty region in central Kerala has an early history of industrialization and high input agriculture. Several industries such as the Government of India Press and Madurai Coats were established long ago followed by latest additions such as Carborandum Universal (CUMI), KINFRA and Infopark along with a multitude of small and medium industries. Heavy metal accumulation in the soils of this region thus assumes significance and hence this study to evaluate the heavy metals and their speciation.

Study Area: The study was conducted in Koratty in Thrissur district of Kerala, India situated between 10^o 19’ and 10^o 32’ N latitudes and 76^o 29’ and 76^o 44’ E longitudes. The region has a history of industrialization and major industries like Government of India Press and Madurai coats were established in 100 acre each though land was scarce even in those days. Modern agriculture was also encouraged in the region with hybrid varieties and high inputs of irrigation, fertilizers and pesticides. The impacts of these are expected to leave their imprints on the environment, especially soil. The soils in the area belong to the Koratty series which is lateritic with high content of sesquioxides. The climate is tropical with bimodal monsoons providing about 300cm of annual precipitation. The atmosphere is warm humid in most of the months.

Methodology

Soil samples to a depth of 40cm were collected from different regions in the study site and composite samples obtained representing each area. The samples were air dried, sieved through 2mm sieve and analysed for heavy metals. Extraction was done following hydrogen peroxide digestion and estimation using Varian

Atomic Absorption Spectrophotometer (AAS). The fractions of heavy metals were determined following the BCR (European Community Bureau of Reference) procedure. Degree of contamination was calculated using the formula $C_{deg=}\sum C^{i}_{f}$ where contamination factors of all the elements are taken into account. Contamination factor of each element was calculated using the formula $C^{i}_{f}= C^{i}_{0\text{-}1}/C^{i}_{n}$. Enrichment factor which gives an indication of heavy metals added to the environment other than from natural sources was determined using the formula, $EF_X=[X_S/E_S (ref)]/[X_c/E_c (ref)]$. Igeo which gives an assessment of contamination with reference to background levels was calculated using the formula Igeo = Log Cmetal/1.5 Cmetal (control).

Results and Discussion

Heavy metal contamination by cadmium, copper, iron, manganese, nickel, lead and zinc in the soils of Koratty region namely Government of India Press compound, Infopark compound and agricultural land is presented below.

Geoaccumulation index of heavy metals: Geoaccumulation index (Igeo) of heavy metals in the study sites is shown in table 1. It can be seen that all the elements studied had negative Igeo values. These negative values indicate that contamination of heavy metals by natural sources is almost absent at these sites.

Heavy metals and its fractions in different sites: Two of the bigger sites which hosted important industries in the region, namely the Government of India Press compound and the Infopark compound were studied along with the adjacent agricultural lands to find out the differences, if any, between the two types of land use. The heavy metal contents and its speciation are discussed below separately.

Site 1. GOI Press Compound: Heavy metals fractionated in different soil components in the compound of the Government of India Press is given in table 2 below.

Cadmium: Cadmium was found to be more in the residual fraction which was followed by organic matter fraction, Fe andMn fractions and exchangeable fraction in soils of GOI press site. But in the Infopark site the exchangeable, Fe andMn and residual fractions were almost equal; the organic matter fraction had the least amount of Cd. The pattern was different in the agricultural area with Fe and Mn fractions dominating which was followed by exchangeable, residual and organic matter fractions in order. There was not much difference between these sites in total fractions of Cd. The content of Cd in the above sites was also low except the agricultural sites which recorded higher Cd values.

Copper: Copper was present mostly in the residual fraction with lesser amounts in the organic matter, Fe and Mn and exchangeable fractions. This pattern was similar in all the 3 sites. The total fraction was not much different in the three sites. Copper was comparatively more in the industrial sites as compared to the agricultural areas. It is low in mobility and hence accumulates at the site of application.

Site 2. Infopark Compound: The different fractions of heavy metals in the soils of Infopark compound are presented in the table 3 below.

Table-1
Geoaccumulation index of heavy metals

Site	Cd	Cu	Fe	Mn	Ni	Pb	Zn
GOI Press	- 1.495	- 0.485	- 0.53	- 0.015	- 0.541	- 0.532	- 0.298
Infopark	- 1.128	- 0.048	- 0.159	- 0.22	- 0.436	- 0.047	- 1.014
Agriculture	- 0.585	- 0.585	- 0.471	- 0.096	- 0.054	- 0.532	- 0.386

Table-2
Heavy metal speciation in GOI press compound

Elements	Exchangeable (mg kg^{-1})	Fe and Mn (mg kg^{-1})	Organic matter (mg kg^{-1})	Residual (mg kg^{-1})	Total (mg kg^{-1})
Cd	1.09	1.32	1.66	2.31	6.39
Cu	0.69	2.80	3.13	14.22	20.84
Fe	178.80	925.60	321.81	39216.50	40642.50
Mn	54.82	106.02	6.74	50.10	435.34
Ni	3.80	12.14	13.70	30.70	60.35
Pb	17.25	30.69	21.75	20.56	101.81
Zn	2.38	2.43	1.88	11.66	18.37

Table-3
Heavy metal speciation in Infopark compound

Elements	Exchangeable (mg kg^{-1})	Fe and Mn (mg kg^{-1})	Organic matter (mg kg^{-1})	Residual (mg kg^{-1})	Total (mg kg^{-1})
Cd	1.87	1.87	0.52	1.72	7.34
Cu	0.45	2.87	4.12	20.45	27.90
Fe	173.50	751.75	260.50	49427.50	50612.50
Mn	49.62	88.87	3.55	43.80	185.85
Ni	3.37	9.45	23.60	36.85	73.27
Pb	23.75	40.50	18.50	36.25	119.00
Zn	2.23	1.36	1.02	8.51	13.12

Table-4
Heavy metal speciation in the Agricultural lands

Elements	Exchangeable (mg kg^{-1})	Fe and Mn (mg kg^{-1})	Organic matter (mg kg^{-1})	Residual (mg kg^{-1})	Total (mg kg^{-1})
Cd	1.92	2.10	1.33	1.47	6.82
Cu	1.36	1.71	3.11	15.04	21.22
Fe	281.80	776.65	296.87	35799.00	37154.10
Mn	15.54	116.34	5.29	43.99	181.16
Ni	12.79	7.31	40.39	207.60	268.09
Pb	5.12	32.37	37.00	15.12	89.62
Zn	2.17	1.68	3.08	13.88	20.81

Iron: Residual fraction of iron was extremely high, Fe and Mn fraction came next which was followed by the organic matter fraction and the exchangeable fraction. This pattern was exhibited in all the 3 sites. The total fraction was only slightly more than the residual fractions and did not differ much between the 3 sites. Soils in the humid tropics are usually rich in sesquioxides which is the case here also and chances of iron pollution are thus more.

Manganese: Manganese was found to be more in the Fe andMn fraction in all the 3 sites. In the GOI site, this was followed by the exchangeable, residual and organic matter fractions. In the Infopark site the Fe and Mn fraction was followed by exchangeable, residual and organic matter fractions while in the agricultural area the pattern was Fe and Mn fraction followed by residual, exchangeable and organic matter fractions. The total fraction was more in the GOI press site but similar in the other two sites.

Site 3. Agricultural Area: Heavy metals present in different fractions of the soil in the agricultural landscape is provided in table 4 below.

Nickel: Most of the nickel occurred in the residual fraction which was followed by the organic matter, Fe and Mn and exchangeable fractions. This pattern existed in both GOI press and Infopark sites. In the agricultural area the residual fraction was the highest as was the case with the other 2 sites but the order of decrease was organic matter, exchangeable and Fe and Mn fractions. The total fraction of Ni was similar in the two industrial sites but was much higher in the agricultural area.

Lead: The fractions of lead in the soil followed a different pattern in the 3 sites. In the GOI press site, it was highest in Fe andMn fraction which was followed by the organic matter, residual and exchangeable fractions. In the case of Infopark site, Fe and Mn fraction was followed by the residual, exchangeable and organic matter fractions. On the other hand in the agricultural site, the organic matter fraction was highest which was followed by Fe and Mn fraction, residual fraction and exchangeable fractions. The total fraction was lesser in the agricultural area as compared to the industrial sites both of which had similar values.

Zinc: The residual fraction of Zn was greater than the other fractions in all the 3 sites. It was followed by Fe and Mn, exchangeable and organic matter fractions in the GOI press site while the pattern of distribution in the Infopark site was in the order of the residual fraction followed by the exchangeable, Fe and Mn and organic matter fraction. In the agricultural area, the organic matter fraction came next to the residual one which was followed by the exchangeable and Fe and Mn fractions.

Discussion: The results obtained was interpreted by calculating the enrichment factor and the contamination factor of heavy metals in the soils of the three sites and is discussed below.

Table-5
Enrichment factor of heavy metals

Site	Cd	Cu	Fe	Mn	Ni	Pb	Zn
GOI Press	5.62	0.71	1.00	0.17	2.6	4.38	0.22
Infopark	4.25	0.77	1.00	0.11	2.54	4.09	0.13
Agriculture	6.47	0.80	1.00	0.32	13.26	4.22	0.20

Table-6
Contamination factor of heavy metals

Site	Cd	Cu	Fe	Mn	Ni	Pb	Zn
GOI	6.52	0.83	1.16	0.19	3.02	5.09	0.26
Infopark	6.12	1.11	1.44	0.17	3.66	5.95	0.18
Agriculture	6.95	0.85	1.06	0.16	13.40	4.48	0.29

Enrichment Factor: Enrichment factor of heavy metals calculated using the continental crust average with Fe as reference element for normalization indicated that Cd, Ni and Pb have accumulated beyond the normal expected levels in the crust in all the three sites. Enrichment factor of Pb was moderate with values slightly less than 5 in all the three sites but that of Ni was moderate in the industrial sites and significantly high in the agricultural areas. Cd enrichment was significant in GOI press site and agricultural areas while moderate in the Infopark area. All the other heavy metals studied had only minimum enrichment factor table 5 and figure 1.

The moderately high enrichment factor of Pb is a potential source of bioaccumulation due to its mobility in the exchangeable fraction. Cd on the other hand has low mobility in all the fractions and hence chances of pollution of ground water is minimum. The enrichment factor for cadmium was more than three in all the sites with negligible Igeo values indicating anthropogenic factors in increasing Cd contamination in these sites. The high enrichment factor of nickel especially in the agricultural land is also a matter of concern due to its mobility and carcinogenic effect.

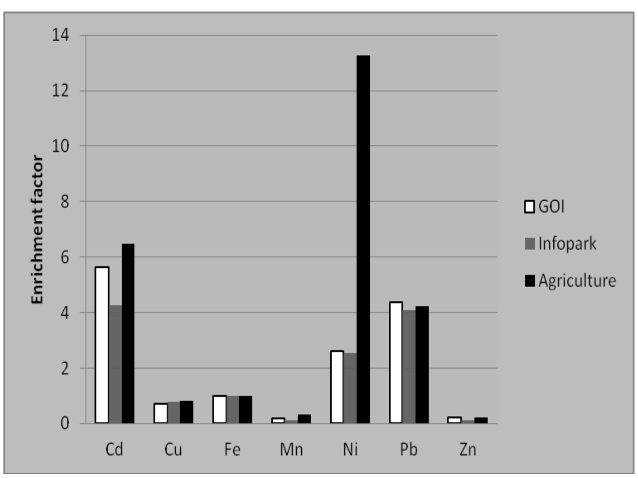

Figure-1
Enrichment factor of different elements in the three sites

Contamination Factor: Contamination factor which gives an idea of concentration of the element in relation to background concentration is shown in table 6 and figure 2.

It can be seen that all the three sites namely GOI press compound, Infopark compound and Agricultural area had moderate to high contamination of cadmium, nickel and lead. Iron, manganese, copper and zinc were low to moderate with respect to the contamination factor. Higher contamination levels of Cd, Ni and Pb in the three sites can be due to fertilizers, industrial effluents and vehicular traffic as well. The high concentration of Ni in the agricultural soil is probably due to phosphatic fertilizers, contaminated irrigation water or sewage water.

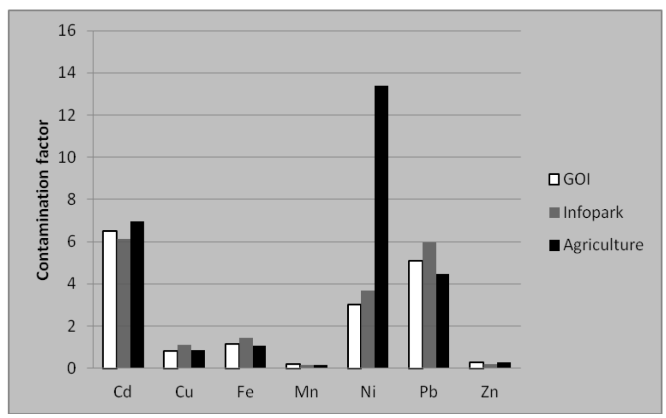

Figure-2
Contamination factor of different elements in the three sites

The speciation of heavy metals in Koratty region revealed different patterns with respect to the elements studied namely copper, iron, manganese, zinc, nickel, lead and cadmium. Copper and iron were mostly restricted to the residual fraction in both industrial and agricultural areas with slightly higher values in the industrial sites. Cu accumulates at the site of addition since it is not a mobile element while iron is comparatively mobile and hence easily transported through the soil. The Fe and Mn fraction contained maximum amount of Mn in both industrial and agricultural sites. Zinc was found to be more in the residual fraction in industrial as well as agricultural areas. Zinc is being enriched from fertilizers, hazardous waste, municipal sludge etc. Electroplating industries making use of electro galvanizing also release considerable amount of zinc into the surroundings. Being mobile, it is easily translocated with percolating water and can lead to pollution when higher amounts are added to the soil.

The residual fraction contained maximum nickel in all the sites irrespective of industrial or agricultural use. The total nickel content in the agricultural soil was much higher than the industrial sites. Fertilizers especially phosphates are a source of nickel in soil. More important is the application of waste disposal including sewage sludge. Predominantly high residual fractions of Ni has been reported by others also[18-21]**.** Nickel may be increasingly bound to organic matter, a part of which forms easily soluble chelates. The solubility and mobility of nickel increases with decreasing pH. Many nickel compounds are soluble at pH less than 6.5 and hence nickel contamination is a cause of concern.

Cadmium was found to be more in the residual and exchangeable fractions in the industrial sites while it was more in Fe and Mn fractions in the agricultural area. Cadmium content was low in most of the sampled sites except the agricultural areas where its values were high which is of concern due to chances of bioaccumulation in the cultivated crops since a preference for Cd is reported among plants[22]**.**

The pattern of speciation of lead was different from the above elements. It was highest in the Fe and Mn fractions in the industrial sites while the agricultural areas recorded more nickel in the organic matter fraction. Lead pollution is expected from printing industry which is reflected in the data also. Vehicular traffic is another major source of Pb through automobile emissions. Paint, plumbing materials, battery etc., also contribute to Pb contamination of the soil. The negative values of Igeo index indicates that enrichment of Pb was not from natural sources. In cultivated soils it was seen that Pb is largely held by organic matter, restricting its availability to the crops. But the acidic soils present in the area may increase the solubility and leaching of Pb to the ground water. Increase in mobility of lead with decreasing pH was also reported by Baranowski *et al*., 2002 [23]**.**

The results show that Cd, Ni andPb are pollutants in the study sites. Fe is the most mobile and Cd the least mobile among the elements and Cu, Mn and Zn contents were found to be low in the area.

Conclusion

Fractions of heavy metals determined using BCR sequencing extraction method showed that the order of mobility of metals was Fe>Mn>Pb>Ni>Zn>Cd>Cu. Contamination factors determined in the study gives an indication of site specific pollution. It was seen that the industrial sites were contaminated by Cd, Pb, Ni, Fe, Cu, Zn and Mn in decreasing order. The agricultural sites were contaminated by Ni, Cd, Pb, Fe, Zn, Cu and Mn in the same order. Enrichment factors reveal that the accumulated Cd, Pb and Ni are due to anthropogenic activities rather than from natural sources. The results show that Cd, Ni and Pb are pollutants in the area.

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