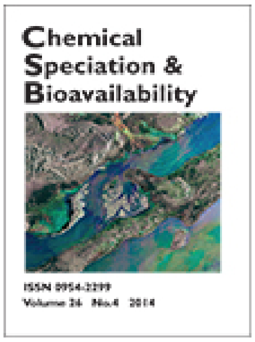

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Chemical fractionation of heavy metals in soils around oil installations, Assam

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ABSTRACT

The chemical fractionation of lead, cobalt, chromium, nickel, zinc, cadmium and copper in soils around Lakwa oil field, Assam, India was studied using a sequential extraction method. It is evident from the study that the residual fraction is the most important phase for the seven heavy metals under study. Among non-residual fractions metals are mostly associated with the Fe–Mn oxides fraction. The association of heavy metals with organic matter was observed in the following order: copper> cadmium> zinc> lead. The concentration of Pb in the carbonate fraction for both the seasons is higher compared with other metals, which may pose environmental problems due to its highly toxic nature. The comparatively low concentration of metals in the exchangeable fraction indicates low bioavailability. Correlations between physicochemical parameters and metal fractions of soil do not show consistent behaviour. The local mean values of metals when compared with the accepted values of normal abundance and geochemical background, indicates two to four fold increases in this area. However, the values are within the range of normal abundance. As well as from natural soil geochemical behaviour, anthropogenic influence might have a close bearing on the association of metals with the soil system in the studied area.

Keywords: Assam, fractionation, Group Gathering Station, heavy metals, oil installation

INTRODUCTION

Soil, which comprised of detritus, inorganic or organic particles, is relatively heterogeneous in terms of its physical, chemical and biological characteristics (Hakanson 1992). Heavy metals are associated with various soil components in different ways, and these associations determine their mobility and availability (Ahumuda *et al.*, 1999). Water soluble and exchangeable forms are considered readily mobile and available to plants, while metals incorporated into crystalline lattices of clays appear relatively inactive. The other forms like carbonate bound, occlusion in Fe, Mn and Al oxides, or complexes with organic matter and Fe–Mn oxides have been found to be the most important in soil and might be the components, which influence the medium to long term effect on lability and bioavailability of metals (Iyenger *et al.*, 1981; Karczewska *et al.*, 1998).

In recent years studies on the speciation or chemical forms of heavy metals in polluted soils using sequential techniques have increased, because these provide knowledge on metal affinity to soil components and the strength with which they are bound to the matrix (Narwal *et al.*, 1999). Numerous extraction schemes have been described in the literature (Chao 1972; Tessier *et al.*, 1979; Sposito *et al.*, 1982; Welte *et al.*, 1983; Clevenger 1990; Ure *et al.*, 1993; Howard and Vandenbrink,1999). The procedure of Tessier *et al.* (1979) is one of the most thoroughly researched and widely used procedures to evaluate the possible chemical associations of metals in sediments and soils. In this method, metal distribution is studied through five major geochemical forms: (i) exchangeable phase; (ii) bound to carbonate phase; (iii) bound to Fe–Mn oxides; (iv) bound to organic matter, and (v) residual metal phase.

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However, the limitations of chemical extraction methods have also been addressed (Jonanneau *et al.*, 1983; Khebonian and Bauer, 1987; Quevauviller *et al.*, 1997; Rauret *et al.*, 1989; 1999). The limitations include technical difficulties associated with selective dissolution and complete recovery of trace metal from chemical phases in soil and sediments. Therefore, the chemical forms of heavy metals from the sequential extraction methods are operationally defined phases only.

The soil around Lakwa (27.3° N Lat., 94.7°E Long.), a major oil producing structure of this region with a number of Group Gathering Stations (GGSs) comprising more than 200 producing wells is considered to be contaminated by the unattended industrial development. The region is located in a humid tropical climate with a high rate of rainfall and perennial flood problems. The advent of unattended industrial development aggravates the situation and warrants implementation of continuous multidisciplinary monitoring approaches with environmental perspectives, as the surface water is the only major source of water for the inhabitants of this thickly populated region. The spillage of oil, untreated formation and drilling water from this field is a matter of great concern for the entire ecosystem. Moreover, the damage caused by the oil field water to the tea planted areas located around the oil field also poses a serious problem. All these, coupled to a necessity for assessment of chemical forms of certain heavy metals and to study their long-term environmental impacts on soil in this area. The importance of studies related to different chemical forms of metals, its potential toxicity and bioavailability needs detailed studies (Forstner, 1983; Tessier and Campbell, 1988; Stamoulis *et al.*, 1996).

The aim of the present study was to investigate the different chemical forms of heavy metals in soil around oil installations i.e., GGSs and to assess the association and bioavailability of certain metals, viz., Cu, Cr, Cd, Co, Ni, Zn and Pb in soil. In order to assess the impacts of soil components on metal associations, relationships between metal accumulation patterns and soil characteristics have also been investigated.

MATERIALS AND METHODS

Study area and sampling

Sampling sites were selected after detailed survey around GGS-I and GGS-III (Figure 1). During the monsoon the water flows through this low-lying area and causes extensive damage to water bodies and agricultural/grazing land. The overflowing water acts as a carrier of the contaminated brines and other waste products from these oil installations. The metals under consideration were selected on the basis of site specific geochemical studies and their expected relationship with the oil field development activities.

Altogether ten sites (five around each GGS) were selected for sampling around the two GGSs I and III and ten sampling sites considerably distant (about 2–5km) from the production area which are considered as unpolluted and were selected for determination of normal soil background and threshold values. Samples were collected once in a month by plastic scoop (Hoffman, 1986) from the topsoil layer (up to 15cm) in the period 1994–1995 and the average of the replicate analysis of total metal content at each point was considered for evaluation in terms of its association and distribution. The generated data were used for this study.

Sample preparation and analysis

All soil samples were air dried and subsequently kept for 1 hour at 100°C for removal of water. The dried samples were ground with agate mortar to below 100 mesh size and were utilised for subsequent analysis. The soil pH was measured at the laboratory with the help of a Global Digital pH meter following the procedure of Faniran and Areola (1978). The carbonate content was determined by the acid neutralization method (Jackson, 1958). Organic matter content was determined by the Walkley Black Method (Faniran and Areola,1978).

Total metals were estimated following the procedure of Sakata (1983) by Atomic Absorption Spectrophotometry (AAS) with a Perkin-Elmer Model-2380 instrument using the hollow cathode lamp as light source. Pb and Cd contents were estimated by electrothermal atomisation i.e. graphite furnace (GF), while Cr, Co, Ni, Cu and Zn were estimated by flame technique (FAAS). Matrix matching, standard addition and background corrections were used to overcome interferences. After every four determinations blanks and reference standards (SO-1 of Canadian Certified Reference Material Project) with 95% confidence interval at ± 2 standard deviation were also run to determine the precision and instrumental uncertainties.

The local background levels of metals were calculated as geometric means (the antilog of the arithmetic average of $\log_{10}$ of the values). The geometric mean reduces the importance of a few high values, is a useful indicator of background for the most geochemical data (Govett, 1983). The threshold or upper limit of normal background fluctuation (Hawkes and Webb, 1965; Karauskopf, 1967) is determined from the background population to know the anomaly by utilizing mean + 2 standard deviations (Govett, 1983).

High purity Certified/Analar or its equivalent grade reagents (obtained from Aldrich, Sigma or E-merck only) were used throughout the work. HNO_3 and HCl used in this study were purified through a sub-boiling distillation unit (all quartz). Stock standard solutions of metals were prepared by dissolving ultrapure metals/compounds (99.99% pure) obtained from Aldrich only.

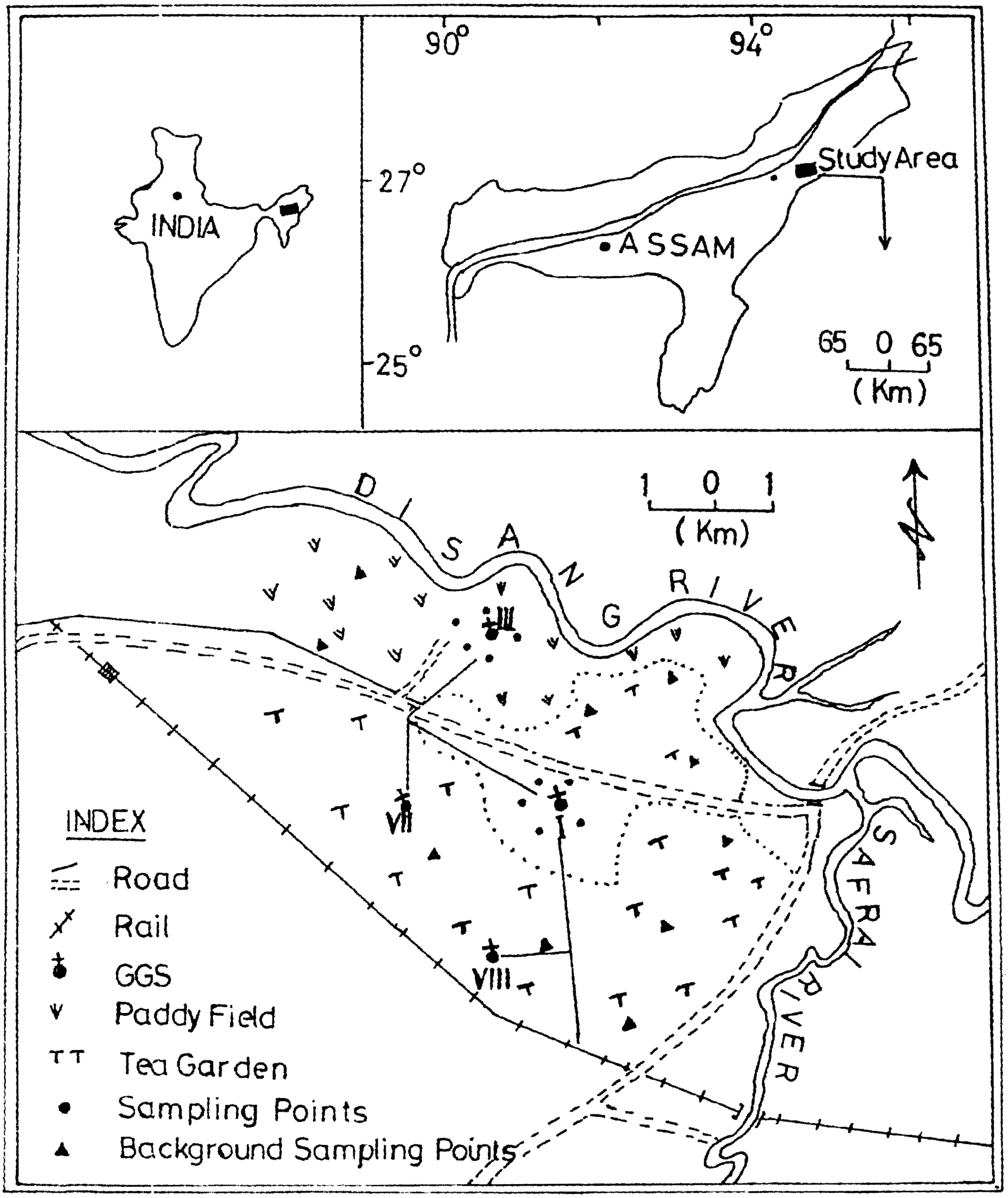

Figure 1 *Location map of the area with sampling points.*

The *t*-test was applied to determine significant correlation coefficients between various pairs of soil components under study at 5% level of significance ($\alpha = 0.05$). The results thus obtained are utilised to understand the interrelationship between them at the existing physicochemical conditions of the soil system under study.

Trace metal fractionation

The procedure of Tessier *et al.* (1979; 1985) was selected for this study. In this method heavy metals are separated into five operationally defined fractions: exchangeable (F_1), bound to carbonate (F_2), bound to Mn oxide (F_{3a}), bound to Fe-Mn oxide (F_{3b}), bound to organic matter (F_4) and residual fraction (F_5).

One gram of soil sample was weighed and extractions have been made through steps (f) by centrifugation at 10,000rpm placing the sample in polypropylene centrifuge tube.

(a) F_1: Exchangeable metals: The sediment samples was extracted for 1 hour with 8 mL of 1M $MgCl_2$ at pH7.0 at room temperature;
(b) F_2: Metals bound to carbonate: The residue from (a) was leached with 1M sodium acetate (NaOHc) adjusted to pH 5.0 with acetic acid (HoAc) for 5 hours;
(c) F_{3a}: Metal bound to Mn-oxide: The residue from (b) was leached for 30 minutes at room temperature with 0.1M $NH_2OH.HCl$ in 0.01M HNO_3;
(d) F_{3b}: Metals bound to Fe-Mn oxide: The residue from (c) was extracted at 96^{0}C for 6 hour with 0.04M $NH_2OH.HCl$ in 25% (v/v) HoAc;
(e) F_4: Metals bound to organic matter: The residue from (d) was extracted at 85^{0}C for 5 hour with 30% H_2O_2 adjusted to pH 2.0 with HNO_3 and then at room temperature with 3.2M NH_4OAc in 20% (v/v) HNO_3;
(f) F_5: Residual metals: The residue from (e) was digested with a mixture of concentrated hydroflouric, nitric and perchloric acids.

Step(c), suggested by Chao (1972), was included to distinguish between manganese and iron oxyhydroxides. The 'selective' extraction was conducted in centrifuge tubes (polypropylene. 50 mL) to minimize losses of solid material. Effective separation was achieved between each successive extraction by centrifuging at 10,000 rpm for 30 minutes. The supernatant was removed with a pipette and analysed for metals under study.

RESULTS AND DISCUSSION

Soil properties

The values of pH (Table1a and b) of soil around GGS-I during non monsoon (NM) and monsoon (M) periods vary from 4.8 to 5.3 and 4.8 to 5.20 and hence do not show any distinct change. Soil pH values below 5.0 to 5.5 warn that soluble level of certain metals, particularly Al^{3+} and Mn^{2+}, may be high enough to be biologically toxic (McBride, 1994). Conversely pH values above 7 are often associated with very low solubility of micronutrient metal cations such as Zn^{2+}. In the case of GGS-III pH values of NM period (4.4 to 8.4) is distinctly higher than M period (4.2 to 5.8). The higher value of pH during NM in S-3 of GGS-III is likely to be related to the higher carbonate content (8.5%) of the sample. However, the overall pH of the soil near two oil installation sites (GGS-I and GGS-III) is within the normal soil pH of the region.

Soil organic matter (SOM) expressed in terms of percentage of organic carbon refers to the sum of all organic carbon containing substances in soils. Organic matter content (Table 1a and b) of GGS-I was higher during M period than the NM period. The high value (7.5%) at S-4 during NM is exceptional and could be related to anthropogenic influences through accidental leakage and release of oil contaminated wastewater from the GGSs. In the case of GGS-III the organic matter content during NM and M periods does not show any appreciable change. Presence of crude oil in soil is harmful since it immobilizes soil N and P, and reduces the population and biomass of soil microfloura. It may also restrict seed germination, possibly, by limiting the inhibition of water and diffusion of gases into the seed. In oil saturated soil, the root hairs get plasmolysed and the root systems of plants get damaged / killed leading to eventual death (Rao, 1992). This might be one of the main causes for stunted growth and decreased yield of crops, particularly paddy crops around these installations.

The carbonate content (Table 1a and b) of the soil is comparatively low. It varies from 1.3 to 2.2% during NM and 1.7 to 2.8% in M period near GGS-I. In case of GGS-III it varies from 1.6 to 8.5% in NM and 1.7 to 3.8% in M periods. The low value of carbonate content is related to the acidic nature of soil with the exception at S-4 of GGS-III during NM period. This might be related to the site-specific geochemical behaviour of the soil profile.

Total concentration of heavy metals

The total concentrations of heavy metals are reported in Table 1a and 1b. The nature of concentrations and distributions of certain heavy metals under study is observed not to be similar for both the GGSs under existing physicochemical conditions. The nature of distribution of Cu, Ni, Co and Cd has shown similar behaviour whilst Cr, Zn and Pb signify a different situation for both the stations. The lower concentration of Co, Ni, Cu and Cd during the monsoon period can be attributed as the dilution and dispersion of metal contents by the flowing water during that period. The

Table 1a Geochemical parameters of soil around GGS-I

Sample points	pH		Carbonate content		Organic content		Pb		Co		Cr		Ni		Zn		Cd		Cu	
	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M
S-1	5.3	4.9	2.2	2.8	2.5	3.9	26.2	44.0	50.4	24.7	74.0	129.7	130.3	72.0	41.4	89.1	0.09	0.09	42.3	29.3
S-2	4.9	4.9	1.9	2.2	2.7	4.1	13.5	46.0	61.3	16.7	96.9	94.1	148.5	52.4	24.3	87.8	0.12	0.05	69.2	31.9
S-3	4.8	4.9	1.4	1.8	2.3	5.7	12.0	38.0	60.6	16.0	105.6	100.6	151.6	45.2	23.6	107.0	0.13	0.07	74.3	34.5
S-4	5.2	5.2	1.9	1.9	7.5	4.54	17.2	46.0	47.6	18.8	102.0	162.5	128.7	53.9	17.2	74.9	0.18	0.17	82.9	26.9
S-5	4.9	4.8	1.3	2.2	3.9	4.8	18.4	42.7	40.6	37.1	91.4	145.5	121.8	85.1	18.4	95.3	0.27	0.10	64.3	33.9

NM, Non -monsoon; M, Monsoon; all concentrations are μg/g except organic matter and carbonate content which are %.

Table 1b Geochemical parameters of soil around GGS-III

Sample points	pH		Carbonate content		Organic matter		Pb		Co		Cr		Ni		Zn		Cd		Cu	
NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	NM	M	
S-1	5.6	5.2	1.4	2.1	4.6	4.7	64.8	42.7	29.2	25.1	112.8	145.5	135.1	58.5	173.9	105.1	0.37	0.86	55.5	32.6
S-2	6.3	5.6	2.2	2.2	4.7	4.7	43.3	47.3	33.4	30.6	98.5	132.6	125.1	53.8	169.5	98.5	0.33	0.24	59.8	31.1
S-3	8.4	5.8	8.5	3.8	4.9	5.6	71.7	42.0	36.8	30.9	94.0	129.8	97.7	56.5	185.7	86.9	0.49	0.28	70.6	25.5
S-4	4.9	4.4	1.7	1.8	5.2	4.6	56.7	56.0	43.8	37.4	188.7	142.7	104.1	69.7	115.9	112.7	0.48	0.26	40.2	26.6
S-5	4.4	4.2	1.6	1.7	6.2	5.6	52.7	37.3	29.0	28.9	116.7	147.1	138.2	65.1	163.2	94.7	0.54	0.16	46.5	30.7

NM, Non -monsoon; M, Monsoon; all concentrations are μg /g except organic matter and carbonate content which are %.

higher concentration of Co, Ni, Cu and Cd during non-monsoon period might have a close relationship with their association with the suspended sediments. With the drop in competency of flowing water the suspended sediments were deposited with the soil profile and thereby causes an increase in total metal concentrations of elements during that period. The total concentration of Zn, Pb and Cr in the non-monsoon period was observed to be lower in GGS I than the concentration in monsoon period. The higher concentration of metals during monsoon period clearly indicates their incorporation from the nearby areas. The total concentration of Cr also exhibits similar behaviour in case of GGS III. However, Zn and Pb have shown a completely different behaviour in case of GGS III. The possibility of incorporation of Cr contents by the flowing water from the overflowing chromite bearing rock types of the catchment areas and from the corrosion-erosion of the chromite bearing fixtures/fittings related to oil exploration-exploitation activities also cannot be ruled out. The enhancement of Zn concentration in soils around GGS I has got definite linkage with the application of fertilizers in the low lying areas and paddy fields existed around it.

Table 2 summarises the background values of seven heavy metals. Comparisons of values with the internationally accepted shale standard (Wedepohl, 1972) and normal abundance values (Hawkes and Webb, 1972) indicate two to four fold increase over the mean values. However, all the values are within the range of normal abundance. On comparison with the two locations under study concentrations of Cd, Cu, Ni, Zn and Cr are lower than the local background. Pb and Co, however, exhibited higher values than the local background. All the values are within the range of background fluctuation and below the calculated threshold values. The high local background values can be interpreted as the presence of less weathered immature soil profiles with abundant soil mineral components coupled with anthropogenic incorporation from the associated development activities nearby.

Chemical fractionation of metals under study

The geochemical behaviour of trace metals and their chemical forms can be ascertained with the help of fractionation. The metals present in exchangeable (F_1) and carbonate (F_2) fractions are considered to be weakly bound and may equilibrate with the aqueous phase thus becoming readily bioavailable. On the other hand, the metals in the residual fraction (F_5) are not easily released under normal conditions. The Fe–Mn oxide (F_{3b}) and organic fractions (F_4) provide a sink or reservoir for heavy metals. The hydrous Mn-oxide fraction exhibits more isomorphic substitution than amorphous Fe-oxide and shows greater conditional equilibrium constants for the heavy metals than Fe-oxide. The distribution of heavy metals in different chemical fractions as evident from the present study is shown in Figures 2a and 2b.

The fractionation of lead shows that a major portion is associated with the residual fraction (F_5), followed by Fe–Mn oxide (F_{3b}), organic matter (F_4), carbonate

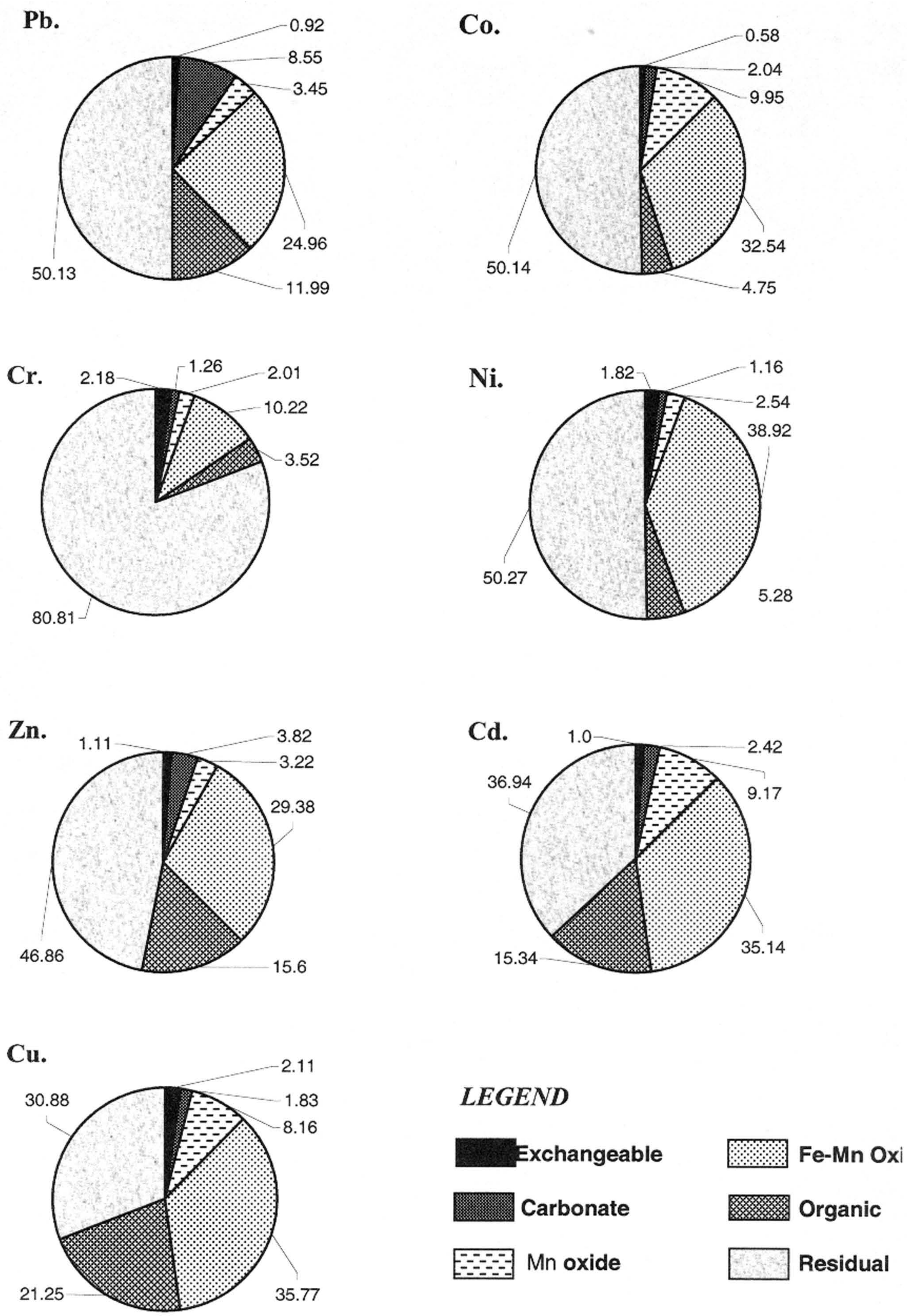

Figure 2a *Chemical partitioning of heavy metals (%) in soil around G.G.S.-I.*

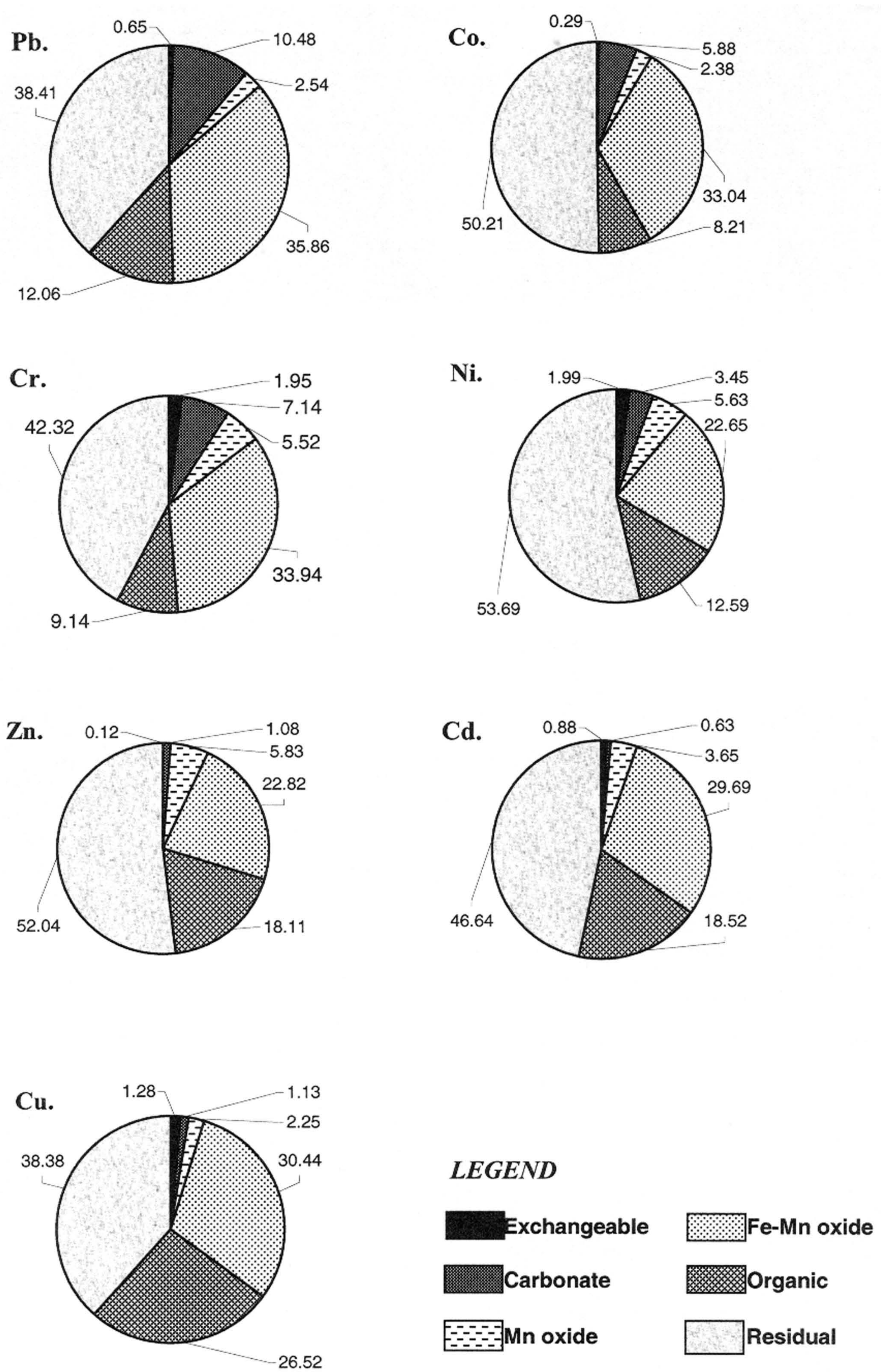

Figure 2b *Chemical partitioning of heavy metals (%) in soil around G.G.S.-III.*

Table 2 Local background and threshold value of heavy metals in soil along with their normal abundance (values are µg/g dw)

Metal	Normal abundance[a]		Average shale values[b]	Background values(present study)		Threshold values (present study)
	Mean	Range		Mean	Range	
Pb	10	2–200	20	18.62	6.8–72.0	81.28
Co	8	1–40	19	19.17	13.6–50. 2	57.54
Cr	100	5–1000	90	120.22	51.8–229.6	250.61
Ni	40	5–500	68	103.21	70–256	281.83
Zn	50	10–300	95	107.76	38.4–310.6	316.22
Cd	0.5	01–0.7	0.3	0.31	0.12–0.64	0.75
Cu	20	2–100	45	48.42	21.8–85.7	90.38

After [a]Hawkes and Webb (1965); [a]Karauskopf (1967); [b]Wedepohl (1972)

(F_2), Mn oxide (F_{3a}) and exchangeable (F_1) fractions. Pb shows different behaviour in relation to pH, carbonate and organic matter contents for the two GGSs. In the case of GGS-I in NM period, Pb shows positive relationship with all parameters, except organic matter content, where it exhibits a negative significant ($r = -0.86$) correlation. The significant positive ($r = 0.81$) correlation with pH during the M period suggests an increasing tendency of sorption with increasing pH. Association of Pb with Fe–Mn oxides (up to 25%) fraction is also supported by their positive correlation. In case of GGS-III, Pb shows non-significant negative correlation with respect to pH and carbonate content for both the periods. However, in case of organic matter content Pb shows significant negative correlation ($r = -0.76$) in M period. The higher concentration of lead in the Fe-Mn oxide is due to the formation of stable complex (Lopez-Sanchez *et al.*, 1996; Jones and Turkie, 1997). The lower concentration of Pb in the exchangeable fraction suggests low bioavailability but slightly higher concentration in the carbonate fraction indicates a problem to the ecosystem as carbonates may dissolve readily with a change in soil characteristics.

The association of cobalt with different fractions was observed in the order: residual > Fe–Mn oxide > Mn oxide > organic > carbonates > exchangeable (Figures 2a and 2b). The higher concentration of Co in the Fe–Mn oxides fractions (up to 42.5%) indicates that Fe–Mn oxides act as a natural sink for cobalt. The correlation matrix for both the GGSs shows a non-significant negative correlation with the physicochemical parameters.Chromium was mostly concentrated in the residual fraction. The partitioning of chromium with different fractions was in the order: residual > Fe oxide > organic > Mn- oxide > carbonate > exchangeable. The significant difference in residual Cr content in GGS-I (80.8%) and GGS-III (42.3%) clearly indicates the role played by soil mineral components in its distribution under the existing physico-chemical conditions. The formation of dichromate at the existing soil pH is minimised and reduces the affinity of sorption by hydrous metal oxides (Fe–Mn). However, at a low pH and concentration, where solubility of Cr (III) is higher, strong specific adsorption on Fe-Mn oxides occurs. Probably because of this reason, we observed a different situation in GGS-I (12.2%) and GGS-III (39.5%) in case of Cr association with Fe-Mn oxides fraction. The relatively higher proportion of organic matter content in the topsoil layer around GGS-III might have clearly indicated its association with the soil system by forming stable organic complexes at the existing physico-chemical conditions. In moderate to highly organic soils, Cr and Cu are present in less mobile and less available forms to soil organisms and plants, the soluble and exchangeable metals (labile fraction) usually being considered as most hazardous (Gupta *et al.*, 1996; Maiz *et al.*, 2000). The higher association with the residual fraction indicates its low bioavailability.

Nickel was mostly concentrated in the residual fraction although it has shown its affinity towards Fe-Mn oxide fractions. The percentage of nickel in the residual fraction ranges from 50.3 to 53.7%. The correlation coefficient (Table 3a and 3b) shows an overall negative effect except carbonate (CO_3^{2-}) content in the NM period of GGS-I. The organic matter associated with the soil fraction also retains a small amount of nickel. The lower concentrations in the exchangeable and carbonate fractions and alternately higher concentration in the residual fraction indicate reduced rate of interactions with the biotic community of the soil.

The sequential extraction showed that residual fraction dominated the Zn distribution in the soil, which ranges from 46.9 to 52.0% for both the GGSs. Similar results for distribution of Zn were also reported by other authors (Gupta and Chen, 1975; Ma and Rao, 1997; Izquirdo *et al.*, 1997; Ramos *et al.*, 1999; Li *et al.*, 2000; Li *et al.*, 2001). As evident from the study the non-residual Zn is likely to be retained in order as: Fe–Mn oxides>organic fraction>carbonate>exchangeable. The organic matter fraction [F_4] also contains a considerable amount of zinc (16–18%) and apparently forms organic complexes. The enrichment of total zinc up to 5% is reported to be bound in the humic acid fraction of the soil (Bodek *et al.*, 1988). The high content of zinc

Table 3a Correlation coefficients of soil properties and heavy metals around GGS-I

Non-monsoon	pH	CO_3^{2-}	#O.M.	Pb	Co	Cr	Ni	Zn	Cd	Cu
pH		–0.03	–0.24	0.48	–0.28	**0.69**	–0.22	**–0.79**	**–0.91**	**–0.91**
CO_3^{2-}			**–0.83**	0.47	0.29	0.07	0.54	–0.29	–0.14	–0.35
S.O.M.				**–0.86**	–0.06	–0.15	–0.30	**0.69**	–0.04	**0.61**
Pb					0.01	0.36	0.16	**–0.91**	0.34	**–0.71**
Co						0.50	**0.96**	0.08	0.14	0.23
Cr							0.49	**–0.60**	**0.92**	–0. 59
Ni								–0.04	0.11	0.07
Zn									**–0.67**	**0.90**
Cd										**–0.71**
Cu										
Monsoon period										
pH		**0.85**	0.33	**0.81**	–0.28	**–0.66**	–0.33	0.57	–0.37	–0.46
CO_3^{2-}			0.04	0.52	0.24	–0.51	–0.32	**0.65**	**–0.73**	–0.40
S.O.M.				0.01	–0.51	0.32	**0.69**	–0.57	0.44	0.58
Pb					–0.54	**–0.93**	**–0.71**	**0.70**	–0.13	**–0.81**
Co						0.35	0.07	0.19	**–0.75**	0.15
Cr							0.90	**–0.82**	0.23	**0.95**
Ni								**–0.87**	0.34	**0.99**
Zn									**–0.72**	**–0.89**
Cd										0.33
Cu										

Table 3b Correlation coefficients of soil properties and heavy metals around GGS-III

Non-monsoon	pH	CO_3^{2-}	#O.M.	Pb	Co	Cr	Ni	Zn	Cd	Cu
pH		**0.92**	–0.51	–0.57	0.17	–0.55	**–0.62**	**0.60**	–0.14	**0.92**
CO_3^{2-}			–0.16	–0.49	0.23	–0.43	**–0.70**	0.50	0.26	**0.78**
S.O.M.				0.22	–0.12	0.20	0.23	–0.23	**0.83**	–0.50
Pb					–0.47	0.18	0.56	–0.06	0.17	–0.44
Co						**0.70**	**–0.85**	**–0.68**	0.20	–0.21
Cr							–0.28	**–0.98**	0.29	**–0.82**
Ni								0.23	0.34	**0.99**
Zn									**–0.72**	**–0.89**
Cd										**–0.89**
Cu										
Monsoon period										
pH		**0.78**	–0.006	–0.12	–0.32	**–0.83**	**–0.91**	–0.51	0.23	–0.09
CO_3^{2-}			0.42	–0.20	–0.05	**–0.80**	–0.56	**–0.70**	–0.02	–0.57
S.O.M.				**–0.76**	–0.20	–0.12	–0.05	**–0.84**	–0.42	–0.27
Pb					**0.78**	–0.11	0.36	**0.73**	–0.10	–0.37
Co						–0.17	0.58	0.36	**–0.60**	**–0.74**
Cr							**0.67**	0.54	0.31	0.48
Ni								0.56	–0.23	–0.27
Zn									0.32	0.18
Cd										0.49
Cu										

in the organic matter fraction is due to its scavenging effect. The present finding can be corroborated with the studies of Tessier *et al.* (1980); Jordao and Hickless (1989); Nriagu and Coker (1980); Gadh *et al.* (1993) and Baruah *et al.* (1996). Fe–Mn oxides seem to play a major role in zinc accumulation in the profile, as precipitation and co-precipitation products. The association of zinc with Fe–Mn oxides in soil has been widely recognised (Kuo *et al.*, 1983; Comber *et al.*, 1995; Jones and Turkie, 1997). The sorption of zinc in soil and sediments strongly imparts its mobility in the environment. For this reason, severe zinc contamination tends to be confined to the region of the source (Li *et al.*, 2000). Hydrous Fe and Mn oxides, clay minerals, carbonate minerals, and, to a lesser extent, organic matter have been noted as sorbents that control the behaviour of zinc in soil. A minor amount is also associated with exchangeable [F_1] and carbonate fractions [F_2]. Calcium carbonate forms complexes with zinc as a double salt ($CaCo_3.ZnCo_3$) in the soil (Li *et al.*, 2000). The association of Zn with carbonate appeared to be less pronounced due to the low content of carbonate in the soil. Lower concentration in the exchangeable fraction indicates low bioavailability.

Association of Cd is observed as maximum in residual fraction. The association of Cd with the different fractions was observed in the following order: residual > Fe–Mn oxides > organic > carbonate > exchangeable. The correlation coefficients (Table 3a and 3b) exhibited wide variation for both the group-gathering stations (GGSs I and III) during NM and M periods. The higher association of Cd with the organic matter fraction (15.3 to 18.5%) is also manifested by the positive correlation coefficients.

Association of copper with different fractions is observed as residual > Fe-Mn oxides > organic > exchangeable > carbonate. Copper is strongly sorbed by hydrous Fe-Mn oxides, clay minerals and organic matter. Because of the high affinity of copper for soil colloids, copper is rated a low-mobility element in near neutral soils. Sorption is probably the most important controlling mechanism determining the association and mobility of copper under the existing physicochemical conditions. Several investigators have demonstrated that the sorption of copper on hydrous Fe–Mn oxides is due to co-precipitation of copper in the Fe–Mn oxide lattice. However, the organic matter fraction [F_4] contains a significant amount (21.3–26.5%) of copper. Copper is preferentially retained on organic matter by complexation rather than by ion exchange (Balasoiu, 2001; Wu *et al.*, 1999). A significant positive relationship between copper and organic matter (Table 3a) is observed in case of GGS-I, however, in case of GGS-III (Table 3b) it shows opposite relationship. This might be related to the local geochemical behaviour of soil. The strong positive effect can be related with the fact that, copper easily form complexes with organic matter due to the high stability constant of organic-Cu compounds. Organic material exhibits a high degree of selectivity for divalent ions and the probable order of binding strength for metals onto organic matter is copper>lead>zinc. Thus, the organically bound form is an important phase for copper in the soil. The carrier effect is more pronounced in the case of copper organic complexes compared to free copper (Cu^{2+}) ions available within the system (Mcbride, 1994). Organically complexed copper (Cu^{2+}) is bound more tightly than any other divalent transition metal; lability of these complexes is rather low, limiting bioavailability. Probably this is the reason why farmers have been able to apply large amounts of copper salts to organic soils over time without causing toxicity to crops (Mcbride, 1994). The higher amount of Cu in the residual fraction [F_5] is suggestive of non-availability to biotic community. The lower concentrations in exchangeable (1.3–2.1%) and carbonate fractions (1.1–1.8%) are also indicative of a low bioavailability.

CONCLUSIONS

The chemical fractionation of metals under study revealed the geochemical nature of seven metals and their probable association with different chemical forms in soils around the group gathering stations of Lakwa oil field, Assam. The study also focused on the influence of soil physicochemical characteristics on the retention and partitioning of seven heavy metals. The heavy metals are mainly associated with the residual and Fe–Mn oxides fractions. The Fe–Mn oxides and organic matter fractions readily form complexes and may provide a sink for heavy metals. The acidic nature of the soils restricts the association with the carbonate and exchangeable fractions. It is evident from the study that the soil characteristics played a significant role in defining the chemical forms of the metals within the system. The present study indicates that the metals under study do not pose environmental risks under the existing physicochemical environment.

However, the present study warrants implementation of a continuous monitoring system in the area, as surface water is one of the major sources of water for this thickly populated area apart from regular use by thousands of cattle and other domestic animals.

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