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RISK ASSESSMENT OF HEAVY METAL POLLUTION AND FRACTIONATION IN SEDIMENT OF A WASTE-FED INDIAN RESERVOIR

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Abstract: Heavy metal pollution in aquatic ecosystem has become a serious concern due to its toxicity, persistence and accumulative behavior. The present study was aimed at studying the levels of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn and their relationships with different physico-chemical parameters like pH, OC, sand, silt and clay to evaluate the risk of heavy metal pollution in Halali reservoir. Data were processed using Pearson's correlation coefficients and factor analysis. Positive relationships among the metals confirmed the anthropogenic sources of pollution in the reservoir. The persistence and fate of the metal depended more on its chemical forms than on total metal concentrations. By applying the sequential extraction method and Risk Assessment Code (RAC) it was found that Ni and Zn were at low risk, while Cu and Mn were at medium risk. By using the freshwater sediment quality guidelines it was established that there was a growing possibility of Cr and Cu toxicity for the aquatic biota of Halali reservoir.

Key words: heavy metals, pollution, toxicity, correlation, factor analysis.

1. INTRODUCTION

Pollution of aquatic environment by heavy metals has become a worldwide problem due to their toxic effects. These metals are introduced in the aquatic system from both natural and anthropogenic sources. Industrial effluents, agricultural runoffs, burning of fossil fuels, animal and human wastes, geological weathering and domestic wastes are the main sources of pollution in aquatic ecosystem. Heavy metals are of high ecological significance since they are not removed from water as a result of self-purification, but accumulate in reservoirs and enter into the food chain (Loska & Wiechula, 2003). Pollution of heavy metals in a reservoir is mainly estimated by their concentrations in the sediments, which play an important role as pollutants. Sediments act as both carriers and sinks for contaminants in aquatic environments. Several studies have demonstrated that the concentration of metals in sediments can be a sensitive marker of contaminants in hydrological systems (Salomons & Forstner, 1980; Luoma, 1990). Sediments are normally the mixture of several components including different mineral species as well as organic debris. The solubility and availability of heavy metals in sediment is affected by pH, concentration and type of ligands, chelating agents, particle size and composition of the sediments (Foster & Hunt, 1975; Throne & Nickless, 1981; Sakai et al., 1986; Jain, 2004). All forms of metals have different bioavailability and toxicity. The environmentalists are rightly concerned about the exact forms of metal present in the aquatic environment. The determination of total metal may not be able to provide information about the exact dimension of pollution and thus the measurements of different fractions have great importance. In 1954, Goldberg introduced the concept of speciation to improve the understanding of the biogeochemical cycling of heavy metals. Several sequential extraction techniques for the fractionation of metals in sediment have been established in Canada (Tessier et al., 1979), England (Jardo & Nickless, 1989; Neal et al., 1996), Egypt (Elsokkary & Muller, 1990), Spain (Rauret, 1998; Pardo et al., 1990) and

Lebanon (Korfali & Davies, 2000). Although the importance of metal speciation and fractionation has been realized in developed countries, the subject has not really taken off in India. Some studies have been done on the fractionation of metals in Indian rivers and lakes (Baruah et al., 1996; Khwaja et al., 2001; Sekhar et al., 2003; Jain, 2004; Singh et al., 2005; Ayyamperumal et al., 2006; Jain et al., 2008; Krupadam et al., 2007; Purushothaman & Chakrapani, 2007), but no study has been conducted on the fractionation of metals in Indian reservoir sediment.

Halali reservoir is situated on the intersect of Bhopal,Vidisha and Raisen districts of Madhya Pradesh, the central province of India. It is constructed on the Halali River and serves as an irrigation dam. It has added economic importance due to large scale fish production. The water of Halali reservoir is also used for drinking purposes in nearby city, Vidisha. Halali and Chamari rivers bring huge amount of wastes from Bhopal and Sehore districts, which are the main source of pollution in this reservoir, and join the reservoir directly as well as through several inlets. No study has so far been conducted to know the heavy metal status in the sediment of the reservoir. So, the aim of the present study was to investigate the levels of different types of heavy metals along with their forms in sediments and the interrelationships amongst the heavy metals and the physico-chemical characteristics of the sediment.

2. MATERIALS AND METHODS

2.1. Study area

The study area was Halali reservoir situated in Bhopal,Vidisha and Raisen districts of Madhya Pradesh at a latitude 23°30’N and longitude 77°30’E. The average water area of the reservoir is 4795 ha, and the full tank level is about 466 m, while the catchment area is about 69900 ha. This study was conducted during 2006-07 at five different stations of the reservoir (referred as H1, H2, H3, H4 and H5), which were selected on the basis of their utility for various anthropogenic activities. Station 1 (H1) is an inlet site, which receives a huge amount of wastes from Bhopal district, mainly containing domestic and municipal wastes, detergents, and also some chemical wastes specially used in dyes. Station 2 (H2) is also an inlet site and is constantly fed with the domestic and municipal wastes, because Chamari river, which mainly carries domestic wastes from Sehore district, join the reservoir at this site. Station 3 (H3) is almost the centre of the reservoir and wastes can accumulate at this site due to the highest depth. Station 4 (H4) is the dam site that is mainly polluted by oil and grease, which are being used in boats by fisherman. Station 5 (H5) has no direct influence of anthropogenic activities, and hence it was referred to as control site. The location of the sampling points is shown in figure 1.

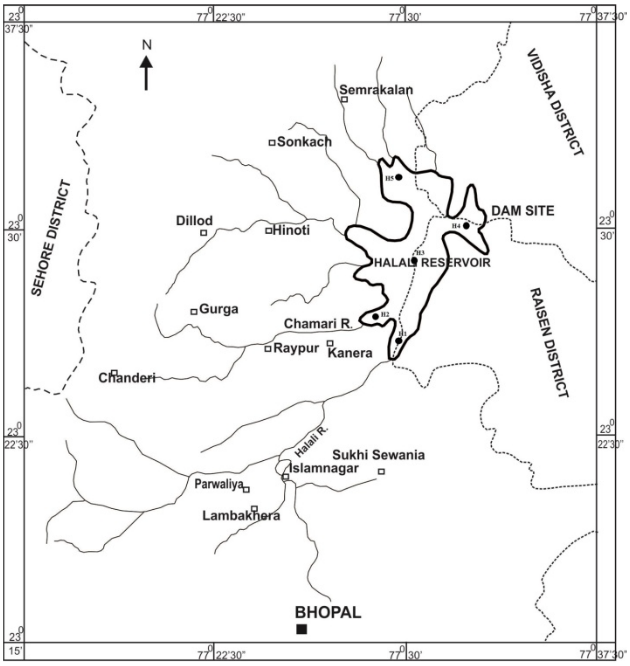

Figure 1. Map showing the inlets and sampling stations of Halali reservoir.

2.2. Sample collection and preparation

The sediment samples were collected with the help of grab sampler- Ekman Dredge. Five samples from each site were collected each time during rainy, winter and summer seasons of 2006-07. The samples were transported to the laboratory in the polyethylene bags and were air - dried. The locations of the sampling points were determined in the field with the help of the Global Positioning System (GPS; Garmin 76 CSx) so as to make repeated samplings from the same points in three different seasons.

2.3. Analytical procedure

The pH of each (1:5 = sediment:water) was determined by equilibration with double distilled water by stirring at regular intervals for 1 hr. The pH of the unfiltered suspension was determined electrochemically using a pH meter (Khwaja et al., 2001).

For organic carbon content, the dried sediment (0.5 gm) was transferred after passing through a 0.25 mm sieve to a 500 ml conical flask. 10 ml of 1N $K_2Cr_2O_7$ and 20 ml concentrated H_2SO_4

were added and the mixture was allowed to react for 30 min. After dilution to 200 ml double distilled water, 10 ml H_3PO_4 was added and titrated against the ferrous ammonium sulphate by using 1 ml diphenylamine indicator (Walkley & Black, 1934). Two blanks were also run along with the samples. Textural analysis was performed in all the samples to estimate the sand, silt and clay contents. It was done by mechanical analysis through Bouyoucous hydrometer method (Bouyoucos, 1962).

The sequential extraction technique proposed by Tessier et al., (1979) was followed for portioning the trace metals into the following five fractions:

Exchangeable

1.0 gm sediment sample was extracted at room temperature for 1 hr with 10 ml of 1.0 M $MgCl_2$ (pH 7.0) with continuous agitation.

Bound to carbonate

The residue obtained from step 1 was leached at room temperature with 10 ml of 1.0 M sodium acetate adjusted to pH 5.0 with acetic acid. The mixture was agitated for 5 hr.

Bound to Fe-Mn oxides

The residue obtained from step 2 was refluxed at 100^oC with 20 ml of 0.04 M $NH_2OH.HCl$ in 25 % (v/v) acetic acid for 6 hr.

Bound to organic matter

To the residue obtained from step 3, 3 ml of 0.02 M HNO_3 and 5 ml of 30 % H_2O_2 were added and pH adjusted to 2.0 with HNO_3. The mixture was refluxed at 100^oC for 2 hr. A second 3 ml aliquot of 30 % H_2O_2 (pH 2 with HNO_3) was then added and the sample was again refluxed for 3 hr. After cooling, 5 ml of 3.2 M ammonium acetate in 20 % (v/v) HNO_3 was added. The sample was diluted to 100 ml and agitated continuously for 30 min. The addition of ammonium acetate is to prevent adsorption of extracted metals onto the oxidized sediment.

Residual

The residue obtained from step 4 was digested with a HF-$HClO_4$ mixture as per procedure followed for the analysis of trace elements.

Different fractions of metals have been expressed as per cent of total metal content. The fraction study was not carried out for Cd and Pb due to their very low concentration in the reservoir sediment. Metal contents in digested samples as well as in different fractions of the sediments were analyzed using ICP–OES (Model- Perkin – Elmer Optima 2100 DV).

2.4. Quality control

All the plastic and glass wares were washed in acid and rinsed with double distilled water before use. Reagents were of analytical grade and double-distilled water was used throughout the study. Before starting the analysis the instrument was calibrated with commercially available chemical standard solutions (Merck, Germany). Analytical blanks were run in the same way as the samples and the concentrations were determined using the standard solutions prepared in the same acid matrix. The quality of the data was checked by the analysis of Standard Reference Materials supplied by Perkin Elmer (NIST 1640, National Institute of Standards and Technology, USA). All the samples were processed in triplicates, to avoid any error.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical properties

The physico-chemical properties of sediment are presented in table1. The average pH of the sediment ranged from 6.9 - 7.5 and was neutral to slightly alkaline. Most of the water bodies have alkaline pH in sediment. Jain (2004) also reported alkaline pH in sediment of Yamuna river. Average organic carbon was in the range of 0.80 - 2.67% at all the sites of the reservoir, which were less than that observed by Sekhar et al., (2003) in Kolleru lake. In all the seasons, sand was found to be dominant at all the stations except at H3 having 34.78 - 56.91% followed by silt (31.73 - 45.32%) and clay (11.36 - 20.22%). This might be due to continuous deposition of alluvium in the reservoir. Similar result was also reported by Singh et al., (2005) for Gomti river.

3.2. Total metal concentration and fractionation

Total concentrations of heavy metals in sediment are presented in table 2. Concentrations of metals were not uniform over the whole reservoir. This variation in concentration might be due to the differences in the sources of heavy metals, physico-chemical conditions and complex reaction with the sediment. The mean concentrations of the metals varied between 0.01 - 0.084 mg kg^{-1} for Cd, 3.57 - 12.31 for Co, 7.69 - 35.42 for Cr, 13.25 - 40.18 for Cu, 1776 - 4591 for Fe, 77.18 - 420 for Mn, 4.55 - 9.91 for Ni, 0.104 - 0.455 for Pb and 42.11 - 94.57 mg kg^{-1} for Zn (Table 2). Metal concentrations varied according to sites and seasons. Station H5 contained the lowest amount of metals in all the seasons probably due to less anthropogenic activities at this site.

Table 1. Characteristics of sediment at different sites during different seasons

Season	Site	pH	OC (%)	Sand (%)	Silt (%)	Clay (%)
rainy	H1	7.11 ± 0.021	2.67 ± 0.058	53.98 ± 5.98	32.67 ± 5.64	13.25 ± 2.71
	H2	7.24 ± 0.028	2.29 ± 0.074	54.68 ± 3.85	33.64 ± 3.98	11.68 ± 1.48
	H3	7.30 ± 0.026	2.56 ± 0.068	34.78 ± 1.55	45.32 ± 1.73	19.89 ± 2.53
	H4	7.19 ± 0.025	2.27 ± 0.081	52.21 ± 2.52	34.22 ± 2.74	13.56 ± 0.683
	H5	7.28 ± 0.023	1.42 ± 0.091	51.93 ± 1.10	35.57 ± 1.53	12.49 ± 1.18
winter	H1	7.28 ± 0.026	1.19 ± 0.051	56.91 ± 6.27	31.73 ± 5.02	11.36 ± 1.29
	H2	7.38 ± 0.024	1.52 ± 0.078	54.80 ± 2.75	33.49 ± 2.96	11.70 ± 0.765
	H3	7.15 ± 0.032	2.37 ± 0.101	34.98 ± 1.38	44.79 ± 1.28	20.22 ± 1.28
	H4	7.14 ± 0.032	2.56 ± 0.067	54.22 ± 1.08	33.23 ± 1.93	12.55 ± 1.47
	H5	7.26 ± 0.037	1.34 ± 0.058	52.82 ± 3.57	34.26 ± 2.35	12.92 ± 2.57
summer	H1	7.54 ± 0.027	0.802 ± 0.052	51.93 ± 8.29	36.14 ± 7.89	11.93 ± 0.983
	H2	7.45 ± 0.034	1.34 ± 0.070	54.34 ± 4.84	33.56 ± 5.02	12.09 ± 0.772
	H3	6.94 ± 0.033	1.48 ± 0.071	36.0 ± 1.11	44.67 ± 1.86	19.33 ± 2.32
	H4	7.16 ± 0.026	2.03 ± 0.091	52.29 ± 3.58	34.49 ± 2.62	13.22 ± 2.93
	H5	7.35 ± 0.031	1.35 ± 0.091	52.63 ± 2.48	34.87 ± 1.96	12.49 ± 1.22

Data represent mean ± SD of 15 observations (5 samples replicated thrice)

Carvalho et al., (1999), Olias et al., (2004), Shomar et al., (2005) and Purushothaman & Chakrapani (2007) reported a variation in heavy metal concentrations with seasons and sites. Most of the metals were higher at site H1 and H2 (Table 2) due to their high potential for heavy metal pollution in the reservoir. Higher concentrations of the metals at site H3 was due to the maximum depth of the reservoir, sedimentation and the textural property of the sediment at this site. Krupadam et al., (2007) also observed a variation in heavy metal concentrations along with the depth of reservoir.

For the tracing of heavy metal enrichment, the heavy metal concentration is generally compared with the standard shale value. In this study, all the metals were lower than the average shale value (Fig. 2) given by Turekian & Wedepohl (1961). In the sediment, heavy metals were found in various chemical forms and they exhibited different physico-chemical behavior. To evaluate the potential and actual impacts of metals, the identification and quantification of the present forms of metals was necessary. Generally, in sediments, heavy metals were found in five forms: exchangeable, carbonate, iron-manganese oxides, organic matter and residual.

The total concentrations of the metals varied according to sites and seasons but in different fractions metals varied only with sites, while so much variation was not found with seasons. Baruah et al., (1996) also did not find variation in heavy metal concentrations in different fractions with seasons, while Krupadam et al., (2007) observed the variation in heavy metal fractionations along with sites. So, the mean values of all the seasons for each site were taken to assess the heavy metal pollution in the studied area. Concentrations of metals in different fractions at different sites are depicted in figure 3.

3.2.1. Exchangeable fraction

Exchangeable fraction serves as the immediate nutrient reservoir for aquatic organisms. The amount of metals in this fraction of the sediment indicated the environmental conditions of the overlying water bodies. Across all sites this fraction of sediment had the mean range of Co from 1.51-5.19 %, Cr 0.99-2.09 %, Cu 2.84-7.29 %, Fe 0.99-1.08 %, Mn 3.37-14.18, Ni 0.451-2.32 % and Zn 0.957-6.11 %. Site H3 contained the highest amount of Mn in this fraction.

3.2.2. Carbonate fraction

In this fraction higher percentages of Cu and Mn (5.57 - 12.59 % and 4.16 - 17.5 %, respectively) were found than those of Co (1.3 - 9.64 %), Cr (1.52 - 8.69 %), Fe (4.68 - 9.38 %), Ni (4.38 - 5.08 %) and Zn (1.39-7.73 %). Mn was the highest accumulating metal in this fraction, but it was higher at site H4 in place of H3.

3.2.3. Fe-Mn fraction

This fraction was proved to be sensitive to anthropogenic inputs (Modak et al., 1992). All sites contained the mean range of Co from 21.10-30.44 %, Cr 19.37-29.42 %, Cu 21.14-31.88 %, Fe 24.44-43.05 %, Mn 12.4-29.28 %, Ni 11.37-21.56 % and Zn 4.13-15.83 % in this fraction. Fe was the highest accumulating metal for this fraction with a maximum of 43.05 % of the total Fe at site H3.

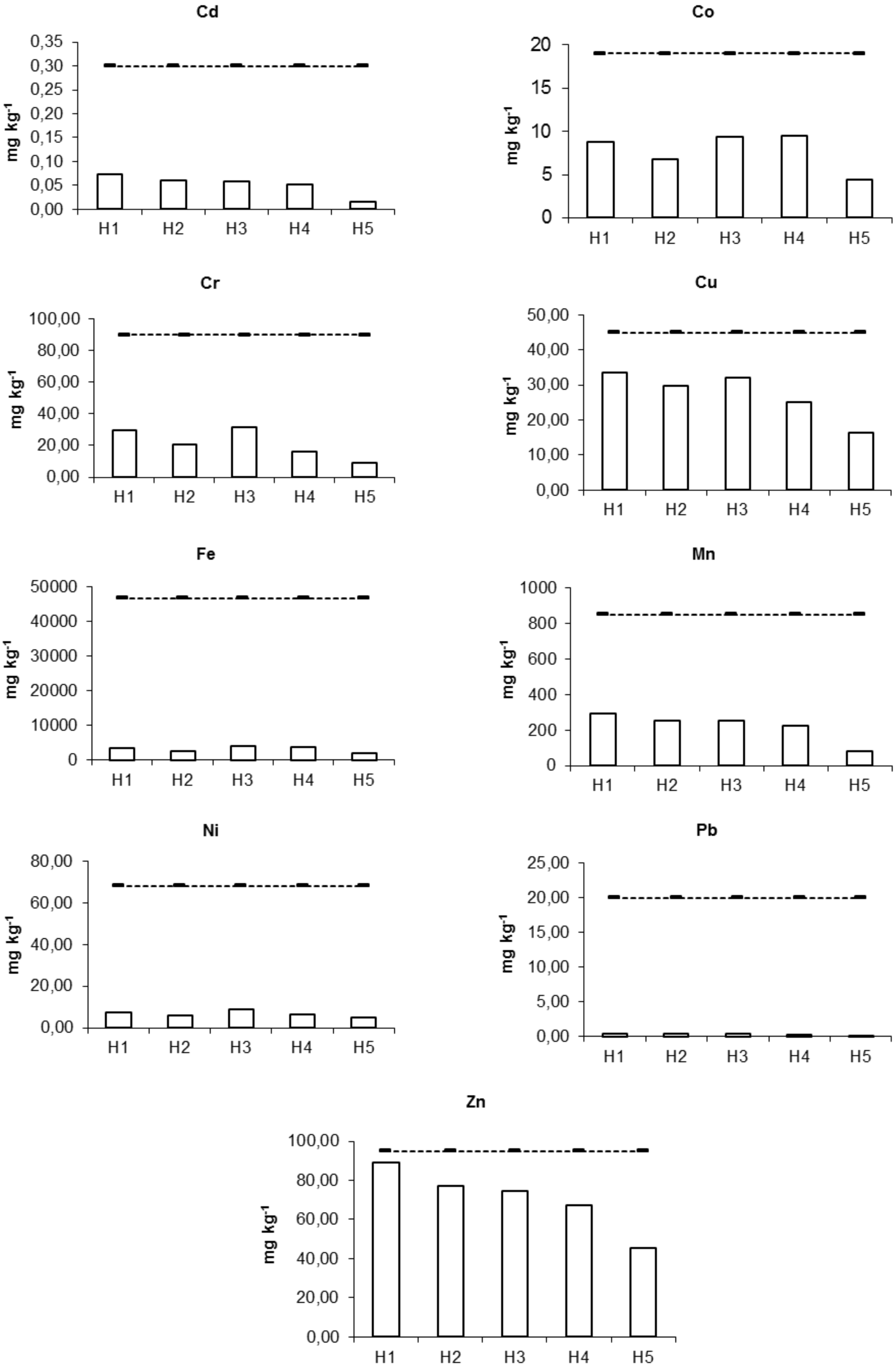

Figure 2. Comparison of total metal concentrations with average shale
(Dotted line shows the average shale value)

Table 2. Heavy metal concentration (mg kg^{-1}) at different sites of the reservoir during different seasons

Season	Site	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
rainy	H1	0.073 ± 0.004	6.24 ± 0.240	28.61 ± 0.292	40.18 ± 0.067	2849 ± 21.31	340 ± 12.18	8.86 ± 0.086	0.328 ±0.006	90.75 ± 1.79
	H2	0.062 ± 0.005	5.83 ± 0.135	18.12 ± 0.094	38.09 ± 0.051	2629 ± 7.78	251 ± 8.68	7.34 ± 0.076	0.309 ± 0.006	80.82 ± 1.84
	H3	0.059 ± 0.006	7.51 ± 0.109	31.64 ± 0.127	33.5 ± 0.121	3234 ± 18.20	114 ± 8.62	9.91 ± 0.118	0.297 ± 0.003	87.33 ± 1.82
	H4	0.049 ± 0.006	8.57 ± 0.173	16.0 ± 0.101	23.63 ± 0.093	3002 ± 8.23	148 ± 7.76	6.45 ± 0.059	0.212 ± 0.004	67.29 ± 1.95
	H5	0.013 ± 0.004	3.57 ± 0.079	7.69 ± 0.076	15.22 ± 0.054	1776 ± 16.16	77.18 ± 1.92	4.55 ± 0.085	0.104 ± 0.002	49.55 ± 1.66
winter	H1	0.059 ± 0.005	8.39 ± 0.061	24.94 ± 0.229	32.18 ± 0.044	3248 ± 13.41	262 ± 6.61	7.22 ± 0.064	0.455 ± 0.004	94.57 ± 0.636
	H2	0.051 ± 0.005	7.34 ± 0.091	14.19 ± 0.068	27.15 ± 0.036	2321 ± 11.78	246 ± 6.31	5.47 ± 0.075	0.378 ± 0.003	77.16 ± 1.05
	H3	0.048 ± 0.006	8.91 ± 0.08	28.73 ± 0.212	27.42 ± 0.073	3884 ± 23.01	420 ± 12.78	7.13 ± 0.088	0.315 ± 0.004	65.48 ± 1.79
	H4	0.036 ± 0.004	7.65 ± 0.074	13.5 ± 0.157	30.22 ± 0.063	3626 ± 16.81	328 ± 13.59	6.17 ± 0.096	0.275 ± 0.003	70.89 ± 1.17
	H5	0.01 ± 0.002	4.28 ± 0.114	8.12 ± 0.049	13.25 ± 0.065	2070 ± 17.20	79.7 2 ± 1.02	4.77 ± 0.089	0.118 ± 0.005	44.21 ± 1.27
summer	H1	0.084 ± 0.004	11.74 ± 0.197	35.42 ± 0.216	28.24 ± 0.086	4091 ± 12.59	276 ± 4.30	6.1 ± 0.061	0.392 ± 0.005	82.24 ± 0.947
	H2	0.069 ± 0.006	7.01 ± 0.124	28.74 ± 0.094	24.3 ± 0.111	3001 ± 9.93	264 ± 6.14	5.57 ± 0.062	0.364 ± 0.003	74.15 ± 0.911
	H3	0.066 ± 0.007	11.57 ± 0.109	34.13 ± 0.091	35.27 ± 0.079	4591 ± 23.26	228 ± 3.81	9.4 ± 0.180	0.344 ± 0.003	70.96 ± 1.41
	H4	0.067 ± 0.004	12.31 ± 0.076	18.26 ± 0.069	21.28 ± 0.092	4376 ± 28.69	202 ± 4.39	6.35 ± 0.133	0.297 ± 0.003	62.82 ± 1.13
	H5	0.024 ± 0.003	5.5 ± 0.087	11.29 ± 0.087	20.89 ± 0.084	2168 ± 21.84	89.86 ± 1.21	5.16 ± 0.157	0.125 ± 0.003	42.11 ± 1.39

Data represent mean ± SD of 15 observations (5 samples replicated thrice)

Table 4. Correlation coefficient matrix of characteristics of sediments and heavy metal concentration in Halali reservoir

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH	OC	sand	silt	clay
Cd	1	0.686***	0.810***	0.678***	0.646***	0.553***	0.570***	0.829***	0.780***	0.041	0.090	-0.093	0.099	0.062
Co		1	0.617***	0.283*	0.930***	0.395***	0.373***	0.595***	0.348*	-0.169	-0.059	-0.282*	0.255*	0.264*
Cr			1	0.638***	0.688***	0.514***	0.712***	0.721***	0.674***	-0.026	0.027	-0.463***	0.415***	0.440***
Cu				1	0.394***	0.588***	0.813***	0.673***	0.826***	-0.312**	0.453***	-0.185	0.145	0.210
Fe					1	0.518***	0.511***	0.569***	0.365***	-0.347**	0.119	-0.411***	0.359**	0.406***
Mn						1	0.298**	0.688***	0.553***	-0.191	0.309**	-0.082	0.054	0.109
Ni							1	0.464***	0.652***	-0.498***	0.508***	-0.550***	0.462***	0.571***
Pb								1	0.859***	0.078	-0.019	-0.033	0.030	0.030
Zn									1	0.025	0.260*	-0.027	0.020	0.032
pH										1	-0.536***	0.341**	-0.237**	-0.435***
OC											1	-0.218	0.125	0.323**
sand												1	-0.950***	-0.860***
silt													1	0.658***
clay														1

*= P< 0.05; **= P< 0.01; ***= P< 0.001

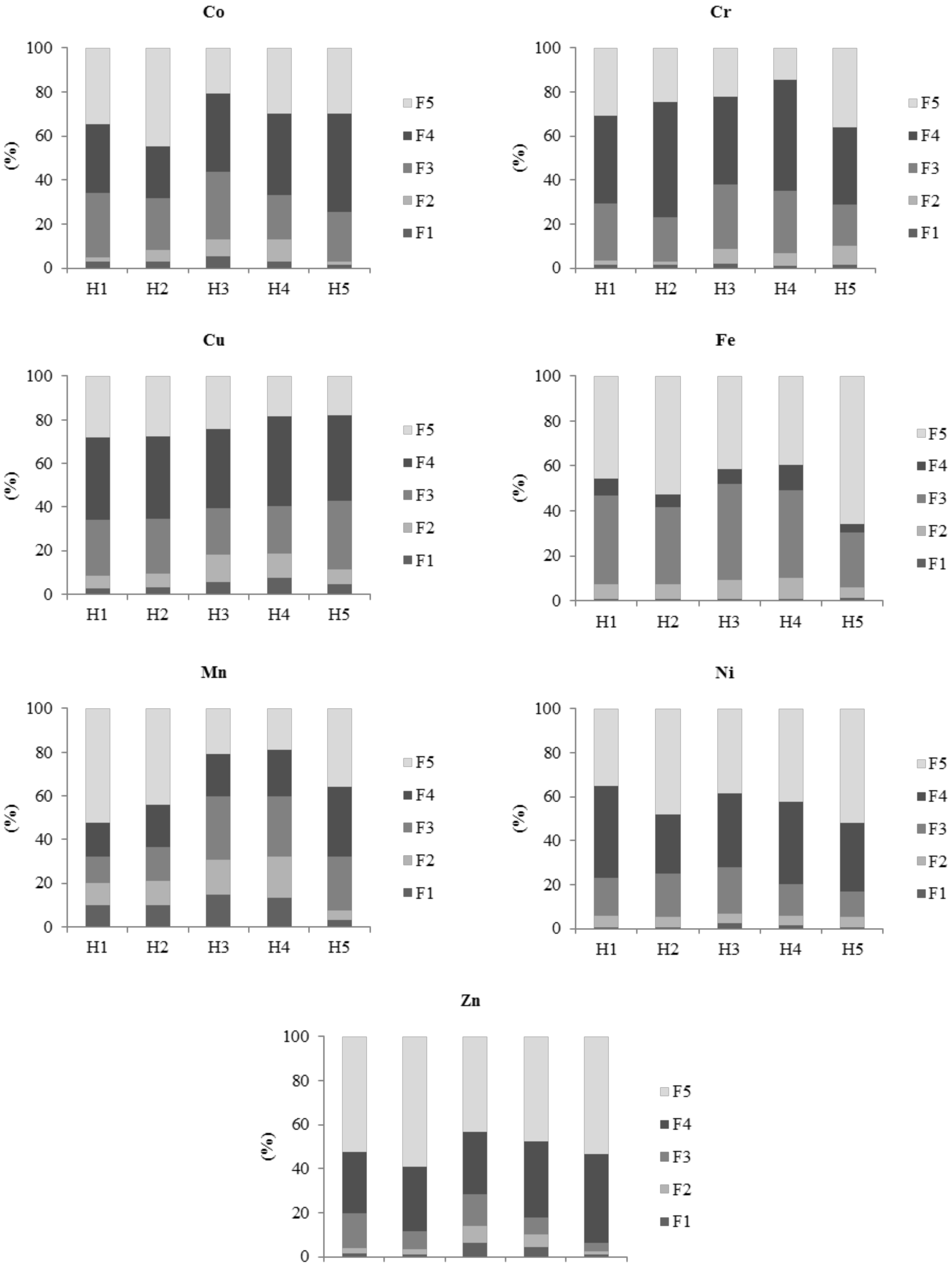

Figure 3. Fractionation of heavy metals in sediments of Halali reservoir

3.2.4. Organic matter fraction

A significant level of metals was found in this fraction with a mean range of 23.64-45.62 % for Co, 35.46-52.81 % for Cr, 36.42-41.75 % for Cu, 4.06-11.65 % for Fe, 15.26-31.92 % for Mn, 26.98-41.66 % for Ni and 27.72-40.20 % for Zn at all sites of the reservoir. The maximum amount of this fraction was found for Cr at site H2. Beside this, all sites contained the highest amount of Cr and Cu in this form probably due to the high affinity of these metals with humic substances, which were a fraction of natural organic matter as was reported by

Pempkowiase et al., (1999) and Forstner (1989a,b). This finding was at variance with that of Olivares-Rieumont et al., (2005) who had reported higher concentration of Cr in residual fraction.

3.2.5. Residual fraction

This fraction is chemically stable and biologically inactive. Most of the metals were the maximum in this fraction at all the sites (Co 21.27-44.95 %, Cr 14.78-35.21 %, Cu 18.14-28.95 %, Fe 39.19-65.73 %, Mn 19.25-52.5 %, Ni 35.35-51.55 % and Zn 43.9-59.19 %). Tessier et al., (1980), Jardo & Nickless (1989), Pardo et al., (1990) and Jain (2004) also reported the highest amount of Zn in residual fraction, while Sekhar et al., (2003) reported higher level of Ni in residual fraction. This form is not soluble under experimental conditions and may therefore be considered as tightly bound and a guide to the degree of contamination of the fluvial system (Singh et al., 2005). Higher percentage of the metal in this fraction is indicative of smaller zone of the pollution.

First two forms of the metals are more mobile and available to aquatic life, while organic, Fe-Mn and residual forms are not so mobile and contained the maximum amount of metals.

The results of the fractionation study showed that the sediments bonded heavy metals in different fractions with different strengths. The strength value can, therefore, give a clear indication of sediment reactivity, which in turns helps to assess the risk connected with the presence of metals in an aquatic environment (Jain, 2004). This criterion is called Risk Assessment Code (RAC; Perin et al., 1985). According to this code, if exchangeable and carbonate fractions have < 1 % of the total metal concentration then it can be considered safe for environment, if it is between 1-10 % it will be at low risk, between 11-30 % at medium risk, 31-50 % at high risk and if it is greater than 50% of the total metal, it will be considered as highly dangerous and can easily enter in to the food chain. According to this code all the sites under study had low risk for Co, Cr and Fe. All the sites had more than 1% of Ni only in carbonate fraction and were at low risk, while Zn was also more than 1% in carbonate fraction along with exchangeable fraction and was at low risk at all the sites. Station H3 and H4 were at medium risk for Mn with high amount in exchangeable and carbonate fractions. In most of the cases the metals were higher at those sites, which contained the highest amount of silt and clay. This might be due to the tendency of silt and clay to act as an adsorbent.

Quantitative measurement of the extent of metal pollution in Halali reservoir was also calculated by using the freshwater sediment quality guidelines, which provided the information in response to adverse effects of metals on the biological components of the reservoir. Table 3 presents a comparative study of the heavy metal concentration in the sediment of Halali reservoir with concentration of lowest effect level (LEL; Persaud et al., 1993) and probable effect level (PEL; Smith et al., 1996). In the LEL, sediments are considered to be clean to marginally polluted. Below this concentration no effects can be seen on sediment – dwelling organisms (Persaud et al., 1993), while the PEL represents the level above which adverse effects to aquatic biota are predicted to occur frequently (Smith et al., 1996). By using this approach in this study, it was established that all the metals were below the PEL threshold value. However, in majority of the sites, Cu and Cr values were higher than LEL values of the concerned metals. Hence, there is a strong probability of the sediment toxicity for the freshwater ecosystem of Halali reservoir from these two metals.

Table 3.Comparision of heavy metal concentration (mg kg^{-1}) in sediment of Halali reservoir with LEL and PEL in sediment of freshwater ecosystem.

Heavy metal	Halali reservoir sediment	Lowest effect level	Probable effect level
Cd	0.05	0.6	3.53
Co	7.06	-	-
Cr	21.29	26	90
Cu	27.39	16	197
Fe	3124	-	-
Mn	222	-	-
Ni	6.69	16	36
Pb	0.287	31	91.3
Zn	70.69	120	315

3.3. Correlation between heavy metals and physico-chemical parameters

In the present study, statistical analysis was carried out to determine the correlation among the heavy metals and the physico-chemical properties of Halali reservoir sediment. Pearson’s correlation coefficients among the physico-chemical parameters of sediment and heavy metals in sediment are presented in table 4. A positive relationship among the metals was clearly observed as has been reported by Singh et al., (2005). pH had no relationship with Cd, Co, Cr, Mn, Pb and Zn and a negative relationship with Cu, Fe and Ni, while OC showed a positive relationship with Cu (r = 0.453), Mn (r = 0.309), Ni (r = 0.508) and Zn (r = 0.26). Sand had negative relationship with all the metals, silt and clay (Table 4), while it showed a positive relationship with pH (r = 0.341). Silt and clay, both showed negative relationship with pH (r = -0.237 and -0.435, respectively), but they were positively related with Co (r = 0.255 & 0.264 for silt and clay) and Cr, Fe and Ni with r values 0.415 and 0.440, 0.359 and 0.406, and 0.462 and 0.571, respectively for silt and clay (Table 4).

Factor analysis was also applied to obtain more reliable information about the relationships amongst the variables (Bartolomeo et al., 2004; Glasby et al., 2004; Ghrefat & Yusuf, 2006). Four factors were obtained in the sediment of Halali reservoir (Table 5). Four significant components, whose eigen values were more than one were considered for cumulative variance (Table5). The communalities for the variable are also shown in Table 5. The communality for a given variable can be interpreted as the proportion of variation in that variable explained by the common factors. For example, 93.3% variation in Co was explained by the four factors. The minimum communality of 60.1% was obtained for Mn and the maximum communality of 97.6% was obtained for sand. Factor one explained 33% of the total variance and was characterized by high level of metals and negative loading of sand (Fig. 4a). Factor two explained 23% of the total variance. It was characterized by the high level of silt and clay and a high negative loading of pH and sand (Fig. 4b). Factor three comprised the data for Co, Fe and Ni and negative values of pH and organic carbon (Fig. 4c). Factor four clearly showed high loading of organic carbon with a high negative value of pH (Fig. 4d).

Generally, the results of correlation analysis and factor analysis corroborated with each other. The results showed a clustering between metals and sediment components like OC and clay, whereas there was a lack of clustering of metals with pH and sand.

4. CONCLUSIONS

The study showed that the sediments of Halali reservoir were alkaline in nature. The total metal concentration in sediments varied according to sites due to different sources of pollution as a result of varying anthropogenic activities and characteristics of the sediments. Variations in heavy metal concentrations with seasons were also reported. Overall, the concentrations of metals were found to be lower than the average shale value.

Multivariate analysis including the correlation matrix and factor analysis applied in the study provides an important tool for better understanding of the complex dynamics of pollutant. The correlation analysis showed a positive relationship among the metals and a negative correlation of sand with metals. pH showed a negative correlation with OC, silt and clay. The factor analysis also confirms these results.

The use of sequential extraction scheme and the risk assessment code in the study also provide valuable information about the availability and mobility of these metals. The data of chemical separation showed that Ni and Zn were at low risk at all the sites, while Cu and Mn were at medium risk at most of the sites of the reservoir. By approaching the freshwater sediment quality guidelines in the study, it has also been established that Cu and Cr may be a cause of sediment toxicity and can adversely affect the aquatic biota of Halali reservoir.

Table 5. Factor analysis of Halali reservoir sediment loading with chemical parameters

Variable	Communality	Factor	Eigenvalue	Total variance (%)	Cumulative (%)
Cd	0.883	1	4.58	32.74	32.74
Co	0.933	2	3.18	22.71	55.45
Cr	0.902	3	2.43	17.39	72.84
Cu	0.911	4	2.02	14.43	87.28
Fe	0.963				
Mn	0.601				
Ni	0.890				
Pb	0.904				
Zn	0.934				
pH	0.850				
OC	0.803				
Sand	0.976				
Silt	0.858				
clay	0.811				

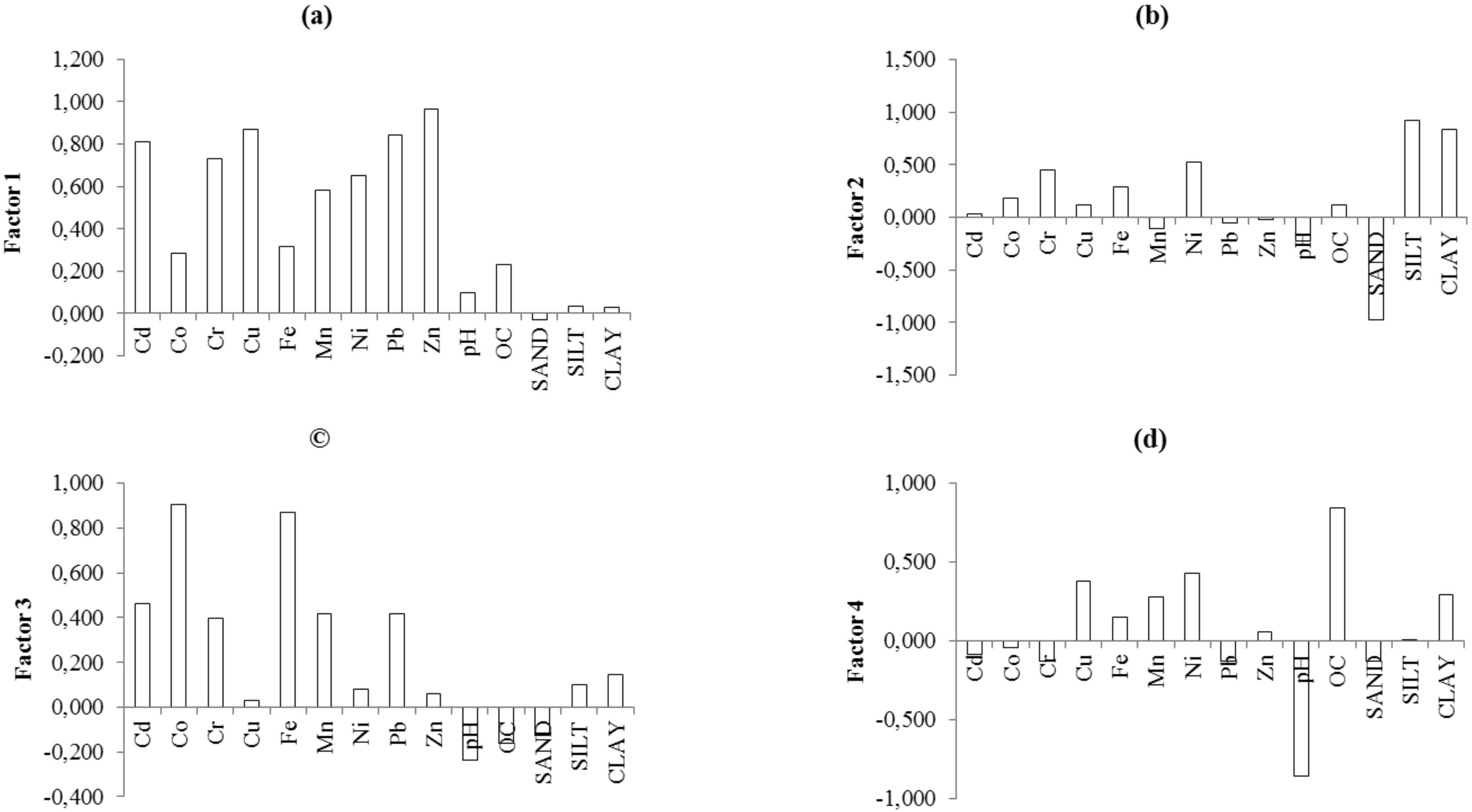

Figure 4. Results of Factor 1 (a), Factor 2 (b), Factor 3 (c) and Factor 4 (d)

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