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Assessment of heavy metal contamination of Amlakhadi: A tributary of Narmada River, Gujarat, India

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Abstract

Aquatic ecosystem throughout the globe is polluted by heavy metals arising from the anthropogenic sources. The study was aimed to investigate the degree of heavy metal pollution in surface sediments and wastewaters from Amlakhadi, India. Designated sampling stations were determined for the collection of wastewater samples and surface sediment samples from khadi and were analyzed for heavy metals using atomic absorption spectroscopy and X-ray fluorescence. The status of pollution in wastewaters and surface sediments of Amlakhadi was assessed using Concentration factor and Geo-accumulation Index. The data analysis indicates variation in heavy metal concentration within sampling stations attributed to the addition of sewage, municipal waste, and industrial effluent from various sources. The distributions of heavy metal in wastewaters were in the following sequence Fe> Zn> Mn> Cu> V> Ni> Co. While the distribution of heavy metals in surface sediments followed the sequence Fe> Si> Al> Ti> K> S> Mn> Co> Zn. The Contamination Factor (CF) showed the highest concentration level of Cu. The mean contamination factor (CF) for metals in the study area followed the order Al> Sr> Ti> Cr> Fe> Mn> V> Zn> Cu. The Geo-accumulation Index (Igeo) value for Cu and Zn was above 4 at most of the sampling stations which indicates high level of Pollution. The Geo-accumulation Index(Igeo) value for metals in the study area followed the order Al> Sr> Ti> Cr> Fe> Mn> V> Cu> Zn. The index of geo-accumulation of the sediment reveals overall pollution in the Amlakhadi area.

Keywords: Tributary, contamination factor, geo-accumulation index, heavy metals.

Introduction

Various kinds of contaminations have been affecting aquatic ecosystems around the world in the recent few years[1]. Contamination of Surface waters due to heavy metals is one of the major concern worldwide[2]. The literature on contamination of aquatic ecosystem by heavy metals around the different parts of the world is well documented[3-8]. From various contaminants heavy metals are of great environmental concern as they are widespread persistent pollutants, non-degradable, bioaccumulate, and are potential toxicant to living organisms[9]. Naturally and through manmade sources the heavy metals are distributed in various compartments of aquatic ecosystems, such as sediment, water, and biota[10]. The contamination of surface water bodies with higher amount of inorganic ions, heavy metals, and pesticides are caused by various anthropogenic sources like runoff from agricultural fields, industrial effluents, and sewage waters[11–15]. The contamination of soil and sediments by heavy metals like cadmium, cobalt, chromium, copper, molybdenum, nickel, lead, and zinc are most frequently observed[16]. The heavy metals tend to accumulate in sediments which come from various water bodies like rivers, lakes, and bays[17,18]. Pollution in the water column is well indicated by the quality of Sediments[11]. However, the assessment of sediments quality is considered as key factor in determining the source of metals in aquatic ecosystems due to their persistency[19,20]. The determination of heavy metal concentration in an aquatic ecosystem is done by measuring metal concentration in water and in sediments[21]. Among various statistical indices the geo-accumulation index (Igeo) and contamination Factor (CF) was used to determine the source and extent of heavy metal pollution [22]. These pollution index methods are widely used to study river and marine sediments[23].

The sediments along the course of Khadi show a high level of contamination due to the longer period of accumulation. The objectives of the study are as follows: i. to determine the physicochemical characteristics of wastewater and sediments of Amlakhadi, ii. to determine the concentration of heavy metal in wastewaters and sediments of Amlakhadi; iii. to determine the degree of contamination by the means of Contamination factor (CF), and geo-accumulation index (Igeo).

Materials and methods

Study area: The Narmada River (1,312 km) is one of the largest west flowing river and in terms of water discharge and drainage area it stands seventh in India[23]. The river basin extends over an area of 98,796 km^2 with a vast area in the state of Madhya Pradesh (81%), Gujarat (12%), and a smaller area in the state of Maharashtra (4%), and Chhattisgarh (2%)[25]. Narmada River has 41 tributaries (22 on left and 19 on right). Out of the total 41 tributaries, Burhner, Ban, Hiran-Tawa, Chota-Tawa, Kundi River, and Orsang are the major tributaries of Narmada[26]. Amlakhadi, a tributary of Narmada River which was once a freshwater source for villages has today become an effluent channel. Amlakhadi is majorly polluted by industrial effluents, untreated domestic sewage, and municipal solid waste as it flows through industrial, urbanized areas and rural areas of Ankleshwar. BEAIL (Bharuch Enviro Aqua Infrastructure Ltd.) collects wastewater from industrial estates like Ankleshwar GIDC, Panoli GIDC, and Jhagadia GIDC which are treated and further discharged into the Amlakhadi. However, the discharge of dark brown to black colored treated water can be observed in Amlakhadi, questioning the effectiveness of wastewater treatment processes.

The study was carried out at Amlakhadi, a tributary of River Narmada, located in Bharuch district of Gujarat, India. It is one of the most polluted tributaries in Gujarat flowing from 21°39' N to 21°31'N latitude and 73°02'E to 72°48'E longitude in the northwest direction of Ankleshwar city. Amlakhadi originates from southeast of Bhadi village, travels a distance of 50km, and then merges into Narmada river 6.8km northwest to Mothiya village near Aliyabet, Hansot. The water in khadi majorly comprises of discharged industrial effluents, domestic sewage, and surface runoffs from agricultural fields and urban areas. The khadi flow's perennial through the basin area but at some of the sampling sites the flow reduces to a minimum due to excessive growth of Hydrophytes. Excessive growth of Cattail (*Typha angustifolia*) and other hydrophytes were observed at Bakrol, Kapodara, Ansar market scrap yard and Mothiya sampling site resulting in waterlogging. The wastewater flowing from Bhadi, Kharod till Kapodara is used for agricultural practices, further gets contaminated as it reaches the Ankleshwar industrial zone. The industrial effluents are discharged into the khadi before Piraman village and at discharge point near Narmada River. The contaminated water of khadi is used in agriculture practices by most of the villages situated near Amlakhadi.

Sample collection and preservation: The sampling areawas divided into three regions. The upper region starts from Bhadi till Kapodara village, the middle region from Piraman village till Kadakiya College, and the lower region from Sajod village till discharge point in Narmada River. A total of twenty sampling stations were selected along the Amlakhadi with an interval of 1.5km downstream to the Narmada River (Figure-1). Each station was identified and marked using portable GPS (Garmin etrex VISTA HCx).

Sampling was carried out during March 2018. Ten wastewater samples and ten surface sediment samples from designated sampling stations were collected along the stretch of the Amlakhadi tributary. Odd-numbered sampling stations were designated for the collection of wastewater samples, while an even-numbered sampling stations were designated for the collection of surface sediment samples. Acid-washed polypropylene containers (1Litre) were used for the collection and storage of wastewater samples. The wastewater samples (1Litre) were preserved in-situ using concentrated nitric acid (HNO_3) by lowering the pH <2. The preserved wastewater samples were stored in an icebox and were transported to the laboratory within 24 hours. The samples were stored in the freezer at 4°C until further analysis.

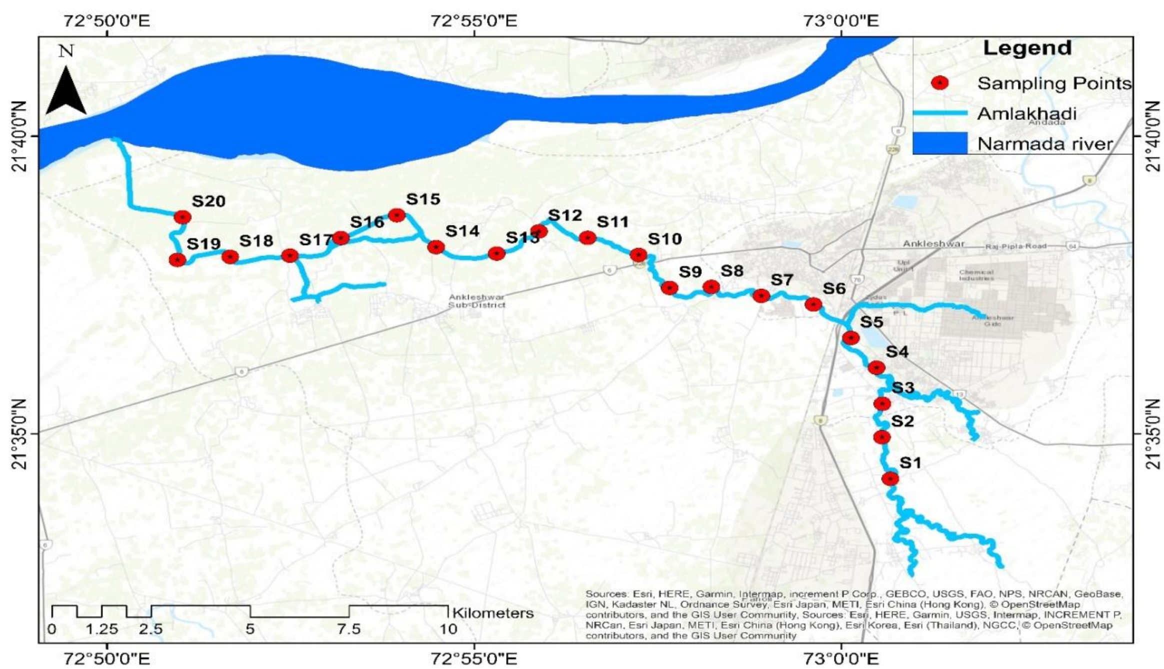


Figure-1: Study area map of Amlakhadi tributary along with sampling stations**.**

Surface sediments were collected from designated sampling stations until the depth of 10cm using portable Polycarbonate tube sampler. Polycarbonate tubes (10cm) were used for the collection and storage of surface sediment samples. The collected sediment samples were stored in-situ in an icebox and transported to the laboratory within 24 hours. The sediment samples were preserved in a freezer at 4°C to avoid microbial contamination. The sediment samples were removed from the polycarbonate tubes, air-dried at room temperature for 14 days, then oven-dried at 105°C for 24hours, ground using mortar and pestle; homogenized using 2mm sieve to remove gravel and debris, labeled and sealed in clean polythene zip lock bags for further analysis.

Determination of heavy metals from wastewaters and surface sediments: The determination of heavy metals from wastewaters was carried out using the standard methods[27]. For metal analysis, 100ml of acid preserved samples were taken in an acid-washed beaker, to that 5mL of concentrated HNO_3 was added and were covered with a watch glass. The mixture was digested in hotplate at 90°C till volume was reduced to 10mL. The samples were again evaporated by adding 10mL concentrated HNO_3 till volume was reduced to 1mL. The final volume was made to 25mL using de-ionized water[28]. For heavy-metal concentration, the digested samples were analyze dusing Atomic Absorption Spectrometer (AAS Elico SL 194, India).

For metal analysis of surface sediments, the column apparatus was pre-cleaned using absorbent cotton and alcohol later air-dried for sample compaction. The sieved sediment samples were pre-treated by pressing and were analyzed using X-ray fluorescence (XRF) spectrometer (Shimadzu EDX 800HS, Europe). Sediment pH and electrical conductivity were analyzed in-situ using pH meter (AQUASOL AM-PH-01, India) and electrical conductivity meter (AQUASOL AM-COND-01, India), respectively.

Geo-accumulation index (Igeo): The Geo-accumulation index was used since the 1960s[23]. This index is used to evaluatethe level of contamination by anthropogenic activity. The equation is as follows:

$$Igeo = Log_2 \frac{(C_n)}{1.5B_n},$$

Where C_n is the examined concentration of heavy metal in sediment samples, B_n is the concentration of heavy metals in the reference sediment sample. While1.5 is a background matrix correction factor introduced to minimize the outcome of variation in background values, which might be due to lithospheric effects in sediments. The factor for Geo-accumulation index involves a log function, and a background multiplication of 1.5, It is not compared to other indices of metal enrichment[29]. The geo-accumulation index is shown in

Table-1.

Table-1: Grades of Geo-accumulation index.

Igeo Grade Value	Pollution Category for geo-accumulation index (*Igeo*)
Igeo<0	Unpolluted
$0 \le Igeo \le 1$	Unpolluted to moderately polluted
$1 \le Igeo \le 2$	Moderately polluted
$2 \le Igeo \le 3$	Moderately to strongly polluted
$3 \le Igeo \le 4$	Strongly polluted
$4 \le Igeo \le 5$	Strongly to Highly polluted
Igeo>5	Extremely polluted

Contamination factor (CF): To determine the status of heavy metal contamination in the sediments of Amlakhadi, The formula was used to calculate the Contamination Factor (CF), as suggested by Hakanson[30].

$$CF = \frac{M_c}{B_c},$$

Where: M_c is the measured concentration of the heavy metals, and B_c is background or pre-industrial concentration of the same heavy metal. Based on the contamination the contamination factor, four contamination categories were documented as shown in Table-2[30].

Table-2: Categories of contamination factor (CF).

CF	CF < 1	1 ≤ CF ≤ 3	3 ≤ CF≤ 6	CF > 6
Degree of contamination	Low	Moderate	Considerable	Very high

Statistical analysis: The statistical analysis was performed using statistical software for Windows software Statistical Product and Service Solutions (SPSS Inc., Chicago, USA). To identify the relationships between physicochemical parameters, heavy metal concentration in wastewater and sediments, Pearson's correlation analysis matrix was conducted. If the value of $p<0.05$ it was considered significant. To describe the relationship between heavy metals in wastewater and sediments a linear regression model was used.

Results and discussion

Variation of nutrients and heavy metals in wastewater: Physicochemical assessment of wastewater samples was carried out using the standard Handbook of Methods for Water and Wastewater Analysis. The results of the physiochemical assessment of wastewater are shown in

Table-3 shows that the pH was in a range of 7.8 to 8.9 which follows the standards given by CPCB. A comparative study on physicochemical parameters of the Narmada river reported by Kumari et al.[31], Gupta et al.[32], and Sharma et al.[33] found that the pH was in arrange from 7.4–9.7 at different sites which is almost similar to the present study. Total dissolved solid was in a range of 722–1570mg/L, which was beyond the permissible limit of 500mg/L. Sampling station No. eight has the highest TDS value of 1570mg/L. Kumari et al.[31] reported similar results of TDS in a range of 136–360mg/L for the Narmada river. The level of dissolved oxygen in the aquatic systems tends to deplete with an increase in levels of dissolved and suspended solids. The values of dissolved oxygen were in a range from 1.11 to 2.51 mg/L. The values for dissolved oxygen reported by Sharma et al.[33] were in a range of 6.5–15mg/L, which was under the permissible limit as per World Health Organization (WHO). Gupta et al.[32] reported that the DO was in the range of 2.4 to 7.8mg/L. The Nitrate-Nitrogen levels were in a range of 0.69 mg/L to 10.42mg/L. Sharma et al.[33] reported the value for Nitrate in the range from 12.6 mg/L to 21.2 mg/L at two sites of Narmada River. Gupta et al.[32] reported the values for nitrate-nitrogen in the range from 0.03mg/L to 3.14mg/L for all the years. The sulfate levels were in the range of 22.07mg/L to 98.64mg/L.

The Table-5 shows the concentrations of heavy metals in the wastewater of Amlakhadi. The concentration of Fe was highest, while the concentration of Co was lowest among the heavy metals studied in wastewater. The concentration of heavy metal

Table-3.

in wastewater samples were compared with the concentration of metal in Narmada, Tapti, and water quality standards. The concentration of metals in wastewater were close to the maximum permissible concentration for the discharge of effluent in inland waters (CPCB[34]; BIS[35]), except for Fe, Mn, and Zn concentrations. The distribution of various heavy metal concentration along the stretch of Amlakhadi tributary is shown in Figure-2. Sharma and Subramanian[36] reported that the concentration of heavy metal in Narmada and Tapti river were below the permissible limit as per BIS[35]; CPCB[34]. Islam et al.[37]; Mohiuddin et al.[38] reported a lower concentration of metals in the river during monsoon resulting due to the effect of dilution of water. The mean concentration of heavy metal in wastewater was in the following sequence of Fe>Zn>Mn>Cu>V>Ni>Co. Islam et al.[37] reported a similar sequence of Cr>Cu>As>Ni>Pb>Cd at korotoa river in Bogra district of Bangladesh. A similar sequence of Zn>Cr>Cu>Pb>Ni>Cd in surface water of Luan river in Northern China was reported by Wang et al.[39].

We conclude that the heavy metal concentration in wastewater show possible variations due to discharge of untreated industrial effluents, surface runoff from the urban and suburban areas of Ankleshwar. Figure-2(a) shows no significant variation in concentration of Fe at various sampling stations along the Amlakhadi tributary. The concentration of Iron was highest at sampling station No. 19. Figure-2(b) shows a possible variation in the concentration of Manganese along with sampling stations of Amlakhadi. The concentration of Mn was highest at sampling station No. 1 and lowest at sampling station No. 9.

Table-3: Chemical composition of Amlakhadi wastewaters.

Sampling stations	pH	E.C. µS cm^{-1}	T. D. S. mgL^{-1}	D.O. mgL^{-1}	Total Hardness mgL^{-1}	Nitrate Nitrogen mgL^{-1}	Sulphate mgL^{-1}
SS 01	8	1000	1270	2.51	505	2.1	36.56
SS 02	9	1320	883	1.5	260	1.41	27.25
SS 03	8	1265	890	1.65	315	0.69	26.2
SS 04	8	1275	1150	1.42	500	6.36	24.66
SS 05	8	1285	811	1.92	365	1.5	98.64
SS 06	9	1285	1230	1.18	375	10.42	32.42
SS 07	8	1348	722	1.49	290	1.29	36.56
SS 08	8	1410	1570	1.56	540	13.3	29.83
SS 09	9	1388	930	1.85	375	1.01	36.56
SS 10	9	1251	1170	1.93	460	6.91	27.25
SS 11	8	1390	757	2.01	300	0.55	57.24
SS 12	9	1316	1270	1.8	375	7.52	35.01
SS 13	9	1172	790	1.91	350	1.23	26.2
SS 14	9	1195	1080	1.72	325	6.33	29.83
SS 15	9	1175	780	1.68	340	1.78	46.92
SS 16	9	1018	950	1.39	235	4.24	22.07
SS 17	9	1178	864	1.38	330	1.92	57.24
SS 18	9	1150	935	1.11	275	4.33	24.66
SS 19	9	1193	850	1.26	340	1.77	49.02

1SS20	9	1125	886	1.14	370	3.95	27.25

SS is a sampling station.

Table-4: Chemical composition of Amlakhadi sediments.

Sampling stations	pH	E.C. $\mu S\ cm^{-1}$	Organic Matter (%)	Organic Carbon (%)	Available Nitrogen mgL^{-1}	Phosphates $kgha^{-1}$
SS01	8	322	3.84	2.91	12.2	2.86
SS02	7	192	2.36	1.3	15.6	2.13
SS03	8	447	4.88	3	12.8	2.59
SS04	7	288	4.64	3.65	11.9	2.01
SS05	7	472	2.81	2.31	13.7	2.82
SS06	7	442	3.56	2.8	14	1.57
SS07	6	315	3.33	2.34	10.6	2.73
SS08	7	310	2.87	1.25	11.2	1.84
SS09	7	337	3.84	2.61	11	0.62
SS10	7	305	2.34	0.32	13.4	0.27
SS11	6	474	3.77	2.67	11.9	1.88
SS12	6	312	2.67	2.45	12.3	0.67
SS13	7	455	3.63	2.56	14.8	0.55
SS14	7	416	3.24	1.39	14.6	1.06
SS15	7	368	3.33	2.53	12.4	1.52
SS16	8	324	3.54	2.4	13.5	1.28
SS17	6	301	3.63	2.45	12.5	0.98
SS18	7	302	4.38	3.98	11.3	0.31
SS19	6	348	3.74	3.27	13.6	1.61
SS20	7	407	3.81	3.7	11.9	1.02

SS is a sampling station.

Table-5: Concentrations of heavy metals in the wastewaters of Amlakhadi compared with other study areas, and water quality standards. All values are in mg^{-1}.

Sampling Stations	Fe	Mn	Co	Zn	V	Cu	Ni
SS01	10.58	5.87	0.0050	5.73	0.0054	0.58	0.0018
SS03	10.79	0.98	0.0008	3.05	0.0073	0.43	0.0033
SS05	10.88	0.97	0.0001	3.06	0.0083	0.47	0.0090
SS07	10.99	1.00	0.0003	6.52	0.0077	0.41	0.0095
SS09	09.30	0.94	0.0004	5.72	0.0079	0.35	0.0109
SS11	10.09	1.15	0.0006	5.91	0.0083	0.40	0.0071
SS13	10.44	1.09	0.0004	3.45	0.0104	0.38	0.0089
SS15	11.38	1.26	0.0012	5.59	0.0174	0.50	0.0104
SS17	10.12	2.07	0.0012	5.74	0.0243	0.47	0.0143
SS19	16.22	2.64	0.000	5.56	0.0165	0.67	0.0104
Reference 36	1.75	0.10	Not detected	0.14	Not detected	0.14	0.068
Reference 36	1.64	0.03	Not detected	0.25	Not detected	0.19	0.054
Water quality criteria (Standards for wastewater discharged into inland surface waters)							
Reference 35	5.00	2.00	No limits	15	0.20	1.5	3.00

Reference 34	3.00	2.00	No limits	5.00	0.20	3.00	3.00

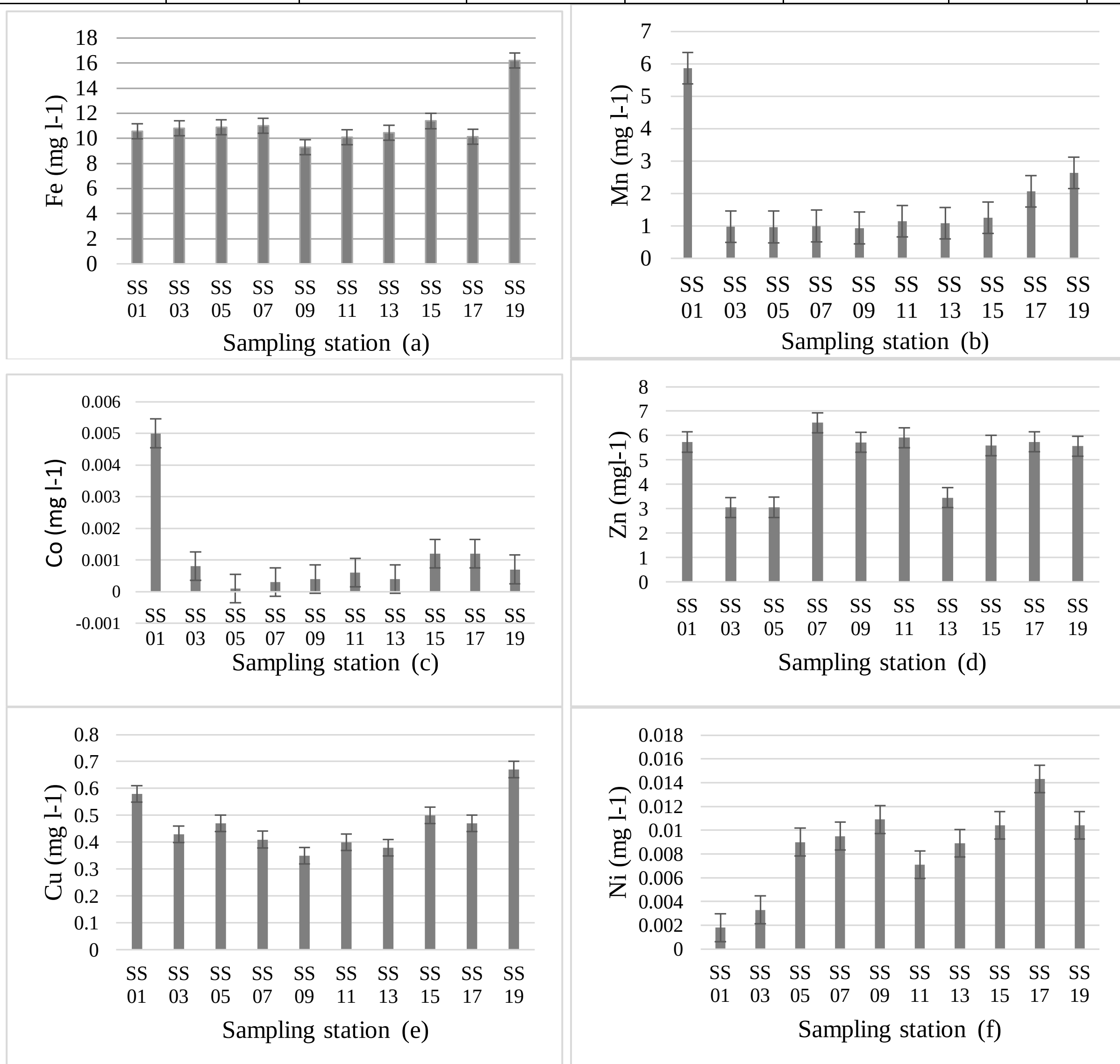


Figure-2: Spatial distribution of metals in wastewaters along the sampling stations of the Amlakhadi tributary. (a) Fe (b) Mn (c) Co (d) Zn (e) Cu (f) Ni.

Similarly, Figure-2(c) and Figure-2(f) show significant variation in concentration of Co and Ni along the Amlakhadi tributary. Wang et al.[39] concluded that the pollution of Cu and Ni in the water was majorly caused by the discharge of wastewater from mine plants and industrial waste discharged from Chengde city. Sharma and Subramanian[36] concluded that Fe, Mn, Ni, Cr, Pb, Zn, and As shows higher concentration in the upstream region, while the concentrations of dissolved metals tend to increase along the downstream sampling point due to anthropogenic activities along the downstream regions such as urbanization, industrialization, and agricultural activities.

Variation of nutrients and heavy metals in sediments: Physicochemical assessment of surface sediment samples was carried out using standard reference. The results of the physiochemical assessment of sediment are shown in Table-4. The sediments of khadi were highly saturated during the sampling period. A few areas showed a decline in flow resulting in the emergence of landmass followed by grasses on the surface. From

Table-4, the pH of the sediments was in a range of 5 to 7. Low variability due to slightly basic sediment pH along the Jarama river was reported by García-Pereira et al. [40]. The content of sediment organic carbon (SOC) ranges from 0.3% to 3.9%. No significant difference in sediment organic carbon among URS, RRS, and RARS for the same sediment layer was reported by Zhang et al.[41]. The organic matter (OM) content ranges from 2.34% to 4.88%. Zhang et al.[41] reported the organic matter content (OM), which was relatively low when compared with the research (Industrial wastewater sludge: 32 ± 5.7%) conducted by Kazi et al.[42].

Table-6 shows heavy metal concentrations in surface sediments of Amlakhadi. The heavy metal concentrations for sediments were obtained in mass % with the standard deviation. The concentration of Fe was highest, while the concentration of Cr was lowest among the heavy metal studied in sediments. The concentration of Cobalt was in a range of 0.327% to 0.431% with a standard error of ±0.017. While Copper, Iron, Aluminium, and Zinc in the sediments were found ranging from 0.05% to 1.496%, 28.73% to 42.21%, 10.71% to 13.228% and 0.121% to 0.627% with standard error ±0.018, ±0.088, ±0.218, and ±0.016, respectively. The maximum concentration of Iron was detected at sampling station No. 1 and No. 5. Whereas the maximum concentration of aluminum was detected at sampling station 3 behind Ansar market scrap yard. The concentration of aluminum was below the detectable limit in sampling stations 6, 7, 8, 9 and 10, respectively. The concentration of copper and zinc were detected highest at sampling station 10 of Mothiya village. The concentration of Fe, Mn, Zn, and Pb was detected in most of the samples, whereas the concentration of Cu, Cr, Ni, Cd, and F was detected in 60% to 70% of samples, respectively in Ganga River as reported by Mandal et al.[43].

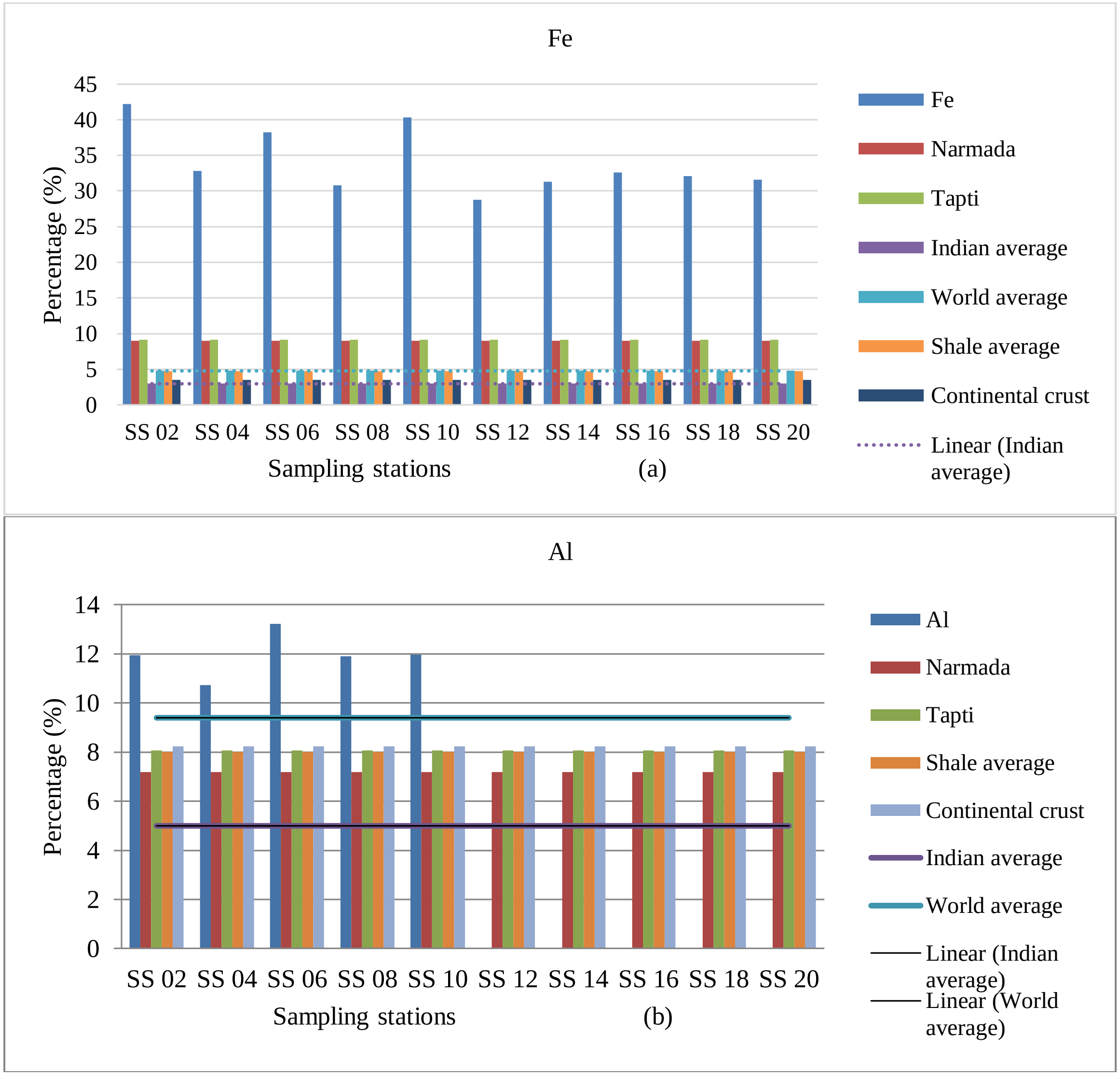
Table-6, Figure-3 (a, b, c, d, e, f) showed that the concentrations of most of the metals exceed the background values of Narmada and Tapti river, Indian average, World average, and geochemical background values (shale average and continental crust). Sharma and Subramanian[36] reported that the concentration of metals in sediment of Narmada and Tapti exceed the geochemical background values as well as it exceeds Indian and world averages. The concentration of metals in sediments were higher due to the presence of Industrial sites in the proximity of khadi, and municipal sewage discharge at various points in khadi. Figure-3(a) shows very minimal variation in concentration of Iron along with sampling stations of Amlakhadi. Figure-3(b) and Figure-3(c) showed minimal variation in the concentration of Aluminium and Cobalt until sampling station No. 5. While the concentration of Al and Co from sampling station No. 6 to 10 were below the detectable limit. The maximum variation in concentration of Zn and Cu along with the sampling station is shown in Figure-3(d) and Figure-3(f).

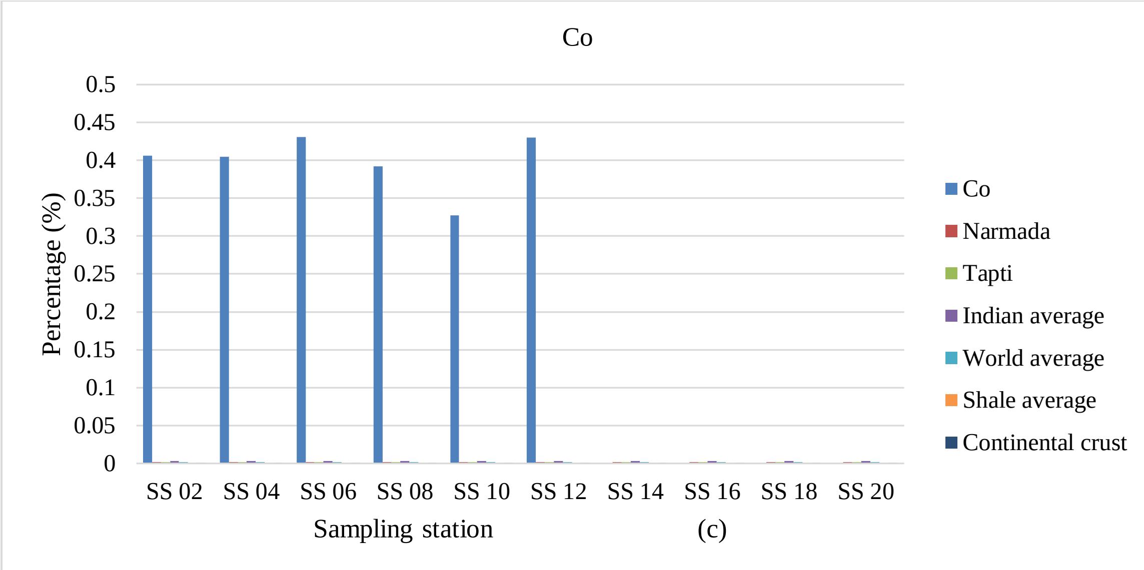
Table-6: Heavy metal concentration in sediments of Amlakhadi, other study areas, and guidelines.

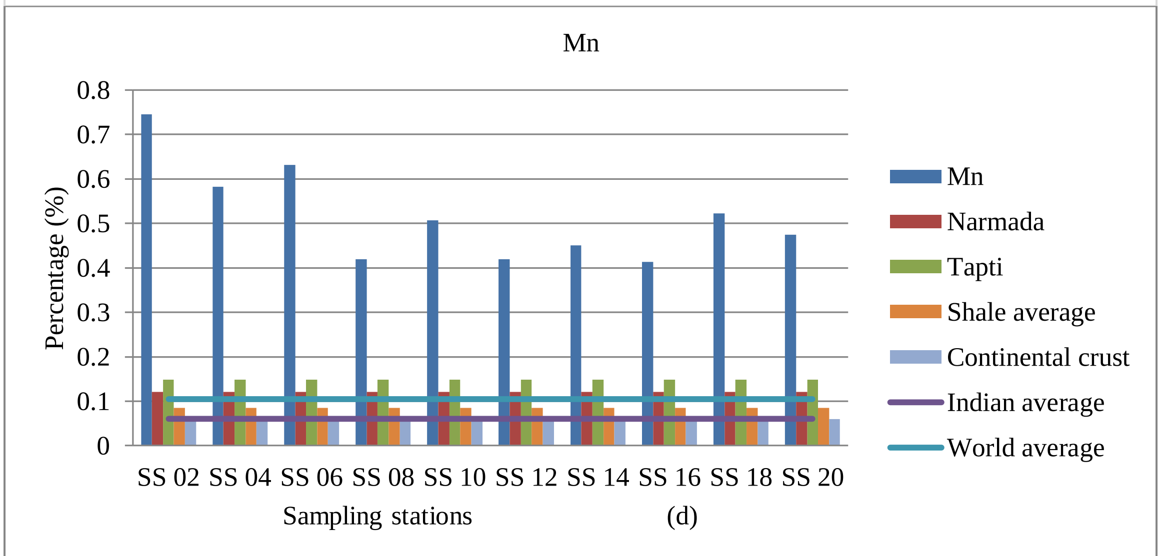
SS	Fe	Si	Ca	Al	Ti	K	Mn	Co	Zn	V	Sr	Zr	Cu	Cr
SS 02	42.21 ±0.10	22.83± 0.11	12.84 ±0.06	11.94 ±0.20	3.509 ±0.03	3.009 ±0.05	0.746 ±0.01	0.406 ±0.01	0.305 ±0.01	0.235 ±0.02	0.186 ±0.007	0.172 ±0.006	0.031 ±0.014	BDL
SS 04	32.84 ±0.089	29.13± 0.114	16.40 ±0.076	10.71 ±0.184	4.712 ±0.037	2.856 ±0.053	0.582 ±0.012	0.405 ±0.018	0.121 ±0.012	0.168 ±0.018	0.152 ±0.007	0.239 ±0.007	0.103 ±0.014	BDL
SS 06	38.22 ±0.103	24.94 ±0.113	11.94 ±0.065	13.22 ±0.207	5.687 ±0.047	2.125 ±0.048	0.632 ±0.029	0.431 ±0.028	0.163 ±0.012	0.602 ±0.027	0.133 ±0.007	0.475 ±0.008	0.05 ±0.013	BDL
SS 08	30.77 ±0.095	28.30 ±0.135	15.97 ±0.089	11.90 ±0.238	4.595 ±0.065	3.153 ±0.068	0.42 ±0.025	0.392 ±0.017	0.457 ±0.016	BDL	0.164 ±0.008	0.386 ±0.008	0.354 ±0.018	BDL
SS 10	40.31 ±0.099	26.58± 0.119	9.503 ±0.060	11.96± 0.213	4.001 ±0.033	2.824 ±0.052	0.507 ±0.011	0.327 ±0.014	0.475 ±0.016	0.388 ±0.022	0.144 ±0.007	0.235 ±0.007	0.46 ±0.018	0.116 ±0.017
SS 12	28.73 ±0.085	51.51 ±1.565	8.856 ±0.062	BDL	3.595 ±0.055	2.265 ±0.058	0.419 ±0.020	0.43 ±0.015	0.419 ±0.013	0.175 ±0.023	0.135 ±0.007	0.264 ±0.006	0.585 ±0.016	0.148 ±0.019
SS 14	31.32 ±0.085	48.27 ±1.651	9.136 ±0.064	BDL	3.392 ±0.051	2.482 ±0.057	0.45 ±0.020	BDL	0.474 ±0.014	0.201 ±0.021	0.139 ±0.006	0.196 ±0.006	0.714 ±0.017	0.159 ±0.017
SS 16	32.60 ±0.089	51.14 ±1.684	6.001 ±0.053	BDL	3.279 ±0.050	2.539 ±0.057	0.413 ±0.020	BDL	0.611 ±0.015	BDL	0.133 ±0.007	0.204 ±0.006	1.492 ±0.022	0.125 ±0.017
SS 18	32.05 ±0.088	52.53 ±1.593	6.594 ±0.054	BDL	2.94 ±0.049	2.612 ±0.056	0.522 ±0.021	BDL	0.543 ±0.015	0.119 ±0.021	0.125 ±0.006	BDL	0.906 ±0.019	BDL
SS 20	31.60 ±0.088	52.47 ±1.657	5.506 ±0.051	BDL	3.271 ±0.051	2.657 ±0.056	0.474 ±0.021	BDL	0.627 ±0.015	0.158 ±0.020	0.121 ±0.007	0.167 ±0.006	1.496 ±0.022	0.148 ±0.017
Ref. 36	8.957	56.17	4.37	7.186	1.189	1.3	0.121	0.002	0.019	0.041	0.054	0.046	0.018	0.019
Ref. 36	9.112	51.45	6.4	8.057	1.518	1.29	0.149	0.002	0.021	0.041	0.105	0.024	0.032	0.021
Ref. 45	2.998	NA	NA	5	0.345	NA	0.06	0.003	0.001	0.021	0.021	NA	0.002	0.008
Ref. 46	4.8	NA	NA	9.4	0.56	NA	0.105	0.002	0.035	0.017	0.015	NA	0.01	0.01
Ref. 47	4.72	NA	NA	8	0.46	NA	0.085	0.001	0.009	0.013	0.017	0.016	0.004	0.009
Ref. 48	3.5	NA	NA	8.23	0.3	NA	0.06	0.001	0.007	0.01	0.035	0.019	0.002	0.008

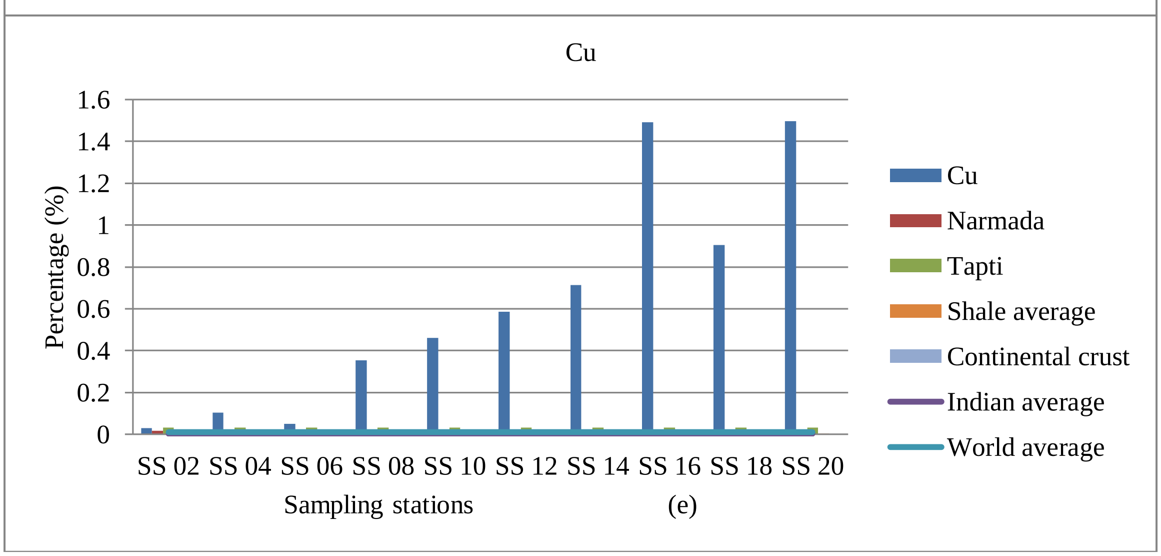
PS	34.07	38.78	10.28	11.95	3.898	2.652	0.516	0.398	0.419	0.255	0.143	0.259	0.619	0.139

SS = sampling station, NA = not available, BDL = below the detectable limit, PS=Present study = Geochemical background average.




Co
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Percentage (%)
SS 02 SS 04 SS 06 SS 08 SS 10 SS 12 SS 14 SS 16 SS 18 SS 20
Sampling station
(c)
Co
Narmada
Tapti
Indian average
World average
Shale average
Continental crust


Mn
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Percentage (%)
SS 02 SS 04 SS 06 SS 08 SS 10 SS 12 SS 14 SS 16 SS 18 SS 20
Sampling stations
(d)
Mn
Narmada
Tapti
Shale average
Continental crust
Indian average
World average


Cu
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Percentage (%)
SS 02 SS 04 SS 06 SS 08 SS 10 SS 12 SS 14 SS 16 SS 18 SS 20
Sampling stations
(e)
Cu
Narmada
Tapti
Shale average
Continental crust
Indian average
World average

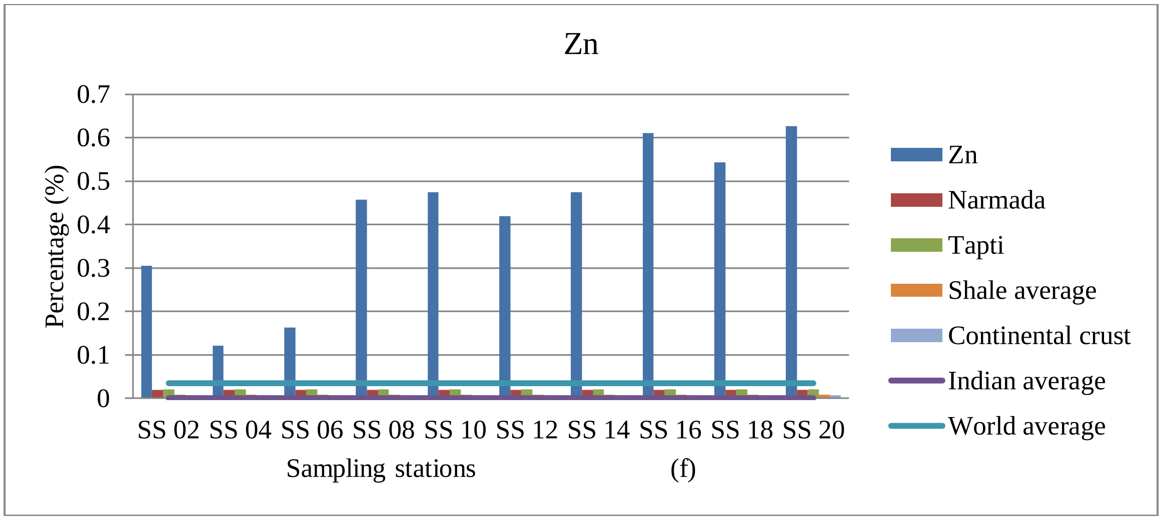


Figure-3: Spatial distribution of heavy metal concentrations in sediments along with the sampling stations of the Amlakhadi tributary. (a) Fe (b) Al (c) Co (d) Mn (e) Cu (f) Zn.

Correlation between the parameters was analyzed using the Pearson coefficient. Correlations within the parameters are shown in Table-7.

The Correlation coefficient value ranges from 1 to -1. If the value is closer to 1, it indicates a strong positive correlation, meaning: one variable is increasing simultaneously with the other. R=0.94 for Co and Mn indicates that, when the concentration of Mn increases, Co concentration also increases. The value close to -1 indicates a strong negative correlation, meaning: one variable is increasing with a decrease in the other. R=-0.57 for Co and Ni indicates that when the concentration of Co increases, Ni concentration decreases, and vice versa. The value close to 0 indicates there is no correlation, no relation exists between two variables and they are independent of each other. R=0.07 for Zn and Fe indicates that there is no relation or dependency between these two variables. Table-8 shows the values for Contamination factor (CF) of heavy metals in sediments of Amlakhadi. The Contamination factor was in a range from <1 to 6> indicating low to very high contamination during the study period. Table-8 shows the Geo-accumulation index for various heavy metals in sediments. The index of geo-accumulation was in a range from 0< to 5<.

Table-7: Heavy metal Correlation in the wastewater of the Amlakhadi.

Correlations								
Elements (mgL^{-1})	Fe	Ca	Mn	Co	Zn	V	Cu	Ni
Fe	1							
Ca	-0.468	1						
Mn	0.189	-0.145	1					
Co	-0.063	-0.108	.943**	1				
Zn	0.072	0.35	0.288	0.25	1			
V	0.298	-0.113	-0.063	-0.149	0.228	1		
Cu	.805**	-0.467	.662*	0.474	0.164	0.312	1	
Ni	0.1	0.076	-0.462	-0.573	0.279	.740*	-0.116	1

** At 0.01 level the correlation is considered significant (2-tailed). * At 0.05 level the correlation is considered significant (2-tailed).

Table-8: Geo-accumulation index and Contamination Factor values for various heavy metals in sediments along with the sampling station of the Amlakhadi tributary.

Elements		Fe	Al	Ti	Mn	Zn	V	Sr	Cu	Cr
SS02	Igeo	1.651	0.146	0.976	2.04	3.42	1.934	1.197	0.197	BDL
	CF	4.71	1.66	2.95	6.17	16.05	5.73	3.44	1.72	
SS04	Igeo	1.291	-0.01	1.401	1.681	2.086	1.451	0.906	1.931	BDL
	CF	3.67	1.49	3.96	4.81	6.37	4.1	2.81	5.72	
SS06	Igeo	1.509	0.295	1.672	1.799	2.516	3.291	0.714	0.89	BDL

	CF	4.27	1.84	4.78	5.22	8.58	14.68	2.46	2.78	
SS 08	Igeo	1.197	0.146	1.364	1.21	4.003	BDL	1.019	3.713	1.197
	CF	3.44	1.66	3.86	3.47	24.05		3.04	19.67	BDL
SS 10	Igeo	1.585	0.155	1.168	1.482	4.059	2.657	0.832	4.091	2.026
	CF	4.5	1.67	3.37	4.19	25	9.46	2.67	25.56	6.11
SS 12	Igeo	1.098	BDL	1.01	1.206	3.878	1.509	0.737	4.437	2.377
	CF	3.21		3.02	3.46	22.05	4.27	2.5	32.5	7.79
SS 14	Igeo	1.222	BDL	0.926	1.31	4.056	1.708	0.777	4.725	2.48
	CF	3.5		2.85	3.72	24.95	4.9	2.57	39.67	8.37
SS 16	Igeo	1.279	BDL	0.88	1.185	4.422		0.714	5.788	2.133
	CF	3.64		2.76	3.41	32.16	BDL	2.46	82.89	6.58
SS 18	Igeo	1.255	BDL	0.72	1.523	4.252	0.951	0.623	5.068	BDL
	CF	3.58		2.47	4.31	28.58	2.9	2.31	50.33	
SS 20	Igeo	1.235	BDL	0.874	1.386	4.459	1.36	0.579	5.792	2.377
	CF	3.53		2.75	3.92	33	3.85	2.24	83.11	7.79

Conclusion

The present study is on the distribution of heavy metals in wastewater and surface sediment of Amlakhadi suggests that the concentration of metals in wastewater and sediments is majorly due to anthropogenic activities such as discharge of sewage, dumping of municipal waste in khadi, and discharge of industrial effluents from the urban areas of Ankleshwar. The concentrations of heavy metals in wastewater were in following sequence Ca>Fe>Zn> Mn>Cu>Ni. While in surface sediments, the concentration of heavy metals was in the following sequence Fe> Si> Ca> Al> Ti> K> S> Mn> Co> Zn. The concentration level of Cu was higher compared to other heavy metals as showed by Contamination Factor (CF), while the mean CF values for the studied metals followed the sequence of Fe> Ca> Cu> Mn> Zn> V. Geo-accumulation Index (Igeo) showed that concentration of Cu and Zn was above 4 at most of the sampling stations which indicate strong level of Pollution. The geo-accumulation index values for metals in the study area was in the following sequence Al> Sr> Ti> Cr> Fe> Mn> V> Cu> Zn.

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References

1. Nazeer S., Hashmi M.Z., and Malik R.N. (2014). Heavy metals distribution, risk assessment and water quality characterization by water quality index of the River Soan, Pakistan. *Ecol Indic*, 43, 262-270. doi: 10.1016/j.ecolind.2014.03.010
2. Yang X., Duan J., Wang L., Li W., Guan J., Beecham S., Mulcahy D. (2015). Heavy metal pollution and health risk assessment in the Wei River in China. *Env Monit Assess*, 187(3), 111. doi: 10.1007/s10661-014-4202-y
3. Sakai H., Kojima Y., and Saito K. (1986). Distribution of heavy metals in water and sieved sediments in the Toyohira River. *Water Res*, 20, 559–567. doi: 10.1016/0043-1354 (86)90019-9
4. Stamatis N., Ioannidou D., Christoforidis A., Koutrakis E. (2002). Sediment pollution by heavy metals in the Strymonikos and Ierissos Gulfs, North Aegean Sea, Greece. *Environ Monit Assess*, 80(1), 33-49. doi:10.1023 /A:1020382011145
5. Akcay H., Oguz A., and Karapire C. (2003). Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Res*, 37, 813–822. doi: 10.1016/S0043-1354(02)00392-5
6. Loska K. and Wiechuła D. (2003). Application of principal component analysis for the estimation of the source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere*, 51(8), 723-733. doi:10.1016/S0045-6535(03)00187-5
7. Woitke P., Wellmitz J., Helm D., Kube P., Lepom P., Litheraty P. (2003). Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. *Chemosphere*, 51(8), 633-642. doi:10.1016/S0045-6535(03)00217-0
8. Singh K.P., Malik A., Sinha S., Singh V.K., Murthy R.C. (2005). Estimation of the source of heavy metal contamination in sediments of Gomti River (India) using principal component analysis. *Water Air Soil Pollut*, 166(1-4), 321-341. doi:10.1007/s11270-005-5268-5
9. Hua X., Dong D., Liu L., Gao M., Liang D. (2012).

Comparison of trace metal adsorption onto different solid materials and their chemical components in a natural aquatic environment. *Appl Geochemistry*, 27(5), 1005-1012. doi: 10.1016/j.apgeochem.2012.01.021

10. Moore J.W. and Ramamoorthy S. (1984). Heavy Metals in Natural Waters: Applied monitoring and impact assessment. Springer Verlag publications, pp 270.

11. Khan B., Ullah H., Khan S., Aamir M., Khan A., Khan W. (2016). Sources and Contamination of Heavy Metals in Sediments of Kabul River: The Role of Organic Matter in Metals Retention and Accumulation. *Soil Sediment Contam*, 25(8), 891-904. doi:10.1080/15320383.2016.1224226

12. European Commission. (2002). Heavy Metals in Waste. DG ENV E3, Proj ENVE3/ETU/2000/0058, pp 1-83. doi:ENV.E.3/ETU/2000/0058

13. Silva-Filho E.V., Santos I.R., Campos L.S., Schaefer CEGR., Albuquerque-Filho MR. (2004). Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. *Mar Pollut Bull*, 50(2), 185-194. doi:10.1016/j.marpolbul.2004. 10.009

14. Kumar A. and Ramanathan AL. (2015). Speciation of selected trace metals (Fe, Mn, Cu, and Zn) with depth in the sediments of Sundarban mangroves: India and Bangladesh. *J Soils Sediments*, 15(12), 2476-2486. doi: 10.1007/s11368-015-1257-5

15. Hu Q., Zhu Y-G., Zhang S., Khan S., Aijun L. (2007). Accumulation of polycyclic aromatic hydrocarbons and heavy metals in lettuce grown in the soils contaminated with long-term wastewater irrigation. *J Hazard Mater*, 152(2), 506-515. doi:10.1016/j.jhazmat.2007.07.014

16. Shikazono N., Tatewaki K., Mohiuddin K.M., Nakano T., Zakir H.M. (2012). Sources, spatial variation, and speciation of heavy metals in sediments of the Tamagawa River in Central Japan. *Environ Geochem Health*, 34(1), 13-26. doi:10.1007/s10653-011-9409-z

17. Scheibye K., Weisser J., Borggaard OK., Larsen M.M., Holm P.E., Vammen K., Christensen J.H. (2014). Sediment baseline study of levels and sources of polycyclic aromatic hydrocarbons and heavy metals in Lake Nicaragua. *Chemosphere*, 95, 556–565. doi: 10.1016/ j.chemosphere.2013.09.115

18. Esmaeilzadeh M., Karbassi A., Moattar F. (2016). Assessment of metal pollution in the Anzali Wetland sediments using chemical partitioning method and pollution indices. *Acta Oceanol Sin*, 35(10), 28-36. doi: 10.1007/s13131-016-0920-z

19. Tuna AL., Yilmaz F., Demirak A., Ozdemir N. (2007). Sources and distribution of trace metals in the saricay stream basin of southwestern turkey. *Environ Monit Assess*, 125(1-3), 47-57. doi:10.1007/s10661-006-9238-1

20. Karbassi AR., Monavari SM., Nabi Bidhendi GR., Nouri J., Nematpour K. (2008). Metal pollution assessment of sediment and water in the Shur River. *Environ Monit Assess*, 147(1-3), 107-116. doi:10.1007/s10661-007-0102-8

21. Camusso M., Vigano L., Raffaella B. (1995). Bioconcentration of trace metals in rainbow trout: A field study. *Ecotoxicol Environ Saf*, 31, 133–141.

22. Krika A. and Krika F. (2018). Assessment of Heavy Metals Pollution in Water and Sediments of Djendjen River, North-Eastern Algeria. *Pollution*, 4(3), 495–502. doi: 10.22059/poll.2018.249394.367

23. Muller G. (1969). Index of geo-accumulation in sediments of the Rhine River. *Geo Journal*, 2, 108-118. doi: 10.1055/s-2007-1023171

24. Jain C.K., Gupta H., Chakrapani GJ. (2008). Enrichment and fractionation of heavy metals in bed sediments of River Narmada, India. *Environ Monit Assess*, 141(1-3), 35-47. doi:10.1007/s10661-007-9876-y

25. Alagarsamy R. and Zhang J. (2005). Comparative studies on trace metal geochemistry in Indian and Chinese rivers. *Curr Sci*, 89(2), 299-309. doi: 10.1016/S0039-9140(01) 00330-7

26. Central Water Commission (2015). PMP Atlas for the Narmada, Tapi, Sabarmati, and Luni River Systems and Rivers of Saurashtra and Kutch Regions including Mahi. India Metrological Department, pp 344.

27. APHA/AWWA/WEF. (2012). Standard Methods for the Examination of Water and Wastewater. Part 1000. Stand Methods. doi:ISBN 9780875532356

28. APHA (American Public Health Association) (2012). Standard Methods for the Examination of Water and Wastewater. 22nd ed. American Public Health, Health Association, Washington, DC. doi:10.1080/1944701300 8687143

29. Singh H., Pandey R., Singh SK., Shukla DN. (2017). Assessment of heavy metal contamination in the sediment of the River Ghaghara, a major tributary of the River Ganga in Northern India. *Appl Water Sci*, 7(7), 4133-4149. doi:10.1007/s13201-017-0572-y

30. Hakanson L. (1980). An ecological risk index for aquatic pollution control.a sedimentological approach. *Water Res*, 14(8), 975-1001. doi:10.1016/0043-1354(80)90143-8

31. Kumari M., Mudgal LK., Singh AK. (2013). Comparative Studies of Physico-Chemical Parameters of Two Reservoirs of Narmada River, MP, India. *Current World Environment*, 8(3), 473-478.

32. Gupta N., Pandey P., Hussain J. (2017). Effect of physicochemical and biological parameters on the quality of river water of Narmada, Madhya Pradesh, India. *Water Sci*, 31(1), 11-23. doi:10.1016/j.wsj.2017.03.002

33. Sharma S., Dixit S., Jain P., Shah KW., Vishwakarma R. (2008). Statistical evaluation of hydrobiological parameters of Narmada River water at Hoshangabad City, India. *Environ Monit Assess*, 143(1-3), 195-202. doi: 10.1007/s10661-007-9968-8

34. The Environment (Protection) Rules (1986). Environment. pp1-10. doi:10.1017/S0033291714000531

35. BIS (Bureau of Indian Standards) (2002). Tolerance Limits of Selected Water Quality Parameters for Inland Surface Water Prescribed for Different uses by Bureau of Indian Standards in India. Bureau of Indian Standards, New Delhi.

36. Sharma SK. and Subramanian V. (2010). Source and distribution of trace metals and nutrients in Narmada and Tapti river basins, India. *Environ Earth Sci*, 61(7), 1337-1352. doi:10.1007/s12665-010-0452-3

37. Islam MS., Ahmed MK., Raknuzzaman M., Habibullah - Al- Mamun M., Islam MK. (2015). Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country. *Ecol Indic*, 48, 282-291. doi:10.1016/j.ecolind.2014.08.016

38. Mohiuddin KM., Otomo K., Ogawa Y., Shikazono N. (2012). Seasonal and spatial distribution of trace elements in the water and sediments of the Tsurumi River in Japan. *Environ Monit Assess*, 184(1), 265-279. doi:10.1007/s10661-011-1966-1

39. Wang Z., Sun R., Zhang H., Chen L. (2014). Analysis and assessment of heavy metal contamination in surface water and sediments: a case study from Luan River, Northern China. *Front Environ Sci Eng*, 9(2), 240-249. doi:10.1007/s11783-014-0646-0

40. García-Pereira FJ., García Giménez R., Vigil de la Villa R., Procopio JR. (2014). Heavy metal fractionation in sediments from the Jarama River (central Spain). *Environ Earth Sci*, 73(5), 2385-2396. doi:10.1007/s12665-014-3587-9

41. Zhang H., Jiang Y., Ding M., Xie Z. (2017). Level, source identification, and risk analysis of heavy metal in surface sediments from river-lake ecosystems in the Poyang Lake, China. *Environ Sci Pollut Res*, 24(27), 21902-21916. doi:10.1007/s11356-017-9855-y

42. Kazi TG., Jamali MK., Kazi GH., Arain MB., Afridi HI., Siddiqui A. (2005). Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test. *Anal Bioanal Chem*, 383(2), 297-304. doi:10.1007/s00216-005-0004-y

43. Mandal SK., Dutta SK., Pramanik S., Kole RK. (2019). Assessment of river water quality for agricultural irrigation. *Int J Environ Sci Technol*, 16(1), 451-462. doi:10.1007/s13762-018-1657-3

44. Subramanian V., Van ’t Dack L., Van Grieken R. (1985). Chemical composition of river sediments from the Indian sub-continent. *Chem Geol*, 48(1-4), 271-279. doi: 10.1016/0009-2541(85)90052-X

45. Martin J. and Meybeck M. (1979). Elemental mass balance of material carried by major World rivers. *Mar Chem*, 7, 173–206.

46. Turekian KK. and Wedepohl KH. (1961). Distribution of the elements in some major units of the earth’s crust. *Bull Geol Soc Am*. 72, 175-192. doi: 10.1130/0016-7606(1961) 72[175:DOTEIS]2.0.CO;2

47. Taylor SR. and McLennan S. (1985). The Continental crust: its composition and evolution. An examination of the geochemical record preserved in sedimentary rocks. Oxford, Blackwell Sci, pp312. doi: 10.1017/S0016756800 032167