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Heavy metals contamination of ground water in and around Joda of Keonjhar district, Odisha, India

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Abstract: *The present study deals with the study of heavy metal contamination of ground water in and around Joda, rich in iron and manganese ore deposits in Odisha. Heavy metals such as Zn, Ni, Cu, Mn, Fe, Co, Cd, Cr and Pb were analysed for 17 ground water samples in pre-monsoon (March-June), monsoon (July-October) and post monsoon (November-February) periods during the year 2011-2012. The average concentration in different periods was in the order pre-monsoon > post-monsoon > monsoon for Zn, Cu, Mn, Fe, Co, Cr and Pb, where as that of Ni and Cd it was in the order post-monsoon > pre-monsoon > monsoon period. The levels of Fe, Mn, Cr, Ni, Cu, Cd and Pb in most of the ground water resources were beyond the standard limits of BIS and WHO indicating their unsuitability for drinking purpose. According to WHO and FAO irrigation standard guidelines, Zn, Ni, Cu, Fe, Co, Cd and Pb content in the studied water samples were well below the standard limits except those of Mn and Cr in some samples. There was positive significant correlation between the metals Zn-Ni, Fe-Mn, Fe-Cr, Cu-Cr, Mn-Cr and Cr-Pb. Clustering of Zn, Ni and Co to one group and Fe and Mn into another group which were associated with Cr and Pb at later stages indicates the similarity of their geochemical as well as anthropogenic input. Along with natural weathering process, mining and industrial effluents arising out of active and abandoned mines and associated industries overburden and waste dumps in the area are the major factors for enrichment of heavy metals in the water bodies.*

Keywords- *cluster analysis, contamination, correlation, heavy metal, water quality*

I. Introduction

Drinking water is a potential source of human exposure to toxic substances. Ground water is one of the major sources of drinking water. Contamination of ground water by domestic, mining and industrial effluents and agricultural activity is a serious problem, faced by developing countries. The quality of water is the concern of the world as there is increasing tendency of pollution of groundwater as a result of leaching of heavy metals generated due to rapid industrialization and urbanization[1]. The toxic metals, released from various sources are concentrated in the biota by bioaccumulation and biomagnifications depending on the accumulation factors of the individual metals. Enrichment of various ions and heavy metals occur leading to degradation of water quality[2-4] is not only detrimental to humans and animals health[1] but also adversely affect such water for domestic, agricultural and industrial use. Heavy metal contamination in aquatic environment has become a critical problem because of their toxicity, persistence and non-degradability as well as biomagnifications at points after being far removed from the source of pollution[5]. The ground water resources in the study area in and around Joda of Keonjhar district of Odisha are contaminated with heavy metals naturally and by anthropogenic activities because of extensive iron and manganese mining and associated activities. Particularly, Keonjhar, being a backward district, dominated by ST and SC population, the local people in the study area do not have insight to the contaminations of water environment and its effects. Various toxic gases, particulate matter, liquid effluents and solid wastes daily enter into the biosphere. Thus, it has become quite important to estimate the extent to which the water, consumed by the residents of the area has been contaminated. In view of the above, the present study is aimed at evaluating heavy metal contamination of ground water in the area to assess the water quality for various uses with the hope that this study can help to develop a better policy and proper planning for groundwater resource management for sustainable development.

II. Study Area

The study area under investigation, in and around Joda is the north-west part of Keonjhar district of Odisha, bounded by 21^0 49′ 55″ to 22^0 03′ 49″ N latitude and 85^0 22′ 08 to 85^0 32′ 52″E longitudes (Fig.1). It comprises Joda Municipality and some part of Joda block as well as Jhumpura block that refers to the Toposheet No. 73 F/8, 73 F/12, 73 G/5 and 73 G/9. The total population of the area is around 1, 50,000. The study area forms a part of Singhbhum-Keonjhar- Bonai iron ore formation belonging to Iron Ore Super Group of Pre-Cambrian age. The major rock types of this area belong to Banded Iron Formation (BIF) mainly represented by Banded Hematite Jasper (BHJ), Banded Hematite Quartz (BHQ), Banded Hematite Chert (BHC) and Banded Ferruginous Shale (BFS). The BIF along with the volcanic and sedimentary rock piles constitute the Iron Ore group. The volcanic rocks constitute Basalt and Tuffite, while meta-igneous rocks like Metagabbro, epidiorite and amphibolites occur in this area. Singhbhum Granite/Hornblende Granite, Pellitic Schist and Amphibolites have also been observed in this area. The younger Kolhan Group of rocks such as sandstone and quartzite overlie Iron Ore group of rocks. The major ore minerals are hematite, goethite, pyrolusite and psilomelane with traces of pyrites. Other associated rocks are dolerites, tuffites and laterites.

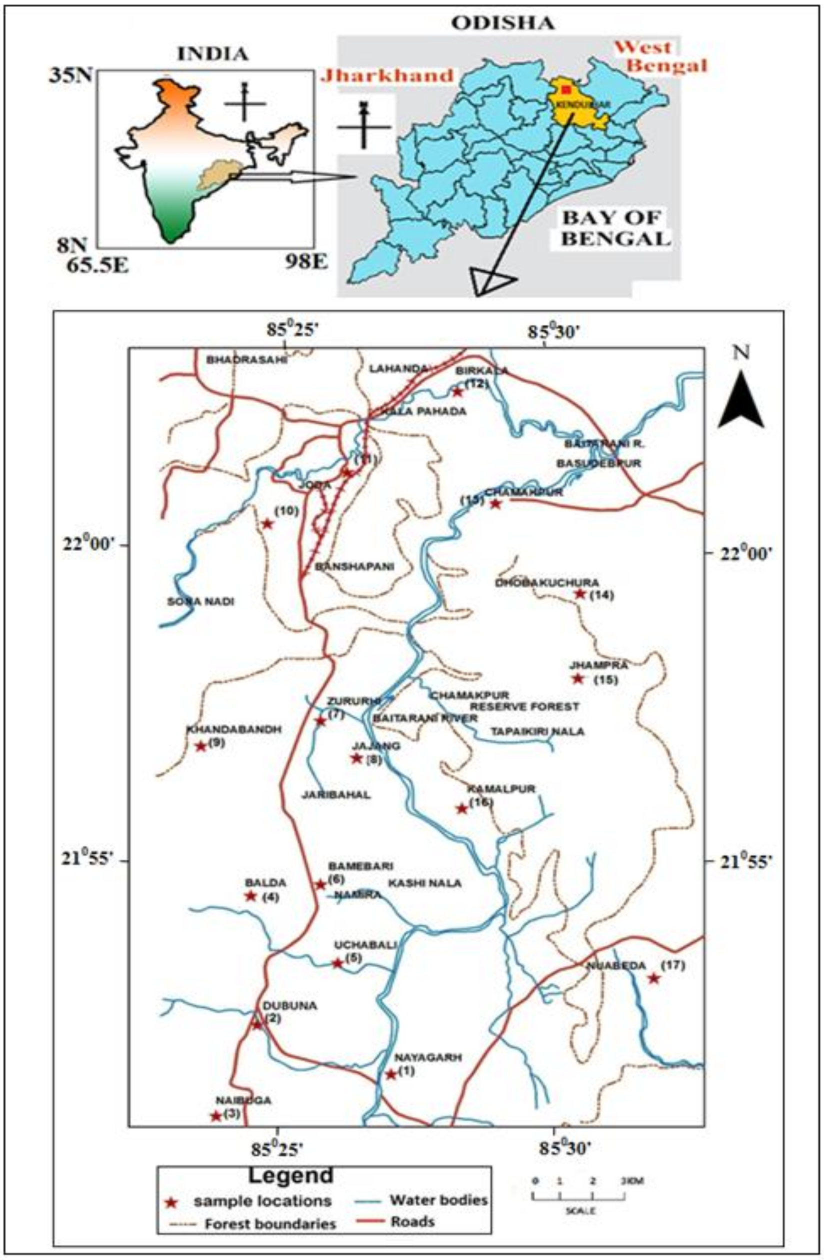

Figure 1. Map of study area with sampling locations of ground water

III. Materials And Methods

The present study was carried out for a period of one year 2011-12. Ground water samples of dug as well as bore wells were collected from 17 different stations (Fig.1) in pre-monsoon (March-June-2011), monsoon(July-October-2012) and post monsoon (November-2011-February-2012) periods at a regular interval of once in a month) in acid-washed plastic bottles of one litre capacity. About two ml. of concentrated HNO_3 was added to each bottle to preserve the heavy metals present in the samples. The collected samples were taken to the laboratory as early as possible. The water samples were protected from direct sunlight and preserved in the refrigerator to carry out chemical analysis following the standard methodology of APHA[6]. Heavy metals like Cu, Ni, Co, Zn, Pb, Cr, Fe, Mn and Cd was done by AAS (Shimadzu AA6300) and ICP-OES (PerkinElmer Optima 2100 DV). The observed values were compared with BIS and WHO standards[7,8] of drinking water

(Table- 4) to assess the drinking water quality. Assessment of irrigation water quality was done by comparing the metal concentrations with WHO and FAO[9] standard guidelines (Table- 4) for irrigation. Statistical analysis like Pearson's Correlation matrix and Hierarchical Cluster Analysis were employed in this study to identify the association and relatively homogeneous groups of heavy metals to predict the possible similar sources of origin of the studied metals in water.

IV. Results And Discussion

The analytical results of heavy metal content in the ground water samples (Table 1-3) under investigation show that variation of the concentration of metals like Zn, Ni, Cu, Mn, Fe, Co, Cd, Cr and Pb was 0.035-1.034, 0.003-0.044, 0.041-0.205, 0.053-0.304, 0.102-2.051, 0.0001-0.0014, 0.001-0.012, 0.042-0.171 and 0.015-0.077 mg/l with average concentrations 0.159, 0.019, 0.159, 0.122, 0.516, 0.0004, 0.005, 0.100 and 0.043mg/l respectively in the study period. The average concentrations in different periods (seasons) was in the order pre-monsoon > post-monsoon > monsoon for Zn, Cu, Mn, Fe, Co, Cr and Pb where as that of Ni and Cd was in the order post-monsoon > pre-monsoon > monsoon period.

Table 1: Heavy metal contents of ground water in pre-monsoon period

Samples	Zn mg/l	Ni mg/l	Cu mg/l	Mn mg/l	Fe mg/l	Co mg/l	Cd mg/l	Cr mg/l	Pb mg/l
S1	0.068	0.011	0.063	0.075	0.263	0.0004	0.002	0.058	0.031
S2	0.135	0.035	0.088	0.118	0.541	0.0002	0.008	0.091	0.056
S3	0.112	0.021	0.049	0.065	0.453	0.0002	0.005	0.073	0.038
S4	0.161	0.023	0.074	0.106	0.955	0.0005	0.004	0.138	0.047
S5	0.065	0.025	0.083	0.172	1.436	0.0004	0.003	0.113	0.061
S6	0.124	0.038	0.055	0.125	0.473	0.0001	0.003	0.068	0.053
S7	0.106	0.020	0.078	0.113	0.711	0.0003	0.004	0.127	0.068
S8	0.074	0.017	0.085	0.157	0.764	0.0011	0.006	0.168	0.077
S9	0.087	0.018	0.072	0.122	0.427	0.0003	0.002	0.091	0.033
S10	0.073	0.039	0.085	0.276	2.051	0.0002	0.004	0.104	0.069
S11	0.215	0.023	0.070	0.184	1.232	0.0004	0.012	0.078	0.028
S12	0.269	0.031	0.081	0.084	0.269	0.0001	0.004	0.066	0.062
S13	0.093	0.008	0.094	0.053	0.137	0.0002	0.004	0.112	0.039
S14	0.080	0.015	0.100	0.155	1.176	0.0014	0.003	0.155	0.057
S15	0.128	0.023	0.073	0.108	0.574	0.0006	0.005	0.073	0.036
S16	0.085	0.017	0.082	0.166	0.615	0.0005	0.003	0.105	0.031
S17	1.034	0.042	0.205	0.304	1.281	0.0001	0.001	0.162	0.066

Table 2: Heavy metal contents of ground water in monsoon period

Samples	Zn mg/l	Ni mg/l	Cu mg/l	Mn mg/l	Fe mg/l	Co mg/l	Cd mg/l	Cr mg/l	Pb mg/l
S1	0.051	0.006	0.043	0.064	0.122	0.0001	0.003	0.046	0.017
S2	0.116	0.018	0.052	0.096	0.326	0.0002	0.004	0.065	0.028
S3	0.073	0.011	0.071	0.102	0.374	0.0001	0.002	0.072	0.046
S4	0.134	0.021	0.078	0.098	0.460	0.0003	0.002	0.117	0.021
S5	0.061	0.016	0.082	0.117	0.515	0.0004	0.001	0.081	0.027
S6	0.057	0.015	0.046	0.073	0.310	0.0002	0.003	0.068	0.036
S7	0.072	0.015	0.055	0.095	0.426	0.0002	0.004	0.123	0.042
S8	0.035	0.008	0.063	0.121	0.568	0.0001	0.003	0.155	0.051
S9	0.049	0.009	0.058	0.086	0.352	0.0003	0.001	0.085	0.025
S10	0.132	0.013	0.067	0.125	0.624	0.0001	0.001	0.092	0.038
S11	0.083	0.011	0.052	0.103	0.447	0.0001	0.002	0.103	0.022
S12	0.088	0.016	0.041	0.082	0.145	0.0002	0.003	0.066	0.015
S13	0.064	0.006	0.055	0.086	0.104	0.0001	0.001	0.094	0.034
S14	0.107	0.012	0.063	0.124	0.353	0.0003	0.001	0.114	0.038
S15	0.101	0.018	0.044	0.073	0.203	0.0002	0.004	0.065	0.027
S16	0.063	0.013	0.050	0.069	0.147	0.0002	0.002	0.097	0.025
S17	0.231	0.024	0.073	0.128	0.361	0.0003	0.002	0.118	0.047

Table 3: Heavy metal contents of ground water in post-monsoon period

Samples	Zn mg/l	Ni mg/l	Cu mg/l	Mn mg/l	Fe mg/l	Co mg/l	Cd mg/l	Cr mg/l	Pb mg/l
S1	0.125	0.013	0.054	0.117	0.306	0.0003	0.003	0.042	0.024
S2	0.664	0.044	0.069	0.134	0.445	0.0009	0.008	0.094	0.045
S3	0.085	0.025	0.083	0.228	0.571	0.0002	0.003	0.101	0.066
S4	0.258	0.031	0.105	0.154	0.543	0.0008	0.004	0.125	0.041
S5	0.113	0.007	0.115	0.191	0.507	0.0007	0.006	0.102	0.048
S6	0.082	0.018	0.092	0.085	0.194	0.0002	0.005	0.070	0.037
S7	0.053	0.021	0.115	0.106	0.371	0.0002	0.006	0.146	0.056

S8	0.039	0.003	0.085	0.147	0.482	0.0004	0.007	0.171	0.059
S9	0.058	0.009	0.079	0.115	0.430	0.0003	0.005	0.113	0.027
S10	0.149	0.015	0.083	0.075	0.203	0.0001	0.004	0.092	0.043
S11	0.108	0.013	0.061	0.141	0.611	0.0002	0.003	0.110	0.032
S12	0.095	0.019	0.066	0.064	0.102	0.0006	0.006	0.084	0.057
S13	0.111	0.017	0.079	0.087	0.108	0.0001	0.004	0.068	0.053
S14	0.265	0.031	0.068	0.123	0.463	0.0007	0.004	0.137	0.065
S15	0.174	0.026	0.062	0.103	0.415	0.0004	0.006	0.103	0.038
S16	0.133	0.020	0.088	0.097	0.392	0.0004	0.007	0.084	0.038
S17	0.482	0.039	0.077	0.174	0.413	0.0005	0.006	0.122	0.051

Table 4: Standard values for drinking and irrigation water

Parameters	Desirable/acceptable value for Drinking water		WHO/FAO(1985) Permissible Value for irrigation water
	WHO(2011)	BIS(2012)	
Zn(mg/l)	3.0	5.0	2.0
Ni(mg/l)	0.07	0.02	0.2
Cu(mg/l)	2.0	0.05	0.2
Fe(mg/l)	0.3	0.3	5.0
Mn(mg/l)	0.1	0.1	0.2
Cr(mg/l)	0.05	0.05	0.1
Co(mg/l)	0.04	-	0.05
Cd(mg/l)	0.003	0.01	0.01
Pb(mg/l)	0.01	0.01	5.0

4.1 Heavy metal contents and drinking water quality

4.1.1 Zn, Cu and Ni

All of the water samples had dissolved Zn level well within the BIS and WHO standard limits for drinking water. Cu content in all of the samples were within the permissible limit of WHO throughout the study period. But its level was beyond the desirable limit of BIS in all samples except S3 i.e. 94.1% in pre-monsoon, all samples other than S1, S6, S12 and S15 comprising 76.5% in monsoon and all samples in post-monsoon period. Ni concentration in all the water samples was within the permissible limit of WHO for drinking water. But, it was beyond the permissible level of BIS for drinking water in water samples S2, S3, S4, S5, S6, S10, S11, S12, S15 and S17 comprising 58.8 % of samples in pre-monsoon, S4 and S17 i.e. 11.8% of samples in monsoon and S2, S3, S4, S7, S14, S15 and S17 i.e. 41.2% of samples in post-monsoon period.

Mining and industrial discharges, domestic construction sources, road dusts, storm water, untreated waste disposal, sewage and runoff, fertilizers as well as organic remains are considerably important sources of Zn, Ni and Cu in the area [5,10-12]. The elevated level of Ni may be due to coal and oil combustion, anthropogenic release and weathering of rocks and minerals like slate, sandstone, clay minerals and basalt, erosion of agricultural soil from adjacent area, where there is use of phosphate fertilizers [10,13]. Leaching from metals in contact with drinking water such as pipes and fittings is an important source of nickel contamination in the water samples [14]. Also, high concentration of Cu may be ascribed to the corrosion of piping system in hand pumps/bore wells [10,12,15].

4.1.2 Fe, Mn and Co

The Mn concentration exceeded the desirable limit of BIS as well as WHO in 82.6%, 47.1% and 70.1% of samples in pre-monsoon, monsoon and post-monsoon period respectively. The values were within the maximum permissible limit (0.3 mg/l) of BIS for all the samples except the sample S17 in pre-monsoon period. However, significantly high level of Mn in samples such as S2, S4, S5, S7,S8, S10, S14,S17 may be due to influence of rocks, mining and industrial effluent and reduction in redox potential caused by influx of readily oxidisable organic matter either from natural or anthropogenic sources[12,16]. Fe content was beyond the desirable limits of BIS and WHO in 82.4% of the samples in pre-monsoon, 70.1% in monsoon and all the samples in post-monsoon period. The samples S5 S10, S11, S14 and S17 comprising 29.4% of the studied samples had Fe level higher than the maximum permissible limit (1.0 mg/l) of BIS in pre-monsoon period. The concentration of Mn and Fe has been found more than the highest desirable limit of drinking water standards at many places in all seasons, which may be derived from iron and manganese mining, sewage and landfill leachate, weathering of ferruginous minerals along with lateritic soil cover of the study area [3,17,18]. Especially water obtained from hand pumps (tube wells) at Balda, Uchabali, Jajang, Dhobakuchura and Nuabeda were of considerably high level of Fe and Mn, which may be attributed to corrosion of iron pipes of hand pumps or due to presence of more iron in ground water. This indicates the poor quality and maintenance of hand pumps in this area. All the samples had Co content far below the desirable limits of both BIS and WHO for drinking water.

4.1.3 Cd, Cr and Pb

Cd level was well below the desired limit of BIS in all the samples in the study period except in the sample S11 in pre-monsoon period. But it exceeded the WHO limit in 82.4% of samples in pre-monsoon, 41.2% of samples in monsoon and all samples in post-monsoon period. The cadmium may occur in groundwater naturally or as a contaminant from sewage sludge, use of phosphatic fertilizers, polluted groundwater or mining and industrial effluents [10,12,15]. Cr content was beyond the desirable limits of BIS and WHO guidelines in all the samples in pre-monsoon and all samples except only one (sample S1) in monsoon as well as in post-monsoon period. Comparatively higher level of Cr was reported in samples S2, S3, S4, S5, S7, S8, S10, S14 and S17 throughout the study period. High level of chromium in the studied water samples may be due to mining and industrial effluents from extensive mining and related industrial activities, overburden and waste dump in the study area [4,5]. Lithogenic sources such as physical and chemical weathering of rocks and soil as well as percolation of domestic waste and sewage effluents of nearby urban and rural areas, runoff from the agricultural sector, mining and industrial effluents, storm water drainage and road dust[5,10,12,14] have significant contribution towards the high Cd and Cr content.

The Pb content exceeded the desirable limits for drinking water specified by BIS and WHO in all samples throughout the study period. Considerably high Pb content in water samples S2, S3, S5, S7, S8, S14 and S17 may be ascribed to atmospheric precipitations due to emissions from sponge iron plant, mining operations and vehicular emissions, gasoline additives, pigments and storage batteries[19-21]. Also road dust, rural and urban runoff, agricultural run-off, household sewages, human as well as animal excreta and corrosion of pipes have considerable contribution to the lead content in ground water in the study area[12,15].

It is observed that the spatial and temporal variations of the studied metals in the water samples are not in a particular trend. Higher concentrations recorded in pre-monsoon than those of monsoon and post-monsoon periods may be due to semi arid type of climate, which promotes higher rate of evaporation causing increase in concentration of these elements[22]. On the other hand, mining operations along with associated activities and domestic activities may contribute more dissolved heavy metals to water during monsoon. Active leaching and subsequent infiltration cause the higher concentration of these parameters in post- monsoon period by percolation of water through various layers of soil, dissolution of minerals from rocks in mining areas[23].

4.2 Statistical analysis

Pearson's correlation matrix and Cluster analysis and have proven to be useful in offering reliable classification of the metals and physicochemical properties of water. Table- 5-7 represent the Pearson correlation matrix, significant at 0.05 significance level of the heavy metals in the studied ground water samples. The water samples exhibit positive significant correlation between the metals such as Zn-Ni, Fe-Mn, Fe-Cr, Cu-Cr, Mn-Cr and Cr-Pb in the study period indicating the similarity of their geochemical sources. Strong positive correlations between Fe and Ni, Mn and Pb, Cu and Mn, Cr and Pb etc. is the indication of same or similar source input likely resulting from mining and industrial waste discharges[5,24]. However, there are no significant correlations among most of these heavy metals, indicating their non-association with each other and their independent or different natural and anthropogenic sources of occurrence in the study area.

The Cluster analysis was done in which the heavy metals were clustered into different groups (Fig. 2) by clustering technique[25]. This figure shows that Zn, Ni and Co had good similarity and were clustered in one group in monsoon as well as post-monsoon periods indicated strong anthropogenic input. Fe and Mn were clustered in one group having strong association between them in all seasons which were associated with Cr and Pb at later stages. This might be due to their lithogenic origin as well as inputs from mining and industrial activities. Also strong association was observed between Cu and Zn in pre-monsoon period. But, Cu formed individual group in monsoon and post-monsoon periods, while Cd was isolated from others throughout the study period. As expected, the individual group of Cd and Cu is indicative of lack of association with the other metals in water[24,26]. The clustering of specific metals can be attributed to nearly same basicity, complexation characteristics and their belongingness in the same transition series. They combine with like anions and enter into the ores, which channel through rain into the water bodies.

Table 5: Correlation matrix for heavy metals of ground water in pre- monsoon period

	Zn	Ni	Cu	Mn	Fe	Co	Cd	Cr	Pb
Zn	1								
Ni	*0.53	1							
Cu	*0.88	0.38	1						
Mn	*0.56	*0.60	*0.66	1					
Fe	0.20	*0.45	0.34	*0.83	1				
Co	-0.30	*-0.48	-0.04	0.02	0.16	1			
Cd	0.02	-0.02	-0.15	0.13	0.21	0.00	1		
Cr	0.33	-0.04	*0.61	*0.46	*0.44	*0.52	-0.20	1	
Pb	0.23	*0.47	0.39	*0.42	*0.43	0.12	-0.33	*0.58	1

Table 6: Correlation matrix for heavy metals of ground water in monsoon period

	Zn	Ni	Cu	Mn	Fe	Co	Cd	Cr	Pb
Zn	1								
Ni	*0.75	1							
Cu	0.36	0.29	1						
Mn	*0.47	0.22	*0.75	1					
Fe	0.16	0.17	*0.68	*0.77	1				
Co	0.29	*0.57	*0.45	0.22	0.13	1			
Cd	-0.06	0.26	*-0.55	-0.41	-0.22	-0.24	1		
Cr	0.15	0.04	*0.51	*0.64	*0.56	0.03	-0.19	1	
Pb	0.18	0.01	0.41	*0.60	*0.46	-0.14	-0.04	*0.64	1

Table 7: Correlation matrix for heavy metals of ground water in post-monsoon period

	Zn	Ni	Cu	Mn	Fe	Co	Cd	Cr	Pb
Zn	1								
Ni	*0.85	1							
Cu	-0.22	-0.15	1						
Mn	0.19	0.15	0.23	1					
Fe	0.17	0.12	0.13	*0.78	1				
Co	*0.63	*0.50	0.06	0.25	0.32	1			
Cd	0.37	0.19	0.21	-0.13	-0.05	*0.45	1		
Cr	0.02	0.03	0.35	0.33	*0.54	0.22	0.28	1	
Pb	0.05	0.23	0.24	0.28	0.02	0.16	0.13	*0.48	1

*Correlation coefficients significant at 0.05 significance level

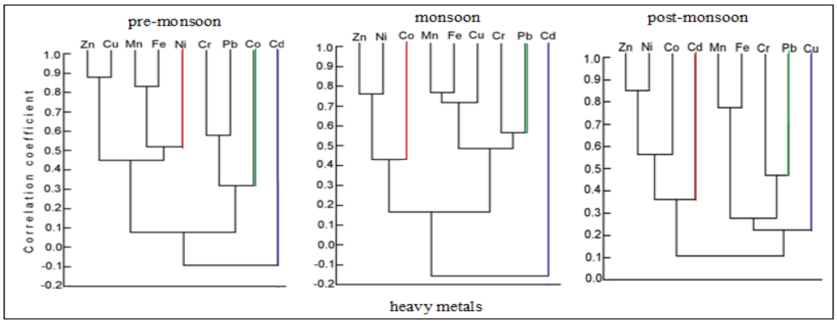

Figure 2. Dendogram showing the cluster analysis for heavy metals

4.3 Irrigational water quality

According to WHO and FAO irrigation standard guidelines, the heavy metal contents Zn, Ni, Cu, Fe, Co, Cd and Pb in the studied ground water were found to be well below the standard limits [27,28] throughout the study period. Manganese content was beyond the limits for irrigation in11.8% of samples (samples S10 at Joda and S17 at Nuabeda) in pre-monsoon and 5.9% sample (S3at Naibuga) in post-monsoon period. But, Cr concentration exceeded both WHO and FAO standard values in most of the water samples i.e. 52.9% in pre-monsoon, 35.3% in monsoon and 58.8% in post-monsoon period.

V. Conclusion

A perusal of the results reveals that there is considerable enrichment of heavy metals particularly, Fe, Mn, Cr, Ni, Cu, Cd and Pb in ground water resources exceeding the drinking water quality criteria, which is of serious concern. This may be due to various active Fe and Mn mines in areas like Dubuna, Kalimati, Balda, Uchabali, Khandbandh, Jururhi, Jilling and Jajang. Strong correlation between the metals such as Zn-Ni, Fe-Mn, Fe-Cr, Cu-Cr, Mn-Cr and Cr-Pb is the indication of same or similar source of natural/anthropogenic input of these parameters. Along with natural weathering process, mining and industrial effluents arising out of active and abandoned mines and associated industries like Ferro manganese plant at Joda, Sponge iron plant at Bileipada and different crusher units, overburden and waste dumps in the area alongwith domestic effluents are the major sources of heavy metals in the water bodies. Cracked hand pump platforms, open dug wells and poor maintenance of the wells are the causes for ground water contamination.Thus, the present study leads to the conclusion that ground water sources of the study area are more or less suitable for agricultural use but not suitable for drinking purpose. This clearly indicates that the water sources of the study area cannot be used for public consumption without proper treatment. This study highlights the dire need to control heavy metals contamination of water bodies of the area and if this need-based issue is left unattended to, it will pose problems to provide safe drinking water and may cause severe health hazards to the inhabitants of the area in the days to come.

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