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SEASONAL ASSESSMENT OF GROUNDWATER QUALITY IN TERMS OF HEAVY METAL CONTAMINATION IN SUKINDA MINING REGION OF JAJPUR DISTRICT, ODISHA

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ABSTRACT

The present study deals with the assessment of heavy metal contamination of groundwater in and around Sukinda region, Odisha, which is rich in chromium, iron and nickel deposits.Mining and industrial effluents arising in this region is due to unrestrained mines, associated industries. Over burden and waste dumps are major factors for heavy metal contamination in groundwater. Ground water samples were collected from ten different locations in monsoon, post monsoon and pre monsoon seasons during the year 2015-2016 and the concentration of heavy metals such as Fe, Mn, Cu, Ni, Co, Zn, Pb, Cr and Cd were analyzed. The average metal contamination load of the above three seasonal periods was in the order of monsoon>pre monsoon>post monsoon for Mn,Co,Cr and Cd whereas, Fe and Ni were in the order of pre-monsoon>monsoon>post-monsoon but forCu and Zn the order was pre-monsoon>post-monsoon>monsoon. Pb is the only metal which is in the order of monsoon>post-monsoon>pre-monsoon. The level of Fe,Cr,Ni,Pb and Mn in most of the ground water resources were beyond the standard limits of BIS andWHO indicating their unsuitability for drinking purpose. There was existence of positive and strong correlation between the metals Zn-Cu,Cu-Co,Cu-Zn,Cu-Cr,Co-Cr,Pb-Cr and Ni-Cr. Clustering of Zn,Co,Cr,Ni in one group; Cu,Cd,Pb,Fe and Mn in another group indicates that the metals under a same cluster group are having common geochemical source and anthropogenic input.

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INTRODUCTION

Water is one of the most significant and precious gift of nature. 75% of our earth is covered by water but only approximately 1% of total water is fresh and usable. It is cardinal for survivability of mankind in the biosphere (Gupta *et al.,* 2014). Ground water is one of the major sources of drinking water. Ground water quality of depends on quality of recharged water, atmospheric precipitation in land surface and subsurface geochemical process (Dash *et al.,* 2014). Contamination of ground water by domestic, mining and industrial effluents and agricultural activity is a serious problem, faced by developing countries.

The Toxic metals released from various sources are concentrated in the biota by bio accumulation and bio magnification depending on the accumulation factors of the individual metal (Gupta *et al.,* 2007; Singh and Pal, 2010; Dutta and Ghosh, 2012). 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 (Dash *et al.,* 2014). Sukinda valley in Jajpur district of Odisha is considered as one of the richest chromite and nickel producing mines area of India (Rao *et al.,* 2003). Several mines are operating for extraction of one mainly through open-cast mining methods (Indian Mineral Book-97) was to rock materials are dumped in open ground without considering its adverse impacts. The ground water of study area is heavily contaminated due to overflow of overburdened

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dumps and leaching of heavy metals especially during rainy season (Dhaket and Singh, 2008).The presence of heavy metals such as Chromium, Orion, Nickel, Lead, Copper and Zinc in high concentration in ground water can cause an adverse effect on human health and making the water unportable (Pandey, 1997). The major problem with the ground water is that once contaminated, it is difficult to restore its quality. Hence there is a need and concern for the protection and management of ground water quality (Gajendran and Thamari, 2008). The study area of this investigation is the Sukinda region which is mainly dominated by backward and tribal population. The area is susceptible to be contaminated directly or indirectly at each segment of environment due to the industrial and mining activities like transportation of ores, burning of coals, domestic activities and automobiles (Dash *et al.,* 2014).In view of the above, the present study is aimed at evaluating heavy metal contamination of ground water in the described 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 ground water resource management to sustainable development (Dash *et al.,* 2016).The quality of ground water was also ensured in respect of its efficacy towards human consumption, agriculture and industrial uses.

MATERIALS AND METHODS

A brief description of study area

The study area under present investigation is in and around the Sukinda valley situated at 21^0 $01^'$ to 21^0 3^1 N Latitude and 85^0 43^1 to 85^0 53^1 E Longitude, which is surrounded by Daitari hills in North and Mahagiri hills in South. The sites in the villages from which the ground water samples were collected are Bhimtangar, Kalrangi, Chingudiapal, Gurujangha, Kaliapani, Chirgunia, Kulipasi, Kaliapani (near Hanuman Temple), Tata steel gate, Kaliapani (near Chandimata Temple) etc. are located in Sukinda region. (Fig.1).The area forms a part of TOPO Sheet No-73G/12, 73G/16,73H/13 and 73H/19.The rock in this area is associated with six sedimentary sequences and each is separated by unconformities. The water level at this area lies between 11 to 15 meters below the ground level (Dhakale et al., Ref (ii).

Collection storage and Analysis of Samples

The ground water samples of dug well as well as bore wells were collected from 10 different stations (named as G-1 to G-10)in three different seasons (monsoon, winter and summer) during the year 2015-2016,at regular interval in acid-washed plastic bottles of one liter capacity. For preservation of heavy metal, 2 ml (appropriately) of concentrated HNO_3 was added to each bottle. The sample were protected from direct sunlight and preserved in the refrigerator for analysis by following standard methodology as described in APHA (1998). Heavy metals like Cr, Fe, Ni, Co, Zn, Cu, Pb and Cd were analyzed by using atomic absorption spectrophotometer (AAS) (SHIMADZU AA7000) and inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer optima 2100 DV). The observed values were compared with BIS (2012) and WHO (2011) standards of drinking water (Table-1). Statistical analysis such as Pearson's correlation matrix (n) and agglomerative hierarchical clustering (AHC) analysis were employed in this study to identify the interdependency and association between relatively homogeneous groups of each analyzed parameters to preservative possible sources of origin of the studied metals in the ground water (Dash *et al.,* 2016).

Figure 1. Location map of ten sampling sites in Sukinda mining region

Table 1. Permissible limit values of heavy metals for drinking water

Heavy metals (mg/l)	Desirable/ acceptable values for drinking water	
	WHO (2011)	BIS (2012)
Zn	3.0	5.0
Ni	0.07	0.02
Cu	2.0	0.05
Fe	0.3	0.03
Mn	0.1	0.1
Cr	0.05	0.05
Co	0.04	-
Cd	0.003	0.01
Pb	0.01	0.01

RESULTS AND DISCUSSION

Heavy metal contents and drinking water quality

The analytical results of heavy metals content in the ground water samples (Table-2,3 and 4) under investigation shows that verification of concentration of metals like Fe, Mn, Cu, Ni, Co, Zn, Pb, Cr, Cd was 0.0121-10.7273 mg/l,0.0103-0.6218 mg/l,0.0001-1.1604 mg/l, 0.0346-0.4717 mg/l, 0.0112-0.5598 mg/l, 0.0001-2.6923 mg/l, 0.043-209259 mg/l, 0.0521-3.0222 mg/l, 0.0001-0.0641 mg/l with average concentration 1.0428, 0.2296, 0.3825, 0.2159, 0.1313, 0.0630, 0.9163, 0.5696 and 0.0353 mg/l respectively. The average heavy metals concentration in ground water in different seasons was in the order monsoon > pre monsoon> post-monsoon for Mn, Co,Cr and Cd whereas Fe and Ni are in the order pre monsoon > post monsoon >monsoon and Pb is the order Monsoon>Post Monsoon>Pre Monsoon.

Table 2. Heavy metal contamination load in ten different ground water samples during Monsoon

Stations	Heavy metal concentration (mg/l)								
	Fe	Mn	Cu	Ni	Co	Zn	Pb	Cr	Cd
G-1	0.3461	0.3628	-0.0486	0.2828	0.5598	0.0121	2.1666	3.0222	-0.0069
G-2	0.3595	0.3901	0.0375	0.4714	0.0848	0.002	2.0222	1.4506	0.0504
G-3	0.7322	0.6078	-0.0108	0.431	0.3901	-0.0223	2.2147	0.4835	0.0206
G-4	0.8345	0.6218	-0.0432	0.2559	0.3053	0.0031	2.1185	1.2361	0.0641
G-5	0.9584	0.5928	-0.0541	0.1212	0.2544	-0.0081	2.9259	0.5403	0.0618
G-6	0.9632	0.4818	0.0811	0.1321	0.2513	0.0018	1.8777	0.0861	0.1306
G-7	0.9756	0.4615	0.0004	0.1123	0.2513	-0.0015	1.927	1.2035	0.0028
G-8	0.8561	0.4365	0.0003	0.1503	0.2614	0.0003	1.8156	2.0235	0.0013
G-9	0.8731	0.512	0.0001	0.1131	0.2403	0.0001	2.1315	1.0982	0.0001
G-10	0.8653	0.4321	0.0001	0.1312	0.2313	0.0003	2.6154	1.0354	0.052

Table 3. Heavy metal contamination load in ten different ground water samples during Post Monsoon

Stations	Heavy metal concentration (mg/l)								
	Fe	Mn	Cu	Ni	Co	Zn	Pb	Cr	Cd
G-1	0.055	0.0224	0.0328	0.1115	0.0334	0.0029	0.4209	0.1077	0.0114
G-2	0.0355	0.0187	0.3398	0.1308	0.0255	0.0077	0.4652	0.431	0.0142
G-3	0.4503	0.0147	0.0316	0.1373	0.0314	0.0117	0.4726	0.2743	0.0146
G-4	0.0301	0.0187	0.0456	0.1501	0.0118	0.0105	0.4947	0.1033	0.0125
G-5	0.0177	0.0212	0.0386	0.1473	0.0334	0.0121	0.5021	0.1371	0.0146
G-6	0.0248	0.0171	0.0292	0.1394	0.0137	0.0121	0.48	0.1502	0.0156
G-7	0.0315	0.0151	0.0215	0.0465	0.0121	0.0114	0.042	0.0521	0.0141
G-8	0.0412	0.0103	0.0131	0.1536	0.0231	0.0062	0.048	0.1426	0.0132
G-9	0.0139	0.0153	0.0121	0.1475	0.0112	0.0051	0.043	0.1324	0.0142
G-10	0.0121	0.0124	0.0016	0.0346	0.0151	0.0101	0.4	0.1124	0.0098

Table 4. Heavy metal contamination load in ten different ground water samples during Pre Monsoon

Stations	Heavy metal concentration (mg/l)								
	Fe	Mn	Cu	Ni	Co	Zn	Pb	Cr	Cd
G-1	0.6029	0.1356	1.0637	0.4462	-0.0196	1.1706	0.2511	0.3193	0.0014
G-2	0.6798	0.0452	1.083	0.3223	-0.0353	2.107	0.2732	0.4088	0.0017
G-3	0.7183	0.0452	1.1604	0.471	-0.0295	2.107	0.2511	0.5192	0.0004
G-4	3.1426	0.3165	1.1217	0.2727	-0.0236	2.176	0.2658	0.4058	0.0017
G-5	10.7232	0.1808	1.0831	0.3347	-0.0216	1.1706	0.2511	0.4297	0.0027
G-6	2.6295	0.2713	1.1024	0.3099	-0.0196	2.6923	0.3397	0.3849	0.0027
G-7	1.2942	0.2451	1.0581	0.2727	-0.2134	1.4123	0.2314	0.2142	0.0025
G-8	2.0154	0.2318	1.1015	0.2651	-0.1246	1.5842	0.1851	0.2341	0.0014
G-9	0.9654	0.2131	1.0854	0.2134	-0.1356	1.1011	0.1635	0.2313	0.0012
G-10	0.0354	0.1314	0.9864	0.1682	-0.2351	0.9856	0.1012	0.1213	0.0011

Contamination of Zn, Cu and Ni in ground water

All the water samples had dissolved Zn level well within the BIS and WHO standard limits for drinking water. Cu content in all the samples are within the permissible limit of WHO throughout the study period. But its level was beyond the desirable limit of BIS in all samples except G-5 and G-6 i.e. 80% in monsoon and all samples in Pre Monsoon period. Ni concentration in all water samples were beyond the acceptable values of WHO as well as BIS value for drinking water. The important sources of Cu, Ni and Zn are mining and industrial discharges, road dusts, storm water untreated waste disposal (Dash *et al.,* 2015; Leung and Jiao, 2006). The Ni concentration exceeds the desirable limit of BIS as well as WHO in all the seasons may be due to chromite mining of Sukinda valley which annually generates around 0-7 million tones of lateritic chromite overburden (COB) containing Ni (0.5-1.0%) (Swamy *et al.,* 2003). Sukinda Valley in the state of Odisha is one of the major chromite reservoirs of the world and is the only known deposit of Nickel in India (Murty *et al.,* 2010). The higher concentration of Ni in water sample may be due to the percolation of the lateritic ore from the weathering zone of the surface. Leaching from metals in contact with drinking water such as pipes and fittings is an important source of Nickel contamination in water sample. High concentration of copper may be ascribed to the corrosion of piping system in hand pumps bore wells (Leung and Jiao, 2006; Tadiboyna and rao , 2016; Jameel *et al.,* 2012).

Contamination of Fe,Co and Mn in ground water

Fe content was beyond the desirable limit of BIS and WHO in 80% of sample in monsoon, 10% of sample in post monsoon and 90% sample in pre monsoon. 50% of total collected sample i.e. G-4,G-5,G-6,G-7,G-8 of monsoon had significantly high value than the maximum permissible limit of BIS (Table-1). The concentration of Mn exceeded the desirable limit of BIS (2012) as well as WHO (2011) in all the samples in monsoon and 60% sample in pre Monsoon. All the samples except the monsoon period have the values within the maximum permissible limit (0.3mg/l) of BIS. The concentration of Fe and Mn has been found more than the maximum desirable limit of drinking water standards at many places in monsoon and post monsoon which may be derived from iron and manganese mining, sewage and landfill leach ate, weathering of ferroginous minerals along with lateritic soil cover of the study site(s). Especially water obtained from Tata steel gates, Balasore alloy gate, OMC Colony Park, has considerably high level of Fe in post monsoon which may be attributed to corrosion of iron pipes of hard pumps or due to the presence of more iron in ground water. Co concentration in all the samples of monsoon exceeded the desirable limit of BIS as well as WHO. But all the samples in pre monsoon and post monsoon had Cobalt content far below the desirable limit of both BIS and WHO for drinking water.

Contamination of Pb, Cr and Cd in ground water

The Pb content exceeded the desirable limits for drinking water specified by BIS and WHO in all the samples throughout the study period. Considerably high Pb content in water samples (G-1 to G-10) of monsoon may be ascribed to atmospheric precipitation due to mining operation and vehicular emissions tailing from ore dressing, petrol particulates, gasoline additives, pigment and storage batteries (Chaterjee, 2011; Singare *et al.,* 2012; Jena *et al.,* 2012). Cd-level exceeded the WHO limit in 60% of sample in monsoon and all the samples in post monsoon period. 40% of samples in monsoon also contain higher value of Cd than BIS prescribed limit. The Cd limit was well below the limit of BIS in all the samples of pre monsoon, 10% of sample in post monsoon and 40% samples in monsoon period. The Cd may occur in ground water naturally or as a contaminant from sewage sludge, use of phosphatic fertilizer, polluted ground water or mining and industrial effluents (Leung and Jiao, 2006; Tadiboyna and Rao, 2016; Jameel *et al.,* 2012). Cr content was beyond the desirable limits of BIS and WHO guidelines in all the samples.

Correlation analysis

Table-5,6 and 7 represents the Pearson correlation matrix at 0.05 significance level of nine heavy metals in the studied ground water samples. The water samples exhibited positive significant correlation between the metals such as Mn-Pb, Ni-Cd, Fe-Mn, Zn-Cr, Fe-Cd, Mn-Cd, Cu-Ni, Cu-Co, Cu-Zn, Cu-b, Ni-Pb, Co-Zn, in the study period indicating the similarity of their geo-chemical sources. Strong positive correlation between Cu-Cr, Ni-Co, Ni-Cr, Co-Pb, Co-Cr, Zn-Pb and Pb-Cr, etc is the indication of same or similar sources of input likely resulting from mining and industrial waste discharge (Dash *et al.,* 2015; Davis, 1986). However there is significant correlation among most of the heavy metals indicating their association with each other and their same natural and anthropogenic sources of occurrence in the study area.

Cluster Analysis

The agglomerative hierarchical clustering (AHC) was performed for a heavy metals collected during three different seasons (i.e. monsoon, post monsoon and pre monsoon). Clustered dendrogram grouping of metals into different clusters according to their similarity pattern is shown in fig. 2 (a,b& c). The Fig. 2 indicates that Cr, Zn, Co and Ni was clustered in one group in which Cr and Zn had good similarity in monsoon which in turn is associated with Co and Ni at later stage. Cu, Cd, Pb, Fe and Mn were clustered in another group where Cu-Cd and also Fe-Mn had good similarity which is associated with Pb in later stage.

Table 5. Pearson Correlation matrix (n) of analysed heavy metals during monsoon

Variables	Fe	Mn	Cu	Ni	Co	Zn	Pb	Cr	Cd
Fe	1	0.533	0.100	-0.762	-0.261	-0.332	0.138	-0.646	0.284
Mn	0.533	1	-0.319	-0.030	0.016	-0.653	0.328	-0.627	0.251
Cu	0.100	-0.319	1	0.014	-0.531	0.040	-0.535	-0.411	0.499
Ni	-0.762	-0.030	0.014	1	0.071	-0.237	-0.150	0.155	-0.072
Co	-0.261	0.016	-0.531	0.071	1	0.084	0.036	0.463	-0.359
Zn	-0.332	-0.653	0.040	-0.237	0.084	1	-0.276	0.633	-0.011
Pb	0.138	0.328	-0.535	-0.150	0.036	-0.276	1	-0.237	0.124
Cr	-0.646	-0.627	-0.411	0.155	0.463	0.633	-0.237	1	-0.661
Cd	0.284	0.251	0.499	-0.072	-0.359	-0.011	0.124	-0.661	1

Table 6. Pearson Correlation matrix (n) of analysed heavy metals during post monsoon

Variables	Fe	Mn	Cu	Ni	Co	Zn	Pb	Cr	Cd
Fe	1	-0.148	-0.066	0.154	0.429	0.238	0.232	0.362	0.226
Mn	-0.148	1	0.293	0.243	0.419	-0.087	0.581	0.088	0.115
Cu	-0.066	0.293	1	0.154	0.210	-0.100	0.297	0.858	0.203
Ni	0.154	0.243	0.154	1	0.273	-0.153	0.169	0.314	0.536
Co	0.429	0.419	0.210	0.273	1	-0.169	0.413	0.384	0.035
Zn	0.238	-0.087	-0.100	-0.153	-0.169	1	0.363	-0.020	0.363
Pb	0.232	0.581	0.297	0.169	0.413	0.363	1	0.366	-0.044
Cr	0.362	0.088	0.858	0.314	0.384	-0.020	0.366	1	0.313
Cd	0.226	0.115	0.203	0.536	0.035	0.363	-0.044	0.313	1

Comparatively higher level of Cr was reported in samples G-1,G-2,G-4,G-7,G-8,G-9 and G-10 in monsoon period. This may be due to the mixing of chromium into the ground water through leaching as well as drainage from over burden during rainy season.

Statistical Analysis

Pearson's correlation matrix and cluster analysis and have proven to be useful in offering reliable classification of metal and physico chemical parameters of water.

The clustering between the above metals may be due their common lithogenic origin and from mining and industrial activities. In pre monsoon Cu, Cr, Zn, Ni, Pb and Co were clustered in one group in which Co and Cr are strongly associated. In another group Fe, Mn and Cd were clustered in which Fe and Cd were strongly associated. Ni, Co, Zn and Cr were clustered in one group in monsoon and pre-monsoon period indicating their strong anthropogenic input. In post monsoon Zn formed individual group. Cu, Cr, Mn and Pb were clustered in one group in which (Cu-Cr) and (Mn-Pb) are forming sub groups.

Table 7. Pearson Correlation matrix (n) of analysed heavy metals during pre monsoon

Variables	Fe	Mn	Cu	Ni	Co	Zn	Pb	Cr	Cd
Fe	1	0.250	0.146	0.065	0.367	-0.086	0.267	0.364	0.596
Mn	0.250	1	0.042	-0.458	-0.106	0.125	0.130	-0.254	0.531
Cu	0.146	0.042	1	0.574	0.678	0.643	0.597	0.794	-0.142
Ni	0.065	-0.458	0.574	1	0.702	0.288	0.583	0.742	-0.171
Co	0.367	-0.106	0.678	0.702	1	0.556	0.783	0.883	0.106
Zn	-0.086	0.125	0.643	0.288	0.556	1	0.770	0.626	0.156
Pb	0.267	0.130	0.597	0.583	0.783	0.770	1	0.757	0.495
Cr	0.364	-0.254	0.794	0.742	0.883	0.626	0.757	1	0.026
Cd	0.596	0.531	-0.142	-0.171	0.106	0.156	0.495	0.026	1

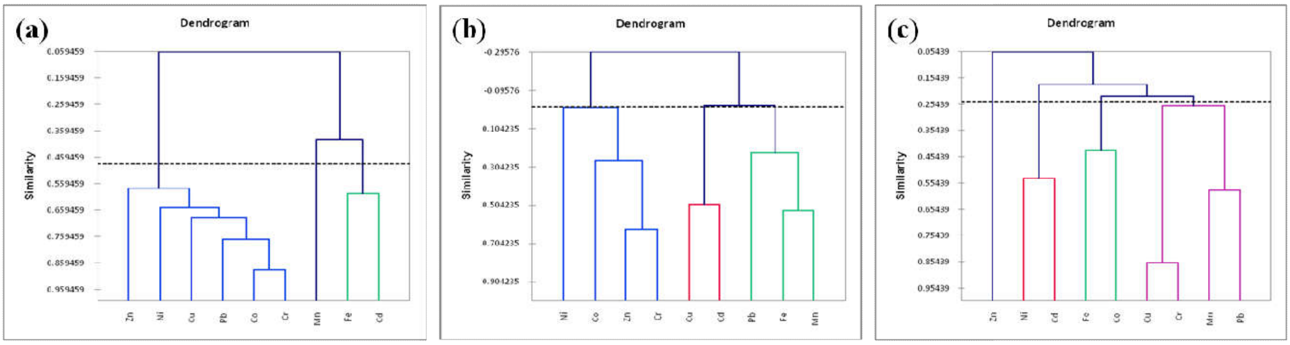

Figure 2. AHC study of all analysed heavy metals concentration in ten ground water samples during Pre monsoon (a), Monsoon (b) and Post monsoon (c)

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 in to the ores, which channel through rain into the water bodies (Dash *et al.* 2016).

Conclusion

The present study reveals that the mining operation has created a lot of damage to ground water of study area. The degree of heavy metal accumulation was found in the order of Fe>Pb>Cr>Cu>Mn>Ni>Zn>Cd (considering the average concentration of all the seasons). Heavy metals such as Fe, Cr, Pb, Ni, Mn and Cd were of much concern because even if they were present in dilute, undetectable quantities, their recalcitration and consequent persistence in water bodies imply that through natural processes such as bio-magnification, concentration (Atkinson *et al.,* 1998) may become elevated to such an extent that they will exhibit toxic characteristics particularly the concentration of these metals (according to the analysed result) causing groundwater to exceed the drinking water quality criteria, which is of alarming concern.

Strong correlation between Zn-Cu, Cu-Co, Cu-Zn, Cu-Cr, Co-Cr, Pb-Cr and Ni-Cr is the indication of similar source of natural/anthropogenic/lithogenic input of these metals. Along with natural weathering process, mining and industrial effluents arising out of active and unrestrained mines, and chrome ore beneficiation industries and over-burden of waste dumps in the area with domestic effluents are the major sources of heavy metals in the water bodies. Hence the present study concludes that there must be restriction of consumption of groundwater of contaminated region by the local villagers and mining workers. Awareness campaign should be arranged regularly by the expert bodies (Govt. and Non-Govt. organizations) to make people conscious and aware about the probable adverse impacts of using contaminated water.

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