

Review

Heavy metal contamination in groundwater due to mining activities in Sukinda valley, Orissa - A case study

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Sukinda Valley, Orissa is known for its chromite ore deposits. The open cast mining for chromium is being carried out since 1950. The extraction of chromite has mostly been carried out by open cast and at few places by under ground mining methods. The possibility of leaching contaminants from the ore material kept in the open ground or from the wastages or degraded ore material produced during the mining processes may contaminate the groundwater in the study area. There is also a high possibility that the contaminants will move to the aquifer system from the seepage of bottom floor of the mining quarry. In order to assess the chemical quality, groundwater samples from different part of the study area for post and pre-monsoon period have been collected and analyzed for various contaminants. This study showed that the groundwater in the study area was nearly neutral to mildly alkaline in pH (6.1 - 7.6) with low to moderate TDS (50 - 507 mg/l). High TSS (4 - 64 mg/l) indicates the influence of mine's waste on the groundwater quality, because the TSS particles remains as suspended colloidal particles in groundwater and are hence toxic as far as the groundwater potability is concerned. TSS levels are higher than the normal permissible limits of potable water and require a proper filtration process before human consumption. Metallic trace elements such as Cu (0.01 - 1.8 mg/l) and Cr(VI) (0.01 to 0.45 mg/l) are more than the permissible limits at some places in different seasons and may cause health hazards. In general, good groundwater conditions as well as simultaneous dissolution and dilution restraint the chromite and other heavy metals in groundwater.

Key words: Heavy metals, dissolution, dilution, ultramafic rocks.

INTRODUCTION

The presence of heavy metals such as Cr(VI), Fe, Cu and Zn in high concentration in groundwater can cause an adverse effect on human health and making that water not potable. The Sukinda Chromite Valley, in Jajpur district, Orissa is well known for its extensive chromite ore deposits. This valley is considered as one of the richest chromite and nickel producing areas and supplies 90% of India's demand (Rao et al., 2003). The area is covered with ultramafic rock of chromite bearing minerals. In this area several mines are in operation for extraction of chromite ore through open cast mining methods. The chromite ores and waste rock material are dumped in the open ground without considering its

impact on the environment. Leaching of heavy metals is possible during the rainy season to the surface water bodies as well as to the groundwater systems.

The ultramafic rocks in the area are highly weathered and metamorphosed at places giving the lateritic soil cover upto a depth of more than 20 m. Lateritic weathering of ultramafic rocks with secondary nickel concentration has been reported in many parts of the world (Zewas-sinck, 1969; Golightly, 1981; Nahon et al., 1982; Colin et al., 1990). Banerjee (1972) has shown the secondary dispersion pattern of Cr, Ni and Co in the soil-laterite overburden. Chackraborty (1976) have suggested that Ni was released due to residual weathering from primary minerals like Olivine, Chromite and was precipitated in the limonite profile in an acidic environment.

James (1972) have studied the migration and leaching of metals from old mine tailings deposits to the groundwater system. Similarly, Ebraheem (1990) have studied

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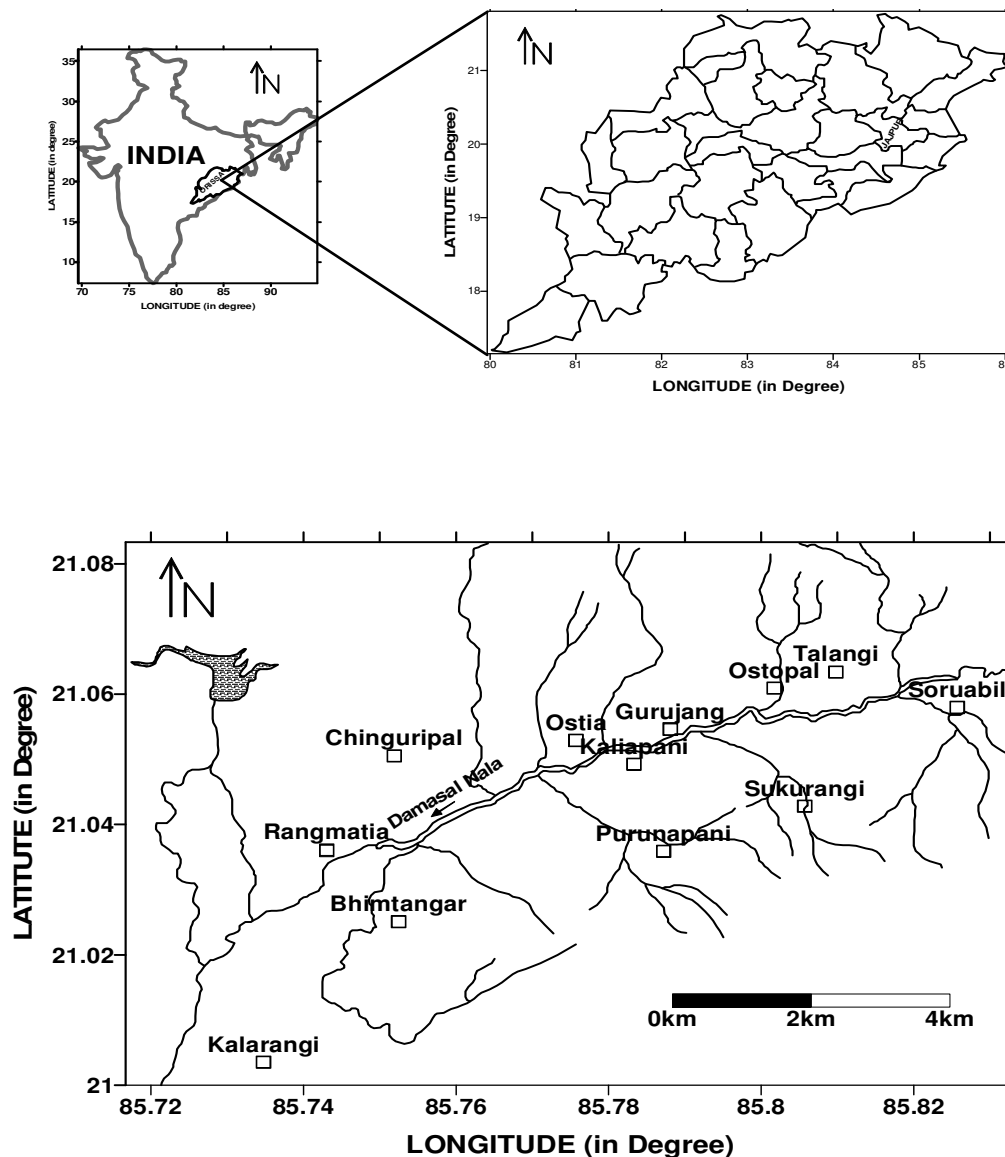


Figure 1. Key map of the study area showing drainage pattern.

acid mine drainage using earth resistivity measurements and they observed contamination in the aquifer system. Several authors have studied the spatial distribution of heavy metal concentration in soil by statistical relationship between soil properties and soil use or derived a model for heavy metal behaviour in soil, subsoil and plant compartment (Schnable and Tietje, 2002).

Recently, Som and Joshi (2003) have studied three vertical profiles at different places in the Sukinda Valley for Ni enrichment and mass balance studies. They collected the rock samples at different depths. Out of these profiles, one is present in our study area. They concluded in their study that these vertical profiles showed changes in mineralogy with depth. Weathering and serpentinite produced a thick lateritic column. Ni was concentrated more in nepouite, derolite, in partially serpentinite, and

mostly in goethite and saprolite. Ni concentration was negligible in topmost part of the weathered column.

Study area

The study area lies between latitude $21^{\circ} 1'$ to $21^{\circ} 4'$ N and longitude $85^{\circ} 45'$ to $85^{\circ} 48'$ E and is a part of famous Sukinda Valley, Jajpur district, Orissa shown in Figure 1. The drainage in the area is towards Northwest and finally join Damsal Nala flowing NE-SW and the stream is perennial in nature. In the southern part, Mahagiri Hill ranges lies with an altitude of 300 m above mean sea level, whereas Damsal Nala lies between 100 to 180 m above mean sea level. The average rainfall of the area is around 2400 mm/year.

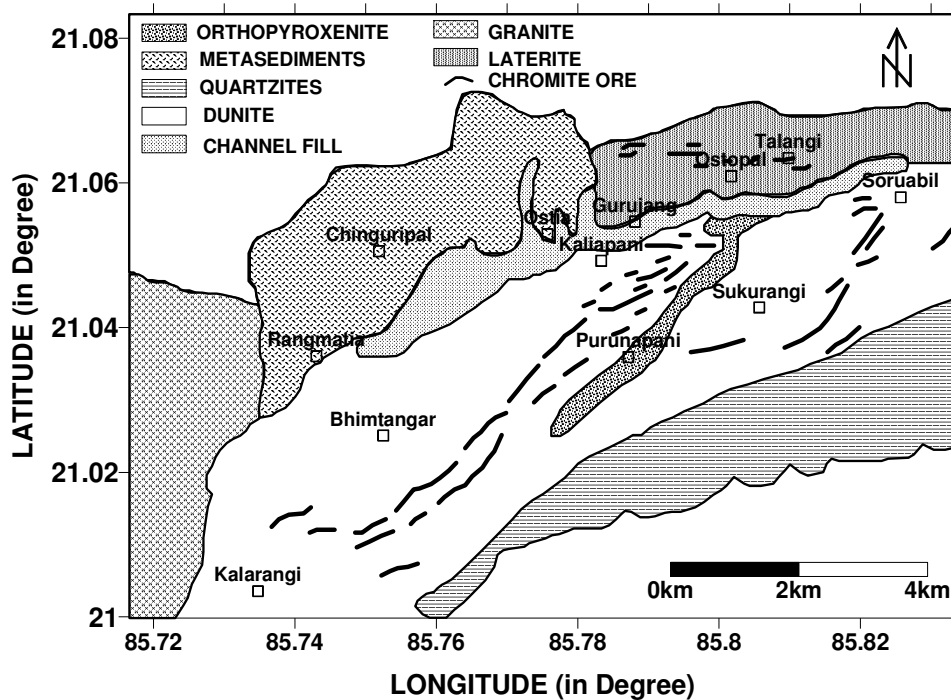


Figure 2. Geological map of the study area.

Geological background

Chromite deposits in Sukinda area are mainly associated with ultramafic rocks – dunite, peridotite and pyroxenite of pre-cambrian age. Chromite minerals consist of primarily of iron and chromium oxides. In addition to these, magnesium and aluminium are also present. The area with chromite deposits has an elevation ranging between 166 - 208 m above mean sea level. These ultramafic rocks are characterized by having fairly thick chromite seams of 10 - 50 m (Acharya et. al., 1998; Rao et. al., 2003).

The chromite deposits form a part of famous chromite bearing ultramafic complex of Sukinda Valley. These ultramafic are highly metamorphosed and belong to pre-cambrian age. The ultramafic appear to have intruded into the quartzites and this layered laccolithic complex is composed of alternate bands of chromite, dunite, peridotite and orthopyroxenite, repeated in a rhythmic fashion. These ultramafic rocks are extensively lateritized and limonitized. The occurrence of numerous chert bands are also found within the ultramafic, which are often completely weathered to a mass of talc-limonite. The geology map of the study area is shown in Figure 2.

Hydrogeology

The weathered Lateritized – Limonite mantle, ultramafics, orthopyroxenite as well as the underlying semi-weathered and fractured country rocks forms the source of groundwater in the area. The groundwater occurrence depends

on the nature, extension and weathering characteristics of the rock formation. The variation in lithology and structural set up control the groundwater potential and movement. The groundwater in the area is generally under semi-confined to confined condition.

Broadly the major hydrogeological units occurs in the area is as follows:

Laterite–Limonite–Chert: These are the altered product of ultramafics, the degree of weathering and meta-morphism is so pronounced that they are almost obliterated down to a depth of 170 m giving rise to a limonite-chert residual. These are the most extensive and potential aquifers and occur in the eastern part of the area. The groundwater in this zone is found in the top aquifer up to 25 m (Chougule, 1981; Das, 1997) under the phreatic condition, whereas the deeper aquifer is (below 25 m) under confined condition. The seasonal fluctuation of water level in this formation ranges from 1.67 - 4.88 m.

Laterite-weathered and fractured ultramafics associated with limonite and chert: This formation occurs in the central and west central parts and covers almost the entire mining tract in the Sukinda valley. These formations lie below a thin and discontinuous capping of the soil and lateritic mantle, which persists up to 20 m. The extent of weathering in this formation is comparatively less than the laterite–limonite–chert formation. The groundwater occurs in this formation under phreatic condition up to a depth of 20 - 25 m below

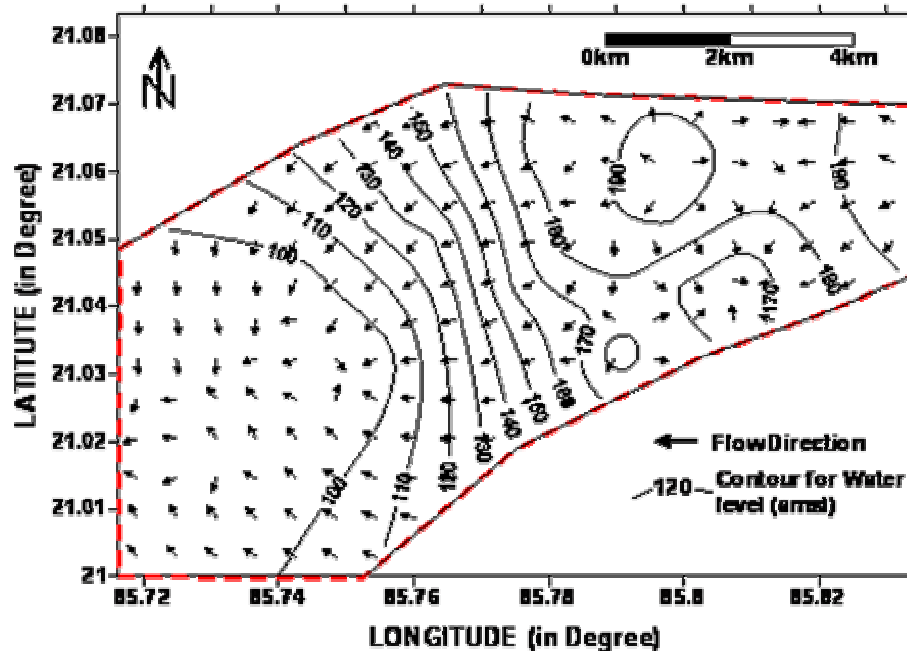


Figure 3. Groundwater flow map for post-monsoon period.

ground level (Chougale, 1981; Das, 1997). The deeper aquifer in this formation is constituted by the weathered–semi weathered and fractured ultramafics generally remains in hydraulic continuity with top aquifer and groundwater generally exists in these deeper horizons near to water table conditions.

Colluvial and channel fill deposits: These formations are generally mixture of boulders, gravels, pebbles, granules etc., highly cemented with ferruginous and siliceous matrix and have restricted occurrences in the foot hill of Mahagiri and Dairi Hill ranges region and along the course of Damsal Nala. The maximum thickness of these formations is around 12 – 15 m (Chougale, 1981; Das, 1997). The average seasonal fluctuation of water level in this formation is around 4 m.

Other hydrogeological units including orthopyroxenites: This group of formations includes orthopyroxenites occurring in the central part around Purnapani village. These formations except the orthopyroxenites are comparatively less weathered and maximum thickness of weathering is up to 15 m below ground level. Whereas orthopyroxenites from low ridge like exposures and the extent of weathering is maximum up to a depth of 10 m (Chougale, 1981; Das, 1997).

The static water level measured during the field investigation varies from 3 to 12 m, based on these a groundwater flow map above mean sea level is prepared shown in Figure 3. It can be seen that most of the groundwater flow in the area was westward. In the northern part, the

flow was towards Damsal Nala, whereas in the north-western part the Damsal Nala water seemed to flow in the aquifer towards the village Chirigunia (Rao et. al., 2003).

Groundwater quality

The water samples were collected from the dug wells, tube wells, mine seepage and from Damsal Nala for post-monsoon and pre-monsoon period and analyzed to study the quality of water with special reference to concentration of Cr(VI). The location of samples is shown in Figure 4. The analysis results of post-monsoon and premonsoon samples are given in Table 1 and Table 2. The groundwater has a low total dissolved solids (TDS) ranging from 50 - 507 mg/l. In general the groundwater was found potable with most of the constituents within the permissible limit for drinking water except for very slight high concentration of Cr(VI) found in a few samples of mine seepage and Damsal Nala.

The concentration of Cr(VI) exceeding the permissible limits was detected from few samples of groundwater, surface water and mine water and mine seepage. The Cr(VI) content was high near the ore bodies during post-monsoon and pre-monsoon period and it decreased with distance away from ore body Figure 5a and b. In groundwater samples, the Cr(VI) concentration varies from 0.001 to 0.018 mg/l in dug wells/bore wells. The Cr(VI) concentration in quarry seepage was found to be in the range of 0.01 to 0.421 mg/l which is on the higher side. In Damsal Nala it ranges from 0.03 to 0.07 mg/l in the upstream side whereas it was 0.104 to 0.147 mg/l in the

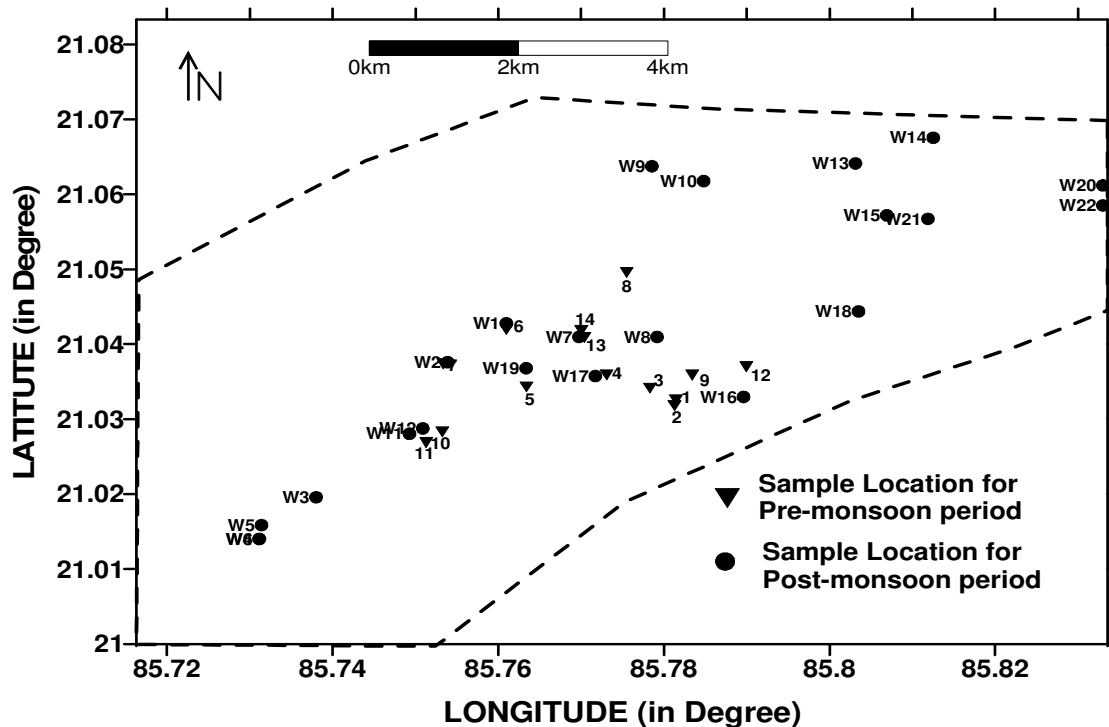


Figure 4. Map showing location of groundwater sample for post and pre-monsoon period.

Table 1. Concentration of pH, EC, TDS, TSS, Fe, Cu and Cr(VI) in Groundwater samples of Sukinda Mine area for post-monsoon period (October – November, 2001)

Sample Code	Parameters (mg/l)					
	pH	TDS	TSS	Fe	Cu	Cr(VI)
W1#	7.6	419	46	0.39	0.016	0.025
W2S#	7.3	386	63	0.41	1.8	0.38
W3#	7.2	421	47	0.54	0.167	0.018
W4#	6.1	309	21	0.29	0.036	0.115
W5#	7.2	215	19	0.21	0.078	0.421
W6\$	6.8	185	15	0.35	0.048	0.049
W7\$	6.8	219	12	0.31	0.03	0.046
W8\$	7.4	310	23	0.29	0.23	0.083
W9#	7.0	419	29	0.28	0.23	0.012
W10*	7.0	507	12	0.18	0.045	0.009
W11*	7.5	422	14	0.21	0.02	0.009
W12*	7.5	305	64	0.24	0.026	0.043
W13*	7.5	232	32	0.27	0.035	0.032
W14*	7.0	386	15	0.34	0.183	0.019

All Parameters are in mg/l except pH

*Groundwater Samples,

#Mine water samples, and

\$Damsal Nala water samples

downstream side; the high concentration of Cr(VI) in Damsal Nala was due to the discharge of mine water and leachate from quarry in the Damsal Nala.

Cross correlation

A cross correlation analysis shown in Table 3a and b was prepared to determine the relation between the various parameters. From these table it is found that there is not strong correlation between any parameters, except between Cr(VI) and Cu shows 60% correlation for postmonsoon samples. Similarly, for pre-monsoon samples shows correlation between Electrical Conductivity (EC) versus Total Suspended Solids (TSS) shows 43% correlation, while TDS and TSS shows 51% correlation, whereas correlation between hardness and alkalinity shows very strong correlation of 96%.

RESULTS AND DISCUSSIONS

Fourteen water samples were collected during post-monsoon period and twenty five water samples for pre-monsoon period were analyzed for various chemical constituents especially Cr(VI), Fe, Cu and Ni using the latest ICP-MS method (Balaram, 2000). The characteristics of the groundwater are presented in Tables 1 and 2. These water samples were found to be nearly neutral to mildly alkaline pH (6.1 - 7.6). The EC of these samples varied from low to moderate (300 - 750 $\mu\text{s}/\text{cm}$) for post-monsoon period, while that for pre-monsoon period (50 - 490 $\mu\text{s}/\text{cm}$). The EC and pH of this water are within the permissible limits of potable water (WHO, 1984). As per the Indian standard the pH permissible limit for drinking water is 6.5 - 8.5 and that of TDS desirable limit is 500

Table 2. Concentration of pH, TSS, TDS, Alkalinity, Hardness, Cr(VI) and Electrical Conductivity (EC) in Groundwater samples of Sukinda Mine area for pre-monsoon period (April, 2002)

Sample Code	Parameters						
	pH	TSS (mg/l)	TDS (mg/l)	Alkalinity (mg/l)	Hardness (mg/l)	Cr(VI) (mg/l)	Electrical Conductivity of water (μ S/cm)
W1*	7.30	35	288			0.032	190
W2*	7.60	23	150	137	150	0.023	210
W3*	6.52	15	111	110	130	0.104	200
W4#	7.49	13	167	68	50	0.043	50
W5#	7.59	14	363	140	170	Nil	190
W6#	7.20	9	30	40	70	Nil	50
W7#	7.06	26	233	72	80	0.057	270
W8#	6.58	29	309	--	--	Nil	490
W9#	7.18	13	105	86	110	0.043	340
W10\$	7.0	29	191	196	210	0.052	290
W11\$	6.62	12	54	72	80	Nil	100
W12\$	6.09	4	35	81	90	Nil	70
W13\$	7.38	21	116	135	150	Nil	150
W14\$	6.87	13	71	49	90	Nil	100
W15\$	7.46	29	152	121	150	Nil	250
W16\$	6.28	28	140	60	90	0.450	110
W17\$	7.41	13	218	41	50	Nil	360
W18\$	6.50	21	187	170	195	Nil	260
W19\$	5.67	26	61	125	140	Nil	50
W20\$	5.88	29	99	59	70	Nil	140
W21\$	6.74	24	369	84	80	Nil	400
W22\$	6.53	34	328	125	130	Nil	370
W23\$	5.96	12	162	185	200	Nil	150
W24\$	5.47	15	123	92	100	Nil	190
W25\$	5.86	28	320	105	120	0.013	320

*Damasal Nala Samples,

#Mine water samples

\$Groundwater samples.

TSS (Total Suspended Solids)

TDS (Total Dissolved Solids)

Cr⁺⁶ (Hexavalent chromium)**Table 3a.** Cross Correlation Matrix of groundwater samples collected during post-monsoon (October - November, 2001).

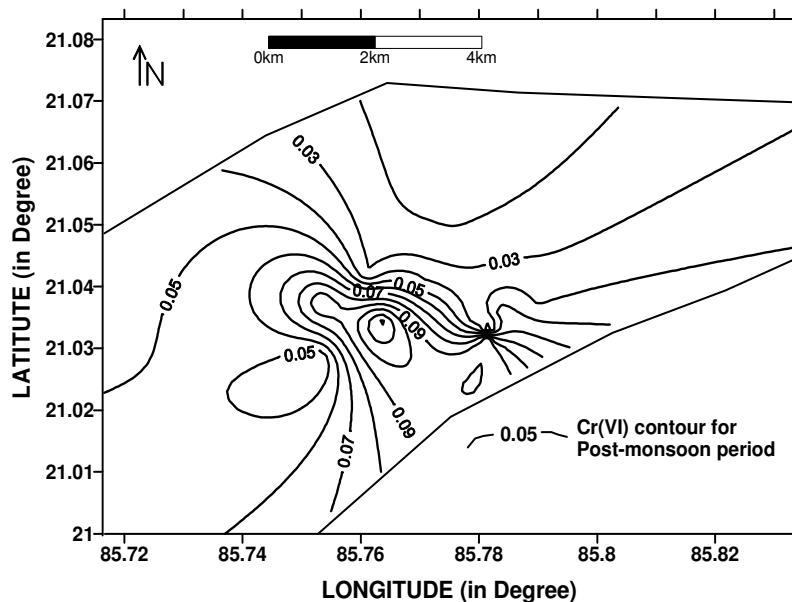
	EC	TDS	pH	TSS	Fe	Cr(VI)	Cu
EC	1.0						
TDS	0.99	1.0					
PH	0.18	0.18	1.0				
TSS	0.16	0.17	0.45	1.0			
Fe	0.1	0.1	0.01	0.45	1.0		
Cr(VI)	-0.29	-0.28	-0.002	0.21	-0.02	1.0	
Cu	0.15	0.17	0.11	0.51	0.35	0.60	1.0

mg/l and permissible range is about 2000 mg/l. The low pH is due to the corrosion and has metallic taste, whereas high pH gives bitter or soda taste. The high TDS is due to livestock waste, landfills, hazardous waste and

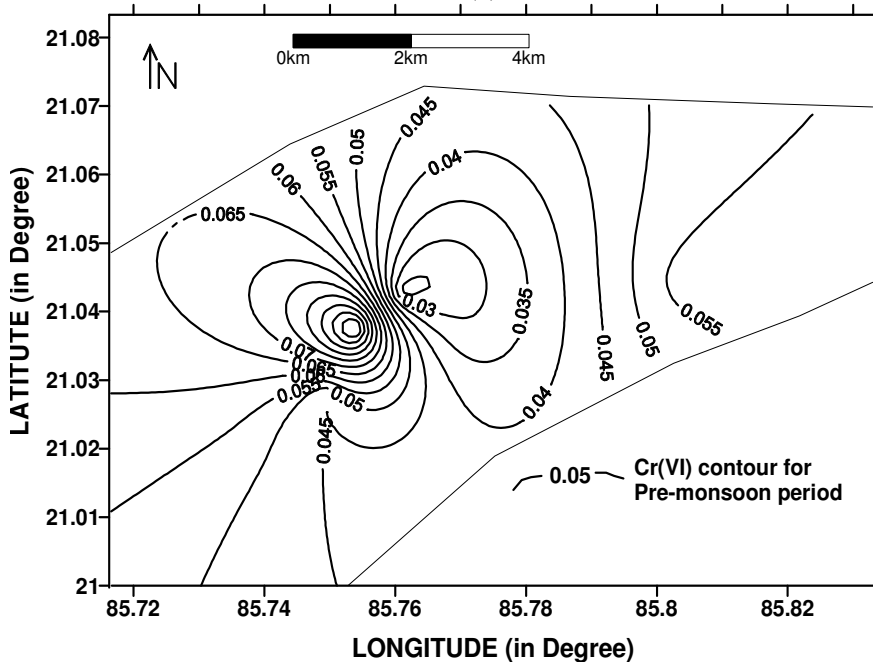
due to dissolve minerals like iron and manganese and give corrosion effects to pipes and fittings. The concentration of total suspended solids (TSS) which plays an important role in the drinking water chemistry is on higher

Table 3b. Cross Correlation Matrix of groundwater samples collected during pre-monsoon (April, 2002).

	pH	EC	TSS	TDS	Alkalinity	Hardness	Cr(VI)
PH	1.0						
EC	0.11	1.0					
TSS	-0.04	0.43	1.0				
TDS	0.18	0.70	0.51	1.0			
Alkalinity	-0.03	0.20	0.28	0.26	1.0		
Hardness	-0.01	0.16	0.25	0.18	0.96	1.0	
Cr(VI)	-0.04	-0.22	-0.25	-0.33	0.06	0.08	1.0



(a)



(b)

Figure 5a and b: Contour pattern for chromium concentration for post-monsoon and pre-monsoon period

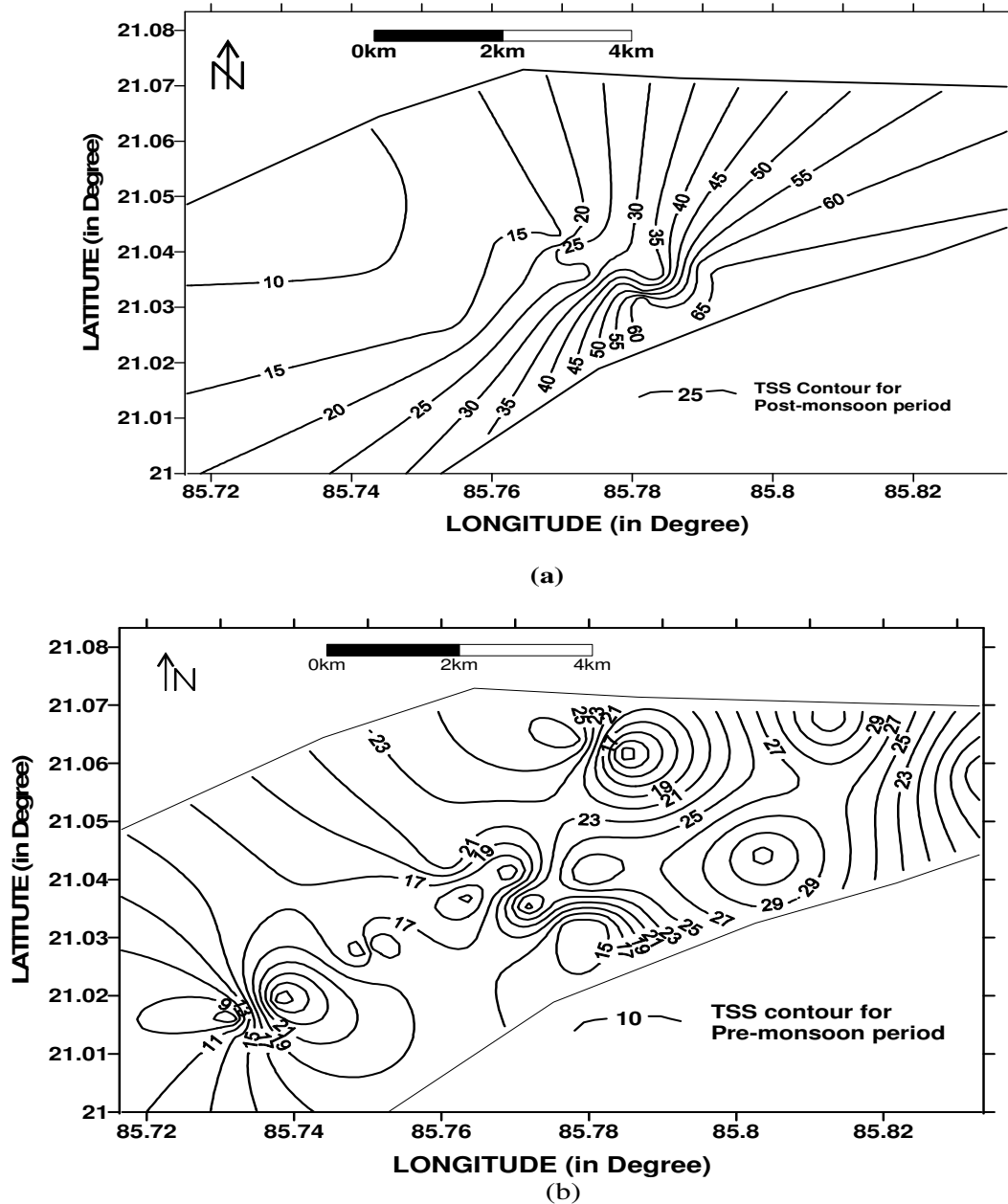


Figure 6a and b. Contour pattern for TSS concentration for post-monsoon and pre-monsoon period.

side and it varies from 12 - 64 mg/l for post-monsoon period and 4 - 35 mg/l for pre-monsoon period, whereas the permissible limits of TSS in potable water is only 10 mg/l. The contour of TSS for post and pre-monsoon period has been drawn for the distribution of TSS in these areas is shown in Figure 6a and b. The high concentration of TSS is may be due to the insolubility of trace element in water and they may be remain in the suspended form. This shows the TSS is comparatively more towards the Southeast direction of mining area and this is further more extended towards Purnapani village. However, the samples were collected from Kaliapani and

South Kaliapani villages which are the main villages of this area have also shown their enrichment of TSS. The high concentration of total suspended solid is more than the permissible limits of potable water (WHO, 1984) is not allowing this for potable use.

The water samples were also analyzed for Fe, cu and Cr(VI) and their results are shown in Table 1 and 2. These tables clearly shows that the water samples are within the permissible limit, Fe concentration is more in the groundwater samples as well as in the Damsal Nala samples due to the top lateritic soil cover which itself is of ferruginous nature. The desirable limit of Fe is 0.3 mg/l

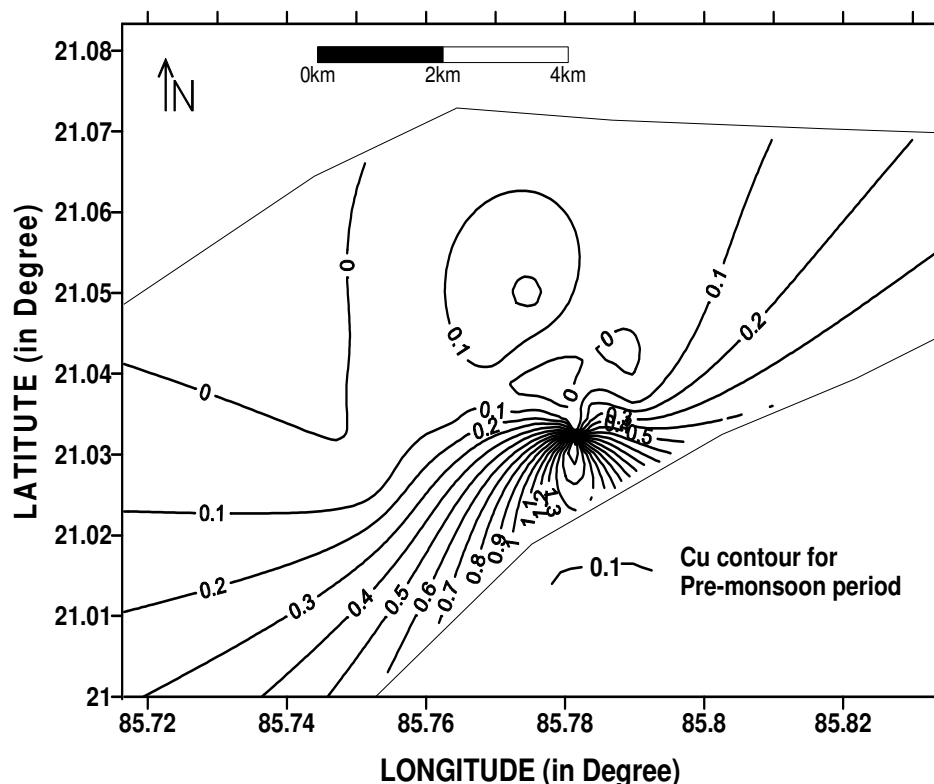


Figure 7. Contour pattern of Copper concentration for post-monsoon period.

and maximum permissible limit is 1.0 mg/l as per Indian standards. If water content more than these limit gives brackish color and bitter or metallic taste, therefore if Fe content is more than these limit would be rejected for drinking purposes. Concentrations of Cu varies from 0.016 to 1.8 mg/l and indicates that 43% samples have more than permissible limit of Cu (<0.05 mg/l). As per the Indian standards the desirable limit of Cu is 0.05 mg/l and permissible limit is 1.5 mg/l, the high concentration of Cu in water causes digestive disturbance, liver and kidney damage and the source is industrial or mining waste, due to this if Cu content is more in water would be rejected for drinking purpose. Copper concentration contours have been drawn and shown in Figure 7. This figure clearly shows the presence of higher contents of Cu in groundwater close to the chromite mining area for the post-monsoon period. The influence of Cu, in the areas such as Chirigunia, Kaliapani and South Kaliapani villages which are close to Damsal Nala have found to be less contaminated during the post-monsoon samples.

Similarly, the Cr contents also varies from 0.001 to 0.38 mg/l for post-monsoon period and about 28% of total samples have been found more than permissible limit of Cr (<0.05 mg/l), in potable water (WHO, 1984), and 0.013 to 0.450 mg/l for pre-monsoon period. The maximum permissible limit of Cr(VI) in water is 0.05 mg/l, if water content than this limit gives skin irritation, skin and nasal ulcers, lung tumors, damage to nervous system and cir-

culatory system and kidney and liver cancer and the source of this constituents is through septic system or industrial or mining discharge. Cr(VI) contour as in Figure 6a and b, clearly indicate the enrichment of Cr in groundwater in various parts of the Sukinda mine area. High level of Cr(VI) is observed close to Chirigunia and Bhimtanagar villages areas which are within the 2 sq.km radius of chromite mining area. In addition to this, the other parts of the mining area close to Purnapani village 2.5 km East of chromite mine are also more or less influenced by Cr(VI) contamination during the first season of samples and for second seasons it is more towards Damsal Nala.

Conclusions

High level of TSS, Cu, Fe and Cr in groundwater indicated the unsuitability of most of these water samples for potable purposes. The villages like Purnapani, Kaliapani, South Kaliapani are more influenced by total suspended solids (TSS) in groundwater and require proper filtration process, prior to use for potable purposes. The ultramafic formation has been highly weathered and metamorphosed giving limonite, chert and laterite. The laterite occur as capping with variable thickness over all formations, which has very low permeability. As the groundwater quality is concerned, the polluted seepage water from mine should not be allowed to spread over the cultivated

or open areas, it should be suitably treated to reduce the Cr(VI) to Cr(III) and then may be discharge to Damsal Nala or may be utilized for industrial or other needs to avoid any future pollution in the area. Dissociation and dissolution of metallic trace elements in particular Cr have been taken place simultaneously with dilution process. For the pre-monsoon period the samples taken in downstream of Damsal Nala shows the high concentration of metallic trace element.

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