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ECOLOGICAL RISK ASSESSMENT THROUGH METAL MOBILITY IN DAMSAL NALA, SUKINDA CHROMITE VALLEY OF INDIA

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ABSTRACT

Damsal Nala, passing through the Sukinda chromite valley, Jajpur of Odisha is carrying the drainage from adjacent mines. Present work estimated the concentration of As, Cd, Cr, Cu, Fe, and Pb, by EDXRF and FAAS from bottom sediments and water samples of different zones of the Damsal Nala. The concentrations of Cd, Cr, Fe, and Pb in UDZ sediments were about 13, 522, 6, and 2 times higher, respectively, than the Indian average values and the concentration were to the tune of Fe>Cr>Cu>Pb>As>Cd. The potential ecological risk assessment (E_r^i and R_I) of sediments of UDZ and downstream zone (DZ) showed a severe risk of Cd and Cr, compared to other sites, which may finally lead to severe risk assessment to human health. These lesions indicated that the mining effluents and leachates not only affect the ecological balance but may also pose health hazards to the local human population.

KEY WORDS : Heavy metals, Potential ecological risk, Chromite mine

INTRODUCTION

In this modern era production of metals increases to cater to the rising needs of human well-being. Metal and mining industries are releasing a large amount of metal ions in the environment and causing their long term accumulation, which is a major concern for potential environmental hazards as well as posing serious health hazards to the exposed human population (Banerjee *et al*., 2016; Naz *et al*., 2016). Mining activities produce a large number of overburden materials consisting of different types of metal ions. Among them, chromium (Cr) is the most abundant one, produced from chromite mines. It is used in various industrial process, *i.e*., tannery, steel alloy, rustproof chrome-plating, dyes, glass manufacture, and paints industries (Das and Singh, 2011; Dutta, 2015; Godgul and Sahu, 1995; Saha *et al.,* 2017). Demand is increasing by the day and the production of Cr has jumped to 0.34 million tons yearly in 2011 from 2009 (IBM, 2012). Sukinda Chromite Valley in Jajpur district of Odisha, accounts for 98% of chromite ore ($FeO.Cr_2O_3$ or $FeCr_2O_4$) deposits of India (Das and Mishra, 2010; Naz *et al*., 2016). So, the huge overburden and subsequent drainage of mining residues contain various metallic ions like Fe, Cr, Ni, Cu, Zn, Pb, As, and Cd, which contaminate our environment (Iyer and Mastorakis, 2010; Mohapatra and Kirpalani, 2017; Rashed, 2010; Saha *et al*., 2017). These metallic ions are harmful to the natural environment because of bioaccumulation and biomagnification (Das and Singh, 2011; Madejón *et al*., 2002; Madejón e*t al*., 2006). Damsal Nala crossing across the Sukinda Chromite Valley carrying most of the drainage from adjacent mines and is polluting the surroundings, including water bodies (Dutta, 2015; Iyer and Mastorakis, 2010). The leaches and drainage containing a huge load of heavy metals cause accumulation in the surrounding habitats, which may lead to acute or chronic deformities in the living body, and finally pose potential threats to human health (Banerjee *et al.*, 2016; Kole *et al.*, 2016; Kumar and Maiti, 2015; Zhang *et al.*, 2016).

In the present study, we intended to find out the magnitude of heavy metal accumulation in water and sediment of Damsal Nala, to calculate the most probable ecological impacts, in the tune of potential ecological risk assessment of Damsal Nala.

MATERIALS AND METHODS

Study area

Sukinda Chromite mine belt of Jajpur district, Odisha (India), was selected to measure the effects and ecological impact of Cr and other associated toxic metals in the different zones of Damsal Nala. The geographical position of the study area (Fig. 1) is within latitudes $21^0 25'$ and $21^0 45'$ and longitudes $85^0 46'2''$ and $85^0 5'8''$. The Damsal Nala carries the total runoff of the adjacent mining and it is also a source of water for agriculture and surrounding residents.

Sample collection

A total of thirty-three samples, from the bottom sediment and water, were collected from eleven sites (three from each site). The sites were named as S1 to S11 of three different zones of Damsal Nala - named as upstream zone (UZ) or without mining drainage zone (as S1 to S3), upstream discharge zone (UDZ) or effluent discharge zone (as S4 to S6), and downstream zone (DZ) or far from discharge zone (as S7 to S11). The present study was conducted during 2018-2019.

Sample preparation

Air-dried, finely grinded (80 µm) bottom sediments were made into pellets of 13 mm diameter using a tabletop palletized (100-130 kg/cm^2) for elemental analysis by EDXRF (Energy Dispersive X-Ray Fluorescence) for elemental assessment *via* FAAS (Flame Atomic Absorption Spectroscopy). All samples were acid digested using concentrated HCl, HNO_3, and $HClO_4$. For bottom sediment and water samples digestion was carried out on hot plate evaporator in 4:2:1 ratio of HCl, HNO_3, and $HClO_4$.

Analytical techniques

Elemental analyses of the collected samples were carried out using two commonly used atomic techniques, namely EDXRF and FAAS. Analytical Grade chemicals from Merck were used for the experiments.

Potential ecological risk assessment

Pollution indices seem to be the most suitable tools to calculate the degree of metal contamination and the most probable potential risk caused by metals in a water-sediment system. The potential ecological risk (R_I) is used to evaluate the toxicity of the metal in the sediment and it is developed by (Hakanson, 1980). The potential ecological risk, R_I of multi-elements in sediment and water can be computed by equations (1), (2), and(3),

$$C_f^i = \frac{C_n^i}{C_0^i} \quad .. (1)$$

$$E_r^i = T_r^i \times C_f^i \quad .. (2)$$

$$R_I = \sum E_r^i \quad .. (3)$$

Where, C_f^i is the contamination factor for the *i*th element; C_n^i is the concentration of the *i*th element in the medium; C_0^i is the concentration of *i*th metal in the water/sediment by upper permissible value or its background value (Indian average value and Shale value is As:10:13, Cd:0.3:0.3, Cr:87:90, Fe:29000, Cu:28:45, Pb:11.2:20 mg/kg)(Patel *et al.*, 2018; Singh *et al.*, 2017); T_r^i represents the toxic response factor for *i*th substance, which accounts for toxic and sensitivity response. Jia *et al.* (2018) recorded the toxic response factor against some metals like As, Cd, Cr, Cu, Pb were 10, 30, 2, 5, and 5 respectively (Jia *et al.*, 2018). The value less than '<1' will not be considered for R_I calculation. is the sum of all risk factors for elements in sediments/ water.

According to Hakanson and Soliman *et al.* (Hakanson, 1980; Soliman *et al.*, 2015), the gradation and degree of toxicity levels of, E_r, R_I are as follows: E_r <40; R_I<150: Low risk; 40<$E_r \leq$ 80; 150<R_I<300: Moderate risk; 80<$E_r \leq$ 160; 300<R_I<600: High risk; 160 < $E_r \leq$ 320; $R_I \geq$ 600: Very high risk; E_r > 320: Disastrous risk.

Statistical analysis

The results of estimated metallic concentration were calculated using the SPSS program v.16.0. to obtain Mean and standard deviation. Analysis of ANOVA-one way at two trial and Tukey test of the respective tables, *viz*, metal concentration present in bottom sediment, and surface water ware also done.

RESULTS AND DISCUSSION

Distribution of metal concentrations in bottom sediments of Damsal Nala

The concentration of metals present in the bottom sediments is presented in Table 1. The results were compared with average Indian values for metal concentrations in sediment (Patel *et al.*, 2018; Subramanian, 1987) and the average concentrations of metals in shale (Rizwan *et al.*, 2016; Turekian and Wedepohl, 1961). The average concentrations of metals like As, Cd, Cr, Cu, Fe, and Pb present in the sediment of UZ were as follows:0.362±0.153, 2.848±0.818, 10244.305±1972.918, 23.272±1.534, 72443.080±28752.207, and 23.398±1.278 mg/kg, respectively. The concentrations of As, Cu, and Pb were lower than the Indian average value and shale value, whereas, the concentrations of Cr, Fe, and Cd were higher than the average values; these were in the order of Fe>Cr>Pb> Cu>Cd>As in UZ. In UDZ, the concentrations of As, Cd, Cr, Cu, Fe, and Pb were 4.170±0.687, 3.980±0.325, 47065.593 ± 7327.727, 26.763±2.783, 181662.408±3089.615, and 21.378±2.165 respectively. All these metals except As and Cu were beyond the Indian average value and shale value (Patel *et al.*, 2018; Singh *et al.*, 2017) and the concentrations of Cd, Cr, Fe, and Pb were about 13, 522, 6, and 2 times higher, respectively, than the Indian average value. Metals' concentration in UDZ sediments were to the tune of Fe>Cr>Cu> Pb>As>Cd. Site S4, the effluent discharge site, displayed the highest metallic load, i.e., Cr, which was nearest to the mines, was 619 times higher.

In the DZ, the distribution of the metals displayed a similar trend but in the reduced form, where it was observed that the concentration was reduced gradually as the distance increased, but Cr, Cd, and Fe concentrations were seriously high. This decreasing trend of metallic constituents was also recorded by many researchers (Rashed, 2010; Samanta *et al*., 2018). It can be inferred that a huge load of metals in sediments are due to the direct drainage of mines, leaches from overburden, and/or from bedrocks, and they are contaminating the underground water also (Krishna *et al.*, 2013; Mohanty *et al.*, 2005; Naz *et al*., 2018).

Physicochemical characterization of surface water from Damsal Nala

The physicochemical characteristics of the water samples of different zones of Damsal Nala are summarized in Table 1 and compared with the inland surface water as per Indian standards (Bureau of Indian Standards, 2003). pH of the water throughout the Nala varied between 8.43 and 5.51, EC between 212.70 and 116.6 µS/cm, total dissolved solids ranged between 143 and 80.9 mg/l, and dissolved O_2 concentration varied from 7.1 to 8.1 during the experimental period (2018-'19). In UZ, the concentration of the metals, such as, As, Cd, Cr, and Fe were as follows: 0.017±0.009, 0.171±0.025, 0.110±0.027, and 1.595±0.305 mg/l, respectively. In

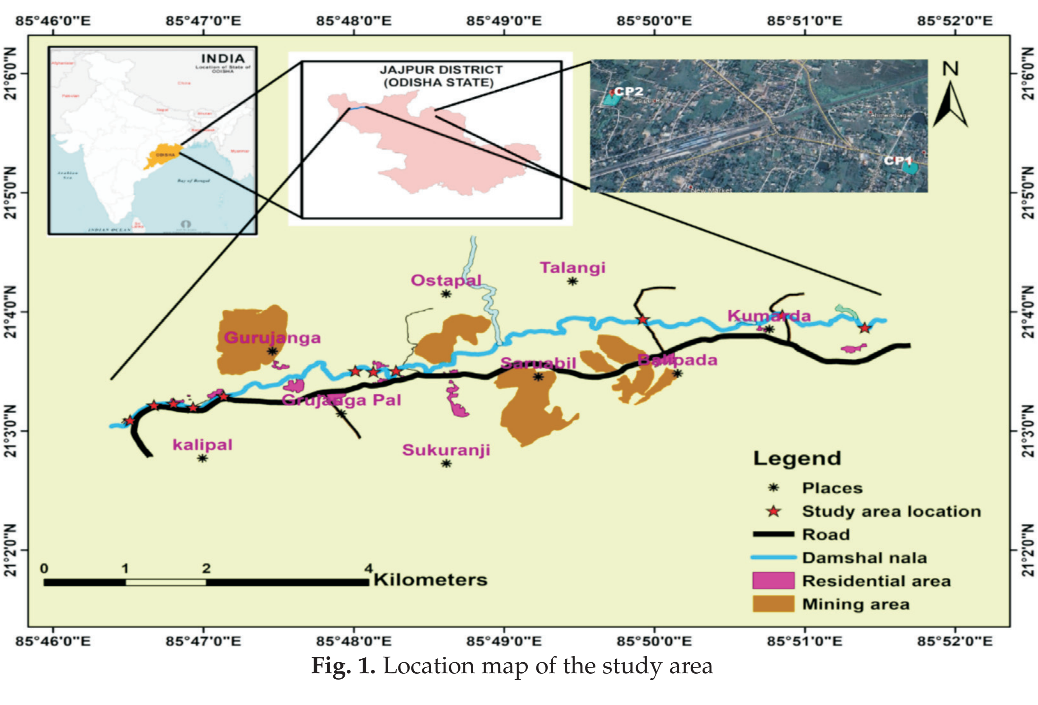

Fig. 1. Location map of the study area

Table 1. Metal concentration in bottom sediments (mg/kg) and physicochemical properties of surface water of Damsal Nala

Bottom Sediments Elements	UZ			UDZ			DZ					IAV	SV
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11		
As	0.21 ± 0.01^{a}	0.36 ± 0.01^{a}	0.52 ± 0.02^{a}	3.52 ± 0.06^{b}	4.11 ± 0.05^{b}	4.885 ± 0.05^{b}	2.63 ± 0.01^{ab}	2.03 ± 0.03^{ab}	1.56 ± 0.02^{ab}	1.42 ± 0.01^{ab}	1.43 ± 0.05^{ab}	10	13
Cd	2.03 ± 0.01^{a}	2.85 ± 0.09^{a}	3.665 ± 0.1^{ab}	4.30 ± 0.01^{b}	3.99 ± 0.11^{b}	3.650 ± 0.14^{ab}	3.66 ± 0.05^{ab}	3.64 ± 0.05^{ab}	3.74 ± 0.02^{ab}	3.91 ± 0.08^{b}	4.13 ± 0.07^{b}	0.3	0.3
Cr	8395.24 ± 176.11^{a}	12321.28 ± 311.34^{a}	10016.395 ± 311.23^{a}	53862.45 ± 223.21^{d}	48031.53 ± 526.99^{d}	39302.805 ± 199.24^{cd}	38388.68 ± 151.51^{cd}	25177.01 ± 439.66^{bc}	15825.13 ± 121.05^{ab}	19540.83 ± 552.72^{b}	30661.10 ± 218.02^{c}	87	90
Cu	24.88 ± 0.08^{bc}	23.11 ± 0.09^{bc}	21.825 ± 0.21^{b}	23.83 ± 0.12^{b}	27.11 ± 0.11^{c}	29.360 ± 0.35^{c}	10.13 ± 0.23^{a}	12.13 ± 0.12^{a}	14.94 ± 0.12^{b}	19.33 ± 0.19^{ab}	22.56 ± 0.14^{b}	28	45
Fe	43638.79 ± 771.2^{a}	72547.54 ± 1777.76^{ab}	101142.915 ± 940.86^{b}	180142.07 ± 1862.34^{d}	179627.56 ± 2512.70^{cd}	185217.600 ± 1469.93^{d}	151575.70 ± 3403.30^{bc}	130817.05 ± 1328.58^{bc}	109837.45 ± 1365.35^{b}	172111.44 ± 868.11^{cd}	173717.50 ± 1074.10^{cd}	-	29000
Pb	21.96 ± 0.98^{a}	23.86 ± 4.74^{a}	24.385 ± 1.73^{a}	19.13 ± 0.88^{a}	21.56 ± 5.54^{a}	23.450 ± 0.41^{a}	14.81 ± 1.28^{a}	18.16 ± 5.16^{a}	22.39 ± 1.60^{a}	19.59 ± 0.58^{a}	17.59 ± 1.34^{a}	11.2	20
Surface Water												IBS	
pH	5.51 ± 0.45^{a}	5.69 ± 0.31^{a}	5.76 ± 0.31^{a}	6.72 ± 0.55^{ab}	6.76 ± 0.55^{ab}	6.89 ± 0.56^{ab}	7.26 ± 0.69^{b}	7.14 ± 0.69^{b}	7.34 ± 0.7^{bc}	7.74 ± 0.7^{bc}	8.43 ± 0.75^{c}	5.5-9.0	
EC	116.60 ± 1.65^{a}	125.70 ± 1.21^{a}	130.10 ± 1.30^{a}	212.70 ± 2.12^{b}	203.00 ± 2.12^{b}	201.00 ± 2.11	168.40 ± 1.61^{ab}	159.00 ± 1.60^{ab}	149.20 ± 1.45^{a}	138.90 ± 1.40^{a}	129.70 ± 1.29^{a}	-	
TDS	$80.90\pm.89^{a}$	82.70 ± 0.88^{a}	90.10 ± 0.89^{a}	143.00 ± 1.41^{c}	137.20 ± 1.33^{bc}	130.00 ± 1.33^{b}	124.51 ± 1.11^{b}	119.40 ± 1.12^{ab}	113.00 ± 1.11^{ab}	104.00 ± 1.0^{ab}	102.50 ± 1.01^{ab}	2100	
DO	7.90 ± 0.71^{a}	8.10 ± 0.81^{a}	8.00 ± 0.81^{a}	$7.90\pm0..65^{a}$	8.00 ± 0.71^{a}	8.10 ± 0.82^{a}	7.40 ± 0.71^{a}	7.10 ± 0.71^{a}	8.10 ± 0.79^{a}	8.00 ± 0.79^{a}	8.10 ± 0.79^{a}	-	
As	0.01 ± 0.00^{a}	0.02 ± 0.002^{a}	0.02 ± 0.006^{a}	0.01 ± 0.001^{a}	0.01 ± 0.000^{a}	0.01 ± 0.001^{a}	0.01 ± 0.001^{a}	0.01 ± 0.001^{a}	0.02 ± 0.001^{a}	0.01 ± 0.001^{a}	0.01 ± 0.001^{a}	0.2	
Cd	0.16 ± 0.00^{ab}	0.20 ± 0.010^{c}	0.16 ± 0.039^{ab}	0.06 ± 0.026^{a}	0.15 ± 0.007^{ab}	0.20 ± 0.003^{c}	0.12 ± 0.003^{ab}	0.18 ± 0.001^{b}	0.18 ± 0.001^{b}	0.17 ± 0.002^{b}	0.19 ± 0.004^{bc}	2	
Cr	0.09 ± 0.00^{a}	0.10 ± 0.000^{a}	0.14 ± 0.069	0.26 ± 0.005^{c}	0.20 ± 0.004^{bc}	0.18 ± 0.014^{b}	0.10 ± 0.007^{ab}	0.09 ± 0.003^{a}	0.07 ± 0.007^{a}	0.05 ± 0.005^{a}	0.05 ± 0.008^{a}	0.1	
Fe	1.30 ± 0.05^{a}	1.57 ± 0.023^{a}	1.91 ± 0.077^{a}	7.25 ± 0.369^{c}	5.42 ± 0.226^{c}	3.52 ± 0.376^{bc}	3.52 ± 0.070^{bc}	3.17 ± 0.014^{bc}	2.62 ± 0.071^{ab}	2.46 ± 0.040^{ab}	2.23 ± 0.037^{ab}	3	

The metal concentration, Indian average value (ISV) and Shale value (SV) for bottom sediments (Patel et al. 2018; Singh et al. 2017) are in mg/kg; All units for water parameter are in mg/l except EC, EC in µS/cm and the standard follows IB Standards for inland surface water (Bureau of Indian Standards, 2003); Different letters indicated significant differences ($p < 0.05$) of the parameters between each site based on Tukey's HSD test.

this zone, all the metals were below and/or equal to the standard levels. In UDZ, the concentrations of Cr and Fe were much higher (0.213±0.042 and 5.392±1.864 mg/l, respectively) than the permissible limit, especially at site S4, the concentrations of Cr and Fe were about 3 and 2 times higher respectively than the standard values. In the DZ, the concentrations reduced gradually, as recorded in bottom sediments (0.011±0.003, 0.167±0.025, 0.071±0.019, and 2.797±0.529 for the metals of As, Cd, Cr, and Fe respectively) and were below the standard values (Table 1).

In comparison with IS standard, all those limnological parameters were under the permissible limit, which inferred that this water quality maintains a permissible limit, but the metallic concentrations are posing an alarming risk. The metallic constituents revealed the influence of mine drainage and leachates from mines and overburden because site S4 had the highest load of Cr and Fe as it is situated nearest to the discharge zone (Dutta, 2015; Rashed, 2010). The reduction of concentrations of metals in the downstream zone as distance increases, and the higher concentrations in the bottom sediments despite the deposition of metals and their accumulation, were higher in the sediments. Similar results were also recorded by various workers in their study (Banerjee *et al*., 2016; Chindah *et al.*, 2009; Giri and Singh, 2015; Ma *et al.*, 2016; Pandey and Singh, 2017; Patel *et al*., 2018; Peng *et al*., 2008).

Potential ecological risk of sediment

The potential ecological risk indices and for each site of Damsal Nala (Fig. 2) were obtained by using equations 5 to 7. According to the data set, Cd and Cr posed a serious ecological risk at all the sites of Damsal Nala. values of these two heavy metals were very high, more than 320 in UDZ and DZ, especially in UDZ, and the of Cr were much higher. So, according to the index, these two metals posed potential 'Disastrous risk' to the ecosystem. The value decreases in DZ but not to less than 320. The illustrates, the potential ecological risk caused by multiple heavy metals in an area. In the current study, values in the UDZ and DZ were in an average of 1497.49 and 1130.83, respectively, which were very high (more than 600). That means these zones possess a very high potential of ecological risks of heavy metals, which are a result of the mining activity (Nargis *et al.*, 2019; Aklima Nargis *et al.*, 2020; Pobi *et al.*, 2019; Samanta *et al.*, 2018). The values of different sites were clearly related to the degrees of anthropogenic disturbances.

CONCLUSION

The present study ascribed that the upstream discharge zone was significantly contaminated with a higher concentration of metals like Cr and Fe in water; and high metallic load of Cd, Cr, Fe, and Pb was observed in the bottom sediments. The present study also suggested, that values of Cr and Cd were very high in UDZ and DZ, so, it can cause potential 'Disastrous risk' to the ecosystem due to mining drainage and the leachates from overburden. These lesions strongly support the ecological impact of heavy metals coming from mining activity on the aquatic ecosystem and its habitat. So, judicial strategic management plan, like easy and potential phytoremediation techniques, *i.e.*, addition of locally available aquatic weeds to minimize the metallic load from the mine drainage, may be adopted to prevent possible health hazards to different life forms, including humans.

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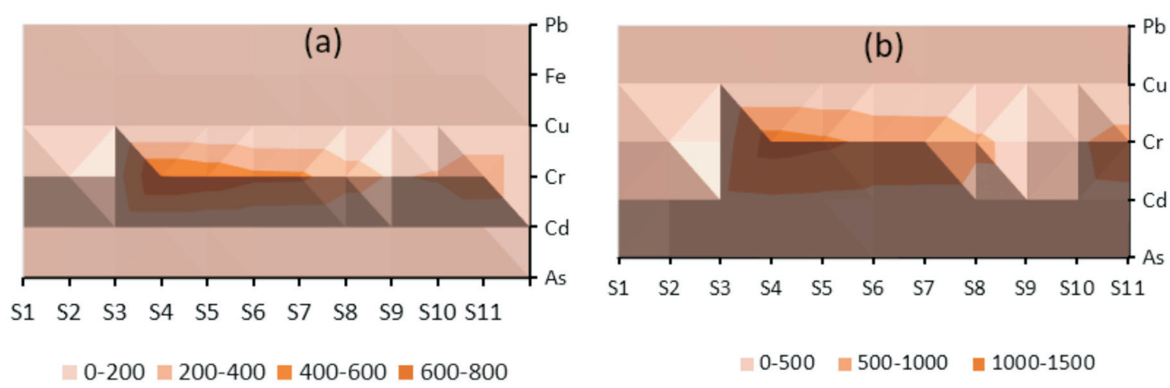

Fig. 2. Potential ecological risk indices (a) and (b) of heavy metals in sediment samples

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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