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Fluctuations in soil contaminations due to monsoon effect –A case study in the Iron Ore Belt of Bolani, Keonjhar district, Odisha, India

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Abstract
Soils in most part of the world are contaminated by anthropogenic activity such as mining, industrial activities. Hence, geochemical monitoring of such soils are necessary for both pre-monsoon and post-monsoon. Bolani and Barbil are well known for mining and industrial activities. Soil samples of both pre-monsoon and post-monsoon were collected from these localities for geochemical assessment with this purpose. Finer fractions (<74 mm) of soils were taken for metal analysis in Atomic Absorption Spectrophotometer. Discriminant analysis on normalized major and trace element data was carried out. Discriminant analysis reveal that the soils of pre-monsoon and post-monsoon are different indicating more contamination in post-monsoon.

Keywords: Geochemistry, soil, pre-monsoon, post-monsoon, discriminant analysis, bolani and barbil

1. Introduction
Soil is the ultimate and most important sink of chemical components in the terrestrial environment (Adriano, 1986; Forstner, 1986) [1, 9]. Several investigations carried out on soils (Bullock and Bell, 1997; Clark *et al.*, 2001; Hren *et al.*, 2001; Krishna and Govil, 2005; Upadhyay *et al.*, 2006; Yuce *et al.*, 2006) [4, 10, 12, 18, 19, 7] reveal that the soils and the sediments of the nearby mining area are severely contaminated by metals in most part of the world. Again, several studies (Nair *et al.*, 1990; Bodo, 1989; and Ansari *et al.*, 2000) [14, 2] reveal that rainfall in the upland regions increases the metal load in lower regions. Ansari *et al.* (2000) [2] recorded higher load of metal pollutants in the sediments and soils of Ganga plain after monsoon. Hence, it is necessary to carryout study of metal load in soils in pre- and post-monsoon periods.

2. Study Area
The present study area (Fig.1) lies in Bolani and Barbil of Keonjhar district, Orissa. between 22º 3'N to 22º 8'N latitude and 85º 18'E to 85º 25'E longitudes falling in the Survey of India toposheet No.73F/8. The climate of the district is tropical to sub-tropical with hot summer, high and well distributed rainfall during the monsoon. The areas are known for their iron and manganese ore deposits. Rocks of the area belong to Iron Ore Group (IOG) comprising mainly Banded Iron Formation (BIF) and associated volcano-sedimentary rocks. The Banded Iron Formation more or less circumscribes the Singhbhum granite batholith. BIF occurrences in Joda-Barbil-Noamundi, Gorumahisani, Daitari are rich in iron ore deposits. The BIF occurs in the form of iron minerals and silica bands. The iron-rich bands mainly comprise hematite, martite, magnetite, specularite and goethite, where as silica-rich bands consist of quartz or jasper (Chakraborty and Majumdar, 1986 and 2002) [5, 6]. The other rock types of the area include shale (with / without Mn-ores), phyllite, tuff, dolomite, mafic lavas. The dolomites of the area are associated with shales.

3. Materials and Methods
3.1 Metal Analysis: Soil samples were collected from 27 locations (Fig.1) during pre- and post-monsoon periods covering the Bolani and Barbil region during 2012-14. From each location about 4kg sample was collected in polythene packet. Then, the samples were dried and sieved. Coarse materials were removed. One gram of <74µm size fraction was taken for metal analysis.

One gram of soil was treated with concentrated acid, dissolved in a closed system. About 25ml of aqua-regia (3 parts HNO_3 and 1 part HCl) was used for dissolution. The reduced volume of the sample solution was then treated with HNO_3 and $HClO_4$ acids in 1:1 proportion and again concentrated to minimum volume. The solution was then extracted with distilled water and the volume was made to 250 ml. The sample solution was then aspirated into atomic absorption spectrophotometer (Perkin Elmer-3100) under optimum operational conditions to measure the concentration of different elements such as Ca, Na, K, Mg, Fe, Mn, Co, Zn, Ni, Cd, Pb, Cr and Cu.

3.2 Multivariate Discriminant Analysis

The soil geochemistry data were processed through statistical technique such as discriminant analysis to differentiate the geochemical soil characteristics of pre- and post-monsoon soils. Prior to the statistical analysis the data were normalized by the transform log[C/(1-C)] for major elements, and log (c) for trace elements, where ‘c’ is the weight fraction of the elements (Kaiser, 1958; Davis, 1986; Ratha and Sahu, 1993) [8, 15, 11]. In order to distinguish the pre-monsoon and post-monsoon impacts for pollution, the discriminant analysis was applied to the normalized major and trace element data of soils.

In discriminant analysis observations may be taken from any of $g \geq 2$ populations or groups. It involves deriving the linear combination of the two (or more) independent variables that will discriminate best between the defined groups. This is achieved by the statistical decision rule of maximizing between the group variance relative to within group variance and is expressed as the ratio of between groups to within group variance. The linear combinations for a discriminant analysis are derived from an equation (linear discriminant function) that takes the following form,

$$R = W_1Z_1+W_2Z_2+ \ldots\ldots\ldots\ldots + W_nZ_n$$

Where, Z = the independent variables; W = the discriminant weights

R = the discriminant score

Thus, a simple linear discriminant function transforms an original set of measurements on a sample into a single discriminant score. By averaging the discriminant scores for all observations within a particular group, group mean can be calculated. The test for the statistical significance of the discriminant function is a generalized measure of the distance (Mahalanobis distance, D^2) between the group means. It is computed by the following formula,

$$D^2 = w_1d_1+w_2d_2+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots+w_nd_n$$

Where, $d_j = \bar{a}_j - \bar{u}_j$

$\bar{a}_j$ = mean of variable j in group-1; $\bar{u}_j$ = mean of variable j in group-2.

Finally, the calculated discriminant scores for both the groups can be plotted along the discriminant function line and the discriminant index ‘R0’ can be obtained which is the point along the discriminant function line exactly halfway between the center of group-1 (R1; pre-monsoon data) and the center of group-2 (R2; post-monsoon data). If the overlap in the distribution is small, the discriminant function separates the groups well. In case of overlapping, misclassification error has to be calculated (Davis, 1986) [8].

Discriminant analysis has been carried out by Ratha et al. (1994) [16], Ratha (1997) [17] to know the variation in chemical concentration of different group of samples in soil.

4. Result and Discussion

4.1. Metal geochemistry of soils

Pre- and post- monsoon soil samples from Bolani and Barbil were analysed for 13 different elements such as Ca, Na, K, Mg, Fe, Mn, Co, Zn, Ni, Cd, Pb, Cr and Cu. The range and mean of these elements were summarized in Table-1. The generated data have been used for discriminant analysis.

Range of values for various metal constituents in pre-monsoon are Ca 20-1130 µg/g, Mg 480-2050 µg/g, Na 300-24500 µg/g, K 500-6500 µg/g, Fe 3.35-48.03%, Mn 0.001-2.67%, Cu 30-185 µg/g , Zn 3-235 µg/g , Ni 8-1025 µg/g, Co 4-178 µg/g, Cr 70-260 µg/g , Pb 15-120 µg/g, Cd 1-120 µg/g. Range of values for various metal constituents in post-monsoon samples are: Ca 10-1420µg/g, Mg 250 - 6750 µg/g, Na 130 - 4200 µg/g, K 267 - 23500 µg/g, Fe 2.12-60.87%, Mn 0.001-10.18%, Co 4-180 µg/g, Zn 3-260µg/g, Ni 8-1025 µg/g, Cd 1-160µg/g, Pb 5-120µg/g, Cr 65-1200 µg/g and Cu 18-230µg/g.

It is observed that iron, manganese, chromium, cobalt, lead and cadmium are higher in most of the samples than world averages. Also, chromium, cobalt, lead and cadmium are more than the thresh hold values of potentially toxic metals prescribed by world Health Organisation (WHO, 1996).

It seems fluvial geomorphic processes play important role for enrichment of heavy metals in post-monsoon soils.

Table 1: The range and mean values of metal constituents in soil, Bolani and Barbil.

Premonsoon				
	Bolani (n=12)		**Barbil (n=15)**	
Metals	Range	Mean	Range	Mean
Fe (%)	5.03-48.03	16.24	3.35-25.13	10.40
Mn (%)	0.065-0.483	0.154	0.001-2.670	0.265
Ca (ppm)	20-1130	498	72-800	316
Mg (ppm)	480-2050	1196	3250-11500	7833
Na (ppm)	300-24500	5459	300-3000	1119
K (ppm)	500-5000	2908	1750-6500	3877
Cu (ppm)	48-100	74	30-185	61
Zn (ppm)	55-230	124	3-235	80
Ni (ppm)	38-105	75	8-1025	147
Co (ppm)	53-160	99	4-178	38
Cr (ppm)	100-230	173	70-260	143
Pb (ppm)	15-25	16	15-120	41
Cd (ppm)	2-120	12	1-2	1
Postmonsoon				
	Bolani (n=12)		Barbil (n=15)	
Metals	Range	Mean	Range	Mean
Fe (%)	10.61-60.87	28.18	2.12-37.50	12.86
Mn (%)	0.05-0.8	0.195	0.021-10.180	1.569
Ca (ppm)	40-900	502	10-1420	647
Mg (ppm)	600-5900	3764	250-6750	2402
Na (ppm)	140-2300	493	130-4200	1693
K (ppm)	267-9500	4732	1170-23500	8135
Cu (ppm)	28-80	54	18-140	73
Zn (ppm)	40-120	73	58-260	100
Ni (ppm)	140-260	175	20-440	117
Co (ppm)	80-180	115	13-120	55
Cr (ppm)	200-1200	563	65-970	231
Pb (ppm)	5-40	14	7-90	32
Cd (ppm)	140-160	149	1-7	3

4.2 Multivariate discriminant analysis

Both pre and post-monsoon soil samples were subjected to discriminant analysis (Table-2 and Fig.2). The D^2 values in case of pre-monsoon soil data versus post-monsoon soil data is though not high (D^2 = 6.4691) but there is clear variation of chemical components from pre-monsoon to post-monsoon in soils. The misclassification error is reported as 26% in case of discriminant analysis of pre-monsoon and post-monsoon soils. This indicates the soils of pre-monsoon and post-monsoon are to some extent chemically closer although clear distinction exists.

Table 2: Discriminant statistics and function for pre- and post-monsoon soil samples, Bolani-Barbil region.

Variable	Constant	% Added
Fe	2.5663	-6.874
Mn	-3.7279	35.3409
Ca	-1.0206	2.1746
Mg	2.6179	7.1006
Na	0.2582	1.5974
K	-4.7228	12.9463
Cu	1.8587	-0.2457
Zn	2.4867	-5.5937
Ni	1.4002	-4.1299
Co	2.4113	-8.1524
Cr	-5.8669	24.716
Pb	0.6398	1.0184
Cd	-3.0224	40.1015

Wilks lambda = 0.37

F = 5.1676 with 13 (NDF1)and 40 (NDF2) Degrees of Freedom

Mahalanobis distance D^2 = 6.4691

R1 = 19.9735
R0 = 16.7389
R2 = 13.5044

Misclassification error = 26%

Discriminant Function (Df) =
2.5663 Fe - 3.7279 Mn - 1.0206 Ca + 2.6179 Mg + 0.2582 Na - 4.7228 K + 1.8587 Cu + 2.4867 Zn + 1.4002 Ni + 2.4113 Co -5.8669 Cr + 0.6398 Pb - 3.0224 Cd.
Group - 1 (Soil Pre-monsoon Chemical Data)
Group - 2 (Soil Post-monsoon Chemical Data)

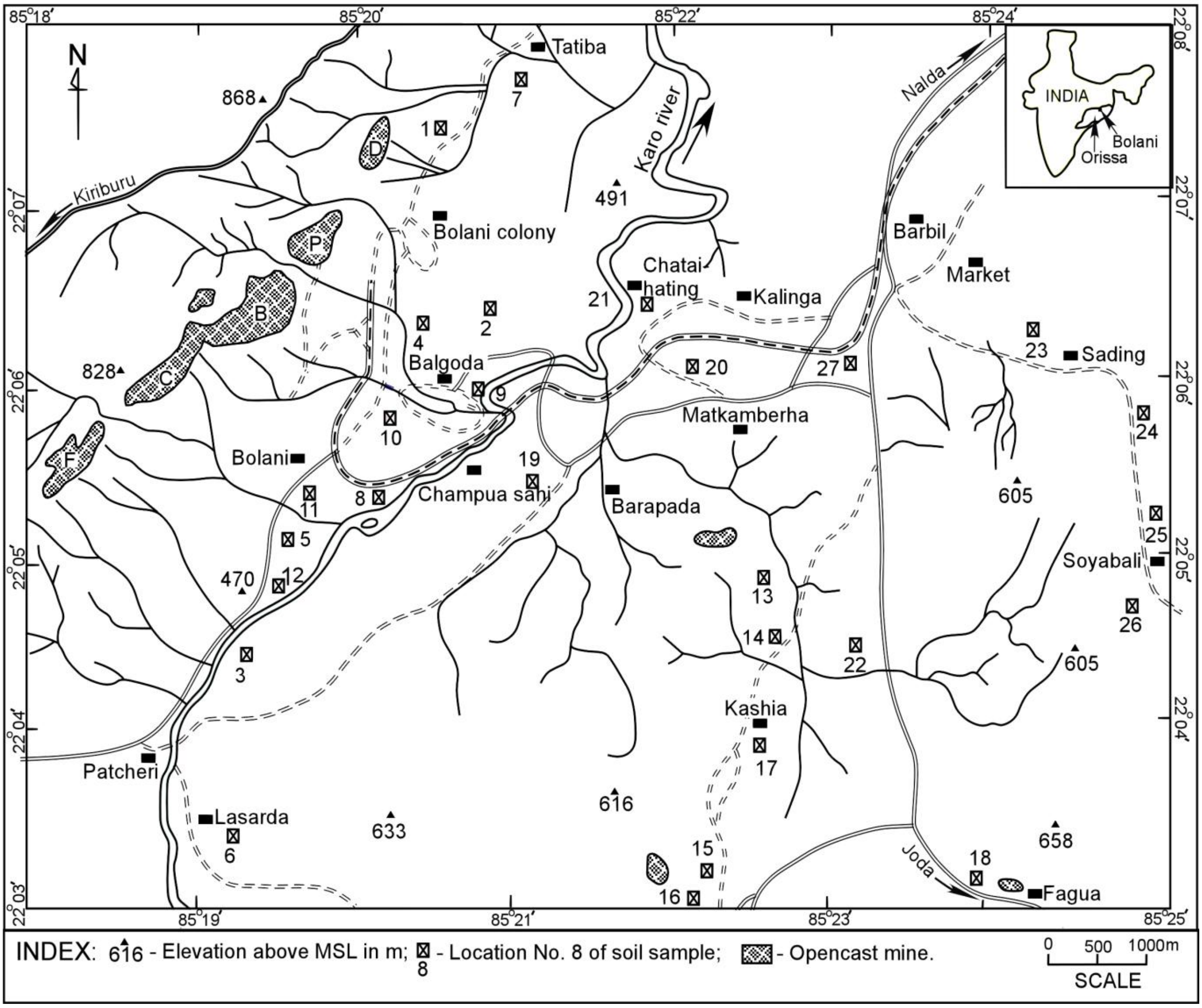

Fig 1: Soil sample locations in Bolani and Barbil area, Keonjhar.

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 8.|            Discriminant Score Plot
 8.|      (Pre and Postmonsoon soils, Bolani-Barbil)
 8.|
 8.|
 9.|    O
 9.|              O
 9.|
 9.|
10.|
10.|      O
10.|       O
10.|
11.|
11.|
11.|              O
11.|      O
12.|     O    O
12.|                   O
12.|       O
12.|             O
13.|
13.|   O
13.|           OO              O        R2=13.5044
13.|
14.|
14.|
14.|            O        O
14.|
15.|
15.|       O
15.|              O
15.|               O
16.|              *
16.|                   O
16.|
16.|               O*                  R0=16.7389
17.|
17.|           *
17.|
17.|                 *
18.|               O    *
18.|
18.|     *      O         *
18.|
19.|                         *
19.|
19.|
19.|         *     O
20.|           *  *  O                 R1=19.9735
20.|            *       *
20.|                    *          *
20.|
21.|           *   * *                 *
21.|
21.|             *  *
21.|
22.|
22.|
22.|                 *                *
22.|                  *
23.|
23.|                                    *
23.|
23.|                    *
24.|
                           * = Soil premonsoon      0 = Soil postmonsoon
```

Fig 2: Discriminant score plot for chemical data of pre and postmonsoon soil samples, Bolani-Barbil area, Keonjhar.

5. Conclusion

Analyses of the metals of the soils of the Barbil and Bolani area show that they are more contaminated due to mining and related industrial activity of the area in post-monsoon. The application of multivariate discriminan tanalysis carried out on geochemical data has led to establish the contribution of chemical components from mine dumps and over burden materials into the soil aided by fluvial geomorphic processes during monsoon. Hence, appropriate remedial steps may be taken to prevent contamination of the soils from mining and industrial activity in the region.

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