Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
e-ISSN: 2395-3454

Vol. 18 | No. 2 | pp. 491-496 | 2019

Original Research Paper **Open Access**

Distribution Characteristics of Micronutrients in Mining Induced Subsided Land of an Underground Coal Mine of South Eastern Coalfields, India

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 05-10-2018
Accepted: 09-12-2018

Key Words:
Coal mining
Subsidence
Micronutrients
Trace elements
Soil texture

ABSTRACT

This paper aims to study the distribution of available micronutrients (Fe, Mn, Cu and Zn) for plants in an underground coal mining induced subsided land of South Eastern Coalfield Limited (SECL), India. Depth-wise changes in soil texture, soil organic matter (SOM) and micronutrient components were evaluated in crack (Profile 2 or P2), slope (Profile 3 or P3) and maximum subsided zone (Profile 4 or P4) of a subsided land and a neighbouring undisturbed land (Profile 1 or P1). Contents of available Fe, Mn, Cu and Zn were in the range of (mg.kg^{-1}) 50.58-85.17, 40.50-64.93, 3.15-10.43 and 2.13-6.20, respectively at P1 and P4, while the contents at P2 and P3 were in the range of (mg.kg^{-1}) 4.10-10.25, 1.26-1.74, 0.12-0.19 and 0.31-0.52, respectively. Considering the critical levels of amounts (mg.kg^{-1}) of DTPA extracted micronutrients, the soils at P1 and P4 were found to have an adequate amount of Fe, Mn, Cu and Zn while P2 and P3 were having lower amounts than the critical levels except the Fe. Positive changes in the content values of the above elements were observed at P4, as demonstrated by increases of 54.90%, 12.98%, 127.02% and 38.30%, respectively. P3 and P2 had shown a negative change. The dispersion patterns of accessible Cu and Zn throughout the soil depth were very similar. By simple linear regression analysis, it was observed that mutual affinity for SOM might influence their distribution in soil. Amount of Fe and Mn displayed different but more consistent distribution within a soil layer.

INTRODUCTION

The forest trees play an important role in the environmental balance on earth, and hence they have the ability of fulfilling relevant ecological functions (Kern & Schmitz 2013). Study about nutritional limits of trees may provide important information regarding the effect of changes taking place in trees after various soil nutritional fluctuations. Coal extraction from underground mining results in land subsidence causing the aboveground forest to face various structural changes in land, consequently the changes in the soil at which they depend for their nutrition. A study based on urban forestry by Lilly (2015) indicates that there is frequently a requirement for treatment with fertilizer in mature stages when trees are not appropriately fertilized at younger stages. A typical mining subsided area has a tensile zone, a slope and a zone of maximum subsidence. The tensile zone where cracks are generated, results in physical damages to the roots causing problems in nutrient uptakes, consequently physiological disturbances in the tree. The slope, where maximum soil erosion takes place causing a disturbance in nutrient equilibrium, soil textural changes etc. and the area of maximum depression where most of the nutrients accumulate due to runoff and mineral weathering. Investigations related to the micronutrient levels in tree species found in the forest ranges are rare.

The heavy metals and trace elements occur naturally in earth's crust and their content depends upon soil's localized changes (Bowen 1979). Due to natural processes like weathering or some anthropogenic processes like application of phosphate fertilizers to the fields, heavy metals enter into the soil (Alloway 2013). It acts as an important source for heavy metals occurrence in the soil and by their continuous application they resulted into the bioaccumulation. Generally, heavy metals are considered as contamination in minerals and natural materials, that is why they might exist in phosphate or other chemical fertilizers. Trace elements necessary for plants such as Fe, Mn, Zn and Cu are the most important micronutrients required in a very small amount for the proper growth of plants. Only chelated, soluble and exchangeable micronutrients are absorbed by the plants, and hence the measurement of total concentrations available in the soil cannot predict the behaviour of micronutrients (Kabata-Pendias 1993, Buccolieri et al. 2010).

Because of the complications associated with the interactions between plants and environmental factors, there is no existence of a common extracting solution for assessment of available micronutrients in soil for plants. The distribution is also affected by soil properties like soil texture, SOM etc. (Milivojeviæ et al. 2002, Kumar & Babel 2011, Belanovic et al. 2012, Yi et al. 2012). There are many findings showing a positive significant correlation between DTPA extractable (Fe, Cu, Mn, Zn) and SOM content. The positive relation depends upon the quantity of chelated heavy metal cations in soluble form by the SOM (Sharma et al. 2003). The SOM plays a key role among various soil parameters in controlling the availability of micronutrients (Bassirani et al. 2011, Yadav 2011).

Because of the similar origin in soil, Fe and Mn show a significant correlation with each other. This close correlation may also be attributed to contaminations from nearby industries. Cu and Zn also show a significant correlation with each other showing a similar variation along the soil depth (Buccolieri et al. 2010). The micronutrients, which are present in soil, are not totally available to the plants for absorption. Only a labile fraction of the total content may be in available form depending upon the nature of the element and the soil.

This paper argues about the distribution pattern of the trace elements along the soil depth and their connection with one another and with SOM in order to better understand trace element behaviour within the soil environment where a significant land subsidence has been met.

MATERIALS AND METHODS

Field information: The study site is located in Anuppur district of Madhya Pradesh (Fig. 1). The coordinates are 23°10'N and 81°57'E. Mine area belongs to humid subtropical climate zone and the climate here is mild and generally warm and temperate. The Köppen climate classification is Cwa.

Field sampling: A plot of about 100×100 m^2 size at P1 and plots of about 10×10 m^2 size, each at P2, P3 and P4 of the subsided land were selected (Fig. 2). Samples of P2 and P3 subsiding around both sides of maximum depression were collected. Soils were sampled from four points at each plot in a zigzag manner in the soil layer 0-15 cm, 16-30 cm, 31-45 cm and 46-60 cm. The samples were air dried and crushed followed by sieving through a 2 mm sieve.

Soil analysis: The available micronutrients (Fe, Cu, Mn & Zn) were extracted with the help of DTPA extracting solution (0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M TEA), pH 7.3 as per the procedure described by Lindsay & Norvell (1978). Textural analysis of the soil was done by Bouyoucos hydrometer method (Bouyoucos 1962). The organic matter content was estimated using the Walkley and Black method (Walkley & Black 1934).

Statistical analysis: All the data were subjected to one way ANOVA to compare the main differences of means of the micronutrient contents along the soil depth or between profiles themselves. Also, the effect of measured soil textures on available micronutrients and their mutual interactions were analysed by correlation coefficients. The software used was SPSS 16.0. Differences which were significant at $p<0.05$ are discussed here.

RESULTS AND DISCUSSION

The depth-wise analysis results at intervals of 15 cm soil layers of studied soil profiles are given in Table 1.

Contents of available Fe, Mn, Cu and Zn were in the range of ($mg.kg^{-1}$) 50.58-85.17, 40.50-64.93, 3.15-10.43 and 2.13-6.20, respectively at P1 and P4, while the contents at P2 and P3 were in the range of 4.10-10.25, 1.26-1.74, 0.12-0.19 and 0.31-0.52, respectively. The critical levels of amounts ($mg.kg^{-1}$) of DTPA extracted micronutrients are considered to be 4.5 for Fe; 2.0 for Mn; 0.2 for Cu and 0.6 for Zn (Lindsay & Norvell 1978). By considering these critical values, the soils at P1 and P4 were found to have an adequate amount of Fe, Mn, Cu and Zn, while P2 and P3 were having below the critical levels of contents except the Fe. The low contents at P2 and P3 might somewhat be ascribed to the soil's runoff, leaching and percolation due to collective effect of damaged vegetation cover and heavy precipitation. The contents may also be affected by soil types, topography and climates (Hamilton 1998, Maitima et al. 2009, Zhang et al. 2011). The cracks at P2 and slope at P3 might have percolated the soil to the deeper layers, ran off the soil nutrients to the subsided zone and subsequently

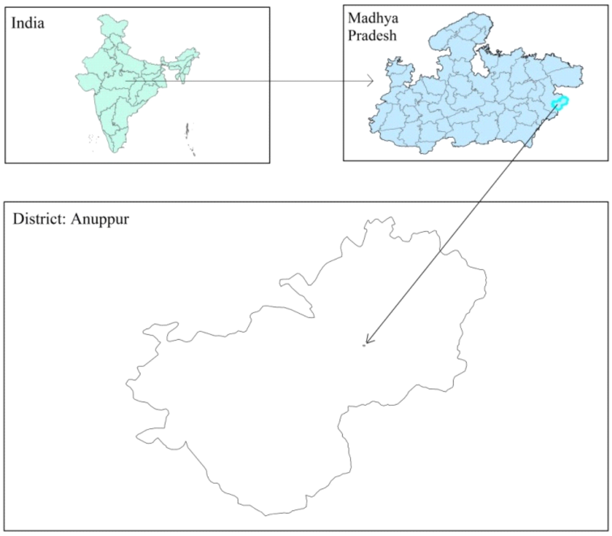

Fig 1: Location map of the study area.

Table 1: Mean values of micronutrients available for plant uptake.

Soil depth (cm)	Fe ($mg.kg^{-1}$)	Mn ($mg.kg^{-1}$)	Cu ($mg.kg^{-1}$)	Zn ($mg.kg^{-1}$)
		Undisturbed Zone (Profile 1 = P_1)		
0-15	56.13	52.04	3.88	4.76
16-30	54.03	49.56	3.52	3.28
31-45	51.73	46.80	3.25	2.57
46-60	50.58	40.50	3.15	2.13
		Cracks (Profile 2 = P_2)		
0-15	4.46	1.85	0.193	0.52
16-30	4.30	1.64	0.189	0.48
31-45	4.21	1.41	0.146	0.41
46-60	4.10	1.26	0.118	0.36
		Slope (Profile 3 = P_3)		
0-15	10.03	1.68	0.176	0.43
16-30	10.25	1.74	0.187	0.48
31-45	9.86	1.63	0.170	0.35
46-60	8.87	1.48	0.124	0.31
		Depression Zone (Profile 4 = P_4)		
0-15	85.17	64.93	10.43	6.20
16-30	83.99	53.40	7.96	4.42
31-45	81.66	49.00	6.77	3.76
46-60	78.28	46.08	6.17	3.24

resulted into the nutrients leaching. The upper first 15 cm layer at P3 was having lower content values than the second 15 cm layer (16-30 cm) and then a decreasing trend was seen from second layer to the subsequent layers, inferring only the surface level translocation of micronutrients, along P3 to P4 (Figs. 3 & 4). Vukašinovic et al. (2015) had shown greater amounts of trace elements in upper 0-20 cm layer and decreasing tendency towards the deeper layers. Similar results were also reported in a study performed by Garcia-Marco et al. (2014) where contents of available Fe and Mn in 0-5 cm soil layer were higher and in 5-30 cm layer, the distribution was homogenous. The higher contents of trace elements in the soil surface were likely a result of higher decomposition of SOM and plant remains, which contribute to a greater accumulation of these elements at surface layers. The distribution is also greatly affected by the rooting depth and root distribution of the plants. The nutrients taken up by the deep roots are transported to the aboveground parts and re-deposited on the soil surface through litter or stem fall (Franzluebbers & Hons 1996, Jiang et al. 2009, Garcia-Marco et al. 2014). Further, greater probabilities of drainage for micronutrients are due to their existence as free ions or dissolved complexes in solution (Huang et al. 2011). Therefore, translocation of these elements along the P3 due to the surface runoff in sloping terrain resulted into the depositions in the subsided zone (P4).

The distribution was statistically compared by evaluating their variance. The findings showed that the available Fe and Mn in soil profiles along the measured depths were more constantly distributed as compared to available Cu and Zn. According to their coefficient of variation (CV) with profiles, the mean variability of available Fe and Mn with depth was 7% and 10%, respectively while for both available Cu and Zn, it is approximately 17% and 15%. These similarities may be due to their similar origin in the soil.

One-way ANOVA test was also performed to indicate the main differences of trace element contents along the soil depth or between profiles themselves. The test results showed no statistically significant differences between means of contents for Fe and Mn in the soil layers of 0-15 cm and 31-45 cm, while in the layers 16-30 cm and 46-60 cm, a significant difference between means of content for Fe were observed at P2 and for Mn, at P1 & P4, respectively. But, in the case of Cu ($p<0.001$) and Zn ($p<0.01$) at P1 and P4, there were statistically significant differences between their means in the 0-15 cm and 16-30 cm layer in respect to the deeper layers examined. In the topsoil layer at P1, mean values of contents were the maximum, 10.43 and 6.20 $mg.kg^{-1}$, respectively.

The amount of all trace elements was found to be statistically different between soil profiles P1 & P4. The influence of measured soil textures on available micronutrients

Table 2: Representing the correlation matrix between the soil properties.

		Sand	Silt	Clay	Cu	Mn	Fe	Zn	SOM
P1	Sand	1	0.160	0.224	-0.034	0.048	0.242	0.130	
P2		1	-0.292	0.324	0.039	0.209	0.359*	0.081	
P3		1	-0.292	0.324	0.039	0.209	0.359*	0.081	
P4		1	0.042	0.178	-0.075	-0.319	-0.125	-0.312	
P1	Silt		1	-0.002	0.486	0.428	-0.332	0.532	
P2			1	-0.169	0.080	0.416*	0.327	0.348	
P3			1	-0.206	0.067	0.351*	0.137	0.352*	
P4			1	-0.755**	0.618**	0.705**	0.726**	0.741**	
P1	Clay			1	-0.598**	-0.430*	0.294	-0.471**	
P2				1	-0.428*	-0.110	-0.274	-0.460**	
P3				1	-0.193	-0.083	-0.059	-0.534**	
P4				1	0.664**	0.542*	0.539*	0.577*	
P1	Cu				1	0.609**	0.437*	0.850**	0.595 (30%)
P2					1	0.377*	0.492**	0.539**	0.346
P3					1	0.173	0.298	0.359*	0.271
P4					1	0.429	0.422	0.440	0.614 (32%)
P1	Mn					1	0.364*	0.637**	0.215
P2						1	0.740**	0.585**	0.291
P3						1	0.102	0.324	0.286
P4						1	0.794**	0.993**	0.317
P1	Fe						1	0.646**	0.233
P2							1	0.872**	0.198
P3							1	0.452**	0.254
P4							1	0.802**	0.316
P1	Zn							1	0.713 (52%)
P2								1	0.417
P3								1	0.385
P4								1	0.728 (59%)
P1	SOM								1
P2									1
P3									1
P4									1

**, Correlation is significant at the 0.01 level (2-tailed).
*, Correlation is significant at the 0.05 level (2-tailed).

and their mutual correlations were evaluated by correlation coefficients derived from SPSS 16.0 (Table 2). The fine textured soils were positively and coarse textured soils were negatively correlated with all the micronutrients at P4 while at P1 the relationship was of the same nature except for the silt where a negative correlation with micronutrients was observed. All the measured elements were highly positively related with each other. Kumar & Babel (2011), Yadav (2011), Yi et al. (2012) and Vukašinovic et al. (2015) reported the similar results except for the moderate relationship between Fe and Mn. The relationship of percent silt with the percent clay was negative at P1 but became significantly positive at P4. All the micronutrients except Fe were positively correlated with silt at P1 but the relationship became highly significant at P4. Clay had a positive relationship with Fe at P1 but this relation became negative and significant at P4. Also, it had a negative relation with all the micronutrients (except Fe) at P1 but became positive at P4. The negative relations of silt and clay with each other and with available micronutrients might be due to their separate correlation assessments. By considering a cumulative percentage of silt+clay together, they showed positive correlations with micronutrients and due to factors discussed above a higher accumulation of nutrients at P4 might be expected.

The variance of SOM highly influenced the availability of Cu (Table 2) along the soil depth with a correlation ($r \sim 0.60$) explaining about 30% of their variability ($p < 0.05$). Available Zn had shown about 52% of its variations ($p < 0.001$) with SOM. SOM appears to influence the availability of Cu and Zn along the measured depth. Due to its sorption nature, SOM plays a dual role for the solubility of the organic ligand. The solid organic form forms insoluble complexes with trace elements resulting in their immobilization while dissolved organic form forms strong soluble com-

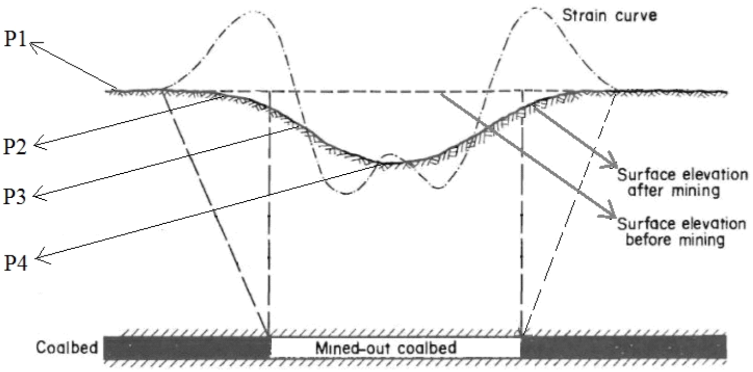

Fig 2: A subsidence profile showing pre and post mining surface status and the sampled zones for study (P1-P4) P1-Undisturbed Zone (Profile 1); P2-Crack (Profile-2); P3-Slope (Profile-3); P4-Maximum Subsidence (Profile-4) (Modified from Lee & Abel 1983, Ingram 1989, Hu et al. 1997).

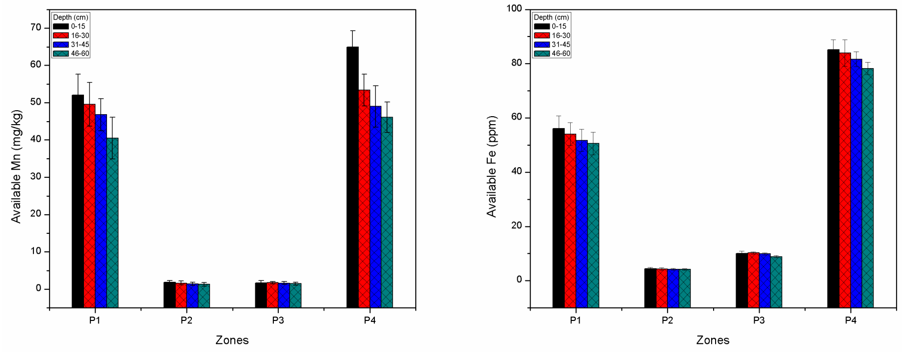

Fig 3: Depthwise zonal distribution of Fe and Mn.

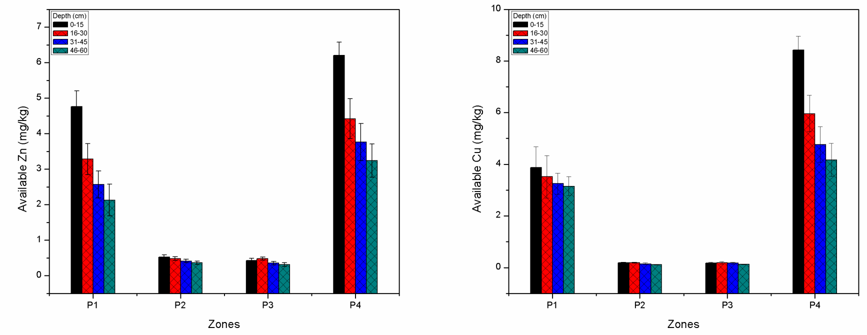

Fig 4: Depthwise zonal distribution of Zn and Cu.

plexes increasing the trace elements solubility (Alloway 2013). Inner-sphere complexes (chelate rings) with SOM might be formed by Cu and Zn. The higher electronegativity of metal ions forms higher stronger bonds with SOM. It implies that chelate stability of Cu with SOM must be higher than Zn (Petrovic et al. 1999) and thus Cu availability at solid soil surface is higher in amount than the Zn.

CONCLUSIONS

The mining subsidence alters the micronutrient contents of the native soil. Although the major nutrient component of soil available to plants may have a profound effect on the soil suitability for vegetation growth, the micronutrients play an eminent role in the quality maintenance of soil to be suitable for plant growth in proper manner. SOM and fine textured soil also play an important role in retaining more nutrients. A positive, as well as a negative impact on the availability of micronutrients, were seen due to mining subsidence. The positive impact may provide an aid in maintaining a healthy soil environment whereas proper mitigation measures should be adopted to alleviate the negative impacts.

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