



THE MOBILITY OF SOME NUTRIENT METAL IONS AS AFFECTED BY HEAVY METALS IN PRESENCE OF ADDED SOIL ORGANIC MATTER IN AN ILLITIC SOIL

N. NAZAR KHAN*

Applied Science Department, BTK Institute of Technology,
(An Autonomous Institute of Uttarakhand Government), DWARAHAT – 263653 (Uttarakhand) INDIA

ABSTRACT

The mobility of some nutrient metals such as Fe, Zn, Mn and Cu have been investigated in an illitic fine sandy loam soil as affected by some toxic heavy metals (Pb, Cd, Cr, and Ni) in the presence of added organic matters using soil thin layer chromatography (Soil TLC). The soil organic matter (SOM) and humic acid (HA) fraction was extracted from the sample soil by standard methods and purified. The heavy metals like Pb, Cd, Cr, and Ni were added to the soil in the form of their SOM and HA complexes to study their effects on the mobility of nutrient metal ions in the soil. The mobility of nutrient metals was found to follow the order as $Mn > Zn > Cu > Fe$. The presence of SOM and its fraction as HA significantly increases the mobility of all the nutrient metal ions in soil. An addition of the heavy metal-SOM and heavy metal-HA complexes in soil further increases the mobility of all the metals except in the case of Cd, which decreases the mobility of all the nutrients. The results so obtained have been explained on the basis of metal ion interactions with soil colloids and their physico-chemical properties in the soil solutions.

Key words: Heavy metals, Illitic soil, Mobility, Nutrient metals, Soil organic matter

INTERODUCTION

It has been well recognized that sewage sludge, industrial and municipal wastes contain many heavy metals^{1,2} like Pb, Cd, Ni, Cr etc. These heavy metals, which are supposed to be highly toxic for plant and animal life, when reaches the soil, form their complexes of variable stability with soil organic matter and its fractions as humic and fulvic acids³⁻⁵. A survey of literature shows that most of the studies on the heavy metals deal with their adsorption-desorption, translocation and their effects on the crop growth and nutrients concentration in plants and/or soil⁶⁻⁹. The major factor affecting the chemistry of metal ions in soil solutions have been recognized as complexation reactions, pH, ionic strength of soil solutions, competing ions, precipitation and binding characteristics with the adsorbent

* Author for correspondence; E-mail: nnazar2000@gmail.com; Mo.: +91-9412928155

surfaces. Again, it is also true that the direct relationship between composition of soil and adsorption characteristics of various metal ions can not be determined specifically due to the strong correlation of soil component interactions. The heavy metals in the form of their organo-complexes of variable stability have been reported to possess a strong competition with nutrient metal ions like Cu, Zn, Mn, Fe etc. for the adsorption and translocation in soils. Lu and Xu¹⁰ have observed that the selectivity sequence of the metal adsorption on to the soil surfaces is $Pb > Cu > Zn > Cd$. Moreira and Alleoni¹¹ have shown the most common sequence of adsorption as $Cu > Cd > Zn > Ni$ in the competitive soil systems. However, the information regarding the movement of micronutrient metals in presence of organo-heavy metal complexes is scanty in literature¹².

Therefore, it was considered worthwhile to observe the effect of these heavy metals in presence of soil organic matter and its humic acid fraction on the mobility of nutrient metals like Mn, Zn, Cu and Fe which are required by plants. The technique used in these experiments was soil thin layer chromatography (Soil TLC), which is widely adopted by the environmental as well as elementological scientists in recent years.

EXPERIMENTAL

Materials and methods

Aeric Halaquept (An illitic fine sandy loam) surface soil (0 to 25 cm) was collected from representative area of Aligarh District of Uttar Pradesh (India) and used in these investigations. The physicochemical properties of the soil as determined by the standard methods are as Sand 66%; Silt 20%; Clay 14%; Soil pH 8.8; Soil Organic Matter (SOM) 0.40%; Electrical conductivity 4.8×10^{-4} mhos cm^{-1} ; Cation exchange capacity 7.8 meq per 100 g soil; DTPA Extractable Zn 0.58 ppm; Mn 0.81 ppm; Cu 10 ppm; Fe 4 ppm; Exchangeable Na 1.0, K 0.5, Ca 3.5 and Mg 1.2 meq per 100 g soil

The soil sample was air dried and passed through 100 mesh sieve (BSS) to obtain uniform particle size for experimental work. It was slurried in distilled water (1 : 2 ratios) and applied on the glass plates of 20 x 5 cm size with the help of conventional TLC applicator to have a uniform 0.5 mm thick soil layer. The plates were air dried and two lines were scribed at 3 cm and 13 cm from the base on all the plates to allow a distance of 10 cm for study. Aqueous solutions (0.01 M) of Mn, Zn, Cu and Fe as nitrates were applied (0.006 mL) on the base line of the plate as a single spot with the help of a micro pipette. The plates were wrapped with a wet filter strip of about 2.5 cm at their bottom to prevent the disintegration of soil. These plates were then developed for the distance of 10 cm in closed

TLC chambers with distilled water as developer/translocator. The plates were then dried and the metal spots were detected on the developed plates by spraying 0.1% (w/v) ethanolic haematoxyline solution for Mn^{2+} , Fe^{3+}/Fe^{2+} and Cu^{2+} , which gave a violet colour spots and Zn^{2+} appeared as blackish red spot with 0.1% ethanolic xylenol orange reagent, which were stable for several hours. The R_f values were measured as a ratio of the distance travelled by the metal spot to that of travelled by the developer.

To study the effects of the soil organic matter, humic acid and their complexes with heavy metals on the mobility of nutrient elements in soil, the SOM and HA fractions was separated out from the sample soil by Stevenson method¹³. The heavy metal-SOM/HA complexes were prepared by using the method of Erdogan et al.¹⁴ The soil samples were then amended with requisite amount of SOM, HA and heavy metal-SOM/HA complexes and used in the preparation of the TLC plates for study. The rest of the procedure was the same as described above. The results were statistically analyzed at 5% confidence level

RESULTS AND DISCUSSION

Table 1 shows that the mobility of nutrient metals in the soil follows the order: $Mn > Zn > Cu > Fe$. It has been observed that ion size and electronegative character of the elements play a significant role in governing the metal ion interactions with soil colloids and hence, the mobility in soil. As the pH of the soil solution is in the alkaline range (8.8), hence, the metal ions are expected to be in their hydrated state. Robert and Hinrich¹⁵ have explained the behavior of metal ions in such solutions. It was shown that the metal ions in alkaline solutions follow the hard soft acid base (HSAB) principle, which states that hard Lewis acids (with high electronegativity, lower polarizability and small ionic size) prefers to complex or react with soft bases. Accordingly, the mobility order of nutrient metals, which was found as $Mn > Zn > Cu > Fe$ can be explained on the basis of HSAB principle by considering the nutrient metal-soil interaction sequence of $Cu > Zn > Mn$ according to their hydrated ion size and electronegativity. However in the case of iron, whose ionic size is varying from 0.66 to 0.78, move to a very little extent and in some cases, it is stationary. It may be due to its variable size and its nature to precipitate as hydroxides in soil solutions. Williams *et al.*¹⁶ have also reported the same sequence of their mobility in soils.

Table 1 also shows that the mobility of all the nutrients increases with increase in the added soil organic matter and its fraction as humic acid. As the pH of the soil remained in the alkaline range and the adsorption sites of the soil colloids already occupied by the indigenous cations, the metal ion interact with added soil organic matter and its fraction as humic acid to form the soluble metal-SOM or metal-HA complexes¹⁷. These soluble organo-

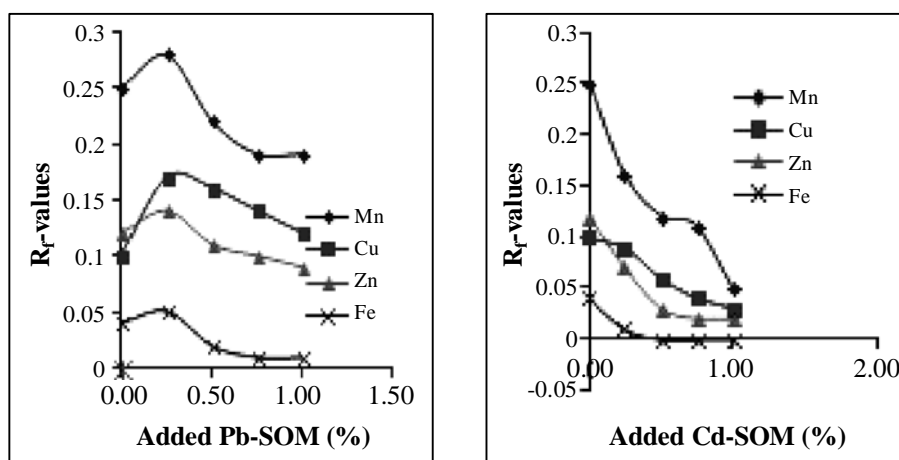
metal complexes move in the soil according to their size and electronegativity. This kind of metal behavior in soil shows that the electronegative character of the metals is an important parameter in deciding the pattern of nutrient translocation in soil plant systems. The results are in agreement with the findings of various workers in this field, who reported transport of metal ions as their HA complexes through soil^{18,19}.

Table 1: Effect of soil organic matter and soil humic acid on the nutrients mobility in soil

Nutrients	R_f -Value										
	SOM added (%)						HA added (%)				
	0.00	0.25	0.50	0.75	1.00	CD*	0.25	0.50	0.75	1.00	CD*
Mn	0.25	0.28	0.30	0.32	0.40	0.01	0.28	0.30	0.32	0.40	0.01
Cu	0.10	0.40	0.42	0.30	0.41	0.02	0.40	0.42	0.30	0.41	0.05
Zn	0.12	0.18	0.21	0.25	0.16	0.01	0.18	0.21	0.25	0.16	0.01
Fe	0.04	0.06	0.12	0.18	0.16	0.01	0.06	0.12	0.18	0.16	0.01

*Critical difference at 5% confidence level

Fig. 1 shows that the introduction of heavy metals in the soil systems altered the mobility of these nutrient metals in the soil. It is clearly seen from the results that except Cd, all other pollutant metals such as Pb, Cr, and Ni when added to soil as their organic matter complexes, enhance the mobility of the nutrient ions. However, Pb-SOM complex increased the nutrient mobility at its low level of addition (0.25%) and then decreases in all the cases.



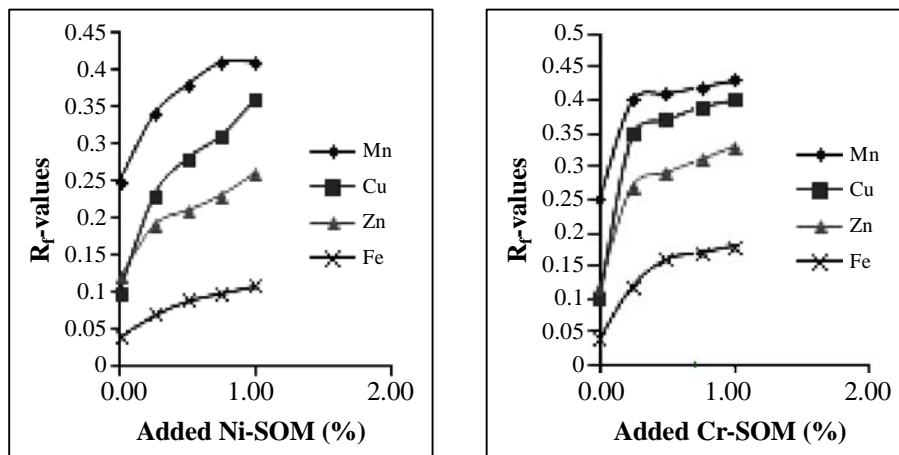
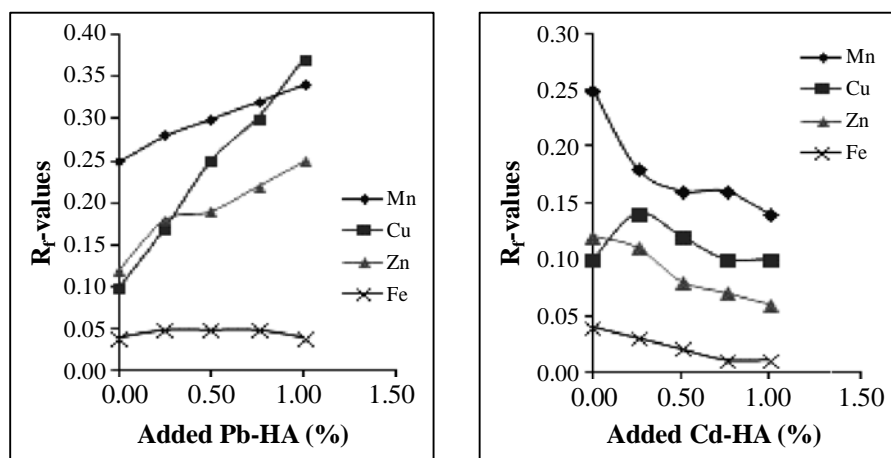


Fig. 1: Effects of heavy metal-SOM complexes on the nutrients mobility in soil

The results could be explained on considering the form of these metals in soil solutions. Suman and Hargrove²⁰ observed that a higher fraction of Fe, Zn, Mn, and Cu at high pH remains as water soluble metal oxides in the form of Mn-oxide and amorphous Fe-oxides. Since the soil in these experiments has low Mn-oxide and amorphous Fe-oxides with a pH ranging between 8.9 and 8.1, it is obvious that these metals remain as water soluble and hence, their mobility increases in organic amended soils.

Fig. 2. shows the mobility of nutrient metals in presence of heavy metal-humic acid complexes. It further indicates that soil organic matter as a whole or its fraction as humic acid behaves in the similar manner in soil solutions except in the case of Pb-HA complex, which enhances the nutrient metal mobility through out the range of added Pb-HA complex.



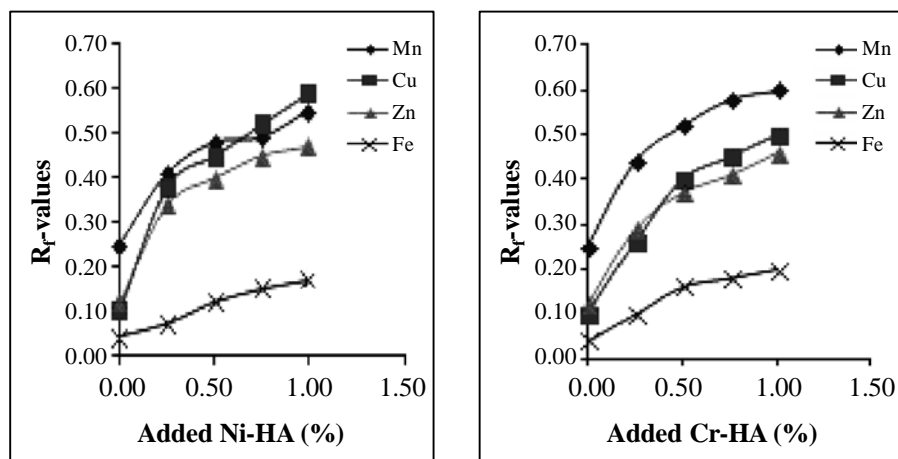


Fig. 2: Effects of heavy metal-HA complexes on the nutrients mobility in soil

The heavy metals in the soil systems also occupied the exchangeable and/or adsorption sites of the soil colloids, which may be an additional factor for the high mobility of nutrient metals in soil. While in the case of Cd-SOM and Cd-HA complexes, which decreases the mobility of all the nutrient metals, it could be said that Cd has a very little affinity with soil colloids²¹⁻²³ in comparison to the nutrient metals like Fe, Zn, Mn and Cu.

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