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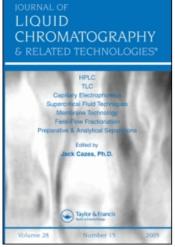
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MOVEMENT OF TRACE ELEMENTS IN SOILS USING THIN-LAYER CHROMATOGRAPHY

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ABSTRACT

The effect of pH, organic matter, autoclaved soil, CaCO₃ and extracts of the different oil-cakes on the mobility of trace elements by employing soil thin-layer chromatographic technique has been studied. Removal of organic matter from the soil increases the movement of trace elements. Similarly, with the increase in the concentration of oil-cake extracts the mobility of trace elements increased. However, autoclaving the soil or addition of CaCO₃ increases the frontal R_f values of certain trace elements and not that of others.

INTRODUCTION

The role of trace elements on the growth of plants hardly need emphasised. Their availability to plants is being influenced

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by a number of factors (8). Recently, Singhal and Singh (13) and Singhal et al. (12) have provided evidence that mobility of trace elements and their availability to plants are greatly influenced by the presence of different salts and organic matter etc. in the soil. The use of oil-cakes which are rich in organic matter for certain cash crops has become very common practice these days. Similarly, plants are grown in soil with different pH and having salts like CaCO. Moreover, in glass house control experiments the soil is naturally autoclaved. The information on the effect of all these factors on the mobility of various trace elements is meagre. Hence, in the present studies an attempt has been made to determine the effect of pH, organic matter, autoclaving, percentageof CaCO, and amended with different oil-cakes on the mobility of Cu2+. Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} in the soil with a view that the information so obtained might help in managing the field for proper fertilizer requirements.

MATERIALS AND METHODS

The important properties of the Ganga Khadir soil type I (0-30 cm) of the Aligarh district that has been used in the present studies were as under:

Sand = 32.30%; silt = 57.56%; clay = 10.06%; pH = 9.0; electrical conductivity = 2.3×10^{-4} m mhos/cm; cation exchange capacity = 9.0 m.e./100 g soil; organic matter = 0.26%; CaCO₃ = 8.85%; bulk density = 1.28 g/cm³ and porosity = 50.76.

B.D.H. Analar pure chemicals were used throughout the studies. The trace elements solutions (0.1M) were prepared

by dissolving requisite amount of sulphates of ${\rm Cu}^{2+}$, ${\rm Co}^{2+}$, ${\rm Ni}^{2+}$, ${\rm Mn}^{2+}$ and ${\rm Zn}^{2+}$. Aqueous 1% potassium ferrocynide was used as detecting ${\rm Cu}^{2+}$, 1% diphenyl carbazide in alcohol for ${\rm Mn}^{2+}$ and ${\rm Zn}^{2+}$ and 0.1% alcoholic dimethyl glyoxime in ammonia for ${\rm Ni}^{2+}$ and ${\rm Co}^{2+}$ (12, 13).

The soils with particle size 100 mesh < 150 m \mu was used as adsorbent phase. For determining the effect of organic matter on the mobility, the soil was treated with 30% ${\rm H_2O_2}$ (2,9). The soil was autoclaved to determine the effect of autoclaving. To the natural soil (which contains 8.85 g CaCO3) 6.15 g CaCO3 was added in order to make the concentration of CaCo, as 15 per cent. The distilled water was used as developer for the studies, while for determining the effect of pH, distilled water with original pH and pH adjusted to 4 and 10 with 0.1N HCl and 0.1N NaOH was used as developer. In the studies dealing with the effect of oil-cakes natural soil slurries were prepared by adding 100 g soil with 100 ml of 1%, 3% and 5% extracts of the caster, groundnut and neem cakes separately. Distilled water was used as developer. In another set of experiments natural soil and soil without organic matter were used as adsorbents and 1%, 3% and 5% extracts of oil-cakes were used as developers.

Glass plates (20 x 20 cm) were coated with the soil slurries to a thickness of 0.5 mm with the help of the TLC applicator and were allowed to air dry at room temperature. Two lines at 3 and 13 cm above the base were scribbled so that the standard development distance of 10 cm was used on all the plates (10,11). The solutions of trace elements were applied on the plates as spots using Lambda pipette at a height of 3 cm from the base. The spots were dried at room tempera-

ture and then plates were developed in the glass tanks with distilled water and extracts of oil-cakes as mentioned above upto a upper line by ascending chromatography. Wet strips of filter paper about 2.5 cm wide were wrapped around the bottom of the plates to prevent the disintegration of the soil layer while it comes in contact with the developers. The developed plates were air dried at room temperature and the mobility of trace elements was detected by spraying the suitable detectors (12,13). The frontal R_f values as recommended by Helling and Turner (5) and Helling (6) were measured.

RESULTS AND DISCUSSION

Development of trace elements spots on the soil TLC plates with distilled water resulted tailings and lateral movements. In autoclaved soil there was an increase in the frontal R, values of Ni $^{2+}$ and Co $^{2+}$ and slight decrease of ${\rm Zn}^{2+}$ and Mn2+ as compare to natural soil (table 1). When the organic matter free soil was used as an adsorbent the mobility of all the trace elements increases. This suggests that the presence of organic matter in the soil may prevent leaching of trace elements. However, CaCO, added soil was used as static phase, the mobility of Cu²⁺, Co²⁺ and Ni²⁺ increases with decrease in Mn²⁺ and Zn²⁺. The decrease in frontal R, values of Mn2+ and Zn2+ could be due to the fact that these ions get fixed over the surface of CaCO, as suggested by Boischot and Durroux (1) and Throne (14). Leeper (7) have also postulated that CaCO_x may act as strong adsorbent of heavy metals. Therefore, these soils need fortification with Z_n^{2+} and M_n^{2+} . When the natural soil was used as an adsorbent and distilled water, pH 4 and pH 10 solutions as developer the mobility of all the trace elements increased.

Frace e lements	Natural soil not auto- claved	Auto- claved soil	Soil without organic matter	6.15 g CaCO ₃ added in 100 g natural soil	pH 4	pH 10
Cu ⁺⁺	0.00	0.00	0.14	0.12	0.06	0.0
3o ⁺⁺	0.10	0.13	0.13	0.15	0.28	0.17
N1 ⁺⁺	0.11	0.13	0.15	0.19	0.26	0.15
√n ⁺⁺	0.15	0.11	0.16	0.12	0.30	0.14
Zn ++	0.11	0.11	0.13	0.10	0.18	0.10

Trace elements	Castor cake extracts in percentage			Groundnut cake extracts in percentage			Neem cake extracts in percentage		
	1	3	5	1	3	5	1	3	5
Cu ⁺⁺	0.10	0.11	0.15	0.11	0.12	0.16	0.07	0.10	0.15
Co ⁺⁺	0.13	0.19	0.25	0.14	0.27	0.30	0.11	0.14	0.23
N1 ++	0.16	0.32	0.38	0.17	0.35	0.48	0.15	0.20	0.36
Mn ++	0.16	0.14	0.22	0.16	0.24	0.26	0.15	0.18	0.19
z _n ++	0.12	0.14	0.20	0.12	0.14	0.16	0.12	0.13	0.15

TABLE 3 Effect on the R_1 Values of Trace Elements When Different Concentrations of Oil Cake Extracts were Used as Developers on Soil having no Organic Matter.

Trace elements	Castor cake extracts in percentage			Groundnut cake extracts in percentage			Neem cake extracts in percentage		
	1	3	5	1	' 3	5	1	3	5
Cu ⁺⁺	0.06	0.08	0.10	0.18	0.38	0.44	0.13	0.30	0.34
co**	0.18	0.20	0.35	0.21	0.25	0.48	0.24	0.32	0.35
N1 ++	0.21	0.35	0.41	0.24	0.41	0.72	0.29	0.39	0.45
Mn ++	0.19	0.21	0.22	0.18	0.22	0.38	0.14	0.20	0.23
zn ⁺⁺	0.14	0.16	0.18	0.16	0.20	0.33	0.18	0.23	0.25

TABLE 4

Effect on the R $_{\mathbf{I}}$ Values of Trade Elements When Different Concentrations of Oil Cake Extracts were Mixed with Natural Soil and Distilled Vater as Developer.

Trace elements	Castor cake extracts in percentage			Groundnut cake extracts in percentage			Neem cake extracts in percentage		
	1	3	5	1	3	' 5	1	3	5
Cu ⁺⁺	0.10	0.11	0.13	0.06	0.05	0.04	0.06	0.09	0.13
Co ⁺⁺	0.10	0.13	0.14	0.14	0.13	0.12	0.11	0.14	0.15
N1 ⁺⁺	0.14	0.16	0.22	0.14	0.13	0.12	0.11	0.15	0.16
Mn ⁺⁺	0.10	0.10	0.13	0.16	0.13	0.12	0.11	0.11	0.13
zn ⁺⁺	0.09	0.10	0.11	0.11	0.10	0.10	0.10	0.12	0.13

TABLE 5
pH of the Extracts of Oil Cakes Used as Developers and Adsorbents.

Extracts	Perce	entage of extra	ets
	1	3	5
Castor	6.50	6.30	6.20
Groundnut	4.80	5.00	5.40
Neem	6.80	6.60	6.40

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The maximum movement of all the trace elements was observed at pH 4. The order of frontal R_f values of trace elements are as follows: ${\rm Mn}^{2+}\!>\!{\rm Co}^{2+}\!>\!{\rm Ni}^{2+}\!>\!{\rm Zn}^{2+}\!>\!{\rm Cu}^{2+}$. This situation is due to the fact that pH of the solution influence the adsorption (4). Doner (3) also reported that the Cl ions increases the rate of mobility of ${\rm Ni}^{2+}$, ${\rm Cu}^{2+}$ and ${\rm Cd}^{2+}$ through soil. Copper was held much stronger than other trace metals.

In natural soil oil-cakes as (table 2), by and large brought about an increase in the mobility of trace elements. An increase in the concentration of the extracts brought about a corresponding increase in the mobility of the elements. Removal of organic matter (table 3) further increased the mobility. Out of the three oil-cake extracts used optimal movement was observed in groundnut extract followed by castor and neem. These differences may partly be due to the fact that groundnut extract has much lower pH as compared to the remaining two extracts (table 5) in addition to other factors.

When oil-cake extracts were used as an adsorbent with natural soil (table 4) and distilled water as developer, there was an increase in the mobility of trace elements only in castor and neem cake extracts. Groundnut cake extract, how-ever, brought about reduction. These differences may be attributed to the variation in the pH values of the three oil-cake extracts. Therefore, it appears that addition of oil-cakes to the soil in a way increases the mobility of trace elements in soil, thereby increasing their availability to plants. This might be one of the reasons that in oil-cake amended soil the plants seldom suffer from deficiency symptoms.

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