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5- SUMMARY

The purpose of this study is to investigate:

1. Single adsorption of zinc, copper, cadmium, and lead by different soils
2. Correlation of some soil properties with metal adsorption.
3. Identifying the direct effect of soil property on metal adsorption by using a statistical technique called path analysis that partitions correlation into direct and indirect effects.
4. Effect of metal (i.e., Zn, Cu, Cd, and Pb) added separately to different soils on its content and growth of corn plant grown in those soils.
5. Relationship between the metal adsorption by soil and the metal uptake by plant.

To achieve these aims, two experiments were conducted in laboratory and greenhouse as follows:

<u>Experiment I</u>:

Twenty-one surface soil samples (0 - 20 cm) were collected from different locations to represent a diverse physical and chemical soil properties. The soil samples were air-dried, ground to pass through a 2-mm sieve, and some soil properties were estimated (e.g., EC, pH, CEC, OM, $CaCO_3$ and particle-size distribution). Metal adsorption was individually determined by equilibrating the soils with varying concentrations of the metal at a 1:10 soil solution ratio in the absence or

presence of 0.01M $CaCl_2$. The suspension was left for 24 h to equilibrate, shaken for 30 min, centrifuged at 4000 rpm and then filtered. The filtrates were analyzed for respect metal by using atomic absorption spectrophotometer. The difference between the initial and final concentration was the quantity of metal adsorption by soil. The data of adsorption isotherm were first calculated according to the Langmuir equation to obtain the adsorption parameters, which are the metal adsorption maxima "b" and the bonding energy "k". The data were also described by the Freundlich equation to estimate the empirical parameters of "n" and "log a".

Experiment II:

This study was carried out as a pot experiment in greenhouse culture with three different selected soils (El-Boussily clayey soil, Burg El-Arab calcareous soil, and El-Boussily sandy soil). Corn as an indicator plant was seeded and plants were thinned up to 2 plants/ pot and received a uniform sufficient application of NPK fertilizers. Metals of Zn, Cu, Cd, and Pb were individually applied at five levels of each after 17 days of cultivation. Each treatment was replicated three times in a randomized complete block design. After 42 days from cultivation, the top plants growths were harvested and dry weight yield were determined after oven drying at $70^{\circ}C$ for 48 h. The plant materials were ground and analyzed for tested metals after digestion.

The obtained results are summarized as follows:

A) – Heavy metals adsorption by soils:

1 – The clayey soils appeared to adsorb the highest amount of metals under study, and followed by calcareous soils and then sandy soils.

2 – Lead was quantitatively the highest metal adsorbed by soils compared to the other studied metals and the sequence was as follows: Pb > Cu > Zn > Cd.

3 – The presence of 0.01M $CaCl_2$ in initial solution reduced the adsorbed quantity of metals especially in sandy soils. This reduction was more pronounced with Zn and Cd, where it was less pronounced with Cu and Pb.

4 – Results showed that the models of Langmuir and Freundlich were greatly significant fitted to the data of metals adsorption by studied soils either in the absence or presence of 0.01M $CaCl_2$.

5 – With respect of Langmuir constants for Zn adsorption, it was found that the b values were higher for clayey soil > calcareous soil > sandy soil, while the k values were higher for calcareous soil > clayey soil > sandy soil. For Freundlich constants, it was found that the log a values were higher for clayey soil > calcareous soil > sandy soil, while n values where higher for clayey soil > sandy soil > calcareous soil.

Statistically, the presence of $CaCl_2$ reduced all values of adsorption constants and the effect was significant with values of log a and k while it was not significant with values of b and n.

6 – Concerning the Langmuir constants for Cu adsorption, it was observed that the b values were higher for calcareous soil > clayey soil > sandy soil, while the k values were higher for clayey soil > calcareous soil > sandy soil. On the other hand Freundlich constants showed that the log a values were higher for clayey soil

> calcareous soil > sandy soil, while the n values were higher for calcareous soil > clayey soil > sandy soil.

The presence of $CaCl_2$ reduced all values Langmuir and Freundlich constants but the effect was not significant.

7 – With regard to Cd adsorption, the Langmuir constants showed that the b values were higher for clayey soil > calcareous soil > sandy soil, while the k values were higher for calcareous soil > clayey soil > sandy soil. On the other hand, the Freundlich constants revealed that both values of log a and n were higher for clayey soil > calcareous soil > sandy soil.

The effect of $CaCl_2$ on adsorption constants was the same to the result that obtained with Zn where the effect was significant for values of log a and k and not significant for values of b and n.

8 – Regarding to Pb adsorption, it was observed that all estimated constants of Langmuir and Freundlich were higher for clayey soil > calcareous soil > sandy soil.

The presence of $CaCl_2$ effect on Pb adsorption constants as similar to that obtained with Cu where the values of all adsorption constants were reduced but this effect was not significant.

B) – Effect of soil properties on heavy metal adsorption:

In contrary to adsorbed quantity (q) of metal, either constant (b) or (log a) has a single and distinct value for each soil, so they often used to study their relationship with other soil properties. In this study two statistical techniques were employed to evaluate the relationship between adsorption parameters and six important properties (i.e., EC, pH, OM%, $CaCO_3$%, clay %, CEC) of 21 soil samples.

1 – The use of statistical path analysis technique revealed the following results:

a – Zinc:

The CEC soil property only had the highest positive direct effect on the values of (b) constant while the $CaCO_3$% soil property had the highest positive effect on values of (log a), either with or without $CaCl_2$.

b - Copper

The b values were directly affected by $CaCO_3$% and followed by pH while values of (log a) were directly affected only by the CEC, either with or without $CaCl_2$.

c – Cadmium:

Without $CaCl_2$, organic matter and calcium carbonates of soils directly affected the (b) values of Cd. The presence of $CaCl_2$ diminished the direct effect of soil properties as indicated from nonsignificant R^2 values. On the other side, the soil properties did not directly affect the (log a) values despite the significance of R^2. This contrary was inferred by the highly intercorrelation between soil properties. Another path analysis constructed and revealed that CEC directly affected values of (log a).

d – Lead:

Generally, the soil properties did not directly affect the values of (b) as indicated from unsignificant values of R^2. The direct effect of soil properties on values of (log a) varied. Soil CEC and $CaCO_3$ had positive direct effect, either with or without $CaCl_2$. On the other hand, Soil EC and clay content had negative direct effect on (log a) values only with $CaCl_2$.

2 – The best multiple regression model was performed to chose only the best three soil properties that correlated with the (b) and (log a) values. The soil properties were differently regressed with adsorption constants. In general, the CEC was the most important variable, followed by $CaCO_3$ and then clay content, while the pH, OM, and EC were less important.

C) - Supply parameter and soil properties:

Supply parameter was used as indicator to express about the adsorbed of metal in the soil, the metal concentration in the soil solution, and the metal buffering capacity in the soil. The supply parameter was calculated for 21 soil samples at different initial concentrations of metal in the aqueous solution and the results were as follows:

1 – The behaviour of supply parameter for soils varied towards the low and high initial concentrations of the metal.

2 – Increasing initial concentrations of metal increased the supply parameter and the increment this study conditions was followed the order: sandy soils > calcareous soils > clayey soils.

3- Statistical correlation between supply parameter and soil properties revealed that CEC, clay content and organic matter correlated highly and inversely with the supply parameter of metals. On the other hand, the supply parameter of metals strongly and directly correlated with sand percentage. Either $CaCO_3$ or pH correlated slightly with the supply parameter for Cu and Pb and no consistent correlation was observed for Zn and Cd.

D) - Soil application of heavy metals in relation to plant growth:

1 – Plant dry weight

Statistical analysis revealed that the tested soils (clayey, calcareous, and sandy) had a significant effect on plant dry weight that was higher in clayey soil > sandy soil > calcareous soil. Compared to the control, the relative dry weight was more pronounced for plants grown on calcareous soil than that grown on clayey and sandy soils.

The metals differently affected plant growth where Cd significantly reduced the dry weight of plant while Zn, Cu and Pb effects did not significantly vary.

With regard to levels of heavy metals application, data showed that Zn and Cd had a significant effect on plant dry weight .Zn addition up to 100 mg/kg soil increased plant dry weight and decreased at level addition of 400 mg/kg soil. Cadmium reduced the plant dry weight at the highest level addition that of 50 mg/kg soil. With for Cu and Pb levels changed plant dry weight, their effects were not significant.

2 – Heavy metal concentration in plant :

Results revealed that the tested soils had significant effect on Zn, Cd and Pb concentration in plant but not on Cu concentration. Generally, the concentration of metals was lower in plants grown on calcareous soil than clayey and sandy soils and the two latter did not significantly differ.

Compared metals concentration in plant illustrated that Zn > Cu > Pb > Cd and the difference was significant over all.

Increasing the level application of metals significantly increased their respective concentration in plant and the variance was more pronounced in sandy soil than clayey and calcareous soils.

3 – Heavy metal uptake by plant:

Results showed that the tested soils had a significant effect on metal uptake by plant. The plant uptake pattern behaved the same trend as the plant concentration where plant grown on calcareous soil taken up less metal than that of clayey and sandy soils and the two latter did not significantly differ.

Also, metals were significantly varied in their uptake by plant and followed the sequence of Zn > Cu > Pb > Cd.

For all metals, the levels of application significantly increased the metal uptake by plant except the latest two levels exhibited non-significant difference.

E) - The relationship between heavy metal adsorption by soil and its uptake by plant:

Results illustrated that the supply parameter was correlated better with plant dry weight, metal concentration in and uptake by plant. Comparing to the equilibrium metal concentration in soil solution, the supply parameter as a measurement scale was easier and improved the predication of growth and metal status of plant.