

Predicted Speciation and Mineral Solid Phases of some Heavy Metals in Sludge - amended Soil

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ABSTRACT

Speciation of heavy metals exerts important controls on chemical behavior, solubility, toxicity, adsorption and even physical properties of solutions (Ure and Davidson 2002). In the present study, speciation and mineral–solid phase of Cd, Ni, and Pb in solution of soil prolonged irrigated with sewage effluent were predicted using GEOCHEM model (Sposito and Mattigod (1980) and constructed stability diagrams (Sposito, 1989 and Lindsay, 1979). The present data indicate that total contents of all tested metals have increased dramatically as a result of sludge amending, particularly, for Cd. In virgin soil solution, the results of speciation indicated that, free species M^{2+} was the prevalent form (60.35%) followed by carbonate species MCO_3aq (20.12%), MSO_4 (5.93%), $MHCO_3^+$ (5.56%), MOH^+ (4.21%) and MCL^+ (4.21%), while in sludge – soil solution the sequence was; M-DOC (41.92%), followed by $MHPO_4$ species (26.74%), M^{2+} (20.07%), $MHCO_3^+$ (4.22%), MSO_4 aq (3.49%) and MCO_3 aq (2.02%). It is clear from the results that amending soil with sludge decreases active portion (M^{2+}) contribution to total speciation of the tested metals. In virgin soil, the majority of both Cd and Ni was (M^{2+}) species. It amounted (79.03%) and (83.8%), respectively. While MCO_3aq was the prominent for Pb (55.86%). In sludge-soil, Pb was almost exclusively in organically complexed forms (88.54%), while the majority species of Ni was M^{2+} (38.56%) and for Cd, $CdHPO_4aq$ (58.72%). The data also showed that in sludge- soil the activities (M^{1+}) of both Pb and Ni decreased by 26% and 72%, respectively, compared to their corresponding values in virgin soil. Meanwhile, the activity of Cd increased. These findings suggesting that amending soil with sludge probably inhibit activities of some metals, while promote activity of others. The data showed that the values of activities of Cd in virgin soil was closed to the solubility of $CdCO_3$ ($\log CO_2 = -2.52$) and $CdSO_4 \cdot 2Cd(OH)_2$ ($\log SO_4 = -2$), while in sludge soil, the value of Cd^{2+} was under saturated with respect the constructed Cd- minerals. This suggested that other possible solid phase of cadmium may be controlling its activity in that soil. Also, the data suggested that activity of Ni^{2+} in virgin soil is governed by $Ni_3(PO_4)_2$ in equilibrium by gypsum. While in sludge-soil, value of Ni^{2+} was controlled by $Ni_3(PO_4)_2$ in equilibrium with Calcium phosphate mineral at ($\log CO_2 = -4.52$). Also, the results indicated that $Pb_3(CO_3)_2(OH)_2$ was the possible solid phase which may be controlled the activity of Pb^{2+} , in both virgin and sludge soil.

Keywords; sewage effluent, heavy metals, speciation, stability diagrams

INTRODUCTION

Many farmers around the world are even compelled to use sewage effluent water to irrigate their crops, due to paucity of fresh water (absence of alternatives). Despite that water contains high levels of organic materials and plant nutrients, and it also contains numerous pathogenic microorganisms, toxic compounds and heavy metals (metalloids). The majorities of heavy metals are toxic even at low concentrations and are capable of entering the food chain, where they accumulate and inflict damage to living organisms (Davis *et al.*, 1992, Katbata-Pendias, 1993, Alloway, 1995).

It is generally recognized that the particular behavior of heavy metals in the environment is determined by their specific physicochemical forms rather than by their total concentration (Cances, *et al.*, 2003 and Yuan, 2009). In addition, Artiola (2005) and Beata, *et al.* (2014) reported that metals exist in a number of different soluble and particulate forms (species), which influence their mobility and bio availability and free metal activity has been shown to be the key factor in determining metal bioavailability and toxicity in most circumstance (Parker and Pedler, 1996, Weng *et al.*, 2001).

There are several methods for determination metal species in soil solution, each method has its advantages and limitations ((Florence, 1986, Apte and Batley, 1995, Mota and Correia dos Santos, 1995) and generally based on a more profound analytical background (e.g., pH, concentration of competing ions, concentration of complexing ligands in solution, and the soil colloid) and characteristics of soil biota (Temminghoff *et al.*, 2000). For instance, Ion selective electrode (ISE) method is simple and cheap and directly measure the free portion of metal in solution (Mota and Correia dos Santos, 1995). But its detection limit is high, and may also suffer from inter-

ferences. The voltammetric and polarography methods is a very sensitive, but the equilibrium of reaction is hardly achieved (Nordstrom, 1996). Competitive chelation could achieve free heavy metal ions concentrations directly with good sensitivity, while chelates attain equilibrium with soils very slowly (Norvell and Lindsay, 1969, 1972, Workman and Lindsay, 1990). The cation exchange resin method is rapid and sensitive, but required some precautions about selected resin (Apte and Batley, 1995). This makes the method complicated (Fotovat and Naidu, 1997). Donnan membrane technique able to measure several free metal ion concentrations at the same time, moreover, all the metals did not interfere each other (Temminghoff *et al.*, 2000 and Li Yi, *et al.*, 2007). They added that attaining equilibrium under procedure circumstances was difficult, beside over estimated due to dissociation of labile species.

Soil solution speciation may be estimated using computer programs like GEOCHEM model (Sposito and Mattigod (1980), MINTEQA model (Allison *et al.*, 1991 and Schecher and McAvoy, 2003) and ORCHESTRA model (Meeussen, 2003). From the computational side, limitations include the uncertainty about the most appropriate equilibrium constants and the measured input data, and the fact reaction kinetics are not considered (Thomas *et al.*, 2005).

Stability diagrams are used as a convenient technique for illustrating how the solubility of metal compounds varies with soil pH and with metal concentration (or activity). The diagrams also allow some prediction of which solid phase regulates metal activity in the soil solution (El-Falaky *et al.*, 1991, El-Gendi, 1994, El-Gendi *et al.*, 2017).

The objectives of this study are to estimate ion speciation of cadmium, Nickel and in sludge-amended soil solution using MINTEQA model (Allison *et al.*, 1991 and

Schecher and McAvoy, 2003) and predict mineral solid phases which may controlling activities of that metals using stability diagrams.

MATERIALS AND METHODS

1-Site description and soil samples

The studied soil samples selected from the agriculture farm of El-Gabal Al-Asfer Sewage station which located at 25 Km north- east of Cairo. This farm has been irrigated with sewage for over 50 years and thereby, provides a possible model of the potential long-term effects of heavy metals on terrestrial ecosystem.

Two sites were selected for sampling the first site represents soils which continuously irrigated with sewage water over 50 years, while the second represent uncultivated area. At each site, five surface soil samples (0 -30 cm) were collected, air-dried, grounded, sieved, mixed to make two composite samples.

2- Soil analysis

The following analysis were carried on the samples;

- 1- Soil organic matter content was determined according to the method of modified Walkley and Black Method, Jackson (1984). Total calcium carbonate content (TCC) in soil was determined volumetrically using Collin's Calcimeter (Jackson 1984). Soil fraction analysis; was carried by pipette method according to Piper (1950). Electrical conductivity, pH and soluble ions were determined in the according to (Page *et al.* 1982). Dissolved organic carbon (DOC) was extracted from 10g fresh soil using 40ml distilled water according to method of Zsolnay (2003). The soil samples were shaken for 30 min at speed of 250 r min⁻¹, the supernatant was centrifuged for 10 min at 15,000 r min⁻¹ and filtered by 0.45µm cellulose ester filters. The extracts were analyzed for C using TOC analyzer. DOC was determined by wet Oxidation which carried out according to the method proposed by Moore (1985). A sample of 25 ml DOC extract was evaporated to dryness at 90°C, and then digested in a boiling water bath for 3 h with 25ml of concentrated H₂SO₄ / H₃PO₄ (2:1 v/v) containing 5g AgSO₄ dm³, and 25ml 0.05 MK₂Cr₂O₇. The amount of dichromate used for the oxidation of DOC was estimated either from back titration using 0.025 M ferrous ammonium sulphate.

2- Soil-solution extraction and chemical speciation

The soil solution of all observed soils was obtained by vacuum displacement method (Wolt and Gravel, 1986), air dried soil samples (100 g each) were wetted with redistilled water to 100% field water capacity and then incubated at room temperature for 72 hours and the soil solution was obtained with the use of a vacuum pump and filtered for the following analysis :

The concentration of major cations ;Na, K, Ca, Mg and major anions (CO₃, HCO₃, Cl, SO₄) were determined according to (page *et al.*, 1982). The concentration of (Co, Cu, Cd, Fe, Mn, Ni, Pb, Si, PO₄ and Zn) were determined by Inductively Coupled Plasma (ICP) Model Ultima-

2-Data treatment:

Speciation calculations were performed using MINTQA2 ver3.11 (Allison *et al.*, 1991). The calculated data are listed in Table (1).

3-Constructing stability diagrams:

Stability diagrams were constructed according to Sposito (1989) and Lindsay (1979).

RESULTS AND DISCUSSION

Soil General properties :

The data presented in Table 1 show that sand fraction is prevailed over the other two fractions. It fluctuates between 58.1% in sludge- soil sample to 82.1% in the virgin soil sample. On the other hand, the data shows that the clay content is higher in sludge - soil (23.4%) compared with virgin soil sample (2.70%). That is may due to sedimentation of fine particles exist in sludge, beside to the influence of organic acids released from sludge's decomposition upon soil particles size.

Table 1. Some of physical and chemical properties of the tested soils

Items	Control soil (virgin)	Sludge- soil (cultivated)
Particle size distribution(%)		
Sand	82.10	58.10
Silt	15.20	18.50
Clay	2.70	23.40
Texture class	Loamy Sand	Sandy Clay Loam
Total calcium carbonate %	1.54	1.09
Soil pH (paste)	7.45	7.01
Soil ECe (dSm-1)	0.82	1.41
Soil organic matter (%)	0.19	5.35

Table (1) refers that the continuous application of sewage effluent markedly reduced both soil pH as well as CaCO₃ content. These findings were probably as a result of organic acids and CO₂ produced during sludge decomposition. Alternatively, electrical conductivity (EC) in sludge soil increased. That is certainly due to salts contained in the applied sludge.

Total metal concentrations in soil solutions are listed in Table (2). It's obvious from the data that concentrations of all tested metals have increased dramatically as a result of sludge amending, particularly, for Cd which increased by 40 times, while Pb increased 3 times and Ni only twice, compared to that concentrations in the virgin soil solution.

Table 2. Chemical Composition of the tested soils calculated as pM*

Item	Virgin soil	Sludge- amended soil
pH	7.54	6.91
Ionic Strength	7.35e-03	0.0207
Cations		
Na	2.690	2.6516
K	3.509	3.154
Ca	3.0300	2.602
Mg	3.119	2.677
	Trace metals	
Cd	7.448	5.846
Co	7.355	5.022
Cu	5.884	4.618
Fe	6.048	4.713
Mn	5.563	4.475
Ni	5.849	5.564
Pb	6.413	5.885
Zn	5.545	4.5036
	Anions	
CO ₃	3.0246	2.3979
Cl	2.720	2.5228
Si (H ₄ SiO ₄)	2.6688	2.6307
SO ₄	3.0135	
NO ₃	-----	2.5528
PO ₄		2.331
DOC		1.8916

* pM = - log M⁻¹

Speciation of the tested metals:

The Speciation of the tested metals were performed using the MINEQL+4.6 program (Schecherand McAvoy, 2003). Table 2 represents the input data of the various ions; calculated as pM (minus log of molar concentration).

The proportions of various species of the tested metals represent as per cent of their corresponding totals, as well as, their activities (M^{1-}) are listed in Table 3.

Table 3. Speciation (%) and activities (M^{1-}) of the tested metals.

Virgin soil			sludge- soil		
Species	% of total	Activity (M^{1-})	Species	% of total	Activity (M^{1-})
Cd species					
Cd ⁺²	79.03	1.96E-08	Cd ⁺²	19.89	1.61E-07
CdCl ⁺	9.97	3.24E-09	CdCl ⁺	3.21	3.97E-08
CdSO ₄ aq	7.46	2.66E-09	CdSO ₄ aq	3.69	5.29E-08
CdCO ₃	1.67	5.97E-10	CdCO ₃	0.36	5.17E-09
CdHCO ₃ ⁺	1.53	4.97E-10	CdHCO ₃ ⁺	1.18	1.46E-08
CuHPO ₄	-----	-----	CdHPO ₄	58.72	8.4E-07
Cd DOM	-----	-----	Cd DOM	12.67	1.65E-07
Ni species					
Ni ⁺²	83.8	8.26E-07	Ni ⁺²	38.56	5.96E-07
NiSO ₄ aq	6.73	9.54E-08	NiSO ₄ aq	6.09	1.67E-07
NiHCO ₃ ⁺	6.31	8.15E-08	NiHCO ₃ ⁺	8.89	2.1E-07
NiCO ₃ aq	2.82	3.99E-08	NiCO ₃ aq	1.11	3.04E-08
NiHPO ₄ (aq)	-----	-----	NiHPO ₄ (aq)	20.23	5.54E-07
Ni DOM	-----	-----	Ni DOM	24.55	6.11E-07
Pb species					
Pb CO ₃ aq	55.86	2.16E-07	Pb CO ₃ aq	4.59	6.02E-08
Pb ⁺²	18.21	4.90E-08	Pb ⁺²	1.75	1.29E-08
Pb OH ⁺	12.18	4.29E-08	Pb OH ⁺	0.29	3.34E-09
Pb HCO ₃ ⁺	8.85	3.12E-08	Pb HCO ₃ ⁺	2.6	2.95E-08
Pb SO ₄ aq	3.59	1.39E-08	Pb SO ₄ aq	0.68	8.9E-09
Pb HPO ₄	-----	-----	Pb HPO ₄ aq	1.28	1.68E-08
Pb DOM	-----	-----	Pb DOM	88.54	1.05E-06

In virgin soil sample, On mean basis, the data show that the tested metals exist mainly in soil solution as free ions M^{2+} (60.35%), followed in decreasing order by carbonate species MCO_3 aq (20.12%). Mean while, MSO_4 aq, $MHCO_3^+$, and MOH^+ species were nearly equal (floculated around 5 %) of their total species, and MCl^+ only amounted (2.76%).

Furthermore, the data of virgin soil show that the free ion (M^{2+}) was the dominate species for Ni (83.8%) and Cd (79.03%). Mean while, the most prominent species of pb was $PbCO_3$ (aq), which accounts more than 55% of total Pb species.

Also, the present results showed that Cd prefers to complex with Cl^+ ligand (9.97%) more than that in SO_4 ligand (7.46%). Mean while the other possible complex ions could be ignored. This results may confirmed by results of Garcia- Miragaya and Page (1976) who mentioned that Cd could make staple complexes with chloride ligands.

In virgin soil, the Table showed that the second most abundant form of Ni was $NiSO_4$ aq and $NiHCO_3^+$ (around 6% for each), followed by $NiCO_3$ (aq) , which exhibits minor part (2.82%).

Meanwhile Pb speciation show that the second order species was Pb^+ (18.21%), followed by $PbOH^+$ (12.48%) , $Pb(HCO_3)^+$ (8.85%) , and $PbSO_4$ aq ((3.59%), (Table 3).

In sewage – amended soil solution, Table (3) indicates that organic complexing exist at appreciable amounts. On mean basis, this species accounted (41.92%), followed by $MHPO_4$ species (26.74%), and M^{2+} species (20.07%). Mean while $MHCO_3^+$, MSO_4 (aq) and MCO_3 (aq) species contribute 4.22%, 3.49%, and 2.02% ,

respectively), while the other possible species could be neglected. It is clear from results that the mean value of uncomplexed species (M^{2+}) decreased from 60.35% (in virgin soil) to 20.07% (in sludge-soil).

The influence of organic amending on metal speciation, was also studied by USMAN *et al.*(2005) and Beata *et al.* (2014) .They concluded that the free portion of metal decreased as amending rate increased. Moreover, Mateusz *et al* (2017) examined the changes in concentrations and speciation of Cu, Zn, and Pb in soil solutions acquired from soils contaminated by emissions and treated with organic materials. They indicated that applying acidic lignite resulted in the release of free metal ions into the solution, while the application of immature compost led to the formation of metal complexes with soluble organic compounds.

Cd speciation in sludge - soil solution (Table 3) showed that the primary species for Cd was $CdHPO_4$ aq (58.72%), followed by Cd^{2+} (19.90%), and Cd -DOC (12.67). In contrast, in Ni speciation the free portion of Ni was the prominent species (38.56%), followed by Ni-DOC (24.55%), $NiHPO_4$ (20.23%), $NiHCO_3^+$ (8.89%), and $NiSO_4$ aq (6.09%).

Pb speciation, (Table 3) indicated that organic complexes was the most prominent species (88.54%), while the contribution of $PbCO_3$ aq was (4.59%) and the other possible species of Pb could be neglected.

The high association of pb with organic ligands may be confirmed with results of Ivanaet *al.*, (2016) who found that Pb^{+2} ions form the most stable complexes with organic ligands. Moreover, they expected that Pb could competing the other investigated M (11) in binding sites of organic ligands.

Activities and prediction of Solid phases which controlling solubility of the tested metals:

The influence of sludge application on activities of the tested metals are listed in Table 3).

As shown from Table (3) that the activities (MI1) of both Pb and Ni decreased by (26% and 72%), respectively , compared with their corresponding values in virgin soil. Meanwhile for Cd, the activity was increased around 8 times more than that in virgin soil. These findings suggesting that amending soil with sludge probably inhibit pollution hazards of some heavy metals and visa versa for some others. In the same connections ,He and Singh , 1993b and Shumun, 1998) reported that certain organic soil amendments had the ability to ameliorate heavy metal toxicity to plants. So, the association of a metal and organic colloids deserve special attention.

Solubility lines of M-ferrite were developed in equilibrium with Fe (OH)₃ (amorphous), Fe(OH)₃ (soil-Fe). Solubility lines of M-aluminate were developed in equilibrium with gypsum, or Al (OH)₃ amorphous . Solubility line of M-silicate were developed in equilibrium with SiO₂ (quartz or soil), while for M-phosphate minerals were developed in equilibrium with gypsum and Ca-phosphate minerals as described by Sposito (1989) and Lindsay (1979) and plotted in Fig 1(a to c).

Plotting the activity values (Cd⁺²) of the tested metals on corresponding stability diagrams (Fig1a). The data show that the solubility of Cd in virgin soil was closed to the solubility of CdCO₃ (log CO₂=-2.52) and CdSO₄-

2Cd(OH)₂ at (log So₄=-2) , while in sludge soil , the value of Cd⁺² was undersaturated with respect the constructed Cd-minerals. This suggested that other possible solid phase of cadmium may be controlling its activity in that soil . In the same connection, Emmerich *et al.*, (1982) reported that activities of Cd, Pb, and Zn in sludge – amended soil were undersaturation with respect the established minerals, suggested that may be another mechanisms involves the solid phase in soil that could control the activity of that metals (as specific adsorption, precipitation, coprecipitation , complexation,...).

Fig 1b shows suggested that the activity of Ni⁺² in virgin soil is governed by Ni₃ (PO₄)₂ in equilibrium by gypsum. While in the value of Ni⁺² in sludgesoil is controlled by Ni₃ (PO₄)₂ in equilibrium with Ca- phosphate mineral at (log CO₂= -4.52). Also, Fig (1c) indicated that Pb₃ (CO₃)₂(OH)₂ is the possible solid phase which may be controlled the activity of Pb⁺², in both virgin and sludge soil. Similar conclusion was also observed by El-Gendi *et al* (2017) who mentioned that values of pb⁺² values were supersaturated with respect of pb(OH)₂, pbCO₃ and pb₃(CO₃)₂(OH)₂ at 0.0003 atm.CO₂. Mean while, In auto exhausted soil, El-Gendi(1994) reported that that the pb⁺² activities were within the range maintained by the formation and /or mixture of PbCO₃, pb₄O(PO₄)₂ , pb₅(PO₄)₃OH , pb₃(PO₄)₂ at equilibrium with (hydroxy apatite) and CaCO₃ at 0.003 atm.CO₂, and pbHPO₄ at equilibrium with (tricalcium phosphate) and CaCO₃ at 0.003 atm.CO₂.

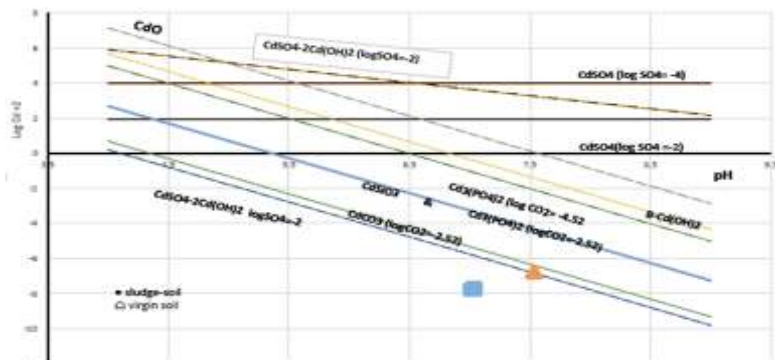


Fig (1a): Stability diagrams of Cd minerals .

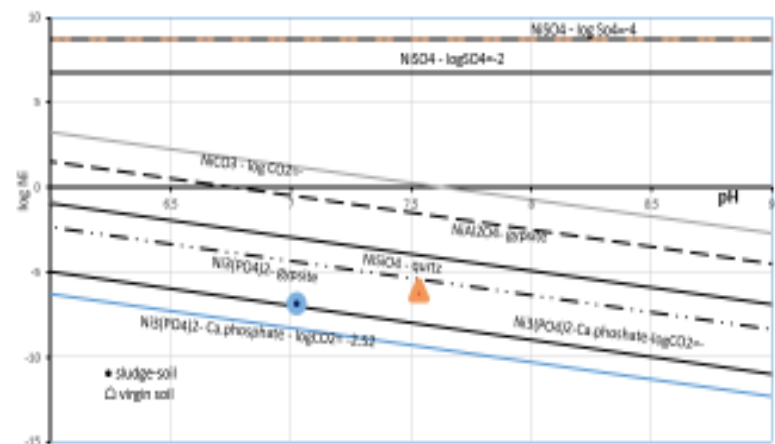


Fig (1b): Stability diagrams of Ni minerals

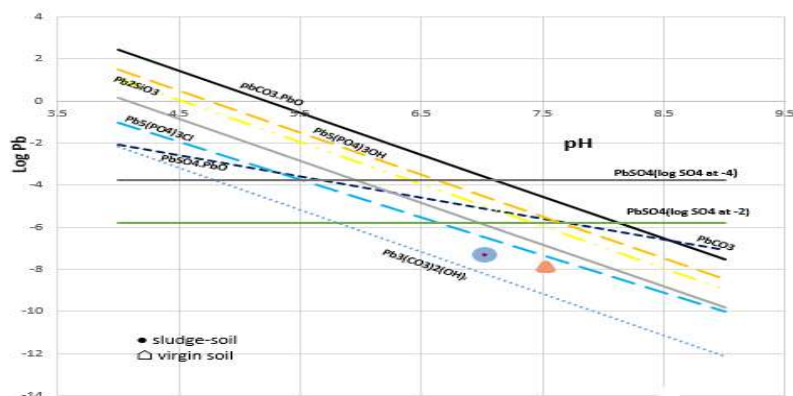


Fig.(1C): Stability diagrams of Pb minerals

REFERENCES

- Allison, J. D., Brown, D. S. and Novo-Gradac, K. J. (1991). *MINTEQA2/ PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 User's manual*; U.S. EPA: Athens, GA.
- Alloway, B. J. (1995). *Heavy Metals in Soils*. Blackie Academic and Professional, Glasgow, Scotland, 368 pp.
- Apte, S. C. and Batley, G. E. (1995). Trace metal speciation of labile chemical species in natural waters and sediments: nonelectrochemical approaches. *Metal Speciation and Bioavailability in Aquatic Systems* (Tessier, A. and Turner, D. R., eds.), 256–306, John Wiley & Sons, Chichester
- Artiola, J.F. (2005). Speciation of copper. In: *Handbook of elemental speciation II. Species in the environment, food, medicine and occupational health*. CORNELIS R. CARUSO J., CREWSH., HEUMANN K. (eds). John Wiley&Sons Ltd., England, 174-187.
- Beata, R., Wieslaw S. and Jan Ł. (2014). Zinc speciation in soil solution of selected Poland's agricultural soils. *Zemdirbyste-Agriculture*. 101(2): 147–152.
- Cances, B., Ponthieu, M., Castrec-Pouelle, M., Aubry, E., Benedetti, M.F. (2003). Metal ions speciation in a soil and its soil solution: experimental data and model results. *Geoderma*, 113: 341-355.
- Chapman, H.D. and Pratt, P.F. (1978). *Methods of analysis for soils, plants and waters*. pp. 50 Univ. of California Div. Agric. Sci., priced publication 4034.
- Davis, A., Ruby, M. V. and Bergstrom, P. D. (1992). Bio availability of arsenic and lead in soils from the Butte, Montana, mining district. *Environ. Sci. Technol.* 26, 461– 468.
- El-Falaky, A.A., Abouloos, S.A., Lindsay, L.W. (1991). Measurement of cadmium activities in slightly acidic to alkaline soils. *Soil Sci.Soc.Am.J.*(55)974-979.
- El-Gendi, S.A., Hassan, M.A. and Elnaka, E.A.(2017). Estimating lead activities in Egyptian alluvial soil using competitive chelation method. *Zagazig J.Agric.Res.*44(4):1315-1323.
- El-Gendi, S.A. (1994). Chemical equilibrium of some heavy metals. Ph.D. thesis. Fac. of Agric., Cairo Univ., Egypt.
- Emmerich, W.E., Lund, L.J., Page, A.L. and Chang, A.C. (1982). Predicted solution phase forms of heavy metals in sewage sludge – treated soils. *J.Environ. Qual.*, 11(2): 182 – 186.
- Florence, T. M. (1986). Electrochemical approaches to trace element speciation in waters: a review. *Analyst* 111, 489–505.
- Fotovat, A. and Naidu, R. (1997). Ion exchange resin and MINTEQA2 speciation of Zn and Cu in alkaline sodic and acidic soil extracts. *Australian J. Soil Res.* 35, 711–726.
- Garcia-Miragaya, J. and Page, A.L. 1976. Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. *Soil Sci. Soc. Am. J.* 40, 658–663.
- He, Q.B. and Singh, R.B. (1993)b. Plant availability of cadmium in soil. II. Factors related to extractability and plant uptake of cadmium in cultivated soils. *Acta.Agric.Scan.* 43: 143-150.
- Ivana, K., Tatjana A., Darko, A.; Ruzica, N., Aleksandar, B., Tatjana, C. and Goran, N. (2016). Interaction of cobalt (II), nickel (II) and zinc (II) with humic-like ligands studied by the ESI-MS and ion-exchange methods. *J. Serb. Chem. Soc.* 81 (3) 255–270. *J. Elem. s.* 695–703.
- Jackson, J. F. C., Nevissi, A. E. and Dervalle, F. B. (1984). "Soil Chemical Analysis". Prentice Hall Inc. Engle Works Cliffs. New Jersey.
- Katbata-Pendias, A. (1993). Behavioural properties of trace metals in soils. *Appl. Geochem.* 2, 3–9.
- Li Yi, Y. H., DuoJun, W. and Yongxuan, Z. (2007). Determination of free heavy metal ion concentrations in soils around a cadmium rich zinc deposit. *Geochemical Journal*, Vol. 41, pp. 235 – 240.
- Lindsay, W. L. (1979). *Chemical equilibria in soils*. John Wiley and Sons. New York.
- Mateusz, C., Anna, K. and Bernard, G. (2017). Speciation of Cu, Zn, and Pb in Soil Solutions Extracted from Strongly Polluted Soils Treated with Organic Materials. *Pol. J. Environ. Stud.* 26(2): 567-575.

- Meeussen, J. C. L. (2003). ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models. *Environ. Sci. Technol.* 37, 1175-1182.
- Moore, T.R. (1985) The spectrophotometric determination of dissolved organic carbon in peat waters. *Soil Sci Soc Am J* 49:1590-1592
- Mota, A. M. and Correia dos Santos, M. M. (1995). Trace metal speciation of labile chemical species in natural waters: electrochemical methods. *Metal Speciation and Bio availability in Aquatic Systems* (Tessier, A. and Turner, D. R., eds.), 205–258, John Wiley & Sons, Chichester.
- Nordstrom, D. K. (1996). Trace metal speciation in natural waters: computational vs. analytical. *Water Air Soil Pollut.* 90,257–267.
- Norvell, W. A. and Lindsay, W. L. (1969). Reactions of EDTA complexes of Fe, Zn, Mn, and Cu with soil. *Soil Science Society of America Proceedings* 33, 86–91.
- Norvell, W. A. and Lindsay, W. L. (1972). Reactions of DTPA complexes of iron, zinc, copper, and manganese with soil. *Soil Science Society of America Proceedings* 36, 773–788.
- Page, A. L., Miller, R. H. and Keeney, D.R. (1982). "Methods of soil analysis". Part 2. Chemical and microbiological properties. 2nd ed. *Agronomy Series 9*, ASA, SSSA, Madison, Wis.
- Parker, D. R. and Pedler, J. F. (1996). Reevaluation of the free ion activity model of trace metal availability to higher plants. *Plant and Soil* 196, 223–228.
- Piper, C. S., (1950). "Soil and Plant Analysis", Interscience Publishing Inc. New York.
- Schecher, W. D., McAvoy, D. C. (2003): MINEQL+. [4.6]. Environmental Research Software, Hallwell, ME, USA.
- Shumun, M.L. (1998). Effect of organic waste amendments on cadmium and lead in soil fraction of two soils. *Commun. Soil Sci. Plant Anal.* 29 (20): 2939-2952.
- Spósito, G. and Mattigod, S.V. (1980). Geochem: a computer program for the calculation of chemical equilibria in soil solution and other natural water systems. *Kearney Found. Soil Sci, Univ of California, Riverside.*
- Spósito, G. (1989). *The chemistry of soils.* Oxford University Press. New York.
- Temminghoff, E. J. M., Plette, A. C. C., Van Eck, R. and Van Riemsdijk, W. H. (2000). Determination of the chemical speciation of trace metals in aqueous systems by WageningenDonnan Membrane Technique. *Anal. Chim. Acta* 417, 149–157.
- Thomas, J., Tjisse, H., Jos, P. and Sjoerde, A. (2005). Modeling of the solid-Solution Partitioning of Heavy Metals and Arsenic in Embanked Flood Plain Soils of the Rivers Rhine and Meuse. *Environ. Sci. Technol.* 39, 7176-7184.
- Ure, A.M. and Davidson, C.M. (2002). "Chemical Speciation in the Environment", Second Edition. Blackwell Science Ltd.
- Usman, A.R.A., Kuzyakov, Y. and Stahr, K. (2005). Effect of Immobilizing Substances and Salinity on Heavy Metals Availability to Wheat Grown on Sewage Sludge-Contaminated Soil. *Soil & Sediment Contamination*, 14:329–344.
- Weng, L., Temminghoff, E. J. M. and Van Riemsdijk, W. H. (2001). Contribution of individual sorbents to the control of heavy metal activity in sandy soil. *Environ. Sci. Technol.* 35, 4436–4443.
- Wolt, J. D. and Graveel, J. 1986. A rapid routine method for obtaining soil solution using vacuum displacement. *Soil Science Society of America Journal*, 50: 602–605.
- Workman, S. M. and Lindsay, W. L. (1990). Estimating divalent cadmium activities measured in arid-zone soils using competitive chelation. *Soil Sci. Soc. Am. J.* 54, 987–993.
- Yuan, G. (2009). Copper, zinc and nickel in soil solution affected by biosolids amendment and soil management. *Aust. J. Soil Res.*, 47: 305-310
- Zsolnay, A., 2003. Dissolved organic matter: artefacts, definitions and functions. *Geoderma* 113, 187–209.

التنبؤ بظهور بعض المعادن الثقيلة في الطور الصلب والسائل في الأراضي المعالجة بالحمأة

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تؤثر صور العناصر الثقيلة في السلوك الكيميائي (الذوبان، السمية، الامصاص) والخصائص الفيزيائية للمحلول. صور الكاديوم والنيكل والرصاص المدمصة على الطور الصلب والذائبة في المحلول الأرضي للأراضي المروية بمياه الصرف الصحي، تم التنبؤ بها باستخدام نموذج GEOCHEM واستنباط حالة الثبات لها. تشير النتائج المتحصلة عليها إلى أن المحتويات الكلية لجميع العناصر المختبره قد زادت بشكل كبير نتيجة استخدام الحمأة خاصة الكاديوم. في محلول التربة غير المعاملة بالحمأة كانت صورة الأيون النشط هي السائدة (60.35%) تليها صورة الكربونات (20.12%) والكبريتات (5.93%) والبيكربونات (5.56%) والهيدروكسيل (4.21%) والكلوريد (4.21%). بينما كان التتابع في محلول التربة المعاملة بالحمأة كالتالي الكربون العضوي الذائب هي السائدة (41.92%) تليها الفوسفات (26.74%) والأيونات النشطة (20.07%) والبيكربونات (4.22%) والكبريتات (3.49%) والكربونات (2.02%). ويتضح من النتائج أن التربة المعاملة بالحمأة تنقل من مساهمة الأيون النشط للصورة الكلية للعناصر المختبره. في التربة غير المعاملة بالحمأة كانت الصورة النشطة لعنصر الكاديوم والنيكل هي السائدة بنسبة 79.03 و 83.8% على التوالي بينما كان الرصاص في صورة الكربونات بنسبة 55.86%. في التربة المعاملة بالحمأة كان معظم صور الرصاص مرتبطة عضوياً (88.54%)، بينما كانت الصورة النشطة لعنصر النيكل هي السائدة (38.56%) والصورة السائدة لعنصر الكاديوم كانت في صورة الفوسفات (58.72%). وقد أظهرت النتائج أن نشاط أيون الرصاص والنيكل انخفض في التربة المعاملة بالحمأة بنسبة 26 و 72% على التوالي بينما زاد نشاط الكاديوم مقارنة بالقيم المناظرة لها في التربة غير المعاملة بالحمأة. هذه النتائج تبين أن التربة المعاملة بالحمأة قد تثبط أنشطة بعض العناصر، في حين تحفز نشاط البعض الآخر. وأظهرت البيانات أن نشاط الكاديوم في التربة غير المعاملة بالحمأة كان قريب جداً من ذوبان كربونات الكاديوم ($\log CO_2 = -2.52$) وكبريتات الكاديوم ($\log SO_4 = -2$)، بينما في التربة المعاملة بالحمأة كانت قيمة الكاديوم غير مشبعة بالمقارنة بالكاديوم المعنى الموجود. وهذا يشير إلى احتمال أن الطور الصلب من الكاديوم قد يتحكم في نشاطه بالترتيب. كما أشارت البيانات إلى أن نشاط النيكل في التربة غير المعاملة بالحمأة يغلف بفوسفات النيكل في حالة الاتزان مع الجيبسيت. بينما في التربة المعاملة بالحمأة نشاط النيكل يغلف بفوسفات النيكل في حالة الاتزان مع معدن فوسفات الكالسيوم عند $\log CO_2 = -4.52$. وقد أوضحت النتائج أن هيدروكسيد كربونات الرصاص هي الصورة الصلبة المحتملة التي تحكم نشاط الرصاص في كل من التربة المعاملة وغير المعاملة بالحمأة.