DETERMINATION OF FREE CD^{2+} SPECIES IN PORE WATER FROM SOIL PREVIOUSLY TREATED WITH SEWAGE SLUDGE USING CATION EXCHANGE RESIN METHOD

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ABSTRACT

Determination of various chemical forms of Cd in soil is important to evaluate its mobility and bioavailability. Little is known about the chemistry of Cd species in soil solution and soil solid phase controlling the Cd^{2+} activity in soil solution. A study was conducted to measure free Cd^{2+} species in soil pore water, previously treated with sewage sludge, using cation exchange resin (Amberlite IR 120-plus resin). The concentration of free Cd^{2+} in soil pore water was very small (less than 2.8 $\mu g l^{-1}$), which represented approximately 0.10, 0.34, and 8.34% of soil total Cd content, DTPA, and NH$_4$NO$_3$ extractable Cd, respectively. However, it represented approximately 90% of soluble Cd. Highly significant positive correlations ($R^2 = 0.83$, $R^2 = 0.98$, $R^2 = 0.73$, and $R^2 = 0.72$, respectively; $p < 0.01$) were found between total, soluble, DTPA, NH$_4$NO$_3$ contents of Cd and pore water free Cd^{2+}, respectively. However, a highly significant negative correlation was found between pore water free Cd^{2+}and soil pH ($R^2 = 0.89$; $P < 0.01$). The solubility diagram suggests that in this study the CdFe$_2$O$_4$ in equilibrium with soil Fe and Fe(OH)$_3$ amorphous regulated the Cd^{2+} activities in soil solution from sewage sludge treated soils.

1. INTRODUCTION

Soil solution in agricultural soils, sludge-amended soils, and industrially polluted soils often contain heavy metals such as Cd. The mobility of these metals in terms of bioavailability to plants and leachability to groundwater may depend not only on the total concentration in soil solution but also on the species of the metals (Bingham *et al.*, 1984 Davies, 1980; Bernhard *et al.*, 1986; Ure and Davison, 1995, Huang *et al.*, 1998). Soil solutions may contain Cd as different chemical species- free divalent cation, inorganic complexes, and organic complexes. Computer predictions of metal species have been successful in well-defined solution with known total concentration of metal and ligand (e.g., McGrath *et al.*, 1986, Hirsch and Banin, 1990, El-Falaky *et al.*, 1991; Badawy, 1992), but these may not accurately predict the species in soil solutions because of the very complex, ill-defined composition of the dissolved organic matter present. Methods for experimentally determining the speciation of Cd in soil solution samples are therefore required.

The mechanisms that control Cd solubility in soils are poorly understood. Adsorption is reported as a likely control mechanism at low levels, whereas perception predominates at a high Cd concentrations (El-Falaky *et al.*, 1991; Badawy, 1992; Street *et al.*, 1977). Santillan-Mmedrano and Jurinak (1975) conducted equilibrium batch studies to obtain solubility data of Cd in soils, and found a decrease in Cd^{2+} activity as pH increases. At a high Cd concentration, the precipitation of $CdCO_3$ or $Cd_3(PO_4)_2$ was believed to regulate Cd solubility, while at low Cd concentration, the equilibrium solution was undersaturated with regard to both minerals. El-Falaky *et al.*, 1991; Badawy, 1992 reported that the Cd activity in soil solution is controlled by $CdFe_2O_4$ in slightly alkaline soils.

The aim of this paper was to determine free Cd^{2+} species in soil pore water using ion exchange resin methods and to identify the soil solid phase controlling Cd^{2+} activities in soil solution in the sewage sludge treated soils.

Theory

The method presented in this study determines the activity of free divalent Cd^{2+} in the samples. This theoretically well-defined determination, is based on the equilibrium established between the activities of the metal ions in the sample solution and the amount of metal ions exchanged onto a cation exchange resin originally saturated with Ca.

The equilibrium chemistry of the Cd in the samples is generally described by the equation:

$$Cd^{2+} + L_n^{j-} \Leftrightarrow CdL_n^{2-j} \tag{1}$$

Where Cd^{2+} is abbreviation for the free Cd ion, L_n^{j-} is a general term for ligands potentially complexing Cd^{2+}, n denotes the number of different ligands that are present in the sample, and CdL_n^{2-j} is the complex formed from Cd^{2+} and L_n^{j-} in the following equation, j is taken to be equal 2. The stability of ML_n complex is characterized by the corresponding stability constant, $K_{c.n}$. For example,

$$K_{c.n} = \frac{(CdL_n)}{(Cd^{2+})(L^{2-})} \tag{2}$$

Where ( ) denotes aqueous phase activities.

The total metal cadmium $[Cd_T]$ in solution before adding resin, determined by atomic absorption spectrophotometer, is

$$\left[Cd_T\right] = \left[Cd^{2+}\right] + \left[CdL_n\right] \tag{3}$$

Where [ ] denotes concentration. The total cadmium concentration $[Cd_T]$ is the only directly measurable parameter in eq.[1] and [2].

The equilibrium of the interaction between the sample in contact with a solid phase such as a resin is described by:

$$RCd \Leftrightarrow Cd_s^{2+} + L_{n.s}^{2-} \Leftrightarrow CdL_{n.s} \tag{4}$$
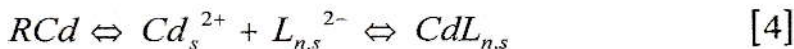
Where RCd refers to the Cd^{2+} exchanged onto the resin and the subscript s denotes the solution phase at equilibrium with the resin. Assuming that only the free divalent metal ion exchanges onto the resin the equilibrium distribution between the resin and the solution can be described by the distribution coefficient, K_d.

$$Kd = \frac{\left[Cd^{2+}\right]_R}{\left[Cd^{2+}\right]_S} \qquad [5]$$

Where $[Cd^{2+}]_R$ is defined as the concentration of Cd^{2+} in the resin phase, and $[Cd^{2+}]_S$ is defined as the activity in the solution phase at equilibrium with the resin.

The total cadmium in solution at equilibrium with the resin is:

$$\left[Cd_T\right]_S = \left[Cd^{2+}\right]_S + \left[CdL_n\right]_S \qquad [6]$$

Assuming that the concentration of metals on the resin is $[Cd_T]_R$, the mass balance yields at equilibrium:

$$\left[Cd_T\right]_R \times W = \left(\left[Cd_T\right] - \left[Cd_T\right]_S\right) \times V \qquad [7]$$

Where

$W =$ the weight of resin

$V =$ volume of the sample solution

The distribution coefficient for the sample experiment is expressed by:

$$Kd = \frac{\left[Cd^{2+}\right]_R}{\left[Cd^{2+}\right]_S} = \frac{\left[Cd_T\right]_R}{\left[Cd^{2+}\right]_S f_2} = \frac{\left[Cd_T\right] - \left[Cd_T\right]_S}{\left[Cd^{2+}\right]_S f_2} \times \frac{V}{W} \qquad [8]$$

Where f_2 is the activity coefficient for divalent ions.

The distribution coefficient of the Cd^{2+} ion onto the resin will depend strongly on the ionic strength, cation composition and pH of the samples. A reference experiment mincing the sample with respect to these characteristics, but without ligands, must be conducted to determine the distribution coefficient as a reference experiment.

$$Kd^* = \frac{[Cd^{2+}]^*}{[Cd^{2+}]^*_S} = \frac{[Cd_T]^*_R}{[Cd^{2+}]^*_S f_2^*} \frac{[Cd_T]^* - [Cd_T]^*_S}{[Cd^{2+}]^*_S f^*_2} \times \frac{V^*}{W^*} \qquad [9]$$

Where superscript * refers to the reference experiment.

Assuming that the free divalent Cd^{2+} has the same affinity for the resin in both the samples and reference experiment, the distribution coefficients for the samples and reference experiment are the same, and that $W = W^*$, $V = V^*$, $f_2 = f_2^*$ the following can be derived from Eq.[8] and [9]:

$$\frac{[Cd_T] - [Cd_T]_S}{[Cd^{2+}]_S} = \frac{[Cd_T]^* - [Cd_T]^*_S}{[Cd^{2+}]^*_S} \qquad [10]$$

Rearranging and dividing by $[Cd_T]_S$ for the sample in equilibrium with the resin yields:

$$\frac{[Cd^{2+}]_S}{[Cd_T]_S} = \frac{[Cd_T] - [Cd_T]_S}{[Cd_T]_S} \times \frac{[Cd_T]^*_S}{[Cd_T]^* - [Cd_T]^*_S} \qquad [11]$$

All variables on the right side of the equation can be measured (Fig.1) and in the following it is shown that the fraction of the total metal in solution present as free divalent ions in the sample in equilibrium with the resin is the same as the fraction of free divalent metal in the original sample.

If the ligand concentration substantially exceeds the total metal concentration, the ratio of Cd^{2+} to the total metal concentration does not change when the sample is exposed to the resin. This statement can be expressed as follows:

$$K_C = \frac{(CdL)}{(Cd^{2+})(L^{2-})} \qquad or = K_C(L^{2-}) = \frac{(CdL)}{(Cd^{2+})} \qquad [12]$$

If $L^{2-} \gg Cd_T^{2+}$, then $L^{2-} = L_T$, where $L_T = L^{2-} + Cd_L$ and

$$K_c(L_T) = \frac{(CdL)}{(Cd^{2+})} \qquad [13]$$

Because the ligand complexed with Cd^{2+} as CdL constitutes only a minor part of the total ligand (L_T). This means that $[CdL] = Kc \times [L_T] \times [Cd^{2+}]$ and that

$$\frac{[Cd^{2+}]}{[Cd_r]} = \frac{[Cd^{2+}]}{[CdL] + [Cd^{2+}]} = \frac{[Cd^{2+}]}{[Cd^{2+}](K_c[L_T] + 1)} \qquad [14]$$

As long as the assumption $L^{2-} \gg Cd_T^{2+}$ is satisfied, the fraction of the total metal in solution present as free divalent ions does not depend on the total metal concentration expressed as:

$$\frac{[Cd^{2+}]_S}{[Cd_T]_S} = \frac{[Cd^{2+}]}{[CdT]} \qquad [15]$$

Relating this to Eq.[11] yields the final equation for determining the free divalent Cd^{2+}

$$\frac{[Cd^{2+}]}{[Cd_T]} = \frac{[Cd_T] - [Cd_T]_S}{[Cd_T]_S} \times \frac{[Cd_T]^*_S}{[Cd_T]^* - [Cd_T]^*_S} \qquad [16]$$

2. MATERIALS AND METHODS

2.1. Soil samples

The soils were sampled in spring 1999 from a long-term sewage field experiment held at ADAS Rosemaund, Herefordshire, United Kingdom. Initially, the experiment was established in 1968 at the Luddington Experimental Husbandry Station, Warwickshire, on a sandy loam textured soil (14% clay). Sewage sludges obtained from sewage works which had sludges 'naturally' rich in either Zn, Cu, Ni

or Cr were applied to attain a range of soil metal concentrations. The Cr-sludge was also contaminated with Cd. Control non-metal enriched sludge was used where necessary to make up quantities, so that all sludged plots received 125 tds ha^{-1} in 1968, or as four annual applications of 31 tds ha^{-1} between 1968 and 1971. Ten metal treatments were established including untreated soil and uncontaminated sludge control treatments (Table 1). The design was a randomised block with four replicate plots per treatment. The initial soil pH was 6.2 and plot sizes were 1.8m x 4.5m. In July 1991, the soils were excavated and transferred to ADAS Rosemaund, Herefordshire, where isolated plots (1.2m x 1.2m) were established using oil tempered hardboard.

Table 1 shows the treatments sampled in April 1999, thirty years after sludge addition ceased. Twenty soil cores were collected from each plot to a depth of 25 cm using a Dutch auger made of tempered steel, and bulked in the field to give representative samples of each plot. The samples were sieved moist to <3 mm, thoroughly mixed and separated into 1 kg (oven dry basis) portions to give triplicate samples for each plot.

2.2. Soil analysis

Representative sub-samples of the soils were air dried, ground to <150 m in an agate ball mill and digested using concentrated HNO$_3$/HCl acids (4:1 v/v), (McGrath and Cunliffe, 1985). Total Cd concentrations were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES; Accuris), and Graphite Furnace Atomic Absorption Spectrometry (Perkin Elmer GF-AAS-4100ZL), with Zeeman background correction, for Cd. Soil pH and EC were determined in deionised distilled water (1: 2.5 w/v), and soil %C and %N using a Leco combustion analyser (Leco® CNS-20000). DTPA-extractable Cd: Cadmium was determined for all tested soils samples using 0.005 M DTPA (diethylene triamine penta acetic acid) extract as described by Lindsay and Norvell (1978). NH$_4$NO$_3$ - extractable Cd: Cadmium was extracted using 1M NH$_4$NO$_3$ and measured for all tested soil samples using GF-AA flame atomic absorption spectrophotometer.

2.3. Determination of free Cd^{2+} concentration in soil pore water

Rhizon soil moisture samplers from Rhizosphere Research Products, Wageningen, Holland were used to extract soil pore water following the procedure of Knight et al., (1998). Briefly, as shown in Fig.1, these samplers consist of a length of inert porous (0.2 μm) plastic tubing, capped with nylon at one end, through which the soil pore water is extracted. The other end is attached to a 5 cm length of polyethylene tubing joined to a female luer lock. Two samplers were placed diagonally opposite each other from the lip of the pot to the base into each of three replicate 1.0 kg (dry weight) pots of soil. Initially, the soil was made up to 50% water holding capacity (WHC) with deionised water, and two weeks prior to extraction, to 75% WHC. Acid washed disposable syringes, attached to the luer lock, and was used to extract pore water from the soil. Free Cd^{2+} concentrations in soil pore water were determined using a calcium saturated cation exchange resin method (Holm et al., 1995).

2.4. Statistical analysis

Genstat 5 (1987, 3rd ed.) was used for all statistical procedures.

3. RESULTS AND DISCUSSION

3.1. *General properties of the soils:* The experiment was established in 1968 at the Luddington Experimental Husbandry Station, Warwickshire, U.K., on a sandy loam textured soil (14% clay), and the samples for this study were collected in 1999. Data in Table (1) show that the soil C%, N%, and C/N ratio in all treatments ranged from 1.42 to 2.03 %, from 0.152 to 0.201 %, and from 9.0 to 11, respectively. Soil pH was ranged from 6.3 to 6.9. However pH of soil pore water were from 6.8 to 7.4. The metal oxides concentration in all plots ranged from 515 to 643 for Al, 2722 to 3152 for Fe, and 201 to 253 mgkg^{-1} for Mn. The dissolved organic carbon (DOC) values ranged from 7.3 to 9.2 mgl^{-1}.

3.2. *Cadmium in soil and soil pore water:* Soil total Cd values (Table, 2) in all plots ranged from 0.33 to 2.60 within an average 0.85 mgkg^{-1}
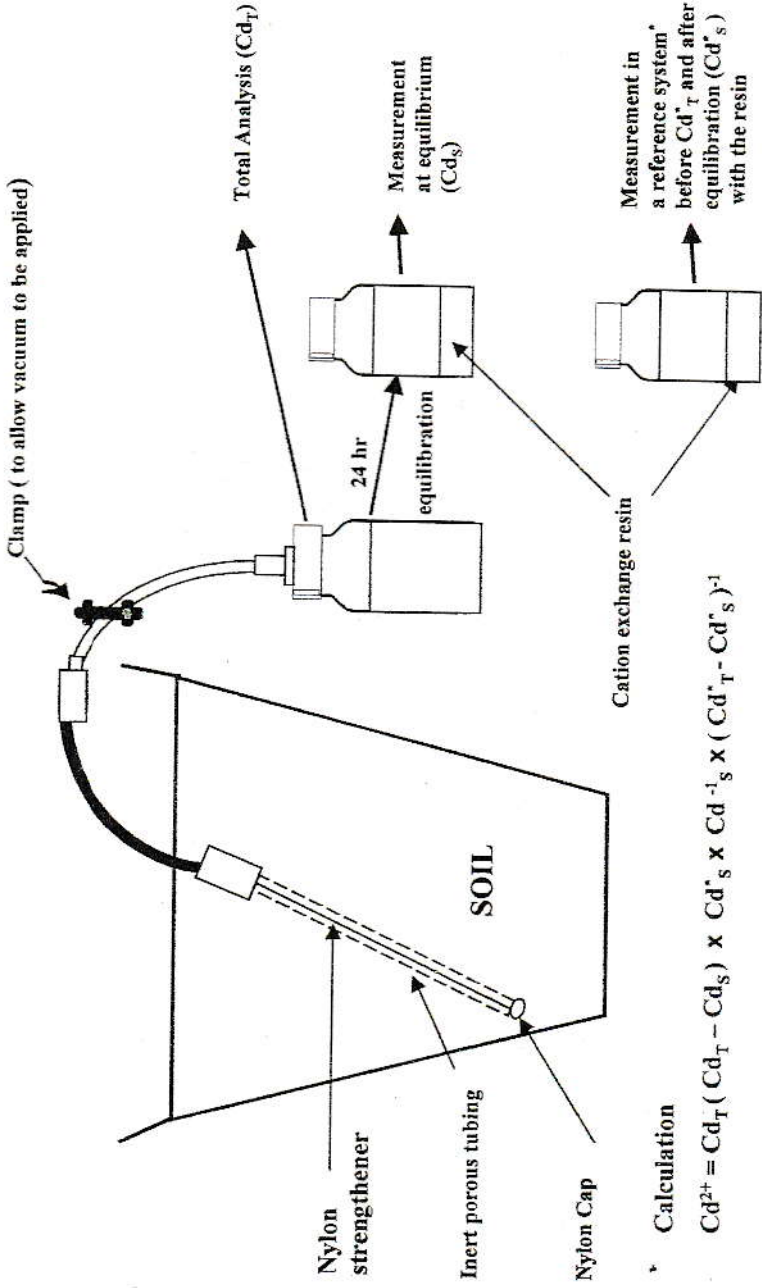
Fig.(1): The experimental procedures and calculation for determination of Cd species in soil pore water.

Clamp (to allow vacuum to be applied)

Total Analysis (Cd_T)

Measurement at equilibrium (Cd_S)

Measurement in a reference system* before Cd^*_T and after equilibration (Cd^*_S) with the resin

24 hr equilibration

Cation exchange resin

SOIL

Nylon strengthener

Inert porous tubing

Nylon Cap

* Calculation

$Cd^{2+} = Cd_T (Cd_T - Cd_S) \times Cd^*_S \times Cd^{-1}_S \times (Cd^*_T - Cd^*_S)^{-1}$

Table (1): Chemical characteristics of studied soils.

No.	Treatment	Soil				Soil pore water			Oxides (mgkg^{-1})		
		pH	C (%)	N (%)	C/N	pH	EC (mScm^{-1})	DOC (mgl^{-1})	Al	Fe	Mn
1	No sludge control	6.9±0.3	1.42±0.04	0.152±0.005	9±0.40	7.1±0.2	1.66±0.12	7.9±0.9	515±3	2730±45	209±6
2	Uncont. Sludge	6.3±0.2	1.79±0.10	0.156±0.004	11±0.45	7.3±0.3	1.55±0.10	7.3±0.3	528±11	2722±55	201±8
3	Low Zn	6.4±0.5	1.69±0.12	0.156±0.009	11±0.33	7.3±0.3	1.79±0.05	8.7±0.6	531±9	2824±65	227±17
4	High Zn	6.3±0.3	1.74±0.06	0.160±0.003	11±0.21	6.8±0.3	1.75±0.13	7.2±0.6	545±11	2884±64	231±24
5	Low Cu	6.7±0.4	1.76±0.07	0.167±0.005	11±0.40	7.4±0.1	1.37±0.11	9.2±0.7	643±20	3152±74	228±22
6	High Cu	6.5±0.4	2.03±0.08	0.201±0.006	10±0.17	7.2±0.2	1.54±0.21	11.9±0.7	642±12	3138±64	225±21
7	Low Ni	6.6±0.3	1.81±0.03	0.161±0.003	11±0.08	7.3±0.1	1.45±0.14	8.8±1.2	565±10	3071±18	253±28
8	High Ni	6.6±0.1	1.68±0.04	0.169±0.004	10±0.06	7.4±0.1	1.49±0.12	8.3±0.4	545±16	3099±109	213±7
9	Low Cr*	6.7±0.2	1.62±0.08	0.152±0.004	11±0.26	7.3±0.2	1.37±0.11	8.6±0.8	533±11	2868±82	209±3
10	High Cr*	6.8±0.2	1.66±0.05	0.177±0.006	9±0.07	7.4±0.1	1.44±0.16	8.6±0.2	579±17	3008±56	213±2

All treatment values are means of 4 replicate plots ± Standard Errors of Means (SEM)

*Cr sludges contaminated with Cd

the highest value was found in high Cr application rate and represented approximately 6 times that of the control treatment. DTPA and NH_4NO_3 extractable values (Table, 2) ranged from 0.08 to 0.80 within an average 0.26, and from 0.002 to 0.033 within an average $0.011 mgkg^{-1}$, respectively. The highest value was found in high Cr application rate and represented approximately 10, and 15 times that of control for DTPA and NH_4NO_3, respectively. The percentage of Cd content extracted by DTPA and NH_4NO_3 ranged from 20 to 42 within an average 32 %, and from 0.44 to 2.2 within an average 1.27% from total content, respectively. Highly significant relationships were found between both DTPA and NH_4NO_3 – extractable with total Cd ($R^2 = 0.86$, and $R^2 = 0.81$, respectively; $P < 0.01$). Also, the data (Fig.2c) shows the linear increase in NH_4NO_3 as increasing in DTPA extractable-Cd ($R^2 = 0.71$; $P < 0.01$). There were increase in soil pore water soluble Cd as increased total soil content (Table2; $R^2 = 0.80$; $P < 0.01$). The percentage value of soluble Cd ranged from 0.05 to 0.13 with an average of 0.12 % from the total.

3. 3. *Free Cd^{2+} species in soil pore water:* Data in Table (2) show that the free Cd^{2+} in soil pore water was very small value (less than 2.8 $\mu g l^{-1}$), which represented approximately, 0.10, 0.34, and 8.34% of soil total Cd contents, DTPA, and NH_4NO_3 extractable Cd, respectively, However, approximately 90% from soluble Cd. Figures 2a, and 2b, 3 shows relationships ($R^2 = 0.98$, $R^2 = 0.73$, and $R^2 = 0.72$, respectively; $p < 0.01$) between each of soluble, DTPA, NH_4NO_3 contents of Cd with the pore water free Cd^{2+} respectively. A highly significant negative correlation was found between pore water free Cd^{2+} and soil pH ($R^2 = 0.71$; $P < 0.01$). El-Falakey *et al.*, 1990; Badawy, 1992, reported the same trend, they found the Cd^{2+} activity in soil solution increased with decreased soil pH.

Cadmium minerals that control the level of Cd in soils were plotted on an equilibrium solubility diagram in terms of Cd^{2+} activity and pH (Fig.4). The thermodynamic data taken from Lindsay, 1979 and El-Falakey *et al.*, 1991 were used to calculate the equilibrium relationships. Figure 5 shows that the measured soil pore water Cd^{2+}

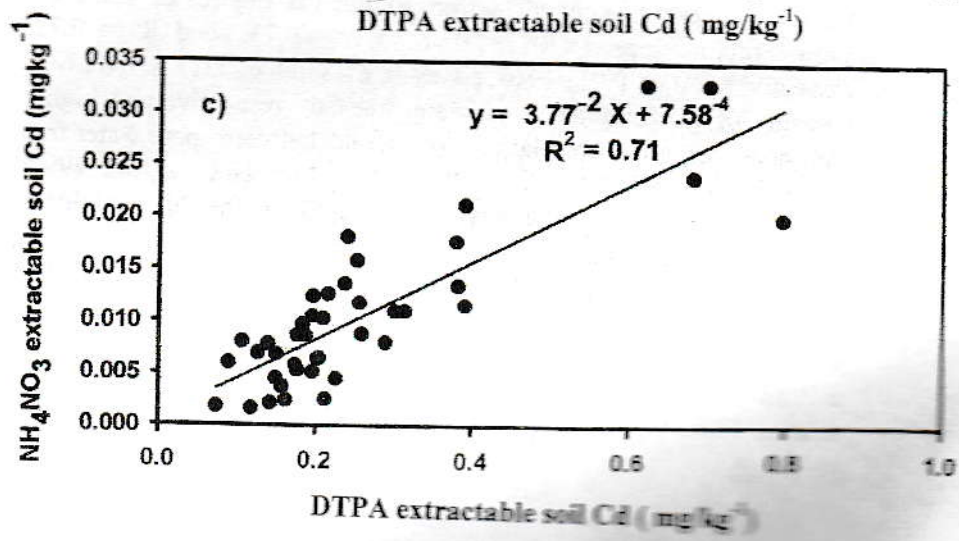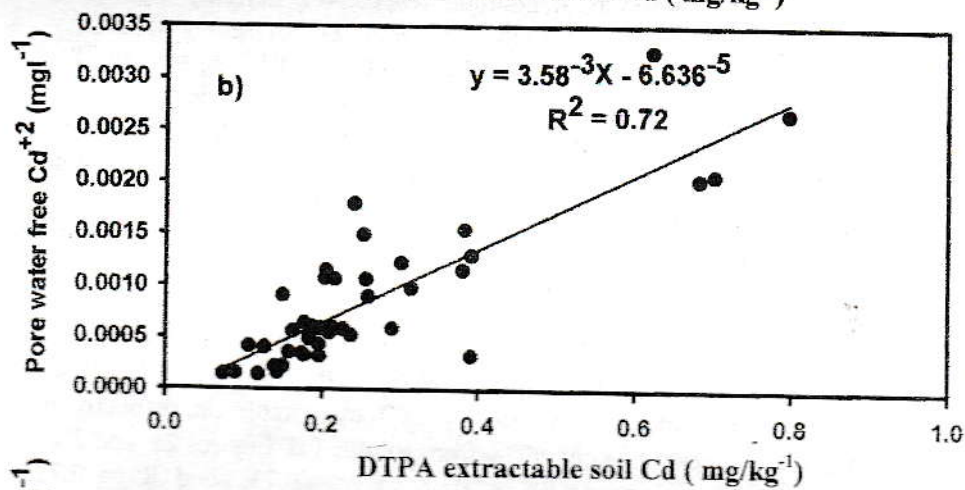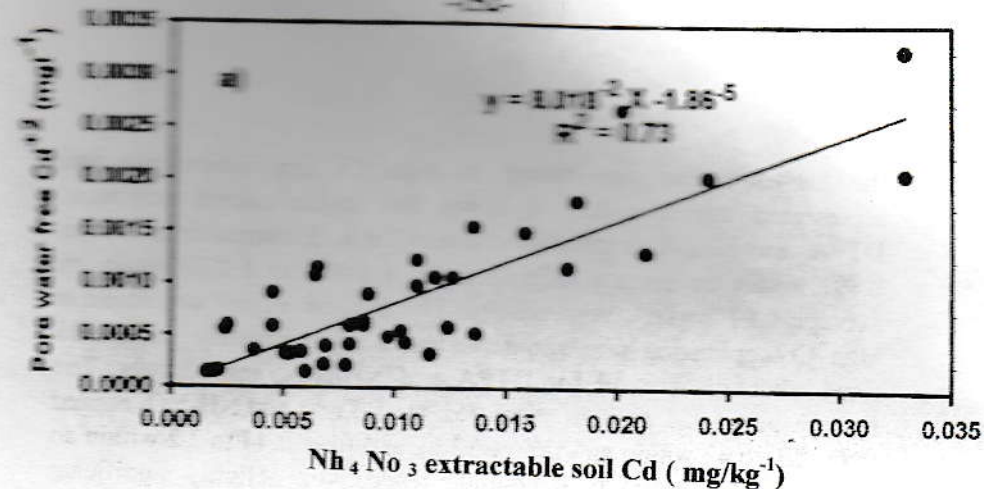Fig. (2): Relationship between free cd^{+2} in soil solution and a) $NH_4 NO_3$ extractable soil Cd. and b) DTPA extractable soil Cd.c) relationship between DTPA and $NH_4 NO_3$ extractable Cd.
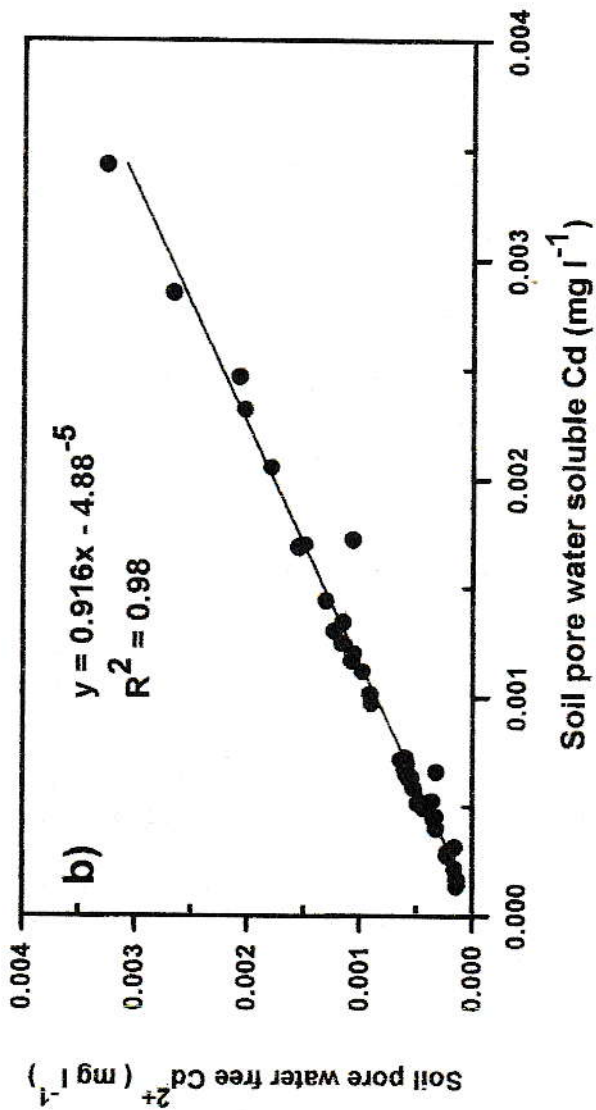
Fig. (3): Relationship between soil pore water Cd and soil pore water free Cd^{2+}

b)

$y = 0.916x - 4.88^{-5}$

$R^2 = 0.98$

Soil pore water soluble Cd (mg l^{-1})

Soil pore water free Cd^{2+} (mg l^{-1})

Table (2): Cadmium content of studied soils.

No.	Treatment	Soil Cd contents (mgkg^{-1})			Soil pore water Cd concentrations (µgl^{-1})	
		Total	DTPA-extractable	NH$_4$NO$_3$-extractable	Soluble Cd	Free Cd^{++}
1	No sludge control	0.40±0.07	0.109±0.03	0.005±0.003	0.28±0.09	0.23±0.06
2	Uncont. Sludge	0.45±0.03	0.153±0.04	0.007±0.002	0.56±0.09	0.44±0.11
3	Low Zn	0.42±0.03	0.194±0.02	0.010±0.003	0.40±0.10	0.34±0.09
4	High Zn	0.53±0.02	0.281±0.03	0.012±0.002	0.57±0.05	0.44±0.06
5	Low Cu	0.67±0.02	0.145±0.03	0.005±0.015	0.54±0.06	0.47±0.06
6	High Cu	0.90±0.04	0.192±0.04	0.006±0.002	1.33±0.13	1.19±0.11
7	Low Ni	0.69±0.06	0.223±0.12	0.010±0.006	1.01±0.25	0.77±0.13
8	High Ni	0.69±0.06	0.223±0.11	0.007±0.003	1.04±0.14	0.93±0.13
9	Low Cr (low Cd)	1.16±0.06	0.348±0.11	0.018±0.007	1.61±0.17	1.45±0.14
10	High Cr (high Cd)	2.43±0.13	0.721±0.130	0.027±0.007	2.77±0.25	2.51±0.29

All treatment values are means of 4 replicate plots ± Standard Errors of Means (SEM)

activities are undersaturated with regard to the solubility of $CdSiO_3$ in equilibrium with SiO_2 (soil) or SiO_2 (quartz) and $CdCO_3$ in equilibrium with CO_2. Also, the measured soil pore water Cd^{2+} activities are undersaturated with regard to the solubility of $Cd_3(PO_4)_2$ in equilibrium with strengite-soil Fe, strengite-$Fe(OH)_3$, TCP-$CaCO_3$, and DCPD-$CaCO_3$. However, the measured Cd^{2+} activity are within the level maintained by $CdFe_2O_4$ in equilibrium with soil Fe, maghmite and $Fe(OH)_3$ amorphous. This represented that the Cd^{2+} activity in tested soils is regulated by $CdFe_2O_4$ .The same trend was found by El-Falakey et.al, 1990; and Badawy, 1992.

CONCLUSION

The method in this experiment is able to determine free Cd^{2+} at low concentration of Cd in soil solution (0.3-2.8 µgl^{-1}). The low metal concentration and the small sample volume were specifically addressed to make the method applicable to soil solutions, but the method is also appropriate for samples with higher concentrations.
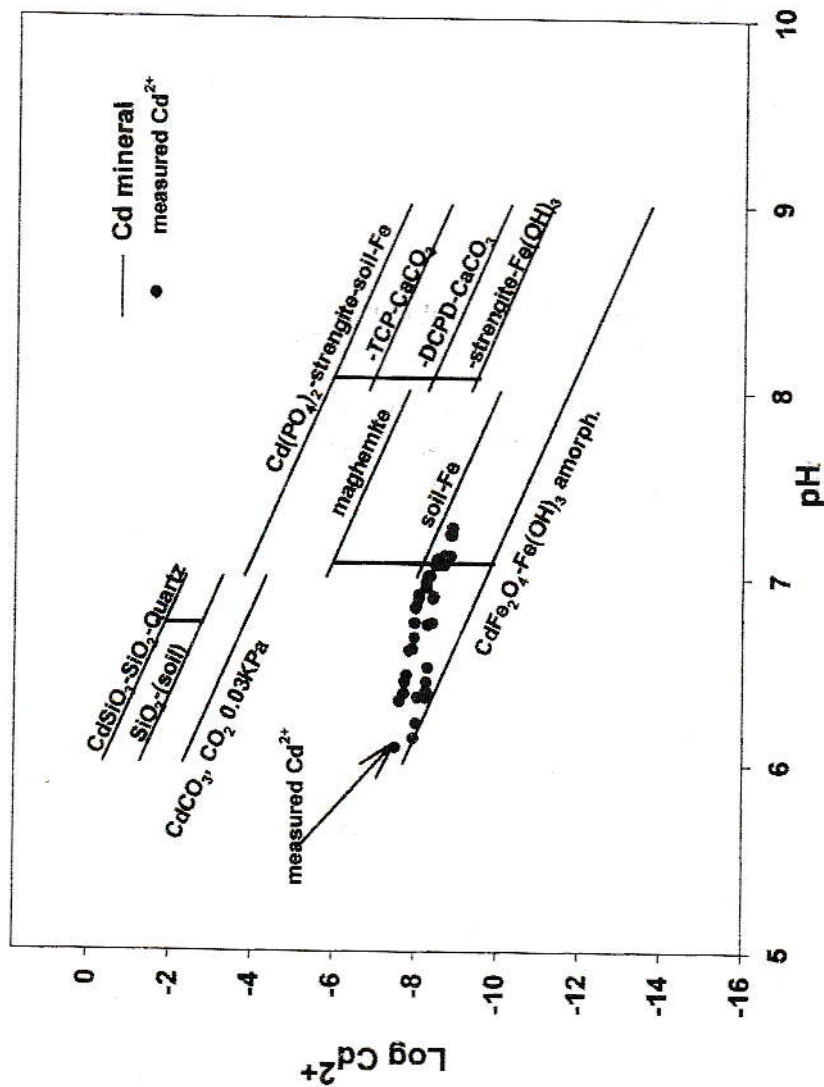
Fig.(4): Measured Cd $^{2+}$ activities of the present study compared with the solubility of various Cd minerals.

The free cadmium species represented a high percentage from soluble form.

ACKNOWLEDGMENTS

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تقدير الصور الحرة للكادميوم فى محلول الأرض المعاملة مسبقا بالحمأة:
باستخدام طريقه التبادل الكاتيوني للراتنجات

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ملخص

أجريت الدراسة بهدف تقدير الصورة الحرة للكادميوم المتواجد فى محلول التربة المعاملة مسبقا بالحمأة (مخلفات الصرف الصحي) وذلك نظرا للأهمية القصوى لدراسة تلك الصورة وتأثيرها على حركه الكادميوم وتوازنه مع الصور الأخرى فى النظام الأرضي. تم جمع 40 عينه من الأرض المعاملة بالحمأة (شملت 10 معاملات مختلفة فى مستوى الكادميوم) وتم تشبيع عينات التربة بالماء المقطر (60–70% من قوه حفظ التربة للماء) وبعد الأتزان تم سحب المحلول الأرضي بواسطة جهاز أخذ عينات الرطوبة المصمم بواسطة جامعه فاجنينج بهولندا. وتم تقدير الكادميوم الحر فى ذلك المحلول بطريقه التبادل الكاتيوني للراتنجات. وقد استخدمت راتنجات مشبعة بالكالسيوم. أما الكادميوم الصالح فقد تم تقديره باستخدام DTPA , NH4NO3 و أوضحت النتائج المتحصل عليها الآتي:

1– تراوح المحتوى الكلى للكادميوم فى الأرض محل الدراسة من 33,–2,6 بمتوسط 85, جزء/مليون وتراوحت الكميات المستخلصة بواسطة محلول ال DTPA من 08,–8, جزء/مليون بمتوسط 26, جزء/مليون أما الكميات المستخلصة بمحلول NH4 NO3 فتراوحت من 002,–033, بمتوسط 011, جزء/مليون.

2– تراوح محتوى الأرض من الكادميوم الذائب من 28,– 2,77 جزء/بليون وتمثل تلك القيم من 05,–13,% بمتوسط 12,% من المحتوى الكلى للكادميوم فى الأرض.

3– كان محتوى المحلول الأرضي من الكادميوم الحر منخفض جدا (أقل من 3,3 جزء/بليون) والذي مثل فقط 1,% ، 34,% ، 34,8 % من المحتوى الكلى , الكميه المستخلصة بمحلول DTPA والكميه المستخلصة بمحلول NH4NO3 على التوالي. بينما كان يمثل 90% تقريبا من صوره الكادميوم الذائب فى المحلول الأرضي. وهذا يبين مدى العلاقة بين كل من الصوره الذائبة والحرة ومالها من تأثير على التفاعلات الكيميائية

المختلفة. وكانت هناك علاقة ارتباط عالية المعنوية موجبــة بين الصورة الحـــره للكادميوم وكل من المحتوى الكلى ومستخلص DTPA ومســـتخلص NH$_4$NO$_3$ والصورة الذائبة ٧٢، ٧٣، ٩٨، ٨٣ على التوالي. بينما كـــانت هنــاك علاقـــة ارتباط عالية المعنوية سالبة مع رقم pH للأرض.

ودلت النتائج الموقعة على منحنى ذوبان المعادن المتحكمـــة فـــى نشـــاط الكادميوم أن القيم المتحصل عليها لنشاط الكادميوم كانت تقع تحت خط ســـليكات الكادميـــوم وفوسفات الكادميوم وكانت تقـــع فى مدى معدن حديدات الكادمـــيوم Cd Fe$_2$ O$_4$. مما يدل على أنه هو المتحكم فى نشاط الكادميوم فـــى الأراضـــي الملوثة بالحمأة.