

COMPARISON OF CD, CU, NI, AND ZN PARTITIONS IN SOILS OF LONG TERM FERTILITY EXPERIMENTS RECEIVING SEWAGE SLUDGE:

I- FRACTIONATION.

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ABSTRACT

The present study was conducted to investigate the chemical fractions of heavy metals in six different soil experiment locations which received sewage sludge for long time. The total contents of Zn, Cu, Ni and Cd, as average of all soils were 251, 83.5, 29.6 and 2.11 ug/g, respectively. The distribution of various fractions for all metals (as % from total content) followed the order: Exchangeable; 2.5 for Zn, 1.6 for Cu, 2.2 for Ni and 2.8% for Cd < Carbonate; 10 for Zn, 11 for Cu, 9.7 for Ni and 11.4% for Cd < Oxides; 14 for Zn, 14 for Cu, 11 for Ni and 11% for Cd < Organically complexes; 21 for Zn, 39 for Cu, 25 for Ni and 24% for Cd. The soluble, exchangeable, organically and oxide forms of Zn, Cu, Ni and Cd represented a negative relationships with soil pH. However, the Carbonate form showed a positive relationship with soil pH and CaCO₃ contents. The soluble form of metals represented a small percentage of total contents (0.37 for Zn., 0.15 for Cu, 0.46 for Ni and 0.25% for Cd). A highly significant correlation ($R^2 = 0.98, 0.98, 0.96, 0.92, p < 0.01$, for Zn, Cu, Ni, and Cd, respectively) was obtained between soluble and exchangeable forms.

Keywords: heavy metals; cadmium, copper, nickel, zinc; fractionation; swage sludge

INTRODUCTION

Addition of sewage sludges (particularly those from town or cities) results in increased concentrations of metals in topsoils. Considerable information is available on the effects after few years and little on chemical forms of metals in the long term when the upper permissible metal concentrations in soil have been reached at a given site. This may take 30 years or more when further sludge applications are then prohibited by law (DoE, UK, 1989). When sludge addition ends, the lack of fresh organic matter and the decomposition of the organic matter previously added may result in large changes in binding of metals due to changes in their chemical forms in soil. Associated changes in bioavailability may then produce large increases or decreases in the risks of potentially toxic metals to crops, animals or man. It is very important to establish what might happen to the chemical forms of metals present in such soils. Existing long-term field experiments can produce vital information at the present time as well as helping to determine what might be the picture in future.

Multi-step extraction methods, although more time consuming compared to single extractants, provide relatively more detailed information about the status of heavy metals in soils (Pickering, 1986; McLaren and Lucas, 2001; Kabala and Singh, 2001; and Lim *et al.*, 2002). Several

sequential extraction methods for soils and sediments have been described in the literature (Gupta and Chen, 1975; Tessier *et al.*, 1979; El-Sokkary, 1979; Shuman, 1985; Beckett, 1989 and Salbu *et al.*, 1998).

The objective of this study is to: (I) investigate the distribution of various heavy metal fractions in soils differing widely in soil properties, which were treated with sewage sludge for long time. (II) investigate the relationship between soil properties and chemical fractions of the heavy metals.

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MATERIALS AND METHODS

Field experiments:

This study was carried out on six different sewage sludge experiments (2 sites from each of UK, Germany, and Egypt) which received sewage sludge for long time. The description of these experiments is as follow:

1- Luddington (UK):

The sludge experiment started in 1968 on a sandy loam soil with 15% clay, 3% organic carbon, a pH of 6.9, and total contents 0.397, 22.9, 18.7, and 92 ug/g soil of Cd, Cu, Ni, and Zn, respectively, (control soil). Sewage sludges were obtained from sewerage works and were 'naturally' rich in either Zn, Cu, Ni or Cr and applied to obtain 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 (ton dry solid) ha⁻¹ in 1968, or as four annual applications of 31 ton dry sludge (tds) ha⁻¹ between 1968 and 1971. Ten metal treatments were established including untreated soil and uncontaminated sludge control treatments. The design was a randomised block with four replicate plots per treatment.

2- Gleadthorpe (UK):

The soil at this site is sandy loam with 6% clay, 2% organic carbon, a pH of 6.5 and total contents 0.185, 8.50, 6.80, and 43.60 ug/g soil of Cd, Cu, Ni, and Zn, respectively, (control soil). This experiment started in 1982 and the sewage sludges used were artificially contaminated by adding metal salts to raw sewage and then dewatering. One application of Zn- or Cu- or Ni-contaminated sludge was made to all plots with a further application to some, but not all, 5 years later. Apart from these single metal treatments, mixed metal treatment of Zn plus Cu and Zn plus Ni were also applied. All sludged plots received 100 tds ha⁻¹. The design was a randomised block with four replicate plots per treatment.

3- Braunschweig1(Germany):

The experiment site was on an old arable soil with plot pH value 6.9, and 0.8% organic carbon content. This soil was silt loam with 5% clay, and

total contents 0.383, 11.90, 8.51, 56.00 and 92 ug/g soil of Cd, Cu, Ni, and Zn, respectively. The experiment began in 1980 and received inorganic fertilizers or 'moderately' contaminated or metal amended liquid sludge added at rates of 100 or 300 m³ ha⁻¹ yr⁻¹ for 10 years; equivalent to 5 or 16 tds ha⁻¹ yr⁻¹ from 1980-1990. the moderately contaminated sewage sludges used were obtained from local sewage works and were naturally contaminated. However, the contaminated sludges were from different works in 1980. From 1981-1990 the same moderately contaminated sludge was artificially contaminated with metal salts and anaerobically incubated for 6 weeks before use. The design was a randomised block with four replicate plots per treatment.

4- Braunschweig2 (Germany):

An old forest soil (ex-woodland) with plot pH value 5.7 and 1.6% organic carbon content. This soil was silt loam with 5% clay and total contents 0.0335, 9.80, 8.60, and 43.00 ug/g soil of Cd, Cu, Ni, and Zn, respectively. The experiment has the same treatment and history like Braunschweig (1).

5- El-Gabal Asfar (Egypt):

The sandy soils of El-Gabal Asfar farm , which is irrigated with sewage effluent of Cairo city since 1911. Control soil content 2.2% clay, 0.19% organic carbon, pH of 8.5, 2.9% of total carbonate content (TCC) and total contents 0.192, 18.60, 15.70, and 58.30 ug/g soil of Cd, Cu, Ni, and Zn, respectively. As general practice, the soil was initially treated with sewage sludge before put under cultivation and irrigation with sewage effluent carried out during the year 1986.

6- Helwan area (Egypt):

The sludge experiment started in 1990 on a desertic (sandy) soil with 3.5% clay, 0.29% organic carbon, pH of 8.5, and 42% of TCC, and total contents 1.11, 9.40, 12.60, and 63.29 ug/g soil of Cd, Cu, Ni, and Zn, respectively which irrigated with sewage effluent of Cairo city and which comprises both municipal and industrial wastes. The soil is treated with sewage sludge at rates of 20- 40 ton/ha for 6 years (sewage sludges obtained from sewage of Helwan station).

Soil samples:

Ten plots were taken from each experimental site. Ten 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 from 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. The changes of the general properties of the soils are given in Table (1).

Soil Analysis:

The general characteristics of soils; pH, organic carbon (OC), total carbonate content (TCC), and clay content were determined using the standard methods outlined by Dewis and Freites (1970).

Sequential Chemical Extraction: The sequential extraction procedure of Tessier et. al.(1979) was used to partition Cd, Cu, Ni, and Zn in soils into five operationally defined fractions; 1) The Exchangeable fraction: soils were extracted with 1M NaOAc, pH 8.2 at room temperature for one hour with continuous agitation; 2) The Carbonate bound fraction: the residue from 1) was leached at room temperature for five hrs with continuous agitation with 1M NaOAc, pH 5.0; 3) The Fe and Mn oxides bound fraction: The residue from 2) was extracted with 0.04 M NH₂OH.HCl in 25% (v/v) HOAc at 96 ± 3 °C with occasional agitation for 5 hrs.; 4) The Organic matter bound fraction: The residue from 3) was extracted with 0.02 M HNO₃ and 30% H₂O₂, pH 2.0, for 2 hrs with occasional agitation at 85 ± 2 °C; then 30% H₂O₂ for 3 hrs with intermittent agitation at 85 ± 2 °C; after cooling 3.2 M NH₄OAc in 20% (v/v) HNO₃ was added.; 5) The Residue fraction: the residue from 4) was digested using the same procedure employed for total. The resulting supernatants from each fractionation step were filtered before analysing the filtrates for metals by GF-ASS. using the standard addition technique.

Table (1): General characteristics in soils.

Location	pH (1:2.5)	OC (%)		CaCO ₃ (%)	
	Range	Range	Average	Range	Average
Ex-Luddington (U.K)	6.10 - 6.85	3.00 - 3.75	3.52	-	-
Gleadthorpe (U.K)	5.32 - 6.50	2.00 - 2.89	2.47	-	-
Braunschweig-1 (Germany)	5.28 - 6.94	0.85 - 1.52	1.25	-	-
Braunschweig-2 (Germany)	4.45 - 5.14	1.65 - 2.63	2.10	-	-
El-Gabal Asfar (Egypt)	5.94 - 8.15	0.19 - 2.65	2.05	2.90 - 0.06	0.19
Helwan (Egypt)	7.38 - 8.25	0.29 - 1.62	1.09	42.52 - 11.82	16.54

All treatment values are means of 4 replicate plots; Average values are means of 120 samples.

Statistical Analysis:

Genstat 5 (1987) was used for all statistical procedures.

RESULTS AND DISCUSSION

The sequential extraction scheme (Tessier, 1979) used here successfully resulted in different fractions according to the chemical nature of each metal, and clear differences between the fractions presented in sludge treated soils at different locations.

Fractionation of soil Cd,

The total Cd content (Table 2) varied between 0.185 and 6.958 within average 2.11 mgkg⁻¹. The sum of the five Cd fractions amounted to 82-115% of the total contents; a coincidence observed with the results of Tessier et. al., 1979; Aboulroos *et al.*, 1991; Badawy and Helal, 2002; Krishnamurti *et al.*, 1995 who reported that the sum of the extractable-Cd fractionations were 88 to 104 % of the total Cd content. Figure (1a) shows closed relationship ($R^2 = 0.93$; $p < 0.01$) between total contents and sum of the five Cd fractions.

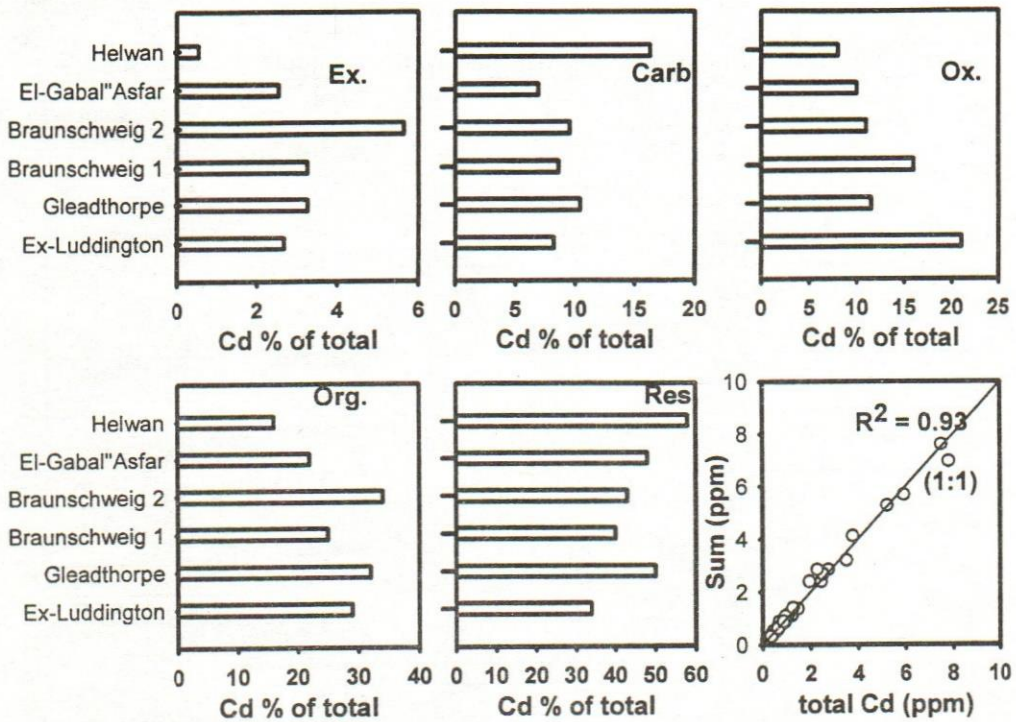


Fig.1a. Percent distribution of particulate-bound Cd species in the different soils

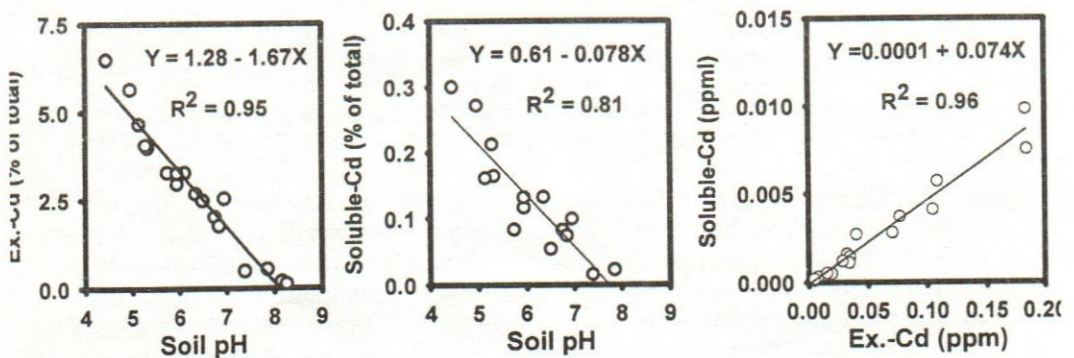


Fig.1b. Relationships between soil pH Vs both of Exchangeable and soluble; Also, Exchangeable vs soluble.

The forms of Cd distribution in soils depend on the physical, chemical and mineralogical properties of soils (Sanchez-Camazano *et al.*, 1994). The environmental effect of Cd is, thus, related to the level of the various forms and the rate with which the less mobile forms are transferred to the mobile ones.

Table (2): Cadmium associated with different chemical fractions in soils.

Location	Soil Cd chemical fractions (mgkg ⁻¹ soil)*							Soluble Cd (µg/L)
	Ex.	Carb.	Ox.	Org.	Res.	Sum	Total	
Ex-Luddington soil (U.K)								
Min.	0.008	0.028	0.073	0.122	0.143	0.374	0.397	0.30
Max.	0.071	0.201	0.564	0.576	1.027	2.437	2.397	2.80
Average	0.032	0.099	0.250	0.344	0.409	1.137	1.205	1.61
Gleadthorpe soil (U.K)								
Min.	0.005	0.037	0.030	0.024	0.096	0.194	0.185	0.10
Max.	0.035	0.088	0.085	0.303	0.438	0.924	0.875	14.40
Average	0.020	0.062	0.069	0.187	0.298	0.634	0.599	5.00
Braunschweig soil from the old arable site (Germany)								
Min.	0.005	0.024	0.032	0.023	0.227	0.311	0.383	0.20
Max.	0.109	0.258	0.462	0.548	1.024	2.500	2.679	5.70
Average	0.040	0.106	0.192	0.326	0.485	1.191	1.230	2.70
Braunschweig soil from the old forest site (Germany)								
Min.	0.016	0.017	0.027	0.062	0.251	0.380	0.335	0.60
Max.	0.184	0.267	0.292	0.940	0.903	2.736	2.840	9.80
Average	0.077	0.130	0.143	0.445	0.598	1.459	1.361	3.70
El-Gabal Asfar farm (Egypt)								
Min.	0.001	0.061	0.072	0.038	0.049	0.229	0.192	0.10
Max.	0.185	0.335	0.485	1.890	3.025	5.920	5.682	7.50
Average	0.105	0.285	0.397	0.952	2.018	3.757	4.359	4.20
Helwan area (Egypt)								
Min.	0.001	0.258	0.243	0.210	0.458	1.192	1.106	0.10
Max.	0.034	1.250	0.658	1.162	4.580	7.812	6.958	1.90
Average	0.029	0.857	0.429	0.856	3.028	5.215	5.269	1.20

All treatment values are means of 4 replicate plots.

*Ex. = exchangeable; Carb. = bound to carbonates; Ox. = bound to Fe and Mn oxides; Org. = bound to organic matter; Res. Residual; Sum = summation of the extracted fractions.

Cd-Exchangeable fraction constituted the least amount of Cd in all tested soils; varying from 0.001 to 0.185 with an average 0.053 mgkg⁻¹ (from 0.09 to 6.5 with an average 2.8% of total). Fig.1a. shows that the highest % of total was found in Braunschweig(2). This reflect is attributed the acidity (pH = 5) of the soil. Aboulroos *et al.*, 1991; Onyatta and Huang, 1999 and Badawy, and Helal, 2002 found that the negative relation between Cd-Exchangeable fraction and soil pH. The Cd-Carbonate fraction (average 0.229 mgkg⁻¹) constituted 11% of total. Fig.1a. shows that the highest % of total was found in Helwan soil. This reflect is attributed to a high CaCO₃ which precipitate and adsorbed Cd. The Cd-Oxides fraction constituted relatively high portion of total (average of 0.25 mgkg⁻¹, equal to 15% of total). This higher value (in Braunschweig2) of Cd-Oxides is related to the Al-, Fe-, and Mn-oxides in the

soils. The same result was found by El-Sokkary, 1979. The Cd-Organic fraction was also high (average 0.50 mgkg^{-1} or 24% of total) and is correlated with organic carbon content in the soil. This higher value was found in Braunschweig2. The Cd-Residual fraction constituted the highest portion of the soil Cd (average 47% of total). This fraction can be considered as the primary form of native Cd in these soils. The average percentage value of each particulate-bound Cd species in all studied soils followed the order: residual (48%) > organic-bound (24%) > oxides-bound (15%) > carbonate-bound (12%) > exchangeable (2.8%) of the total present in the soils. The values for the particulate-bound Cd species can be considered as basic information for the Cd status of soils (Ramos *et al.*, 1994; Onyatta and Huang, 1999).

The soluble Cd represented a small percentages of the total (average 0.249%). Figure 1b shows a high significant correlation found between soluble Cd and both of soil pH ($R^2 = 0.81$, $p < 0.01$) and Exchangeable Cd ($R^2 = 0.96$, $p < 0.01$).

Fractionation of soil Cu:

The results of the sequential extraction technique are presented in Table (3). The sum of the five fractions of Cu amounted 89-112% of the total contents. The same trend was found by Tessier *et al.*, 1979; Aboulroos *et al.*, 1991. They reported that the sum of the extractable-Cu fractionation were 88 to 104 % of the total Cu content. Figure (2a) shows closed relationship ($R^2 = 0.96$; $p < 0.01$) between total contents and the sum of the five fractions of Cu. Average values of the various fractions of Cu in the soil (Table 3) showed that the Cu-Exchangeable fraction constituted the least amount of Cu in all tested soils (average 1.66 mgkg^{-1} , making some 1.56% of total). Fig.1a. shows that the highest % of total was found in Braunschweig2 (pH = 5). The Cu-Carbonate fraction averaged 12 mgkg^{-1} (11% of total). Fig.1a. shows that the highest % of total was in Helwan soil with the highest CaCO_3 content which precipitated and adsorbed Cu. The Cu-Oxides fraction constituted relatively high portion of total Cu (14% of total). This higher value (in Braunschweig2) of Cu-Oxides can be related to the Al-, Fe-, and Mn-oxides in the soils. The same results were found by McLaren and Crawford, 1973; El-Sokkary, 1979. The Cu-Organic fraction was also high (average 37 mgkg^{-1} as 38% of total) and correlated with organic carbon content in the soils. The Cu-Residual fraction constituted the highest portion of the soil Cu (average 39% of total). This fraction can be considered the primary form of native Cu in soils. The average percentage value of each particulate-bound Cu species in all studied soils followed the order: residual (39%) > organic-bound (38%) > oxides-bound (14%) > carbonate-bound (11%) > exchangeable (1.6%) of the total present in the soils. The values for the particulate-bound Cu species can be considered as basic information for the Cu status of soils.

The soluble Cu represented a small percentages of the total (average 0.15%). Figure 1b show high significant correlations between soluble Cu and both soil pH ($R^2 = 0.81$, $p < 0.01$) and Exchangeable Cu ($R^2 = 0.96$, $p < 0.01$).

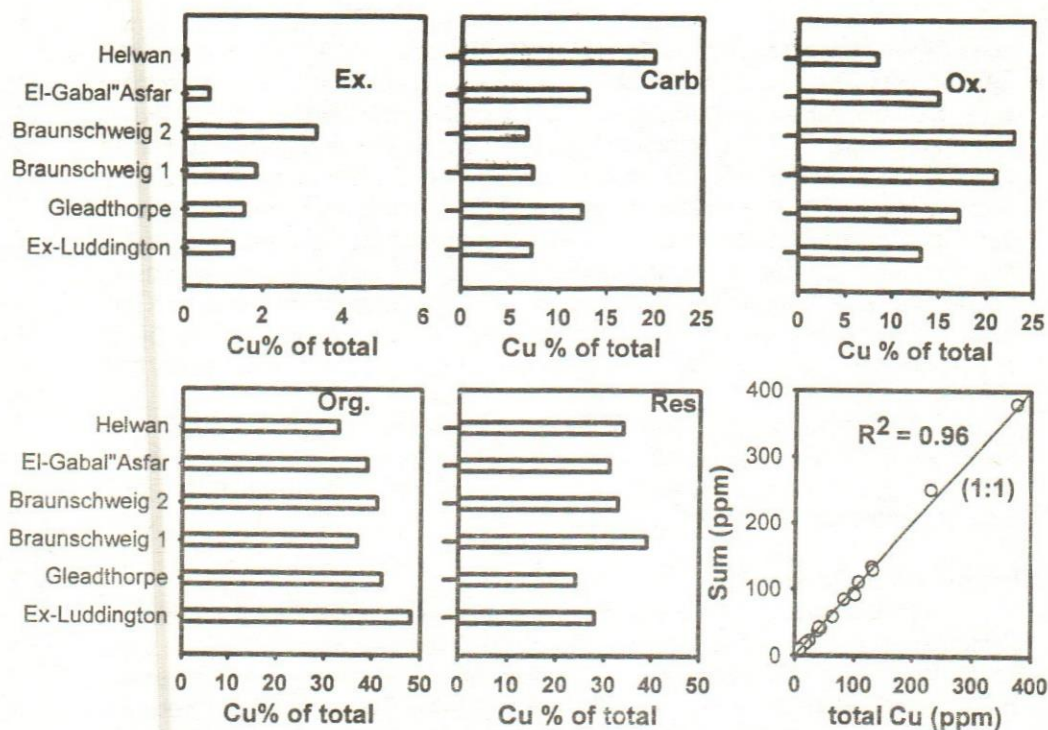


Fig.2a. Percent distribution of particulate-bound Cu species in the different soils

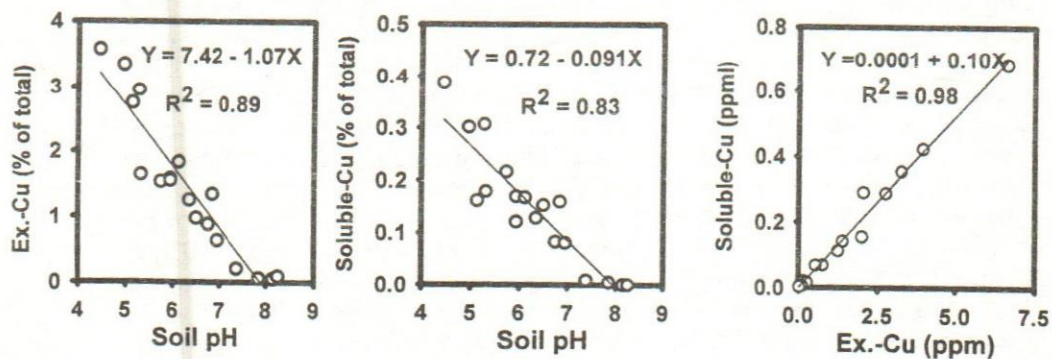


Fig.2b. Relationships between soil pH Vs both of Exchangeable and soluble; Also, Exchangeable vs soluble.

with different chemical fractions in soils.

	Cu chemical fractions (mgkg ⁻¹ soil)						Soluble Cu (mg/L)	
	Carb.	Ox.	Org.	Res.	Sum	Total		
Ex-Luddington soil (U.K)								
Min.	204	0.610	2.60	7.57	14.7	22.5	22.9	0.019
Max.	978	21.9	35.8	123.1	50.1	232	249	0.423
Average	395	7.97	14.5	53.95	31.1	108	111	0.142
Gleadthorpe soil (U.K)								
Min.	0.084	0.280	0.500	1.95	6.36	9.14	8.50	0.013
Max.	10.56	85.14	66.1	156.8	64.5	376	349	0.681
Average	2.56	16.58	22.9	56.8	32.6	130	134	0.292
Braunschweig soil from the old arable site (Germany)								
Min.	0.161	0.750	0.720	3.09	6.65	11.5	11.9	0.019
Max.	2.76	8.72	22.15	41.8	25.7	100	93.7	0.287
Average	0.759	3.03	8.59	15.4	16.4	44.4	41.3	0.069
Braunschweig soil from the old forest site (Germany)								
Min.	0.268	0.480	0.954	2.45	5.67	9.61	9.80	0.016
Max.	3.28	7.74	15.45	43.9	33.6	102	91.6	0.354
Average	1.26	2.51	8.56	15.1	12.5	39.4	37.5	0.113
El-Gabal Asfar farm (Egypt)								
Min.	0.009	1.85	2.56	6.58	7.23	18.6	18.6	0.005
Max.	2.01	18.57	22.45	56.3	33.6	132	129	0.156
Average	0.544	10.98	12.83	32.5	26.4	83.4	84.7	0.069
Helwan area (Egypt)								
Min.	0.008	1.65	1.12	3.57	2.65	9.23	9.40	0.001
Max.	0.120	9.52	4.26	26.6	22.2	63.9	58.6	0.005
Average	0.026	8.56	3.59	14.3	11.6	41.4	42.6	0.002

All treatment values are means of 4 replicate plots.

*Ex. = exchangeable; Carb. = bound to carbonates; Ox. = bound to Fe and Mn oxides; Org. = bound to organic matter; Res. Residual; Sum = summation of the extracted fractions.

Fractionation of soil Ni

The sum of the five Ni fractions amounted to 88-109 of the total Ni contents. This coincidence was observed with the results of Tessier *et al.*, 1979; Abouloos *et al.*, 1991, who reported the sum of the extractable-Ni fractionation were 88 to 104 % of the total Ni content. Figure (3a) shows closed relationships ($R^2 = 0.94$; $p < 0.01$) between total contents and the sum of the five fractions of Ni.

The average values of the various fraction of Ni in the soils are given in Table (4). The Ni-Exchangeable fraction constituted the least amount of Ni in the all tested soils (average 0.58 mgkg^{-1} , 2.2% of total). Fig.3a. shows that the highest % of total was in the acid Braunschweig(2) soil (pH = 5). Abouloos *et al.*, 1991 and Badawy, 1987 reported a negative relation between Ni-Exchangeable fraction and soil pH. The Ni-Carbonates fraction in the tested soils (averaged 2.9 mgkg^{-1} , as 10% of total). Fig.3a. shows that

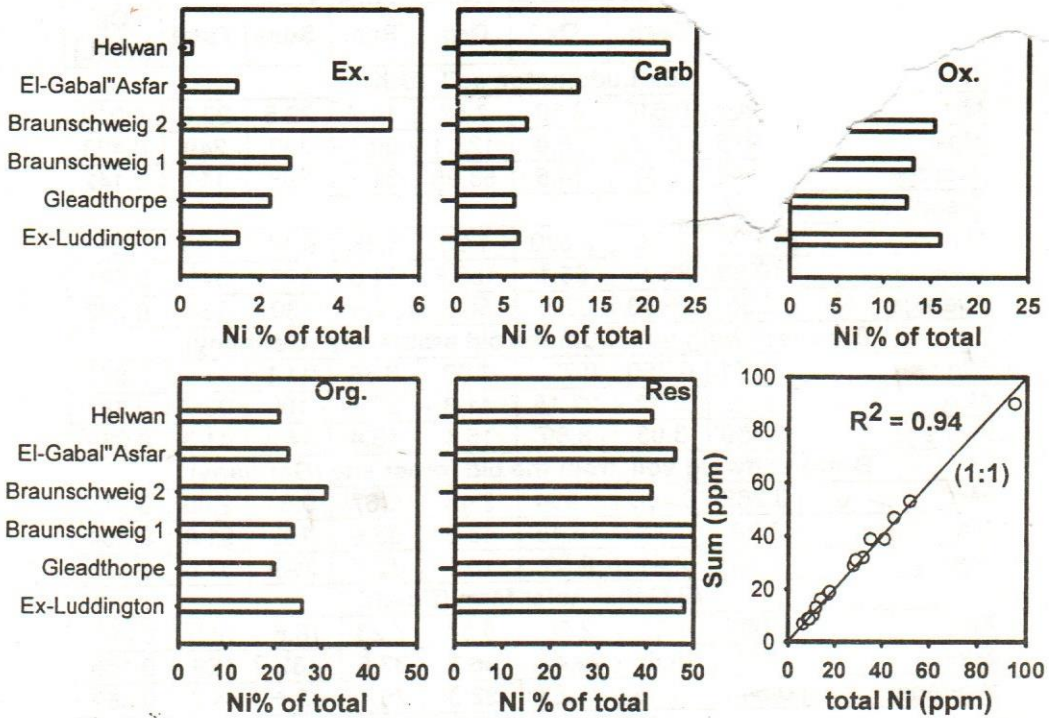


Fig. 3a . Percent distribution of particulate-bound Ni species in the different soils

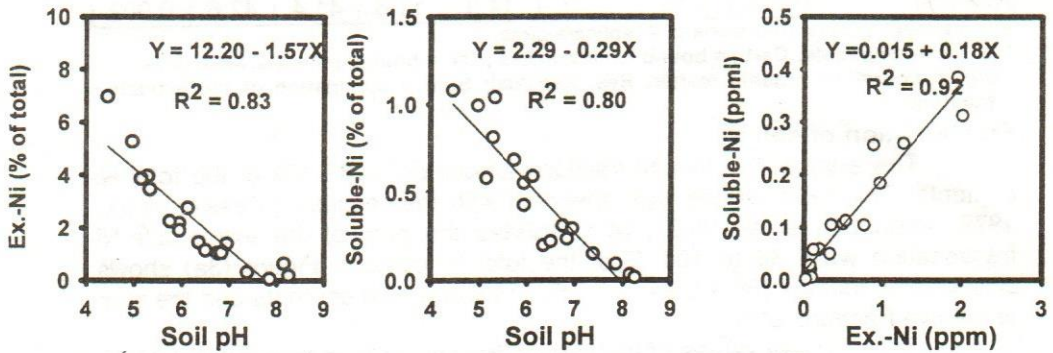


Fig. 3b Relationships between soil pH Vs both of Exchangeable and soluble; Also, Exchangeable vs soluble.

the highest % of total was found in Helwan soil rich in CaCO₃ which precipitates and adsorbs Ni. The Ni-Oxides fraction constituted relatively high portion of the total (average of 4.0 mgkg⁻¹ which makes 12% of total). This higher value (in Braunschweig2) of Ni-Oxides is related to the Al-, Fe-, and Mn-oxides in the soils. Similar results were found by McLaren and Crawford, 1973; El-Sokkary, 1979. The Ni-Organic fraction was also high (average 7.3 mgkg⁻¹ which equal 26% of total) and correlated with organic carbon content in the soils. This higher value was found in Braunschweig2. The Ni-Residual fraction constituted the highest portion of the soil Ni (from 24 to 76 with an average 49% of total). This fraction can be considered as the primary form of native Ni in these soils. The average percentage value of each particulate-bound Ni species in all studies soils followed the order: residual (49%) > organic-bound (25%) > oxides-bound (12%) > carbonate-bound (10%) > exchangeable (2.2%) of the total present in the soils. The values for the particulate-bound Ni species can be considered basic information for the Ni status of soils (Ramos *et al.*, 1994; Onyatta and Huang, 1999).

Table (4): Nickel associated with different chemical fractions in soils.

Location	Soil Ni chemical fractions (mgkg ⁻¹)							Soluble Ni (mg/L)
	Ex.	Carb.	Ox.	Org.	Res.	Sum	Total	
Ex-Luddington soil (U.K)								
Min.	0.196	0.580	1.23	5.48	10.3	17.7	18.7	0.058
Max.	1.96	7.35	17.6	27.6	41.5	95.0	89.9	0.385
Average	0.771	3.45	8.38	13.7	25.8	51.9	53.2	0.105
Gleadthorpe soil (U.K)								
Min.	0.078	0.380	0.64	1.52	3.80	6.37	6.80	0.015
Max.	0.350	0.810	1.45	2.85	5.20	10.7	10.1	0.105
Average	0.195	0.520	1.08	1.68	4.90	8.34	8.62	0.059
Braunschweig soil from the old arable site (Germany)								
Min.	0.090	0.408	0.450	1.28	6.48	8.64	8.51	0.020
Max.	1.27	2.67	4.14	10.6	12.7	31.4	32.0	0.260
Average	0.500	1.03	2.40	4.27	9.57	17.8	18.1	0.107
Braunschweig soil from the old forest site (Germany)								
Min.	0.332	0.580	0.450	2.38	5.67	9.19	8.60	0.050
Max.	2.02	3.02	5.40	10.5	6.94	27.9	28.9	0.313
Average	0.973	1.35	2.85	5.57	7.60	18.2	18.5	0.184
El-Gabal Asfar farm (Egypt)								
Min.	0.100	1.12	1.24	3.25	8.05	14.0	15.7	0.005
Max.	0.890	6.58	4.80	12.6	20.9	45.7	46.5	0.257
Average	0.540	4.85	2.80	8.94	17.9	35.1	38.5	0.113
Helwan area (Egypt)								
Min.	0.023	2.05	1.12	2.57	5.6	11.8	12.6	0.002
Max.	0.120	8.95	5.48	10.5	16.2	41.3	38.5	0.058
Average	0.076	6.58	3.59	6.40	12.6	29.3	30.5	0.028

All treatment values are means of 4 replicate.

*Ex. = exchangeable; Carb. = bound to carbonates ; Ox. = bound to Fe and Mn oxides; Org. = bound to organic matter; Res. Residual; Sum = summation of the extracted fractions.

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The soluble Ni represented a small percentages of total Ni (average 0.249%). Figure 1b show high significant correlations between soluble Ni and both of soil pH ($R^2 = 0.81$, $p < 0.01$) and exchangeable Ni ($R^2 = 0.96$, $p < 0.01$).

Chemical fractionation of soil Zn:

The sum of the five fractions of Zn in the studied soils amounted to 90 – 110% of the total contents Fig. (4a). This coincidence was observed with the results of El-Sokkary, 1979; Tessier et. al., 1979 and Badawy and El-Motaium, 2003. They reported that the sum of the extractable-Zn fractionations were 90 to 105 % of the total Zn content.

Average values of the various fractions of Zn in the soils (Table 5) show that the Zn-Exchangeable fraction constituted the least amount of Zn in all tested soils (average 5.94 mgkg^{-1} which gave 2.5% of total). Fig.4a. shows that the highest % of total was in Braunschweig(2), and the lowest in Helwan soils. Aboulroos *et al.*, 1991; Badawy, 2001 found a negative relation between Zn-Exchangeable fraction and soil pH. The Zn-Carbonate fraction in the tested soils averaged 30 mgkg^{-1} (10% of total). Fig.4a. shows the highest % of total in Helwan and El-Gabl Asfar soils and the lowest in Gleadthorpe soil. This reflect attributed to a high CaCO_3 of the soils which precipitate and adsorbed Zn. This Zn-Oxides fraction constituted relatively high portion of the total zinc (average of 35 mgkg^{-1} or 14% of total). This high level of Zn-Oxides in Braunschweig2 is related to the Al-, Fe-, and Mn-oxides. Similar results were found by McLaren and Crawford, 1973; El-Sokkary, 1979. The Zn-Organic fraction was also high (55 mgkg^{-1} or 21% of total) and correlated with organic carbon content in the soils. The highest value was found in Braunschweig2. The Zn-Residual fraction constituted the highest portion of total soil Zn (from 33 to 63 with an average 52% of total). This fraction can be considered as the primary form of native Zn in these soils. The average percentage value of each particulate-bound Zn species in all studies soils followed the order: residual (52%) > organic-bound (21%) > oxides-bound (14%) > carbonate-bound (10%) > exchangeable (2.5%) of the total present in the soils. The values for the particulate-bound Zn species can be considered as basic information for the Zn status of soils (Ramos *et al.*, 1994).

The soluble Zn represented a small percentages of total Zn (from 0.03 to 1.11 with an average 0.37%). Figure 1b shows a high significant correlations between soluble Zn and both of soil pH ($R^2 = 0.80$, $p < 0.01$) and exchangeable Zn ($R^2 = 0.98$, $p < 0.01$).

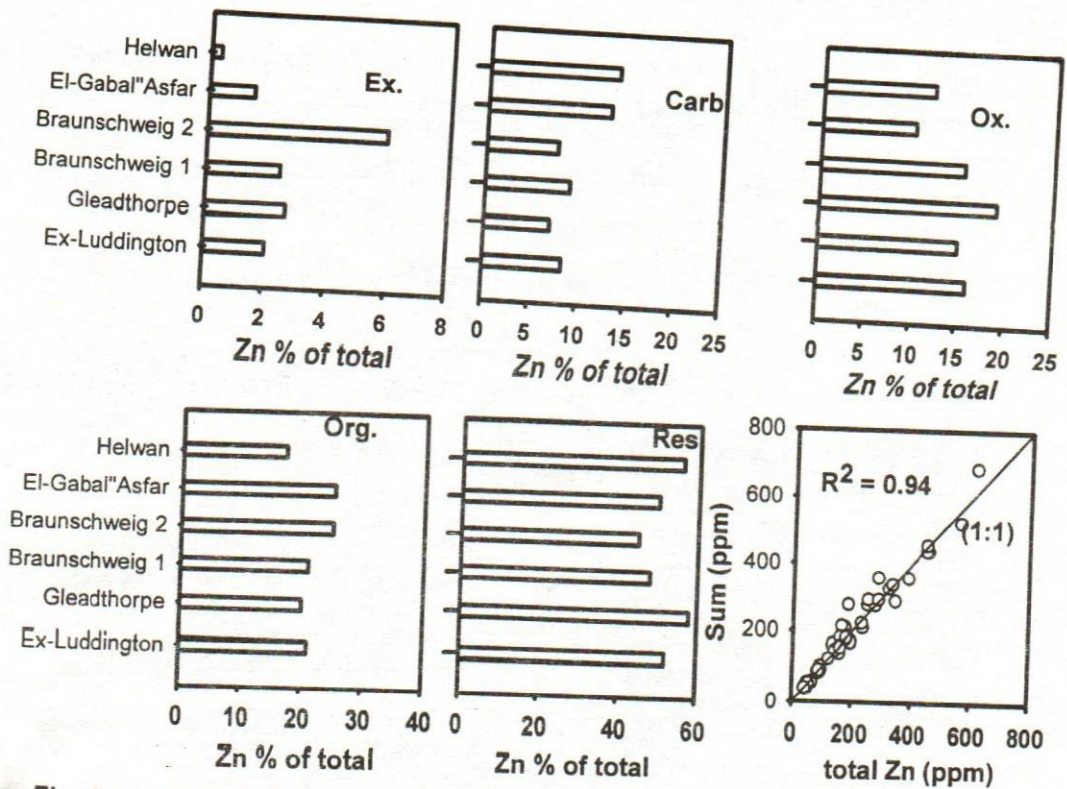


Fig. 4a Percent distribution of particulate-bound Zn species in the different soils

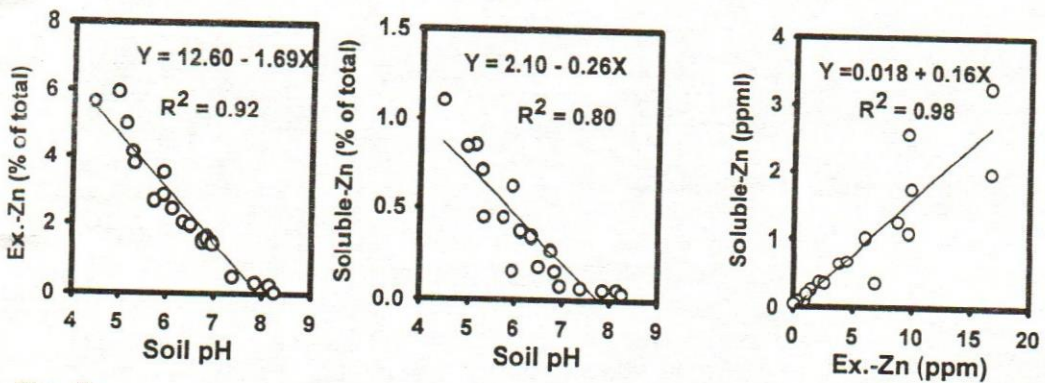


Fig. 4b Relationships between soil pH Vs both of Exchangeable and soluble; Also, Exchangeable vs soluble.

Table (5): Zinc associated with different chemical fractions of studied soils.

Location	Soil Zn chemical fractions (mgkg ⁻¹)							Soluble Zn (mg/L)
	Ex.	Carb.	Ox.	Org.	Res.	Sum	Total	
Ex-Luddington soil (U.K)								
Min.	1.44	6.90	16.80	15.60	48.50	88.50	92	0.257
Max.	9.88	28.9	36.50	61.50	156.0	292.0	279	1.740
Average	3.83	15.6	29.50	39.80	96.80	183.0	187	0.652
Gleadthorpe soil (U.K)								
Min.	0.86	2.76	8.50	11.40	23.60	47.00	43.6	0.080
Max.	16.72	49.8	45.60	77.40	275.0	454.0	440	1.980
Average	6.04	15.8	34.80	47.20	132.5	233.0	225	1.015
Braunschweig soil from the old arable site (Germany)								
Min.	0.92	4.47	5.87	8.70	34.50	54.00	56	0.089
Max.	14.90	41.9	74.35	79.60	185.6	388.0	359	2.560
Average	4.48	16.8	34.43	38.60	87.50	180.0	183	0.685
Braunschweig soil from the old forest site (Germany)								
Min.	2.14	2.89	3.65	7.77	25.60	40.60	43	0.368
Max.	16.62	29.8	54.00	67.80	126.50	287.0	294	3.250
Average	8.77	11.25	22.94	36.40	66.80	141.0	148	1.250
El-Gabal Asfar farm (Egypt)								
Min.	0.13	5.85	8.80	12.20	26.20	60.80	58	0.031
Max.	9.68	98.6	89.50	202.0	221.0	616.0	691	1.084
Average	6.88	59.5	46.50	115.5	229.0	453.0	459	0.354
Helwan area (Egypt)								
Min.	0.025	7.69	6.82	11.20	35.10	61.90	63.29	0.022
Max.	2.58	89.5	76.50	95.80	301.0	565.0	527	0.352
Average	1.08	46.5	39.50	56.80	189.5	333.0	340	0.189

All treatment values are means of 4 replicate plots

*Ex. = exchangeable; Carb. = bound to carbonates ; Ox. = bound to Fe and Mn oxides; Org. = bound to organic matter; Res. Residual; Sum = summation of the extracted fractions.

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مقارنة بين المفصولات الكيميائية لكل من الكاديوم والنحاس والنيكل والزنك فى اراضي الحقول المعاملة بالحماة لفترات زمنية طويلة

١- الصور الكيميائية

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أجريت هذه الدراسة لاختبار تأثير إضافة الحماة للأراضي المختلفة الخواص لفترات زمنية طويلة علي توزيع الصور الكيميائية للفلزات الثقيلة.

تمت هذه الدراسة علي ٦ مواقع حقلية تمثل أراضي مختلفة في صفاتها ، وسبق أن أضيفت إليها الحماة لفترات زمنية طويلة (وصلت في بعض المواقع إلي ٩٠ سنة). جمعت عينات ممثلة من المواقع وقدرت الصور الكيميائية المختلفة للفلزات الثقيلة باستخدام طريقة الاستخلاص المتتابع (Tessier,1979) وأظهرت النتائج الآتي:

١- احتوت الأراضي علي الكميات الكلية الآتية من الفلزات الثقيلة (كمتوسط عام): ٢٥١، ٨٣،٥ ، ٢٩،٦ ، ٢،١١ جزء / مليون لكل من الزنك والنحاس والنيكل الكاديوم علي التوالي.

٢- اختلف توزيع كل فلز من الفلزات الثقيلة اختلافا كبيرا بين الصور المختلفة. وكان ترتيب التوزيع النسبي لجميع الفلزات المختلفة كالآتي:

الجزء المتبادل > الجزء المرتبط بالكربونات > الجزء المرتبط بالاكاسيد > الجزء المرتبط عضويا.

٣- اختلف التوزيع النسبي داخل كل صورة من الصور السابقة (النسبة المئوية من المحتوى الكلي) لتلك الفلزات في الأراضي المختلفة متأثرا بنوع الأراضي ومحتواها من المادة العضوية والطين وكربونات الكالسيوم ورقم ال pH . وكانت الصورة العامة كما يلي:

• في الجزء الذائب: الكاديوم (٢،٨ %) < الزنك (٢،٥ %) < النيكل (٢،٢ %) < النحاس .
• في الجزء المرتبط بالكربونات: الكاديوم (١١،٤ %) < النحاس (١١ %) < الزنك (١٠ %) < النيكل (٩،٧ %).

• الجزء المرتبط بالاكاسيد: الزنك = النحاس (١٤) < الكاديوم = النيكل (١١).
• الجزء المرتبط عضويا: النحاس (٣٩ %) < النيكل والكاديوم (٢٤ %) < الزنك (٢١ %).

٤- كانت الصورة الذائبة من الفلزات تمثل أجزاء ضئيلة جدا من الكمية الكلية (٠،٣٧ % للزنك ، ٠،١٥ % للنحاس ، ٠،٤٦ % للنيكل ، ٠،٢٥ % للكاديوم). وقد اظهر التحليل الإحصائي وجد علاقة ارتباط مؤكدة بين الكمية الذائبة وتلك المتبادلة لكل من الزنك والنحاس والنيكل والكاديوم ($R^2 = 0.98, 0.98, 0.96, 0.92, P > 0.01$)

٥- ارتبط تواجد الفلزات في الصور المختلفة برقم ال pH في الأراضي حيث كانت هناك علاقة عكسية بين الجزء المتبادل والذائب مع رقم ال pH في الأرض.