

Determination of the Heavy Metals in the Contaminated Soil Zones at College of Education Ibn Al-Haitham -University of Baghdad

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Abstract

Soil is a crucial component of environment. Total soil analysis may give information about possible enrichment of the soil with heavy metals. Heavy metals, potentially contaminate soils, may have been dumped on the ground. The concentrations of soil heavy metals (Cd, As, Pb, Cr, Ni, Zn and Cu) were measured in three zones thought to be deeply contaminated at different depths (5, 25, 50 cm) at Ibn Al-Haitham College. The highest concentration of heavy metals Pb (63.3ppm), Cr (90.7ppm), Ni (124ppm) and Cu (75.7ppm) were found in zone (A) location-1, where the highest concentration of Zn (111.7ppm) was found in zone (C). Cd and As were detected in small amounts in all zones.

PH value, organic matters, carbonates, sulphates, chlorides and total soluble salts were also studied to get better understanding of mobility and displacement of the contaminating compounds in soil under study.

Key words: soil pollutant, heavy metals (Cd, As, Pb, Cr, Ni, Zn and Cu), soil parameters (pH, organic matters, carbonates, sulphate, chlorides and total soluble salts).

Introduction

Soil is a natural body consisting of layers of mineral constituents and composed of finely divided rocks mixed with decayed vegetable and animal matters [1].

Soil contamination is a result of man-made chemicals getting into the soil. This occurs in several different ways. Soil contamination can occur when an underground storage tank is punctured, when waste is leaked from landfills or when an industrial waste is discharged into the soil. This can be a huge concern since soil contamination can seep into the water supply if not cleaned up in time.

Soil contaminants are either solid or liquid hazardous substances mixed with the naturally occurring soil. The contaminants in the soil are physically or chemically attached to soil particles, or, if they are not attached, are trapped in the small spaces between soil particles [2].

Motivation for controlling heavy metal concentrations is diverse. Some of them are dangerous to the health or the environment as they are carcinogenic or toxic, affecting, among others, the central nervous system (Hg, Pb, As), the kidneys or liver (Hg, Pb, Cd, Cu) or skin, bones or teeth (Ni, Cd, Cu, Cr). Through precipitation of their compounds or by ion exchange into soils, heavy metals can localize and lay dormant [3, 4].

Bohan Liao and et al. determine releases and changes in speciation fractions of heavy metals (especially Cd, Cu and Zn) when the soils are contaminated with heavy metals from the tailings waste of collapsed dam in China and affected moreover by simulated acid deposition[5].

Ioan Suciuc and et al., measured five soil heavy metals (Pb, Co, Cr, Cu and Hg) in sampling sites in central Transylvania, Romania using the Inductively Coupled Plasma Spectrometry method and the data were verified by using the Neutron Activation Analysis method [6].

Tomoyuki Makino determined the Cd-content in the digested solution in Japanese soils obtained from the plow layers of paddy fields through Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [7].

Anna Maria Polcaro and et al. considered Pb^{+2} , Zn^{+2} and Cd^{+2} as most representing the pollution of a Sardinian (Italy) area. Their work was to evaluate the exchangeable fraction of metal retained in the soil, when it is contaminated by multicomponent heavy metal solutions [8].

Foundations are subject to attack by destructive compounds in the soil. Concrete in foundations may have to withstand by sulphates in the ground or in chemical waste. The severity of attack on foundation depends on the concentration of the aggressive compounds [9].

The main soil parameters governing process of sorption and desorption of heavy metals can be **presented as follows:**

pH: This is affected by the changes in redox potential which occurs in soils that become waterlogged periodically. Reduction conditions generally cause a pH increase and oxidation brings about a decrease. In general heavy metal cations are most mobile under acid conditions and increasing the pH by limiting usually reduces their bioavailability [10, 11].

Organic matters (O.M.): The nonliving portion of soil organic fraction. They are a heterogeneous mixture of products resulting from microbial and chemical transformation of organic residues (plants and animals). Although the soil organic matters are in most cases, only a small part of the total solid phase, they are of major importance in defining the physical, chemical, and surface properties of the soil material [11, 12].

Carbonates: Greatly dispersed and have a major influence on the pH of soils and therefore on heavy metals behavior. The heavy metals may co-precipitate with carbonates being incorporated

in their structure, or may be sorbed by oxides that were precipitated onto the carbonates or other soil particles. The greatest affinity for reaction with carbonates has been observed for Co, Cd, Cu, Ni, Pb and Zn [13].

Sulphates: They are readily soluble and therefore are greatly involved in soil equilibrium processes. In considering sulphate attack on concrete foundation, it is, usually sufficient to determine the sulphate content and pH value of soil [9, 13].

Chlorides: They are the most soluble salts occur only in soils of arid and semiarid climate zones. Chlorides affinity for forming easily soluble complexes with Cd is of environmental concern [13].

Total Soluble Salts (T.S.S.): They consist mostly of various proportions of the cations calcium, magnesium, sodium and potassium, and the anions chloride, sulphate, carbonate and bicarbonate. A very high percentage of total soluble salts may cause cavities caused by removal of salts with seeping water [12, 14].

Preventing heavy metal pollution is critical because cleaning contaminated soil is extremely expensive and difficult. The main goal of this study is to assess the heavy metals in number of contaminated zones at College of Education / Ibn Al-Haitham.

Experimental

Apparatus

pH211 Microprocessor equipped from HANA Instrument was used to measure the pH values.

Atomic Absorption Flame Emission Spectrophotometer model AA-680 Shimadzo was used for determination of the heavy metals Cd, As, Pb, Cr, Zn, Ni and Cu concentrations.

Crushing machine, Pulverizer, Drying Oven, Analytical Balance (Sartorius BL210 d=0.1mg), Heater and Muffle Furnace.

Sieves, Filter Paper, Silica Crucible and Desiccator.

Reagents & Materials

Hydrochloric acid (37%), Ammonia (25%, sp.g. 0.91) and Nitric acid (65%).

Barium Chloride, Potassium dichromate, Silver nitrate solution and Potassium chromate.

All of these reagents and materials were provided from Fluka and BDH or Ibn Sina companies with high purity.

Procedure

The concentrations of soil heavy metals were measured in three zones at Ibn Al-Haitham College around and behind number of concrete foundation of the department of chemistry as it is

thought to be deeply contaminated due to the vandalism of laboratories during the immoral state of anarchy that coincide with the end of the battle operations in 2003. These hazardous substances are either spilled or buried directly in the soil or migrate to the soil from a spill that has occurred elsewhere.

These abandoned contaminated zones were marked for the purpose of research as below:

Zone A – location 1: 2 meters away from the concrete foundation of general chemistry lab / first stage.

Zone A – location 2: 6 meters away of the same lab above.

Zone B: 2 meters away from the concrete foundation of organic chemistry lab/ first stage.

Zone C: 2 meters away from the concrete foundation of organic identification lab/ fourth stage.

Sampling of soil before analyzing is of great importance to get good homogenized specimen, the steps applied for sampling were as follows:

Step 1: Holes with an area of $50 \times 50 \text{ cm}^2$ were dug.

Step 2: Soil samples were taken from each hole at three separated depths (5 cm, 25cm and 50cm) except zone B only (5cm and 15cm) as a hard concrete ground appeared at depth of 15cm.

Step 3: The samples individually were sifted and homogenized after drying then they were being crushed, pulverized and prepared for analysis.

The parameters of soil samples pH value, organic matter, sulphate, carbonate and chloride (Mohr method) were considered according to BS 1377[15], while total soluble salts content was conducted according to the methods mentioned in Earth manual [16].

The heavy metals of the soil specimen under study were determined after the prepared samples were dissolved in hydrochloric acid and/or nitric acid then the solution samples measured using the Atomic Absorption Flame Emission Spectrophotometer that mentioned above.

It is important to mention that all samples were taken for analyses in 2010.

Results and Discussion

Table (1) demonstrates the parameters of the soil samples under study with their RSD% respectively. The pH values of all samples at different depths exceed 7 which indicate the soils are more prone to dispersion [12].

Organic matter content (O.M.) in zone A is ranged between (5.36%-6.25%) more than zones B and C (0.66%-0.8%) at different depths. Soils high in organic contents have tendency to develop voids by decay and that make them undesirable for engineering use [16].

Sulphate content is less than 1% in all zones except for zone B (1.26%-1.34%) and this also applies to the chlorides that also present in less than 1% for all zones at different depths.

Carbonate content is ranged between (18.5%-35%) at different depths in all zones, when present in appreciable amounts, they influence the texture of the soil. Carbonates are important

for they constitute a potential source of soluble calcium and magnesium for the replacement of exchangeable sodium [14].

Total soluble salts (T.S.S.) are presented in appreciable amounts in zone B (3.01%-3.39%) and less in zone A location-1 (1.38%-2.03%) at different depths, while they are in much lesser degree in zone C (0.83%-1.49%) and zone A location-2 (0.73%-0.94%). Soils with high T.S.S. lead to higher permeability [14].

Table (2) shows the concentrations of the heavy metals of the soils under study in ppm (Cd, As, Pb, Cr, Zn, Ni, and Cu) with their RSD% respectively. These concentrations were illustrated in figures (1-4) at depths (5 cm, 25 cm and 50 cm).

Cadmium concentrations for all zones are not exceeding 10ppm. Cadmium content of soil in non-polluted area is usually below 1ppm. Cadmium may form complexes with various anions, such as chloride, sulphate and carbonate ions. Such complexity might contribute to the mobilization of cadmium in the environment. Cadmium is susceptible to chelation that may affect its displacement in soils [7, 17].

Arsenic concentrations are 1ppm or 2ppm for all zones. Arsenic accumulation in soils is usually found in the top 10 cm due to strong fixation. Arsenic mobilization is mainly controlled by adsorption/desorption processes. These phenomena are linked mainly to pH and also to redox conditions, mineral nature and arsenic state oxidation [17, 18].

Lead concentrations are between (14-28ppm), (16-33ppm) and (30-63ppm) with increasing downward depths for all zones respectively. The danger of excess lead is probably decreased after deposition on the soil due to the formation of relatively insoluble compounds like $PbCO_3$, $Pb_3(PO_4)_2$, and to a lesser degree $PbSO_4$. Because of the formation of the solids and of the adsorption of lead when present as divalent cation, lead displacement in soils is mostly small. Soils of high pH may release fixed lead when becoming acidic especially if $PbCO_3$ is involved in the lead immobilization [17].

Chromium concentrations are between (20-48ppm), (28-66ppm) and (82-90ppm) with increasing depths for all zones respectively. The mobility of chromium is extremely slow. At the pH values and redox potentials prevailing in most soils, Cr^{+6} is readily reduced to Cr^{+3} , mainly occurring as the poorly soluble $Cr(OH)_3$ [17].

Zinc concentrations are between (30-82ppm), (44-101ppm) and (69-111ppm) with increasing depths for all zones respectively. One of the major factors controlling zinc availability is the pH. The zinc species in soils below 7.7 is Zn^{+2} and at higher pH values the neutral zinc hydroxide $Zn(OH)_2$. Large pH influence on zinc solubility is indicated by the fact that the zinc activity in

solution at equilibrium conditions decreases 100-folds for each unit increase in pH. Zinc may be adsorbed on the adsorption complexes of clays and organic matter. Chelation may influence Zn-soil interactions [17].

Nickel concentrations are between (52-89ppm), (71-111ppm) and (116-124ppm) with increasing depths for all zones respectively. Being a divalent cation, Ni^{+2} must be expected to be

adsorbed on the soil complex. Silicate ions of soil govern the nickel concentration in soil solution, immobilization of nickel thus being caused by the formation of nickel silicate minerals. The abundance of silicate ions in soils provides an almost infinite storage capacity when time is available for the formation of these nickel solids. Nickel is susceptible to chelation which may considerably affect its displacement in soils [17].

Copper concentrations are between (19-46ppm), (31-75ppm) and (25-43ppm) with increasing depths for all zones respectively. Mobility and displacement of copper in soils are low. It is strongly bound by organic matter and as a result of this bonding, downward movement of copper in soils is almost nil; and this may explain to some extent the concentrations of copper at 50 cm depth is less than that at 25 cm depth. A large number of copper complexes are known to occur in soils. Copper also has been susceptible to chelation that affect its displacement in soils [17].

Conclusion

The concentrations of the heavy metals (Cd, As, Pb, Cr, Zn, Ni and Cu) were measured in three zones at College of Education / Ibn Al-Haitham thought to be deeply contaminated. The parameters of soil pH value, organic matter, sulphate, chloride, carbonate and total soluble salts were carried out to get better understanding of specifying the chemical forms and mobility of the contaminating compounds in the soil. The research concluded that the highest concentrations of the heavy metals in soils of the contaminated zones under study were arranged as follows:

Zone A > Zone C > Zone B concerning metals Pb, Cr, Ni, Cu and Cd

while the highest concentrations concerning metals Zn and As were arranged as follows:

Zone C > Zone A > Zone B

The heavy metals Cd and As were detected in small amounts.

Heavy metals do not decay and thus pose a different kind of challenge for remediation. In situ fixation is a process that creates new chemical compounds in which heavy metals are less available to living things. Prevention still is the best method to protect the environment from contamination by heavy metals.

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Table (1): Parameters of soil with their relative standard deviations in contaminated zones at different depths (cm)

Zone	Location	Depth	pH	RSD %	O.M. %	RSD %	Sulphate %	RSD %	Chloride %	RS D%	Carbonate %	RSD %	T.S.S %	RSD %
A	1	5	7.81	0.07	6.25	0.18	0.70	0.81	0.89	0.64	25	0.2	2.03	0.74
		25	7.84	0.12	5.96	0.33	0.42	2.38	0.53	1.07	33.5	0.45	1.38	0.39
		50	7.79	0.12	5.54	0.18	0.62	1.61	0.71	0.80	24	0.41	1.79	0.55
A	2	5	7.71	0.34	5.72	0.36	0.04	2.5	0.36	0.55	18.5	0.08	0.83	0.13
		25	7.55	0.40	5.36	0.28	0.10	2.5	0.53	0.37	25.5	0.04	0.94	0.60
		50	7.84	0.12	5.78	0.26	0.09	1.66	0.36	0.30	24.7	0.06	0.73	0.20
B		5	7.66	0.32	0.80	0.71	1.26	0.45	0.84	0.13	26	0.38	3.01	0.33
		15	7.54	0.07	0.73	1.36	1.34	0.42	0.67	0.37	25	0.06	3.39	0.03
C		5	7.62	0.06	0.77	0.14	0.45	0.22	0.63	0.17	35	0.28	1.49	0.13
		25	7.73	0.06	0.66	0.22	0.05	2	0.52	0.29	31	0.32	0.83	0.12
		50	7.84	0.04	0.74	0.13	0.10	2	0.58	0.17	27	0.21	0.95	0.15

Table (2): Concentrations of soil heavy metals (ppm) with their relative standard deviations in contaminated zones at different depths (cm)

Zone	Location	Depth	Cd	RSD %	As	RSD %	Pb	RSD %	Cr	RSD %	Zn	RSD %	Ni	RSD %	Cu	RSD %
A	1	5	8.7	6.65	1	0	16.7	3.45	20.3	2.84	30.7	1.88	52.7	2.19	19.7	2.93
		25	7.7	7.52	1	0	24.3	2.37	28.7	4.02	44.3	1.30	71.3	1.61	75.7	1.52
		50	1	0	1	0	63.3	9.11	90.7	1.27	69.3	0.83	124	0.46	25.3	2.27
A	2	5	1	0	1	0	15.3	3.17	39.7	2.90	44.3	2.60	72.3	0.79	21.7	2.66
		25	1	0	1	0	22.7	2.54	66.7	1.73	60.3	1.91	91.3	0.63	54.7	1.05
		50	1	0	1	0	30.3	1.90	87.3	0.66	79.7	0.72	116.7	0.49	34.3	3.36
B		5	4	0	2	0	14.3	4.03	48.6	2.37	50.3	1.98	71.7	2.13	26.7	3.74
		15	4	0	2	0	16.7	3.46	63.7	1.81	63	1.58	89.7	1.70	31	3.22
C		5	7	0	2	0	28.3	2.04	47.6	2.42	82.6	2.52	89.3	1.71	46.7	1.23
		25	6	0	2	0	33.3	1.73	66.3	1.74	101	1.73	111	2.38	51.3	1.12
		50	5	0	2	0	38.7	1.49	82.3	1.85	111.7	1.86	117.3	1.30	43.3	4.80

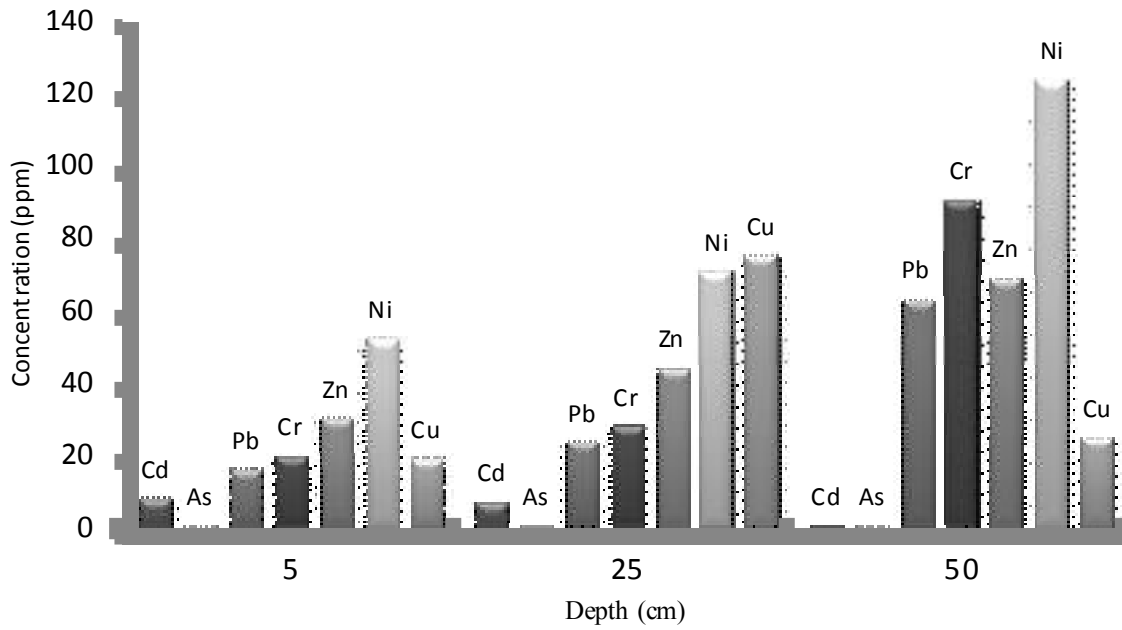


Figure 1: Soil heavy metal concentrations in Zone (A) location -1 at different depths

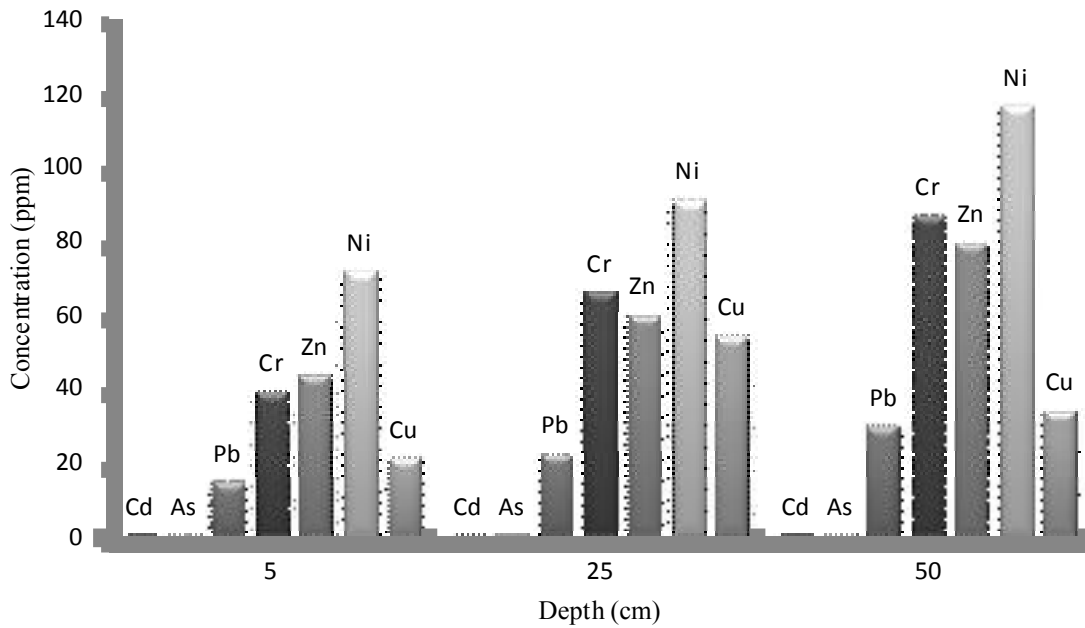


Figure 2: Soil heavy metal concentrations in zone (A) location-2 at different depths

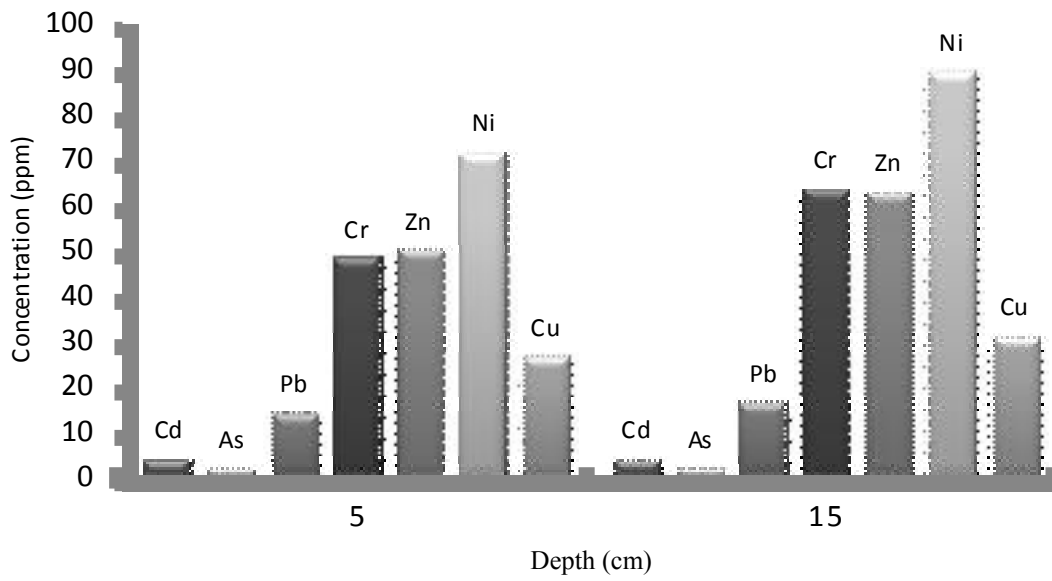


Figure 3: Soil heavy metal concentrations in Zone (B) at different depths

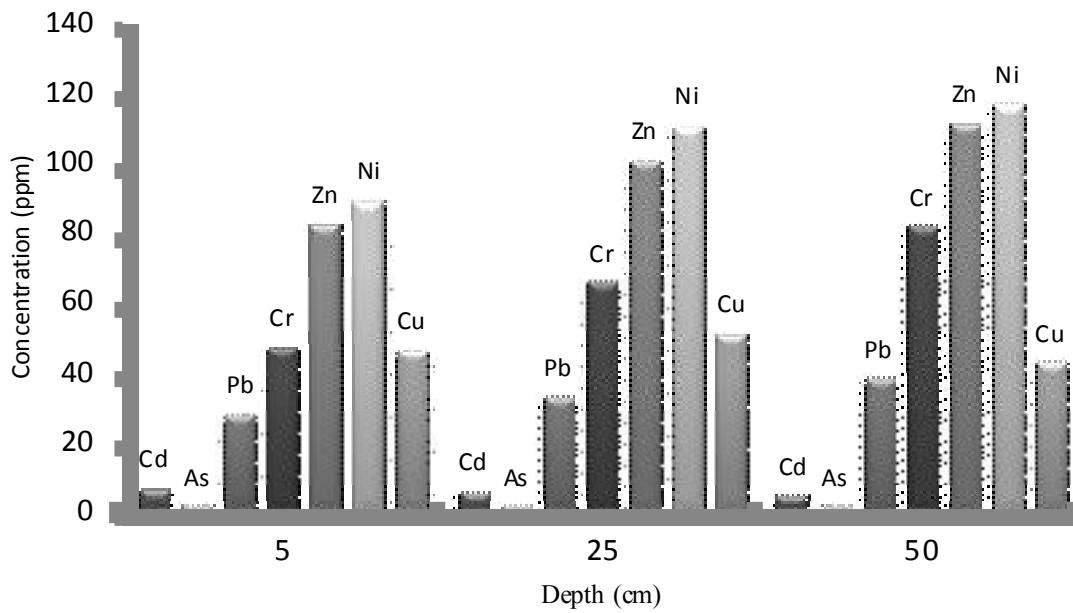


Figure 4: Soil heavy metal concentrations in Zone (C) at different depths

تقدير تراكيز العناصر الثقيلة في مساحات ملوثة في كلية التربية / ابن الهيثم - جامعة بغداد

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الخلاصة

التربة هي أي ترسب طبيعي تكون جزء من قشرة الارض وبيئتها الذي يتألف من تجميع جسيمات منفصلة غير مترابطة، عادة تكون معادن وفي بعض الاحين مواد عضوية. ملوثات التربة ومنها العناصر الثقيلة قد ترتبط فيزيائيا أو كيميائيا مع جسيمات التربة أو أنها تستقر في الفراغات الصغيرة بين جسيمات التربة. أجري التحليل الكيميائي لنماذج من التربة وبأعمق مختلفة (5سم و 25سم و 50سم) في ثلاث مساحات، جرى سكب أو دفن الملوثات في تربتها أو أنها عرفت طريقها الى التربة من خلال مجرى مائي معين، نتيجة لأعمال التخريب التي رافقت العمليات الحربية في العراق في عام 2003 والتي طالت مختبرات قسم الكيمياء في كلية التربية/ ابن الهيثم إذ قدرت تراكيز الكاديوم، والزرنيخ، والرصاص، والكروم، والخاصين، والنيكل، والنحاس فيها.

نتائج التحليل بينت أعلى تركيز (Pb (63.3ppm), Cr (90.7ppm), Ni (124ppm), Cu (75.7ppm) في zone (A) location-1، بينما كان أعلى تركيز Zn (111.7ppm) في zone (C) كما سجلت تراكيز محسوسة من عناصر As و Cd أيضا.

للحصول على وصف كامل لحركة الملوثات داخل التربة أجرى قياس قيم الاس الهيدروجيني، وتقدير محتوى المواد العضوية، والكاربونات، والكبريتات، والكوريدات، والاملاح الذائبة الكلية.

