Assessment of Heavy Metal Pollution in Greenhouse Soils

Bülent TOPCUOĞLU

***Abstract*—**Repeated amendments of organic matter and intensive use of fertilizers, metal-enriched chemicals and biocides may cause soil and environmental pollution in greenhouses. Specially, the impact of heavy metal pollution of soils on food metal content and underground water quality has become a public concern. Due to potential toxicity of heavy metals to human life and environment, determining the chemical form of heavy metals in greenhouse soils is an important approach of chemical characterization and can provide useful information on its mobility and bioavailability. Total metal concentration were determined and a single and a Nemerow comprehensive pollution index method were used to assess pollution level, and also a sequential extraction procedure was used to estimate the availability of heavy metals (Zn, Cd, Ni, Pb and Cr) in greenhouse soils of Antalya Aksu.

According to evaluation grading standarts of the single-factor pollution index method, soil samples were in clean quality grade. But based on Nemerow comprehensive index method, pollution grade of soil samples were in warning limit.

The study of the distribution of metals showed that the greatest percentages of all metals were present in the residual phase. Cd seemed to be the most mobile element, and was largely associated with organic matter and Fe-Mn oxides. Although Ni and Pb were largely associated with residual phase, the second important percent of these metals were in exchangeable form. Although Ni concentration of most of soil samples were above the pollution limits, the mobility factor of Ni in these soils were found the least. Results of the present study suggest that the mobility and bioavailability of metals probably decrease in the following order: Cd>Zn>Cr>Pb>Ni.

Although soils have a small range of heavy metal contamination, due to low metal bioavailability these greenhouse soils could be safely cultivated for crop production.

***Keywords*—** Pollution index**,** Metal speciation, Metal mobility, Greenhouse soils.

I. Introduction

HEAVY metal contamination of soil is a major environmental problem. Due to intensive use of agrochemicals in greenhouse soils, heavy metals are become to common pollutants in greenhouse soils and near environment. Repeated amendments of organic matter and intensive use of fertilizers, metal-enriched chemicals and biocides may cause soil and environmental pollution in greenhouses. Specially, the impact of heavy metal pollution of soils on food metal content and underground water quality has become a public concern.

Bülent TOPCUOĞLU is with the Akdeniz University Vocational School of Technical Sciences, 07058 Antalya TURKEY (phone: 0090242-3106751; fax: 0090242-2274785; e-mail: btoglu@ akdeniz.edu.tr).

The maximum permissible concentrations of heavy metals in surface soils are normally based on total concentration, although it is the bioavailable metal fraction that posses environmental concern [1]. Nevertheless, these criteria are insufficient since mobility, environmental diffusion and bioavailability largely depend on soil physico-chemical characteristics and, likewise, on trace metal chemical forms ([2]. Heavy metals are often adsorbed or occluded by carbonates, organic matters, Fe-Mn oxides and primary or secondary minerals [3]. Since plants take up most nutrients from the soil solution, it is often assumed that the dissolved metals are readily available to organisms [4]. Due to potential toxicity of heavy metals to human life and environment, determining the chemical form of heavy metals in greenhouse soils is an important approach of chemical characterization and can provide useful information on its mobility and bioavailability. From an environmental point of view, the evaluation and forecast of food contamination is related to the bioavailable fraction of heavy metals in soil.

Although total heavy metal content in soils provide a convenient means of expressing a measure of pollution, such measure are generally deficient in predicting toxicity of metal pollutants. Therefore, the chemical form is of great significance in determining the potential bioavailability and remobilization of the soil metals [5].

Although greenhouse areas a have great impact on environment due to intensive use of agrochemicals, little attention has been paid to heavy metal speciation and metal bioavailability in greenhouse soils. The aim of this study was to provide information on the metal speciation and metal bioavailability in the greenhouse soils.

II. Material And Methods

The experiment was conducted on the major greenhouse vegetable growing area located at Aksu in the eastern part of Antalya, Turkey. The site studied is intensively cultivated and is not industrialized area. The experiment was carried out at greenhouse region and soil samples were taken from eight sampling points (Fig. 1).

The geological materials of greenhouse area are mainly of calcareous nature. The land is influenced by a Mediterranean climate with a high average annual rainfall (1100 mm/year), the annual average temperature being around 18,7 °C, 67 % average humidity and 300 sunny days. As for greenhouses, the annual temperature is higher inside than outside, and all are watered by sprinklers. All greenhouses have passive ventilation to control temperature and humidity inside. A great

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number of greenhouse soil is artificially built up with a different layer of sand, organic matter and other soil source.

Fig. 1. Map of greenhouse regions of Aksu, Antalya

Soil samples were taken at a depth of 10-20 cm and these were air-dried, sieved (< 2 mm) and stored in polyethylene bags sealed awaiting analysis.

Electrical conductivity (EC) and pH were measured a soil:water ratio of 1:2. cation exchange capacity (CEC) was determined by 0.1 M NN4AoC extraction; CaCO3 content was determined by the calcimeter; organic carbon was measured by wet oxidation; and texture was determined by Bouyoucos hydrometer method.

Sequental extraction proposed by Tessier et al. [6] was applied to soil samples to identify metal fractions.

The heavy metal sequential extraction procedure had the following steps:

F1. 1 M $MgCl_2$ (1:8 w/v, pH 7) for 1 h at room temperature; metals in soil solution and in exchangeable forms.

F2. 1 M NaOAc (1:8 w/v, pH 5) for 5 h at room temperature; metals mainly in the carbonate fraction.

F3. 0,04M NH2OH/HCl in 25 % (v/v)HOAc (1: 20 w/v) for 6 h at 96 °C ; metals associated with Fe and Mn oxides.

F4. 3 ml 0,02 M HNO3+5 ml 30 % H2O2 (pH 2) for 3 h at 85 °C; metals associated with organic matter.

F5. HNO3-HCl digestion; residual fraction.

For the determination of 'total' heavy metal concentrations, soil samples were digested in aqua regia (1:3 HNO_3/HCl) and $HCLO_4$ according to the international standard [7]. Zn, Cu, Ni, Pb and Cd concentrations of greenhouse soil were analysed using ICP-MS under optimised measurement conditions, and values were adjusted for oven dried (12 h at 105 °C) material.

Degree of soil pollution was evaluated by using single factor index and Nemerow comprehensive index methods [8].

Variance and correlation analysis and least significant difference test at P<0.05 level were performed by using SPSS-16 for Windows program.

III. Result And Discussion

*Soil Properties***:** Certain soil characteristics of greenhouse area are shown in Table 1. These greenhouse soils have generally sandy loam texture, slightly alkaline reaction, moderate CEC, in a wide range of EC and lime values. These soil characteristics, together with irrigation by sprinklers and agricultural practices, suggest that intensive greenhouses agriculture is the main cause of soil contamination by heavy metals and that theoretically the heavy metal availability will be changeable [9].

Total metals: The total metal contents of the experimental soil and their pollutant limits was given in Table 2. The results of Table 2 ranged (μg g^{-1}) from 76.33 to 112.25 for zinc with a mean of 87.99, 0.19 to 1.36 for cadmium with a mean of 0.59, 42.25 to 112.33 for nickel with a mean of 73.12, 15.02 to 23.30 for lead with a mean of 18.89 and 33.26 to 62.33 for chromium with a mean of 50.66.

Soil samples obtained from site 4 and site 8 had the highest concentration of Ni and Zn, respectively. In these sites Ni and Zn concentrations were exceeded soil pollution limits referenced by 86/278/EEC directive to agricultural soils with pH>7[10]. The average concentrations of Cd and Pb in soils were higher than typical soil concentration reported by literature [11]. This suggest an accumulation of heavy metals in greenhouse soils due to agricultural practices.

According to these data, the order for the average content of metals in analysed samples is Zn>Ni>Cr>Pb>Cd.

Soil pollution index: Single-factor index analysis of soil samples were given in Table 2. According to evaluation grading standarts of the single-factor index method, soil samples were in clean quality grade. But based on the analysis of the Nemerow comprehensive index method, pollution grade of soil samples were 0.75, and this value refers to warning limit [8].

Metal Speciation: Concentrations of Zn, Cd, Ni, Pb and Cr in soil fractions were given in Table 3. Irrespective of sampling point, the distribution of metals in greenhouse soil samples generally followed the order below for the metals studied.

Zn: F5>F4>F2>F3>F1
Cd: F5>F3>F4>F1>F2
Ni: F5>F4>F1>F2>F3
Pb: F5>F4>F1>F2>F3
Cr: F5>F4>F2>F3>F1

The study of the distribution of metals showed that the greatest percentages of all metals were present in the residual phase. The residual phase represents metals largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh conditions [5].

Although Ni and Pb were largely associated with residual phase, the second important percent of these metals were in exchangeable form. On the other hand second important percent of Zn ad Cr were associated with Fe_Mn oxides.

Cd seemed to be the most mobile element, and was largely associated with organic matter and Fe-Mn oxides. High amount of Cd associated with the non-residual phases shows that it may be easily transferred into the food chain through uptake by plants growing in the soils. Under oxidizing conditions, metals present in organic matter may be easily remobilized into the environment. Fe/Mn oxides exist as nodules, concretions, cement between particles or as a scavengers [12]. These fractions include Cd held by electrostatic adsorption (exchangeable) and that specifically adsorbed [13].

TABLE I
THE ANALYTICAL CHARACTERISTICS OF THE EXPERIMENTAL SOIL

Sampling point	$CaCO_3$, %	pH (H_2O)	EC, micS cm^{-1}	CEC, mmol ^{kg}	Organic carbon, g^{-kg}	Particle size distribution (%)		
						Sand (2-0.02 mm)	Silt (0.02-0.002 mm)	Clay (<0.002 mm)
1	0,2	6,95	2038	64	0,61	72,44	19,08	8,48
2	0,9	6,96	1862	90	0,88	65,22	25,9	8,88
3	10,6	7,8	963	181	1,52	61,44	31,08	7,48
4	25,5	7,82	721	192	2,86	56,44	35,88	7,68
5	29,3	7,84	824	160	3,78	64,44	27,48	8,08
6	39,0	7,93	1471	320	2,44	53,44	38,88	7,68
7	30,4	7,83	862	192	1,83	60,44	31,28	8,28
8	7,8	7,38	4520	320	2,02	66,44	25,28	8,28

TABLE II
THE TOTAL METAL CONTENTS (µG G-1 DRY WT) OF THE EXPERİMENTAL SOİL AND THEİR POLLUTANT LİMİTS.

Sampling sites of Aksu, Antalya	Zn	Cd	Ni	Pb	Cr	Pollution Index
1	93,03	1,27	44,25	22,64	56,33	0,39
2	95,03	1,36	42,25	23,12	52,31	0,39
3	76,33	0,25	43,25	23,30	37,29	0,27
4	74,38	0,51	112,33	16,51	62,33	0,52
5	76,33	0,56	96,33	17,12	55,63	0,47
6	88,25	0,26	81,25	17,34	48,56	0,40
7	88,33	0,33	77,02	15,02	59,63	0,42
8	112,25	0,19	88,26	16,05	33,26	0,40
Mean metal concentration	87,99	0,59	73,12	18,89	50,66	
Limit values in soil (pH>7) [10]	150-300	1-3	30-75	50-30		
Typical soil contents, [11]	20-300	0.03-0.3	50	2-20	70	

TABLE III
CONCENTRATIONS OF ZN, CD, NI, PB AND CR IN SOIL FRACTIONS

Metal Fraction	Metal Concentration of Sampling Sites (µg $g^{-1\ dry\ wt}$)								Fraction, %
	1	2	3	4	5	6	7	8	Mean
Zinc									
F1	0,52	0,54	0,5	0,23	0,35	0,31	0,34	0,33	0,51
F2	0,33	0,32	2,28	1,38	7,63	2,65	1,33	0,43	2,57
F3	1,92	1,85	0,18	0,23	0,02	0,81	0,09	0,04	0,74
F4	7,88	7,7	0,02	0,6	0,35	0,9	4,72	0,02	3,04
F5	77,8	81,25	74,53	67,25	70,96	82,89	96,33	41,33	93,15
Cadmium									
F1	0,008	0,009	0,019	0,004	0,002	0,002	0,002	0,002	1,57
F2	0,004	0,004	0,001	0,003	0,007	0,005	0,002	0,006	1,12
F3	0,023	0,021	0,018	0,019	0,016	0,019	0,026	0,016	6,28
F4	0,088	0,051	0,004	0,011	0,006	0,001	0,001	0,033	4,58
F5	1,011	1,17	0,213	0,445	0,505	0,224	0,133	0,118	86,52
Nickel									
F1	0,3	0,29	1,08	0,29	0,21	0,32	0,36	0,04	0,56
F2	0,12	0,13	0,38	0,23	0,49	0,23	0,12	0,19	0,34
F3	0,13	0,15	0,2	0,14	0,15	0,14	0,12	0,12	0,23
F4	4,3	4,16	0,39	0,88	1,03	1,01	0,77	0,56	3,45
F5	35,14	33,27	67,73	99,7	91,55	69,6	82,33	55,36	95,41
Lead									
F1	0,13	0,12	0,23	0,1	0,1	0,14	0,07	0,07	0,74
F2	0,11	0,13	0,0005	0,0005	0,08	0,0005	0,11	0,01	0,30
F3	0,06	0,05	0,06	0,04	0,03	0,04	0,05	0,03	0,27
F4	1,9	1,97	1,91	1,84	1,86	1,8	1,98	1,82	12,09
F5	18,88	19,32	13,46	13,02	14,25	13,52	13,32	8,05	86,61
Chromium									
F1	0,27	0,26	0,2	0,19	0,18	0,1	0,14	0,14	0,53
F2	1,15	0,16	0,45	0,77	0,86	0,17	0,73	0,12	1,39
F3	0,07	0,08	0,39	0,23	0,18	0,14	0,14	0,17	0,54
F4	2,13	2,1	2,11	1,18	3,69	2,9	1,71	1,3	5,88
F5	40,77	38,63	28,25	53,65	44,87	43,89	26,36	12,97	91,67

Mobility of metals: Due to some metal forms are strogly bound to soil components than those exracted in F1 and F2, the mobility of metals in soil samples may be evaluated on the basis of absolute and relative content of fractions weakly bound to soil component. Relative index of metal mobility was calculated as a 'mobility factor' (MF) on the basis of the following equation [14]:

$$\text{MF: } \frac{(F1+F2+F3) \text{ x } 100}{(F1+F2+F3+F4+F5)}$$

This equation is largely describes the potential mobility of metals. Among the elements studied, Cd were appeared to be the most readily soluble and potentially bioavailable metals and these metals may carry a potential risk for metal transfer in food chain and contamination to ground water.

The high MF values have been interpreted as symptoms of relatively high lability and biological availability of heavy metals in soils [14]. The results of the present study suggest that the mobility of the metals declines in the following order (Figure 2): Cd>Zn>Cr>Pb>Ni

Although average Ni concentration of all soil samples was above the pollution limits, the mobility factor of Ni in these soils were found the least.

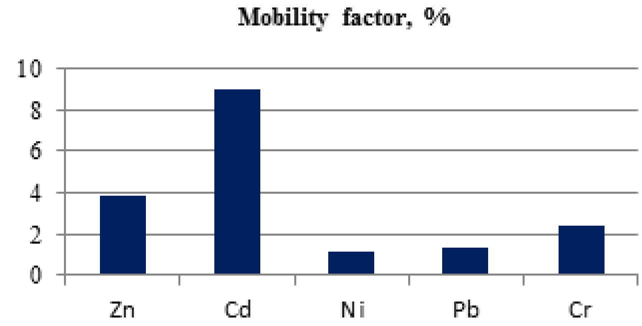

Fig. 2 Metal mobility of greenhouse soils

Correlation analysis: In the current study, correlation analysis between total metal concentrations and soil properties ($CaCO_3$, pH, CEC, organic matter and clay) of grenhouse soils was performed (Table 4).

$CaCO_3$ content of soil was significantly correlated with pH, organic matter, Ni and Pb. Soil pH correlated with organic matter, clay and Cd concentration. EC value positively correlated with Zn and Cr concentrations. Organic matter were positively correlated with Pb, but negatively correlated with Ni. Among the elements Cd and Ni concentrations were negatively correlated with CEC. Clay content is significantly correlated with concentrations of Cd. Clay is the main soil component related with heavy metals [15].

TABLE IV
CORRELATION COEFFICIENTS (R), OF TOTAL METAL CONCENTRATIONS WITH SOIL PROPERTIES AND AMONG ELEMENTAL CONCENTRATIONS IN AKSU GREENHOUSE SOILS

	$CaCO_3$	pH	EC	OM	CEC	Clay	Zn	Cd	Ni	Pb	Cr
pH	**0,877****	1									
EC	- 0,493	- 0,497	1								
OM	**0,749***	**0,751***	- 0,284	1							
CEC	0,529	0,569	0,374	0,442	1						
Clay	- 0,557	**- 0,815***	0,384	- 0,500	- 0,493	1					
Zn	- 0,452	- 0,580	**0,924****	0,448	0,276	0,597	1				
Cd	- 0,615	**- 0,830****	- 0,030	- 0,555	**- 0,839****	**0,732***	0,106	1			
Ni	**- 0,717***	- 0,596	- 0,059	**- 0,682***	**- 0,643***	0,214	- 0,066	**0,633***	1		
Pb	**0,673***	0,608	- 0,059	**0,856****	0,537	- 0,377	- 0,188	- 0,535	**- 0,874****	1	
Cr	0,330	0,052	- **0,651***	0,168	-0,500	0,177	- 0,476	0,409	- 0,193	0,261	1

**and * : Correlation is significant at the 0.01 level and 0.05 level, respectively

IV. CONCLUSIONS

The concentration of heavy metals with the exception of Zn and Ni in soils of Antalya Aksu greenhouses is generally lower than referenced by the 86/278/EEC directive [11] to agricultural soils. Results showed that the anthropogenic input of Cd was primarily in the organic matter and Fe-Mn oxides. Although total Cd concentration was below the pollution limits, a important portion of Cd concentration was in mobile form. Therefore Cd bound to organic matter may be readily solubilized, thus making this element the most potentially bioavailable. Inputs of Zn are mainly in the carbonate and Fe/Mn oxides form. Obtained results with greenhouse characteristics and area conditions generally suggest a very low contamination of soils. However, pollution index based on 86/278/EEC directive soil metal limits, indicates that multielement contamination in soils is low and implies that the sampled soils could be safely cultivated for greenhouse crop production.

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