Heavy Metal and Pollution Characteristics of Soils and Underground Waters in Intensive Greenhouse Areas

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 greenhouse areas. 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. A study was carried out in intensive greenhouse area of Kumluca to determine the relation between soil metal characteristics and underground water metal contents and also other quality and pollution levels. Additional to routine water and soil analysis, a sequential extraction procedure was used to estimate the availability of heavy metals (Zn, Cd, Ni and Pb) in greenhouse soils. Underground waters of greenhouse area have high conductivity and nitrate content, but heavy metal contents were below the permissible levels. Soil total metal contents, exception of Zn were below the pollution limits. Metal fractionation showed that Zn was predominantly associated with Fe-Mn oxide fraction, major portion of Cd and Pb associated with organic matter fraction, a major portion Ni was associated with residual fractions. Results of the present study suggest that the mobility of metals probably increase in the following order: Ni<Pb<Cd<Zn. Although metal contents of soil exception of Zn were below the pollutant limits, among the elements studied, Zn and Cd were appeared to be the most readily soluble and potentially bioavailable metals.

***Keywords*—** Metal speciation, metal mobility, greenhouse soils, underground water.

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.

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 Kumluca in the western 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 ten sampling points (Fig. 1).

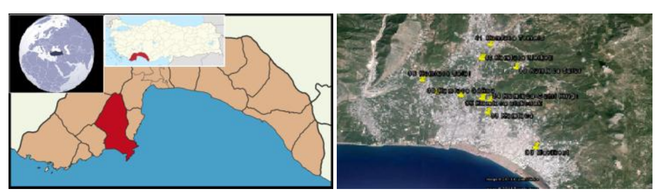

Fig. 1 Map of greenhouse regions of Kumluca, Antalya

The geological materials of greenhouse area are mainly of calcareous nature and near to Mediterranean sea with average 4-10 m altitude . 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 most of them are watered by sprinklers with underground water source at the same point. All greenhouses have passive ventilation to control temperature and humidity inside. A great number of greenhouse soils is artificially built up with a different layer of sand, organic matter and other soil source.

Underground water samples were collected from all the ten sites to analyze for heavy metals. Water samples were collected in polyethylene bottles (washed with detergent then with double-distilled water followed by 2 M nitric acid, then double-distilled water again and finally with sampled water). Water samples were acidified with 10% HNO3 for metal analysis, brought to the laboratory and kept refrigerated until needed for analysis. pH, electrical conductivity (EC) and nitrate were measured on site.

To determine heavy metals in water samples, 10ml of aqua regia and 1 ml of perchloric acid added to 100ml of water samples in a culture test tube, then incubated at 80°C in a water bath, after total digestion and subsequent cooling, the solution was diluted to 50ml and analyzed for heavy metals.

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 method [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, Cd, Ni and Pb concentrations of water and greenhouse soil samples were analysed using ICP-OES under optimised measurement conditions, and values were adjusted for oven dried (12 h at 105 °C) material.

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

A. Underground Water Properties

Certain underground water characteristics of greenhouse areas are shown in Table 1. Groundwaters in greenhouse areas have generally slightly alkaline reaction, high electrical conductivity and high nitrate content. Specially, total nitrate content of groundwater has exceeded maximum permissible limits for drinking waters.

Table I
The Analytical Characteristics Of The Underground Waters In Greenhouse Areas.

Sampling point	pH	EC, micScm^{-1}	NO3, mg L^{-1}	Zn, µg L^{-1}	Cd, µg L^{-1}	Ni, µg L^{-1}	Pb, µg L^{-1}
1	7.40	1089	39	<1,86	<1,18	<4,57	<4,03
2	7.67	526	40	<1,86	<1,18	<4,57	<4,03
3	7.39	852	48	6,9	<1,18	<4,57	<4,03
4	7.37	815	33	<1,86	<1,18	<4,57	<4,03
5	7.61	717	15	<1,86	<1,18	<4,57	<4,03
6	7.60	945	19	27	<1,18	9,30	<4,03
7	7.39	997	20	<1,86	<1,18	<4,57	<4,03
8	7.07	804	45	<1,86	<1,18	<4,57	<4,03
9	7.24	727	189	<1,86	<1,18	<4,57	<4,03
10	7.59	599	102	<1,86	<1,18	<4,57	<4,03
Permissible limits [8]			10	200	3	20	10

*: < values refer to below the analytical detection limit

High concentration of nitrate and conductivity values are of course may be due to highly intensive agricultural practices for all season and also low altitude of region and may be cause of seawater intrusion to aquifer. Total Zn, Cd, Ni and Pb contents were below the permissible pollution limits and also most of samples were below the detection limits of analytical apparatus.

B. Soil Properties:

Certain soil characteristics of greenhouse areas are shown in Table 2. These greenhouse soils have generally slightly alkaline reaction, moderate CEC, high EC values and slightly calcareous. 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 lower [9].

Table II
The Analytical Characteristics Of The Experimental Soil.

Sampling point	CaCO3, %	pH	EC, micS cm^{-1}	CEC, meq$^{-100\,g}$	Organic carbon, g^{-kg}	Clay
1	6.88	7.79	951.0	36.21	0.609	17.0
2	2.48	7.18	2568.0	29.83	1.706	23.5
3	3.21	7.25	1967.0	36.22	4.568	35.0
4	6.79	7.67	920.0	36.22	1.218	38.0
5	5.04	7.57	991.0	25.57	2.655	22.3
6	8.71	7.81	1584.0	19.17	0.913	22.3
7	3.85	7.73	1178.0	29.82	0.913	24.6
8	5.73	7.43	1320.0	46.87	2.465	21.6
9	7.52	7.64	1117.0	17.04	3.532	33.0
10	3.67	7.63	767.0	29.83	2.971	44.0

C. Total metals

The total metal contents of the experimental soil and their pollutant limits were given in Table 3. The results of Table 3 ranged (µg g^{-1}) from 355 to 772 for zinc with a mean of 496, 0.04 to 0.48 for cadmium with a mean of 0.24, 9,7 to 78.8 for nickel with a mean of 43.2 and 4,2 to 10.9 for lead with a mean of 6.7. The metal levels except Zn in these all soils are lower than referenced by 86/278/EEC directive to agricultural soils with pH>7. The average levels of Zn in greenhouse soils were higher than the limit values of European Union [10].

This suggests 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.

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

Sampling sites	Zn	Cd	Ni	Pb
1	359	0.48	9.7	5.2
2	600	0.04	37.8	6.4
3	409	0.04	50.7	3.9
4	772	0.03	68.8	4.2
5	476	0.17	41.8	6.8
6	493	0.10	26.3	5.8
7	670	1.32	26.5	8.8
8	402	0.05	36.8	7.5
9	421	0.13	54.8	10.9
10	355	0.06	78.8	7.8
Mean	496	0,24	43,2	6,7
Limit values in soil (pH>7) [10]	150-300	1-3	30-75	50-30
Typical contents [11] [12]	20-300	0.03-0.3	50	2-20

D. Metal Speciation

Concentrations of Zn, Cd, Ni and Pb in soil fractions were given in Table 4. Irrespective of sampling point, the distribution of metals in greenhouse soil samples generally followed the order below for the metals studied.

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

The study of the distribution of metals showed that the greatest percentage of Zn (50.79 %) was present in the Fe/Mn oxides. Fe/Mn oxides exist as nodules, concretions, cement between particles or as a scavengers (Ikem et al., 2003). Fe/Mn oxides are excellent scavengers of trace metals and sorption by these oxides tend to control Cu, Mn and Zn solubility in soils [13]. It is reported that Zn was strongly bound to Fe/Mn oxide fraction [14].

Cd (51.63 %) and Pb (32.17 %) were largely associated with organic matter. Under oxidizing conditions, metals present in organic matter may be easily remobilized into the environment.

Ni largely (62.56 %) associated with 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].

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

Metal Fraction	Metal Concentration of Sampling Sites (μg $g^{-1\ dry\ wt}$)										Fraction % mean
	1	2	3	4	5	6	7	8	9	10	
Zinc											
F1	8.5	9.3	11.2	6.5	4.6	3.7	5.6	4.9	6.6	7.7	1.35
F2	33.1	42.1	55.6	44.9	39.4	77.5	55.2	70.3	42.6	55.6	10,39
F3	188	215	233	288	188	255	388	256	255	244	50,79
F4	33.3	19.6	22.6	48.5	39.8	65.3	88.6	39.6	44.3	25.6	8,62
F5	95.8	313.6	86.5	384.0	203.3	91.1	132.0	31.3	72.0	21.5	28,85
Cadmium											
F1	0.015	0.01	0.01	0.01	0.03	0.02	0.01	0.02	0.01	0.01	4.58
F2	0.115	0.03	0.01	0.01	0.02	0.02	0.18	0.02	0.09	0.02	16.99
F3	0.077	0.06	0.01	0.01	0.05	0.05	0.06	0.02	0.09	0.09	16.99
F4	0.19	0.06	0.02	0.02	0.05	0.05	0,89	0.08	0.05	0.03	51.63
F5	0.086	0.03	0.01	0.01	0.02	0.02	0.05	0.02	0.01	0.01	9.80
Nickel											
F1	0.06	0.08	0.05	0.09	0.12	0.14	0.09	0.08	0.07	0.14	0,21
F2	2.3	2.2	1.8	2.1	1.9	1.7	1.88	2.4	2.6	1.8	4,80
F3	4.5	12.3	5.9	8.9	12.3	13.5	6.9	8.7	9.6	11.2	21,73
F4	1.9	8.8	3.6	5.6	2.6	3.3	1.3	5.9	7.8	5.4	10,70
F5	0.9	14.4	39.4	52.1	24.8	7.6	16.3	19.6	34.7	60.2	62,56
Lead											
F1	0.05	0.06	0.05	0.06	0.07	0.09	0.02	0.06	0.04	0.01	7,10
F2	0.7	0.5	0.66	0.48	0.44	0.55	0.6	0.55	0.33	0.28	6,96
F3	0.9	0.8	1.2	1.2	1.8	1.3	3.9	1.8	2.8	3.4	26,74
F4	2.3	2.2	0.89	1.55	2.2	2.2	1.9	2.8	3.3	3.8	32,17
F5	1.1	2.8	1.1	0.8	2.2	1.6	2.3	2.3	4.4	0.2	27,01

E. 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) [15] on the basis of the following equation:

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

This equation is largely describes the potential mobility of metals. The MF values were considerably higher (particulary for Zn) for all metals. The high MF values have been interpreted as symptoms of relatively high lability and biological availability of heavy metals in soils [15]. The results of the present study suggest that the mobility of the metals declines in the following order (Figure 2):

Zn>Cd>Pb>Ni

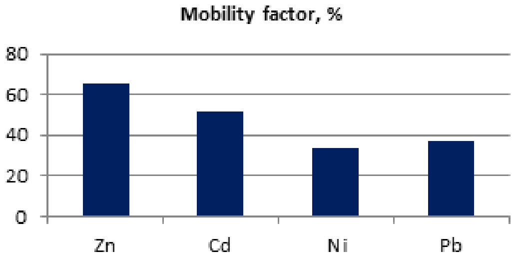

Fig. 2 Metal mobility of greenhouse soils

F. Correlation analysis of soil parameters

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. $CaCO_3$ content of soil was significantly correlated with pH. Soil pH correlated with CEC. Organic matter is significantly correlated with concentrations of Ni. No other correlation was found between soil metals and chemical parameters.

IV. Conclusions

The concentration of heavy metals with the exception of Zn in soils of Antalya Kumluca greenhouses is generally lower than referenced by the 86/278/EEC directive to agricultural soils. Results showed that although total Cd concentration was below the pollution limits, a high 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 Fe/Mn oxides form, and also total concentration was above the pollution limits. On the other hand Zn and Cd were found to be most mobile element. Nevertheless, there is no heavy metal pollution problem in underground waters of greenhouse area, but nitrate and conductivity values seem the most dangerous threath in this araea. Obtained results with greenhouse characteristics and area conditions suggest a contamination of soils by agricultural practices.

Table V
Correlation Coefficients (R), Of Total Metal Concentrations With Soil Properties And Among Elemental Concentrations In Kumluca Greenhouse Soils

	$CaCO_3$	pH	CEC	OM	Clay	Zn	Cd	Ni
pH	**0,705***	1						
CEC	-0,425	**-0,752***	1					
OM	-0,217	-0,094	-0,228	1				
Clay	-0,309	-0,339	0,006	-0,073	1			
Zn	-0,057	0,041	0,124	0,064	-0,016	1		
Cd	-0,136	0,408	-0,213	-0,317	-0,030	0,289	1	
Ni	-0,216	-0,198	-0,224	**0,938****	-0,044	0,090	-0,480	1
Pb	0,052	0,177	-0,230	0,025	-0,442	-0,164	0,294	0,074

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

Acknowledgements

This research was sponsored by TUBITAK (The Scientific and Technological Council of Turkey). Author would like to thank to TUBITAK for the financial support of the project (TOVAG-111O711).

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