

# Heavy Metal Mobility and Bioavailability on Soil Pollution and Environmental Risks in Greenhouse Areas

BÜLENT TOPCUOĞLU

**Abstract**---A survey study was conducted on greenhouse soils and plants in intensive greenhouse areas of Antalya to assess the heavy metal mobility and bioavailability on soil pollution, and to understand the ecological risk, transport processes of heavy metals and the relations with the soil characteristics. Additional to routine water and soil analysis, a sequential extraction procedure and a DTPA-extraction was used to estimate the mobility and bioavailability of heavy metals (Zn, Cd, Ni and Pb) in greenhouse soils and several environmental pollution indexes were used to evaluate the size of pollution and risks.

The concentration of heavy metals with the exception of Ni in soils of greenhouses were generally below the referenced limits. Soil metal speciation showed that the greatest percentage of all metals was present in the residual form, and the mobility of metals declined in the following order: As>Cd>Zn>Pb>Ni. DTPA-extractable metal levels were not coincided with the tendency of total metal levels in soil and there were not a strictly relations between total and DTPA-extractable metals for all elements studied. Single factor and composite pollution coefficient values of all metals with the exception of Ni were not exceeded critical limit. Anthropogenic and enrichment factor indexes of greenhouse soils indicate that both two parameter showed similar trends and 1 to 5 fold metal enrichment by anthropogenic inputs compared to uncontaminated soil. Potential ecological risk indexes of soil metals except Ni were found below the threshold value that indicate these metals have a low risk to surrounding environment.

Mean Zn and Cd concentrations in tomato leaves were exceeded referenced limits. But all heavy metal concentrations were found below the phytotoxic heavy metal limits for culture plants. Although soil Ni concentration was exceeded the pollutant limits, possibly due to low soil mobility factor of Ni, concentration of Ni in tomato fruit was found very low. However, target hazard quotient (THQ) of tomato fruits was found below the critical value and thus it can be presumable no health risk for Cd metal in short or medium terms.

In a comprehensive manner, in addition to total concentrations referenced, environmental risk evaluation methods, soil speciation studies and determination of efficient extraction methods may provide useful information for assessing metal bioavailability and environmental risks.

**Key words:** Greenhouse Soils, Metals, Mobility, Bioavailability

## I. INTRODUCTION

**H**EAVERY metals are of considerable concern due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviours [1]. Due to intensive use of agrochemicals in greenhouse soils, heavy metals are become to common pollutants in greenhouse soils and adjacent environment. Repeated amendments of organic matter and intensive use of fertilizers, metal-enriched chemicals and biocides may cause soil and environmental pollution in greenhouses. Especially heavy metals can be accumulated over the acceptable limits and plant heavy metal concentrations may reach phytotoxic levels. Therefore, there is a necessity to monitor heavy metal content of soils.

Most of recently reported studies dealing with the evaluation of heavy metal contamination in soils use only the total content of heavy metal as a criterion for determining their potential effect on the environments.

Bülent TOPCUOĞLU is with the Akdeniz University Vocational School of Technical Sciences, 07058 Antalya TURKEY. (phone: +90242-3106751; fax: +90242-2274785; e-mail: btoglu@akdeniz.edu.tr).

However, it is common conception nowadays that the total concentrations of metals in soils are not a good indicator of bioavailability, or a good tool for potential risk assessment either, due to the different and complex distribution patterns of metals among various chemical species or solid phases [2].

Intensive efforts have been directed at the development of sequential fractionation schemes that quantitatively partition the total amount of a heavy metal into soil pools that may be interpreted for predicting metal phytoavailability from contaminated soils. Many studies have indicated that soil-test-extractable heavy metals can be correlated with their associated levels in plants. DTPA (diethylenetriaminepentaacetic acid) extraction provide a fairly rapid procedure for determining trace elements in soils. This procedure has been used to assess metal solubilities and contamination in soils. Evidence indicates that the DTPA-extractable metals are generally related to plant availabilities. Considerable research has been done on the extracting of heavy metals from contaminated soils by chelating agents, primarily DTPA [3].

Today many environmental pollution risk indexes developed for water and sediments can be used for soils, organic matter and other environmental materials. Although several establishment criteria developed for soils depend on total concentrations, these criteria were frequently unsatisfied for a comprehensive environmental risk prediction. Although greenhouse areas have a great impact on environment due to intensive use of agrochemicals, little attention has been paid to metal accumulation in greenhouse plants and heavy metal speciation and metal bioavailability and environmental pollution assessment in greenhouse soils with respect to comprehensive and integrated environmental evaluation.

The objectives of this study were to provide information on the metal accumulation in greenhouse plants, metal speciation and metal bioavailability in the greenhouse soils, and to compare the DTPA extraction procedure to sequential extraction for the removal of metals from soil and, to determine the relationships between DTPA-extractable metals of soil and the metal contents in greenhouse tomato grown in the same soil, and also to evaluate metal enrichments in greenhouse soils and plants and soil pollution indexes versus to soil characteristics in greenhouse soils.

## II. MATERIAL AND METHODS

The experiment was conducted on the major greenhouse vegetable growing area located at 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 8 sub-region and 30 sampling points (Fig. 1).



Figure 1. Map of greenhouse regions of Antalya, Turkey.

The geological materials of greenhouse area are mainly of calcareous nature and adjacent to Mediterranean sea with average 59 m altitude. The land is influenced by a Mediterranean climate with a high average annual rainfall (1038,8 mm/year), the annual average temperature being around 18,4 °C, 63,2 % average humidity and average 148,6 sunny days per year. As for greenhouses, the annual temperature is higher inside than outside, and most of them are watered by sprinklers with ground 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.

Greenhouse 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  $\text{NH}_4\text{Ac}$  extraction;  $\text{CaCO}_3$  content was determined by the calcimeter; organic carbon was measured by wet oxidation; and texture was determined by Bouyoucos hydrometer method.

Sequential extraction method [4] was applied to soil samples to identify metal fractions.

For the determination of 'total' heavy metal concentrations, soil samples were digested in aqua regia (1:3  $\text{HNO}_3/\text{HCl}$ ) and  $\text{HClO}_4$  according to the international standard [5]. Bioavailable fractions (DTPA-extractable) of metals were extracted from soil with diethylenetriaminepentaacetic acid- $\text{CaCl}_2$ -triethanolamine adjusted to pH 7,3 [6]. Total and bioavailable Zn, Cd, Ni and Pb concentrations of greenhouse soil samples were analysed using ICP-MS under optimised measurement conditions, and values were adjusted for oven dried (12 h at 105 °C) material.

Selected environmental pollution indexes for soil samples 'Mobility of Metals' [7], 'Single-Factor and Composite Pollution Index of Soils' [8], Anthropogenic Factor (AF) [9] and 'Enrichment Factor (EF) Indexes of Soil' [10], 'Potential Ecological Risk Factor Indexes' [11], and as for plant samples 'Heavy Metal Transfer (Bioconcentration) Factor' and 'Target Hazard Quotient (THQ) of Food' [12] were used for comprehensive and integrated evaluation of parameters.

Statistical analyses were performed by using SPSS-16 for Windows program.

## II. RESULT AND DISCUSSION

### 1. Soil Properties

Certain physical and chemical characteristics of greenhouse soils are shown in Table 2. These greenhouse soils have generally slightly alkaline reaction, moderate CEC, low EC values and highly 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 [13].

TABLE 1. THE ANALYTICAL CHARACTERISTICS OF GREENHOUSE SOILS

Site	Lime, %	pH, $\text{H}_2\text{O}$	EC, $\mu\text{mS cm}^{-1}$	CEC, $\text{meq}_{100\text{g}}$	Org. C., $\text{g}^{-\text{kg}}$	Clay, %
1	15,0	7,85	574	15,25	1,28	10,05
2	17,2	7,49	892	28,80	2,64	8,20
3	40,8	7,57	2020	19,40	3,53	11,02
4	20,9	7,57	1444	22,47	3,17	11,01
5	19,5	7,56	1914	31,85	4,20	9,76
6	25,1	7,80	1076	23,98	3,19	8,76
7	5,7	7,50	1535	17,80	2,59	9,39
8	35,9	7,96	374	13,80	1,52	8,88
Mean	22,51	7,66	1229	21,69	2,77	9,63
St.D.	1,13	0,18	601	6,36	0,98	1,03

The total and DTPA-extractable metal contents of the experimental soil and their pollutant limits was given in Table 2 and Table 3, respectively.

TABLE 2. TOTAL METAL CONTENTS ( $\mu\text{G G}^{-1}$  DRY WT) OF THE GREENHOUSE SOILS AND THEIR POLLUTANT LIMITS.

Site	Zn	Cd	Ni	Pb	As
1	173	0,50	118	12,3	6,5
2	249	0,35	215	13,7	6,6
3	170	0,23	90	9,3	8,7
4	126	0,45	130	20,0	7,5
5	112	0,62	129	25,1	34,3
6	88	0,78	56	30,4	17,9
7	127	0,33	64	28,6	4,0
8	57	0,25	175	15,9	9,9
Mean	138	0,44	122	19,4	11,9
St.D.	5,9	0,19	5,39	7,8	9,9
Limits [14]	20-300	0.03-	50	2-20	1-7

TABLE 3. DTPA-EXTRACTABLE METAL CONTENTS ( $\mu\text{G G}^{-1}$  DRY WT) OF THE GREENHOUSE SOILS

Site	Zn	Cd	Ni	Pb	As
1	5,265	0,030	0,826	0,092	1,090
2	5,940	0,020	0,730	0,662	0,205
3	4,550	0,024	1,192	0,328	0,980
4	4,750	0,026	0,388	0,515	1,903
5	3,195	0,028	0,404	0,631	2,275
6	3,482	0,008	0,770	0,521	0,071
7	3,845	0,018	0,735	0,381	0,100
8	11,600	0,020	0,956	8,200	0,170
Mean	5,338	0,021	0,750	1,416	0,849
St.D.	2,694	0,007	0,266	2,747	0,866

The results of Table 2 ranged ( $\mu\text{g g}^{-1}$ ) from 57 to 249 for zinc with a mean of 138; 0.23 to 0.78 for Cd with a mean of 0.44; 56 to 215 for Ni with a mean of 122; 9,3 to 30,4 for Pb

with a mean of 19,4; and 4 to 34,3 for As with a mean of 11,9. Average total metal contents except zinc were above the limits of European Union (86/278/EEC) [14] directive to agricultural soils with pH>7. Ni concentration in all soil samples were higher than limit values. According to these data, the order for the average content of metals in analysed samples is Zn>Ni> Pb>As>Cd.

DTPA-extractable metals ( $\mu\text{g g}^{-1}$ ) representative of available soil metals taken by plants were ranged from 11.6 to 3.195 for zinc with a mean of 5,338; 0.018 to 0.03 for Cd with a mean of 0.021; 0.388 to 1.192 for Ni with a mean of 0.750; 0.092 to 8.2 for Pb with a mean of 1.416; and 0.071 to 2.275 for As with a mean of 0.849. According to these data, the order for the average content of DTPA-extractable metals in analysed samples is Zn>Pb>As>Ni>Cd. Pearson's correlation coefficient showing relationship between soil total metal contents and DTPA-extractable metals was given in Table 4. DTPA-extractable metal levels were not coincided with the tendency of total metal levels in soil (Table 4). Extreme ranges in DTPA-extractable metal levels as in Pb and As were determined. This possibly may cause of metal mobility differences or/and soil conditions affecting extraction process.

Pearson's correlation matrices between total and DTPA-extractable metals were computed and the significant correlations obtained for the criterion values of probability  $P<0.05$  and  $P<0.01$  were presented in Table 4. Correlations between total metal form and DTPA-extractable form for an element are cross underlined in its column and row, and other correlations matrices of elements are neglected. According to results significant correlations between total metal form and DTPA-extractable form for an element can be seen only for Zn and As. This results show that there were not a strictly relations between total and DTPA-extractable metals for all elements studied.

TABLE 4. PEARSON'S CORRELATION COEFFICIENT SHOWING RELATIONSHIP BETWEEN SOIL TOTAL METAL CONTENTS AND DTPA-EXTRACTABLE METALS

		Soil Total Metals				
		Zn	Cd	Pb	Ni	As
Soil DTPA-Ext. metals	Zn	<u>0,175*</u>	-0,136	-0,105	-0,140	-0,147
	Cd	0,010	<u>-0,124</u>	0,003	-0,073	0,165*
	Pb	-0,198*	<u>-0,296**</u>	0,119	-0,177*	-0,138
	Ni	0,169*	-0,050	<u>-0,030</u>	-0,019	0,010
	As	0,121	0,095	-0,114	0,034	<u>0,256**</u>

\*: Significant with  $P\leq 0.05$ ; \*\*: Significant with  $P\leq 0.01$

**Metal Speciation**

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

- Zn: F1<F3<F4<F2<F5
- Cd: F2<F3<F4<F1<F5
- Ni: F3<F1<F2<F4<F5
- Pb: F3<F2<F1<F4<F5
- As: F3<F4<F2<F1<F5

The study of the distribution of metals showed that the greatest percentage of all metals was present in the residual

fraction (F5). However, F1 and F2 fractions of Zn; Cd and As metals were higher than other metals. This property possibly give these metals a high mobility. The most mobile metal fraction was detected in As and the most immobile metal fraction was detected in Ni. Ni largely (97,6 %) 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 [7].

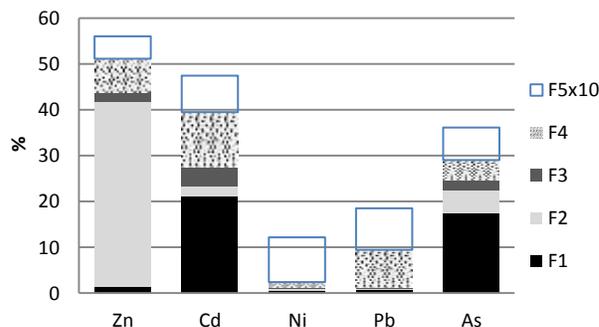


Figure 3. Concentrations of Zn, Cd, Ni, Pb and As in soil fractions (F5 values are higher 10 fold than given values)

**Mobility of metals**

Due to some metal forms are strongly bound to soil components than those extracted in F1, F3 and F3, 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:

$$MF = \frac{(F_1 + F_2 + F_3)}{(F_1 + F_2 + F_3 + F_4 + F_5)} \times 100$$

This equation is largely describes the potential mobility of metals. The MF values were considerably higher for As, Zn and Cd. 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: As>Cd>Zn>Pb>Ni (Figure 4).

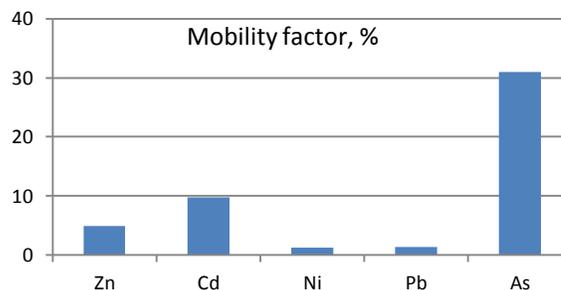


Figure 4. Average metal mobility of greenhouse soils

**Contamination Evaluation of heavy metals**

*Anthropogenic factor (AF) and Enrichment factor (EF) indexes of soil*

Anthropogenic and enrichment factor indexes of greenhouse soil were given in Figure 5. Estimated values of AF for the heavy metals determined in the soil samples with

respect to the uncontaminated soil in the same area were generally greater than one and range from 1,48-0,81 (Zn), 2,70-1,64 (Cd), 2,56-1,38 (Ni), 2,62-1,41 (Pb) and 5,53-3,00 (As). This indicates a, 1 to 5 fold metal enrichment by anthropogenic inputs compared to uncontaminated soil.

Enrichment factor values showed similar trends with anthropogenic factor values. Mean Enrichment factor Zn was below the moderate level and approximate to depletion level.

Although total Ni concentration of greenhouse soils were above typical soil concentrations and permissible contaminant limits, enrichment factor is very low and also in some sampling sites enrichment factor of Ni were in depletion level. This may be inferred that Ni abundance of parent material of soil is very high and there are less Ni contaminant sources.

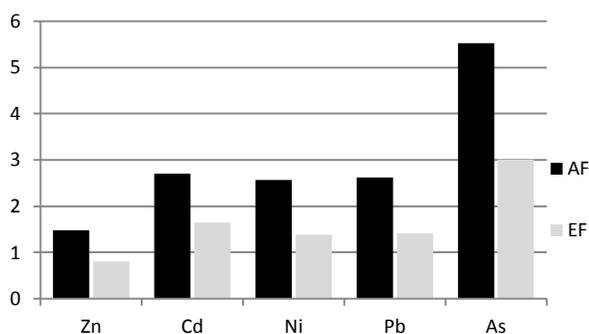


Figure 5. Anthropogenic (AF) and enrichment factor (EF) indexes of the greenhouse soils

*Single-factor index, composite pollution index and single ecological and potential ecological risk factor index*

Single-factor ( $P_i$ ) and composite pollution ( $P_N$ ) indexes, single ecological risk ( $E_r$ ) and potential ecological risk ( $R_i$ ) indexes of heavy metals in greenhouse soils are summarized in Figure 6. It is clear that all contamination coefficients ( $P_i$  and  $P_N$ ) with the exception of Ni were not exceeded critical value 1. Contamination coefficient of Ni was exceeded critical value in all sampling sites. Although contamination coefficient of other metals were low, due to higher coefficient value of Ni, composite pollution index was determined in heavy pollution risk group.

The average single ecological risk factors,  $E_r$  of heavy metals in greenhouse soils were ranked in the following order  $Zn < Pb < As < Cd < Ni$ . The average monomial risk for heavy metals were found below the 40 that indicate all metals posed low risk to surrounding ecosystem. In order to quantify the overall potential ecological risk of observed metals in the greenhouse soils, general ecological risk factor (RI) value was calculated as the sum of all the risk factors. Average RI value were found 19,17 and below the ecological risk level.

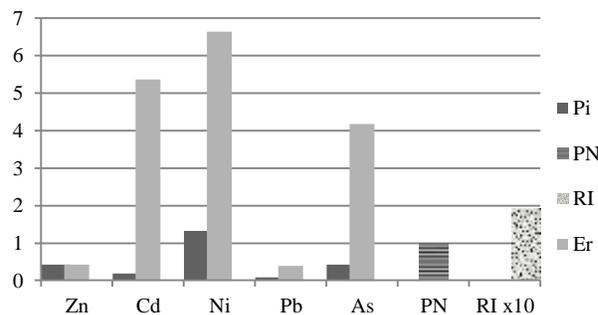


Figure 6. Single factor index of each metal, composite pollution index, single ecological and potential ecological risk indexes of metals in greenhouse soils.

**2. Plant Properties**

*Plant heavy metal content*

Heavy metal concentration of leaves and tomato fruits were presented in Table 5 and Table 6, respectively.

TABLE 5. TOTAL METAL CONTENTS ( $\mu\text{G G}^{-1}$  DRY WT) OF TOMATO LEAVES GROWN IN GREENHOUSE SOILS.

Site	Zn	Cd	Pb	Ni	As
1	114	0,099	1,89	1,115	0,156
2	120	0,520	5,25	0,622	0,182
3	74	1,214	2,14	0,530	0,994
4	145	1,204	2,51	0,763	0,429
5	238	0,892	2,34	1,202	0,288
6	40	0,622	2,75	0,934	0,663
7	124	0,802	4,60	0,798	0,237
8	244	0,087	2,36	0,914	0,228
Mean	137,3	0,680	2,98	0,860	0,397
St.D.	71,8	0,437	1,412	0,230	0,292
PL	100-400	5-30	30-300	10-100	
BL	40	<0,5	3	2	0,02-5

\*: PL: Phytotoxic levels [16]; BL: Background levels [17].

TABLE 6. TOTAL METAL CONTENTS ( $\mu\text{G G}^{-1}$  DRY WT) OF TOMATO FRUITS GROWN IN GREENHOUSE SOILS.

Site	Zn	Cd	Ni	Pb	As
1	15.1	0.167	0.28	2.64	0.15
2	7,4	0,036	0,10	1,18	0,03
3	10,6	0,146	0,08	1,31	0,15
4	10,2	0,103	0,09	1,16	0,09
5	13,1	0,338	0,08	1,32	0,32
6	12,6	0,109	0,17	1,17	0,13
7	11,3	0,178	0,09	1,69	0,20
8	1,3	0,056	0,29	1,46	0,06
Mean	10,20	1,416	0,147	1,491	0,141
St.D.	4,252	0,938	0,090	0,497	0,090
LV	20	0,05	2	3	<0,5

LV: Limit values for edible foods [18].

Mean Zn and Cd concentrations in tomato leaves were exceeded referenced limits [17]. But all heavy metal concentrations were found below the phytotoxic heavy metal limits for culture plants [16]. This results show that plants grown in greenhouse soils were contaminated with the some of heavy metals by antropogenic or natural sources. All heavy metal concentrations with the exception of Cd were found below the permissible heavy metal limits for fresh vegetables [18]. Average Cd concentrations in tomato fruit were exceeded referenced limit (0,05  $\text{mg kg}^{-1}$ ). Although soil Ni

concentration was exceeded the soil pollutant limits, possibly due to low soil mobility factor of Ni, concentration of Ni in tomato fruit was found very low.

**Heavy metal transfer factor (TF) and Target Hazard Quotient (THQ) of Tomato Fruit**

TF and THQ values are presented in Figure 8. The trend of TF value ranges were: Cd>Zn>Pb>Ni>As. The highest average TF was found 3,58 for Cd in tomato fruits. The second high TF was found for Zn in the either tissues of tomato plant. These possibly might be due to higher mobility factor of Cd and Zn in the greenhouse soil (Figure 4) and may be due to soluble metal participations by agricultural practices or antropogenic factors. The mobility of metals from soil to plants is a function of the physical and chemical properties of the soil and of plant species, and is altered by innumerable environmental and antropogenic factors [19].

High Cd accumulation in tomato fruits may be possibly caused by high metal mobility and high enrichment factors of soil Cd. However, although As has the most mobile metal in greenhouse soils, bioconcentration factor was low.

As can be seen mean THQ values were found below the critical value 1 with the exception of Cd metal in sampling site 8 resulted as 1,13 THQ ratio. According to these results there can not be proposed a health risk for Cd metal in short or medium term.

Pearson's correlation matrices between soil total metal concentrations and leaf metal concentrations; Pearson's correlation matrices between DTPA-extractable metal concentrations and fruit metal concentrations and Pearson's correlation matrices between plant metal transfer factor and soil metal mobility factor were presented in Table 7, Table 8 and Table 9, respectively. Correlations between for an element are coss underlined in its column and row, and other correlations matrices of elements are neglected in Tables.

According to results significant correlations between soil total metal concentrations and leaf metal concentrations for an element were detected for Cd, Pb and As; whereas significant correlation coefficient between leaf metal concentrations and soil DTPA-extractable metal concentrations were only determined for As. However, significant correlations were determined between plant metal transfer factor and soil metal mobility factor for all metals except Zn. This results show that there were not a strickly relations between DTPA-extractable metals and plant metal content for all elements studied, and can be assumed that DTPA extraction procedure is inadequate to determine bioavailable metals in greenhouse soils of studied region. Results also show that the importance of soil metal mobility on metal transfers to plants.

TABLE 7. PEARSON'S CORRELATION COEFFICIENT SHOWING RELATIONSHIP BETWEEN SOIL TOTAL METAL CONCENTRATIONS AND TOMATO LEAF METAL CONCENTRATIONS

		Tomato Leaf Metals				
		Zn	Cd	Pb	Ni	As
Soil Total Metals	Zn	-0,028	-0,108	0,133	-0,102	-0,074
	Cd	-0,093	<b>0,205*</b>	-0,090	0,016	0,265**
	Pb	-0,184*	-0,096	<b>0,213**</b>	-0,033	-0,132
	Ni	0,150	-0,072	<b>0,213**</b>	-0,069	-0,068
	As	-0,102	-0,055	-0,116	0,054	<b>0,283**</b>

\*: Significant with P≤ 0.05; \*\*: Significant with P≤ 0.01

TABLE 8. PEARSON'S CORRELATION COEFFICIENT SHOWING RELATIONSHIP BETWEEN SOIL DTPA-EXTRACTABLE METAL CONCENTRATIONS AND TOMATO LEAF METAL CONCENTRATIONS.

		Tomato Leaf Metals				
		Zn	Cd	Pb	Ni	As
Soil DTPA-Ext. metals	Zn	0,090	-0,003	0,009	0,047	-0,173*
	Cd	0,115	-0,057	-0,130	0,040	-0,076
	Pb	0,142	-0,117	-0,054	0,092	-0,255**
	Ni	0,125	-0,141	-0,010	0,066	0,044
	As	0,009	-0,005	-0,089	-0,007	<b>0,227**</b>

\*: Significant with P≤ 0.05; \*\*: Significant with P≤ 0.01

TABLE 9. PEARSON'S CORRELATION COEFFICIENT SHOWING RELATIONSHIP BETWEEN SOIL METAL MOBILITY FACTOR AND PLANT METAL TRANSFER FACTOR OF TOMATO.

		Plant Metal Transfer Factor				
		Zn	Cd	Pb	Ni	As
Soil Metal Mobility Factor	Zn	0,095	-0,028	0,194*	0,112	-0,029
	Cd	-0,015	<b>0,390**</b>	-0,009	-0,100	0,129
	Pb	0,010	-0,072	<b>0,279**</b>	0,153	0,076
	Ni	0,145	-0,020	0,080	<b>0,845**</b>	-0,023
	As	-0,054	0,242**	0,335**	-0,012	<b>0,389**</b>

<sup>1</sup>MF: Soil metal mobility factor; <sup>2</sup>TF: Metal transfer factor of tomato; \*: Significant with P≤ 0.05; \*\*: Significant with P≤ 0.01

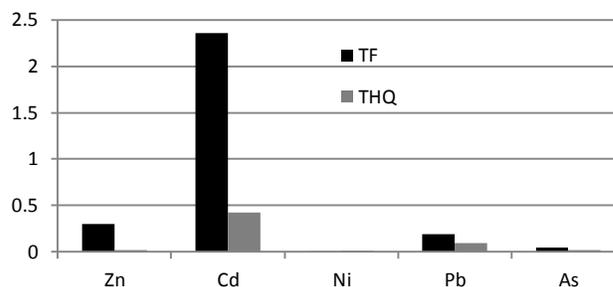


Figure 8. Heavy metal transfer factor and Target Hazard Quotient (THQ) of tomato.

III. CONCLUSIONS

The concentration of heavy metals with the exception of Ni in soils of Antalya greenhouses were generally below the limits referenced by the 86/278/EEC directive to agricultural soils with pH >7. Ni concentrations in all soil sample were higher than limit values. Soil metal speciation showed that the greatest percentage of all metals was present in the residual form, and the mobility of metals declined in the following order: As>Cd>Zn>Pb>Ni. Thus, although Ni was the most important threatening metal as total concentration, its mobility was found very low.

DTPA-extractable metal levels were not coincided with the tendency of total metal levels in soil and there were not a strickly relations between total and DTPA-extractable metals for all elements studied.

Single factor and composite pollution coefficient values of all metals with the exception of Ni were not exceeded critical limit. However, due to high total concentration of Ni in greenhouse soils, composite pollution index was determined in heavy pollution risk group. Anthropogenic and enrichment factor indexes of greenhouse soils indicate that both two

parameter showed similar trends and 1 to 5 fold metal enrichment by anthropogenic inputs compared to uncontaminated soil. Mean Enrichment factor Zn was below the moderate level and approximate to depletion level. Potential ecological risk indexes of soil metals except Ni were found below the threshold value that indicate these metals have a low risk to surrounding environment.

Mean Zn and Cd concentrations in tomato leaves were exceeded referenced limits [20]. But all heavy metal concentrations were found below the phytotoxic heavy metal limits for culture plants. Although soil Ni concentration was exceeded the pollutant limits, possibly due to low soil mobility factor of Ni, concentration of Ni in tomato fruit was found very low. High Cd accumulation in tomato fruits may be possibly caused by high metal mobility and high enrichment factors of soil Cd. However, according to target hazard quotient value of tomato fruit, it was found that THQ of tomato fruits is below the critical value and thus it can be presumable no health risk for Cd metal in short or medium terms.

As it is seen, the comparison results of risk values of heavy metals based on different methods show that there are several disagreements. Most of these paradoxes in evaluation are mainly depend on the total content of heavy metals as a criterion for determining their potential effect on the environments. Whereas in a comprehensive manner, in addition to total concentrations, environmental risk evaluation methods and soil speciation studies will provide useful information for assessing metal bioavailability or toxicity. Results also show that the importance of soil metal mobility on metal transfers to plant, and determination of efficient extraction methods to assuming bioavailable metals.

#### 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-1110711).

#### REFERENCES

- [1] Yu Rui-lian, Yuan Xing, Zhao Yuan-hui, Hu Gong-ren, Tu. Xiang-lin. 2008. Heavy metal pollution in intertidal sediments from Quanzhou Bay, China [J]. *Journal of Environmental Sciences*, 20(6): 664–669. [http://dx.doi.org/10.1016/S1001-0742\(08\)62110-5](http://dx.doi.org/10.1016/S1001-0742(08)62110-5)
- [2] Chen, B., Shan, X. Q., Qian, J. 1996. Bioavailability index for quantitative evaluation of plant availability of extractable soil trace elements. *Plant and soil*, 186(2), 275-283. <http://dx.doi.org/10.1007/BF02415523>
- [3] Olaniran, A. O., Balgobind, A., Pillay, B. 2013. Bioavailability of heavy metals in soil: impact on microbial biodegradation of organic compounds and possible improvement strategies. *International journal of molecular sciences*, 14(5), 10197-10228. <http://dx.doi.org/10.3390/ijms140510197>
- [4] Tessier, A., Campbell, P.G.C., Bison, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844-851. <http://dx.doi.org/10.1021/ac50043a017>
- [5] ISO 11466 International Standard, 1995. Soil quality-extraction of trace elements soluble in aqua regia. 03-01.
- [6] Lindsay, W.L., Norwell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil sci. Soc. Am. J.*, 42, 421-428. <http://dx.doi.org/10.2136/sssaj1978.03615995004200030009x>

- [7] Yusuf, K.A., 2007. Sequential extraction of lead, copper, cadmium and zinc in soils near ojota waste site. *Journal of Agronomy* 6(2):331-337. <http://dx.doi.org/10.3923/ja.2007.331.337>
- [8] Cheng, J.L., Shi, Z., Zhu, Y.W., 2007. Assessment and mapping of environmental quality in agricultural soils of Zhejiang province, China. *Journal of Environmental Sciences*, 19:50-54. <http://dx.doi.org/10.1007/s11767-005-0098-6>
- [9] Adamu, C., I., Nganje, T.N., 2010. Heavy metal contamination of surface soil in relationship to land use patterns: A case study of Benue state, Nigeria. *Materials Science and Applications*, 1:127-134. <http://dx.doi.org/10.4236/msa.2010.13021>
- [10] Reimann, C., de Caritat, P., 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: Regional geochemical surveys versus enrichment factors. *The science of the total environment*, 337:91-107. <http://dx.doi.org/10.1016/j.scitotenv.2004.06.011>
- [11] Hakanson, L., 1980. An ecological risk index for aquatic pollution control: A sedimentological approach. *Water Research*, 14: 975-1001. [http://dx.doi.org/10.1016/0043-1354\(80\)90143-8](http://dx.doi.org/10.1016/0043-1354(80)90143-8)
- [12] United States, Environmental Pollution Agency (USEPA), 2007. Integrated risk information system. Available from: (<http://cfpub.epa.gov/ncea/iris/index.cfm?fuseaction=iris.showSubstanceList>).
- [13] Gil, C., Boluda, R., Ramos, J. 2004. Determination and evaluation of cadmium, lead, and nickel in greenhouse soils of Almeria (Spain). *Chemosphere*, 55, 1027-1034. <http://dx.doi.org/10.1016/j.chemosphere.2004.01.013>
- [14] C.E.C. (Council of the European Communities) 1986. Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when SS is used in agriculture (86/278/CEE). *Official Journal of the European Communities*, L181, 6-12.
- [15] Soon, Y.K., Abboud, S., 1990. Trace elements in agricultural soils of North-western Alberta. *Can.J. Soil Sci.* 70, 277-288. <http://dx.doi.org/10.4141/cjss90-029>
- [16] Davis, R.D., Carlton-Smith, C.H., 1980. Crops as indicators of the significance of contamination of soils by heavy metals. *Water Research Centre, Technical Report TR140*, WRd Medmenham, Marlow.
- [17] Kabata-Pendias, A., Pendias, H. 2000. Trace elements in soils and plants. CRC Press, Boca Raton, FL. <http://dx.doi.org/10.1201/9781420039900>
- [18] WHO/FAO, 2007. Joint FAO/WHO food standard programme codex alimentarius commission 13<sup>th</sup> session. Report of the thirty-eight session of the codex committee on food hygiene, Houston, USA.
- [19] Zurera, G., Estrada, B., Rincon, F., Pozo, R. 1987. Lead and cadmium contamination levels in edible vegetables. *Bull. Environ. Cont. Toxicol.*, 38:805-812. <http://dx.doi.org/10.1007/BF01616705>