Risk Assessment of Metal Pollution in the Greenhouse Soils and Crops

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***Abstract*— A case study was conducted on greenhouse soils and plants in intensive greenhouse areas of Antalya, one of the major greenhouse production regions of Turkey to assess the heavy metal pollution, and to understand the ecological risk, transport processes of heavy metals and the relations with the soil characteristics.**

All total heavy metal concentrations except Ni in the greenhouse soils were generally below the referenced limits. Anthropogenic and enrichment factor indexes of greenhouse soils showed that there were an 1 to 18 fold metal enrichments by anthropogenic inputs compared to uncontaminated soil in the same geographic region. Through to greenhouse soils of Antalya territory, no pollution was determined with regard to evaluations of composite pollution and potential ecological risk indexes. Soil metal speciation studies showed that the residual form of all metals was the greatest percentage of metal fractions, and the metal mobility was 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. Significant correlations were determined between soil metal mobility factor and plant metal transfer factor of all metals with the exception of Zn

In reference to FAO/WHO limitations, only As and Cd concentrations were excessed limits in greenhouse tomato fruits. Heavy metal pollution in tomato fruits in several greenhouses of Serik, Kumluca, Alanya, Gazipaşa, Finike and Kaş regions were determined with regard to evaluation of hazard indexes of metals. Although total Ni concentration of greenhouse soil was exceeded the reference pollutant limits, Ni had the low mobility factor and lower concentration of Ni in tomato fruit was recorded. According to general pollution evaluation results, no health risk for heavy metals is expected in short or medium terms.

***Keywords*— Greenhouse soils; Metal pollution; Risk Assessment.**

I. INTRODUCTION

Mediterranean region has an important agricultural potential especially greenhouse cultivation with its special climate and geographical characteristics in Turkey. Greenhouse cultivation has resulted in increasing usage of mineral fertilizers and in recent years, many research findings have indicated that an extreme fertilizer and pesticide consumptions in the greenhouse soils of Mediterranean region. Crop plants which are cultivated in contaminated soils can accumulate contaminants and transfer them to animals and human beings via food chain which are eventually result in various health problems [1].

Heavy metals are of considerable concern due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviours [2]. 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 [3].

Most of the 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 [4]. 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 [5].

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 [3]. DTPA (diethylenetriaminepentaacetic acid) extraction provides a fairly rapid procedure for determining trace elements in soils. This procedure has been used to assess metal solubility 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 [6].

Today many environmental pollution risks indexes developed for water and sediments can be used for soils, organic matter and other environmental materials. Although several pollutant limits developed for soils depending on total concentrations, these criteria were frequently unsatisfied with a comprehensive environmental risk prediction. Although greenhouse areas had great impact on environment due to intensive use of agrochemicals for all season, little attention has been paid to metal accumulation and health risks in greenhouse plants and

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heavy metal speciation in greenhouse soils with respect to comprehensive and integrated environmental evaluation.

The objectives of this study were to provide information on the metal contamination in greenhouse soil and plants, metal speciation and metal bioavailability in the greenhouse soils, and to compare the DTPA extraction procedure to sequential extraction for the availability and removal of metals by plants from soil, and to evaluate several metal pollution risks in greenhouse soils.

II. Material And Methods

A. Geography of study region

The experiment was conducted on the major greenhouse vegetable growing areas located at Antalya, Turkey. The study region is intensively cultivated and is not industrialized area. The geological materials of greenhouse area are mainly calcareous nature, mostly consist of ‘Red Mediterranean soil’, and nearby to Mediterranean sea with average 57,8 m altitude. The land is influenced by a Mediterranean climate with a high average annual rainfall (1081,5 mm/year), the annual average temperature being around 18,7 °C, 63,8 % average humidity and average 164 sunny days per year [7]. In the greenhouse, the annual temperature is higher inside than outside, and most of greenhouses are watered by sprinklers with ground waters source of the same point. All greenhouses have passive ventilation to control temperature and humidity inside. A great number of greenhouse soils are artificially built up with a different layer of sand, organic matter and other soil source for conditioning soil texture (Figure. 1).

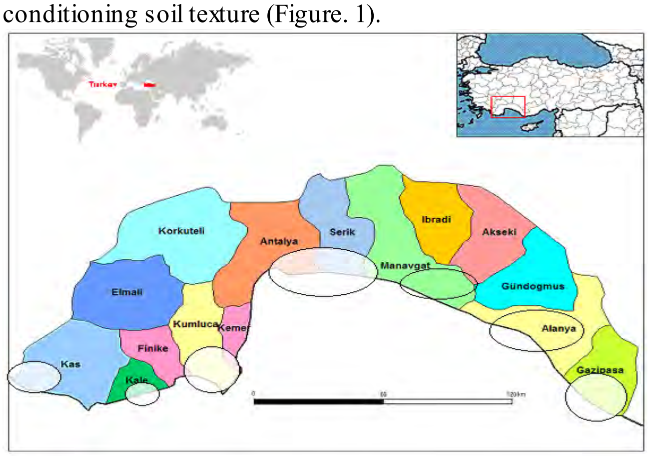

Fig. 1: Map of greenhouse regions in Antalya, Turkey

B. Material Sampling and Analysis

The experiment was carried out at greenhouses of Antalya region and soil and plant samples were taken from 10 sub-regions and 148 sampling points. Greenhouse soil samples were taken at a depth of 0-20 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 NN_4AoC extractions; $CaCO_3$ content was determined by the calcimeter; organic carbon was measured by wet oxidation; and texture was determined by Bouyoucos hydrometer method.

Sequental extraction method [8] 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 NH_2OH/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 HNO_3+5 ml 30 % H_2O_2 (pH 2) for 3 h at 85 °C; metals associated with organic matter.

F5. HNO_3-HCl digestion; residual fraction.

Bioavailable fractions (DTPA-extractable) of metals were extracted from soil with diethylenetriaminepentaacetic acid-$CaCl_2$-triethanolamine adjusted to pH 7,3 [9] 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 method of international standard [10].

For the plant pollution evaluation in greenhouses, tomato fruit samples were collected at the full ripening stage from each greenhouse. The samples were washed throughly with tap water and rinsed with deionized water. Fruit samples were dried at 70 ºC in a oven, ground in an agate mortar and then digested in aqua regia (1:3HNO3/HCl). After cooling to the room temperature, the mineralized residue was diluted with deionized water.

Heavy metal (Zn, Cu, Cd, Pb, Ni, As) concentrations of greenhouse soil and greenhouse plant samples were analysed using ICP-MS under optimised measurement conditions, and all values were adjusted to oven dried (12 h at 105 °C) material.

C. Evaluation Methods of Contamination

Several environmental pollution indexes for soil samples; ‘Metal Mobility Factor’ [11], ‘Anthropogenic Factor [12], ‘Enrichment Factor’ [13], ‘Single-Factor Pollution Index’ and ‘Composite Pollution Indexes’ [14], ‘Single Factor Ecological Risk’ and ‘Potential Ecological Risk’ Indexes’ [15], and as for plant samples ‘Heavy Metal Transfer Factor’ [16], ‘Target Hazard Quotient’ and ‘Hazard Index of Food’ [17] were used for comprehensive assessment of pollution and health risks.

D. Statistical Analysis:

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. Soil Analytical Characteristics

Certain analytical characteristics of greenhouse soils are shown in Table 1. These greenhouse soils have generally high lime content, slightly alkaline reaction, low EC values, poor organic carbon, moderate CEC and ranged sandy-loam to loamy textures. There were detected significant differences in the sample sites with regard to lime, pH, EC, organic carbon and CEC values. Manavgat, Kale and Kaş regions generally have the higher lime, pH, EC values. İt is stated stated that unless any other natural reason, intensive greenhouse agriculture is the main cause of soil contamination by heavy metals and that theoretically heavy metal availability will be expected low due to slightly alkaline reaction and calcareous nature of the soil [18].

TABLE I. THE ANALYTICAL CHARACTERISTICS OF GREENHOUSE SOILS IN ANTALYA REGION

Sites	Sample number	$CaCO_3$, %	pH	EC, micS cm^{-1}	Org. C., g^{-kg}	CEC, $meq^{-100\ g}$	Clay, %	Silt, %	Sand, %
1. Center	29	21,41	7,67	1267	2,97	22,42	9,59	37,21	53,20
2. Aksu	24	17,57	7,58	1592	2,21	18,32	8,69	34,98	56,32
3. Serik	13	16,21	7,61	1103	2,02	19,85	9,20	38,62	52,18
4. Kumluca	28	5,53	7,63	1333	2,66	26,98	9,91	37,80	52,30
5. Manavgat	4	29,03	7,60	1253	1,92	20,88	10,82	42,34	46,84
6. Alanya	9	1,64	7,33	2055	3,38	17,70	10,47	32,85	56,68
7. Gazipaşa	12	3,68	7,46	1124	3,23	24,75	10,08	40,62	49,30
8. Finike	7	11,73	7,62	1714	2,27	27,71	10,52	37,66	51,82
9. Kale	12	28,34	7,65	2066	2,24	16,17	8,78	29,23	61,99
10. Kaş	10	32,27	7,62	1922	2,58	21,50	8,84	38,03	53,13
Mean		15,64	7,60	1484	2,60	21,93	9,52	36,66	53,81
F degree and significancy		17,641 **	1,952 *	3,115 **	3,097 **	5,421 **	1,242 öd	1,739 öd	1,638 öd

*: P<0,05, **: P<0,01, ns: no significancy

The total and DTPA-extractable metal contents of the greenhouse soils and their pollutant limits were given in Table 2.

TABLE II. TOTAL (T) AND DTPA-EXTRACTABLE (D) METAL CONTENTS (μG G-1 DRY WT) OF THE GREENHOUSE SOILS AND THEIR POLLUTANT LIMITS.

Sites	Sample number	TZn	DZn	TCu	DCu	TCd	DCd	TPb	DPb	TNi	DNi	TAs	DAs
1. Center	29	125,0	4,4	38,2	4,7	0,535	0,018	23,3	0,74	99,5	0,69	12,5	0,75
2. Aksu	24	76,4	5,5	34,3	5,8	0,434	0,030	17,0	2,50	72,7	0,59	21,5	0,96
3. Serik	13	83,3	3,5	37,6	5,6	0,473	0,027	18,0	0,62	101,6	0,41	7,7	0,12
4. Kumluca	28	93,3	5,5	53,1	8,2	0,184	0,018	24,0	2,56	112,1	0,66	4,5	0,10
5. Manavgat	4	91,9	8,7	21,1	4,5	0,302	0,025	18,9	4,36	95,6	0,86	10,8	0,23
6. Alanya	9	72,3	9,4	66,1	10,2	0,192	0,029	21,1	6,41	36,9	0,55	5,8	0,19
7. Gazipaşa	12	104,2	8,4	40,6	8,3	0,214	0,022	36,4	7,91	35,8	0,83	11,3	0,22
8. Finike	7	94,3	9,5	57,0	8,1	0,176	0,021	16,7	4,96	106,2	0,87	4,0	0,24
9. Kale	12	64,1	18,3	27,1	4,9	0,329	0,036	19,6	4,13	9,0	0,42	11,2	0,10
10. Kaş	10	86,7	14,4	33,8	6,3	0,274	0,020	35,7	4,11	161,2	0,47	5,5	0,09
Mean		92,7	7,5	41,5	6,6	0,342	0,024	23,0	3,09	85,8	0,62	10,5	0,39
Limits[1]		300		140		3		300		75		20	
F degree and significancy		6,490 **	14,929 **	5,717 **	4,147 **	3,195 **	2,165 ns	5,091 **	15,201 **	10,163 **	4,386 **	5,037 **	6,442 **

[1]: CEC (1986) [19]; *: P<0,05, **: P<0,01, ns: no significancy

Differences in total heavy metal concentrations of greenhouse regions soils were found significantly important. Total heavy metal concentrations were ranged (µg g^{-1}) from 64.1 to 125 for Zn with a mean of 92.7; 21.1 to66.1 for Cu with a mean of 41.5; 0.535 to 0.176 for Cd with a mean of 0.342; 16.7 to 36,4 for Pb with a mean of 23; 9 to 112.1 for Ni with a mean of 85.8 and 4 to 21.5 for As with a mean of 10.5. All Average total metal contents except Ni were below the limits of European Union (86/278/EEC) directive to agricultural soils with pH>7 [19]. Ni concentrations of Center, Serik, Kumluca, Manavgat and Finike regions were higher than limit values. Also total As content of Aksu was detected above the limit. According to these data, the order for the average content of total metals in analysed soil samples is Zn>Ni> Cu>Pb>As>Cd.

Differences of DTPA-extractable all heavy metal concentrations with the exception of Cd of greenhouse regions soils were found significantly important. DTPA-extractable metals (µg g^{-1}) representative of available soil metals taken by plants was ranged from 3.5 to 18.3 for Zn with a mean of 7.5; 4.5 to 10.2 for Cu with a mean of 6.6; 0.018 to 0.036 for Cd with a mean of 0.024; 0.62 to 7.91 for Pb with a mean of 3.09; and 0.41 to0.87 for Ni with a mean of 0.62 and 0.09 to 0.96 for As with a mean of 0.39. According to these data, the order for the average content of DTPA-extractable metals in analysed samples is Zn>Cu>

Pb>Ni>As>Cd. Although total Ni concentrations in many greenhouse soils were high and above the critical limit, DTPA-extractable concentrations were recorded lower than Cu and Pb metals.Clay, lime and pH are effective on the soil metal availability; due to the high binding capacity of clay, slight alkaline and calcareous soil usually has low metal mobility and bioavailability [20]. It has been reported that greenhouse cultivation reduces the soil pH value and increases the availability of soil metal over time and increases the accumulation of heavy metals, especially Cd, Zn and Cu, in greenhouse soils [21].

Pearson's correlation matrices between total and DTPA-exractable 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 3. 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, Cu and As. DTPA-extractable metal levels for all elements were not coincided with the tendency of their total metal levels in the soil. These results show that there were not a strictly relations between total and DTPA-extractable metals for all elements studied. This possibly may cause of metal mobility differences or/and soil conditions affecting extraction process.

B. *Soil Metal Speciation*

Heavy metal concentrations in soil fractions were given in Figure 3. Irrespective of greenhouse regions, the distribution of metals in greenhouse soil samples generally followed the order below for the metals studied.

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

TABLE III. PEARSON'S CORRELATION COFFICIENT SHOWING RELATIONSHIP BETWEEN SOIL TOTAL METAL CONTENTS AND DTPA-EXTRACTABLE METALS[1].

		Soil Total Metals					
		Zn	Cu	Cd	Pb	Ni	As
Soil DTPA-Ext. metals	Zn	**0,175***	-0,108	-0,136	-0,105	-0,140	-0,147
	Cu	-0,064	**0,453****	-0,205	-0,002	0,046	-0,176*
	Cd	0,010	-0,048	-0,124	0,003	-0,073	0,165*
	Pb	-0,198*	0,021	-0,296**	0,119	-0,177*	-0,138
	Ni	0,169*	0,145	-0,050	-0,030	-0,019	0,010
	As	0,121	-0,042	0,095	-0,114	0,034	**0,256****

[1]: Total sample number is 148. *: Significant with P≤ 0.05; **: Significant with P≤ 0.01

The study of the distribution of metals showed that the greatest percentage of all metals was present in the residual fraction (F5). 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 [22]. F1 and F2 fractions of Zn and As metals were higher than that of other metals. This property gives these metals a high mobility. Only the soluble, exchangeable and chelateable metal fractions in the soil have been reported to produce labile fractions that plants can benefit from [23]. 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. It has been reported that the potential bioavailability of heavy metals is strictly controlled by the chemical forms of the metals, that the metal uptake of the plant is typically correlated with the extractable form relative to the total concentration of metal [24].

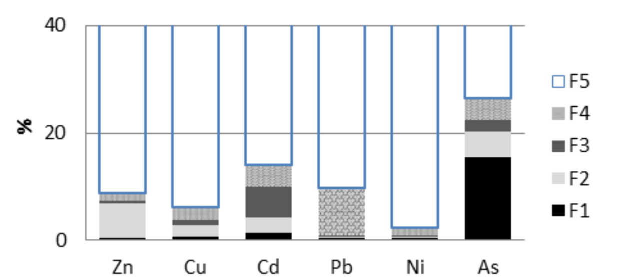

Fig. 2. Concentrations of Zn, Cu, Cd, Ni, Pb and As in soil fractions

C. *Mobility Factor of Metals*

Mobility Factor (MF) values of metals were specially higher for As, Cd and Zn. The high MF values of metals have been interpreted as symptoms of relatively high lability and biological availability of heavy metals in soils [25]. The results of the present study suggest that the mobility of the metals declines by the following order: As>Cd>Zn>Ni>Cu>Pb (Figure 4).

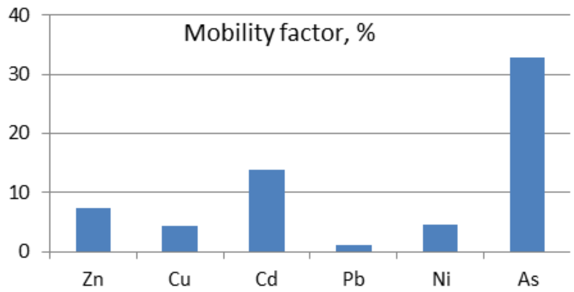

Fig. 3. Average metal mobility of greenhouse soils

Although total Ni concentration of soil was exceeded the pollutant limits (Table 2), soil mobility factor of Ni was recorded low. As and Cd elements have a higher mobility factor. It has been reported that the main pollutants in greenhouse soils are Cd, Pb, Cu and Zn, which are the most mobile elements in greenhouse soils according to the proportional values of the available fractions of these metals [26]. The fact that the Cd metal is the most easily soluble metal in the elements makes the Cd element potentially bioavailable and poses a threat to the transfer of Cd element into the food chain [22].

D. Contamination Evaluation of heavy metals

E. Anthropogenic and Enrichment Factor Indexes of Soil

Anthropogenic factor (AF) and enrichment factor (EF) indexes of greenhouse soils were given in Figure 5. AF values for the heavy metals determined in the soil samples with respect to the uncontaminated soil in the same area were found generally high. Values indicate that there were 1 to 18 fold enrichments for various metals by anthropogenic inputs compared to uncontaminated soil. Increasing order of heavy metal EF value was followed by Pb<Cu<Zn<As<Cd<Ni. ER values showed similar trends with AF values. Mean EF of Pb metal was recorded below the moderate level. It has been reported that there is a continuous enrichment of heavy metals and especially increase in the metal availability in the greenhouse soils due to anthropogenic effects [26] and the most prominent results in heavy metal contamination are seen in the enrichment of Zn, Pb, Cd and Hg [27].

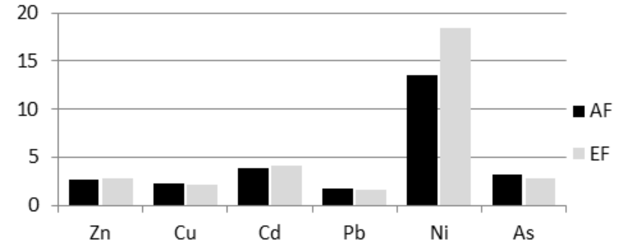

Fig. 4. Anthropogenic factor and Enrichment factor indexes of the greenhouse soils

F. Single-factor composite pollution indexes and single ecological and potential ecological risk factor indexes

Single-factor (Pi) and composite pollution (PN) indexes, single ecological risk (Er) and potential ecological risk (RI) indexes of heavy metals in the greenhouse soils are summarized in Figure 6. Figure 6 summarizes all contamination coefficients (Pi and PN) of metals with the exception of Ni were not exceeded critical value 1. Contamination coefficient of Ni was exceeded critical value in all regions. Although Pi coefficients of all other metals were low, due to higher Pi coefficient value of Ni, PN index of greenhouse soils in regional size was determined in heavy pollution risk group.

The average Er values of heavy metals in the greenhouse soils were ranked as Ni>As>Cd>Cu> Pb>Zn. The average risk value for all heavy metals was found below the 40 that indicates all metals posed low risk to surrounding ecosystem. Average RI value that calculated as the sum of all the risk factors and represents overall potential ecological risk of observed for all metals in the greenhouse soils was found 17,26 and below the ecological risk level.

Figure 7 summarizes RI values according to greenhouse regions. There were important differences in RI indexes among the regions. RI indexes of all greenhouse region soils except Kaş region were below the critical value 40. Thus greenhouse soils of Kaş region have moderate potential ecological risks in the short term. It has been reported that the ecological risk indices in the metals follow Cd> Pb> Cu> Cr> Zn [28] and the Cd element is the key factor causing the risk, while other metals carry little ecological risk [29].

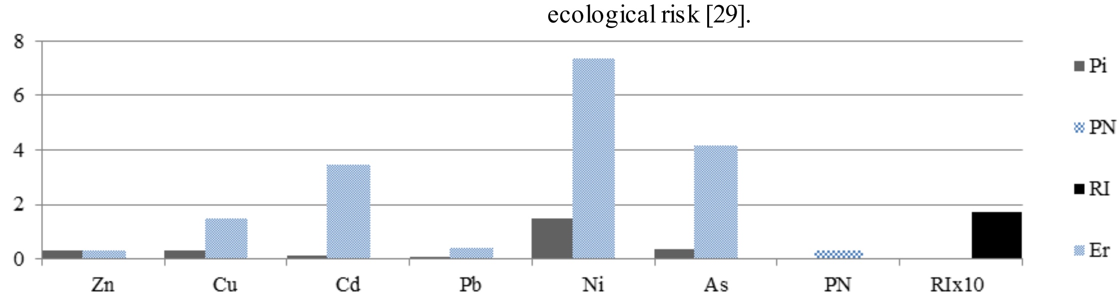

Fig. 5. Single factor index of each metal, composite pollution index, single ecological and potential ecological risk indexes of metals in greenhouse soils

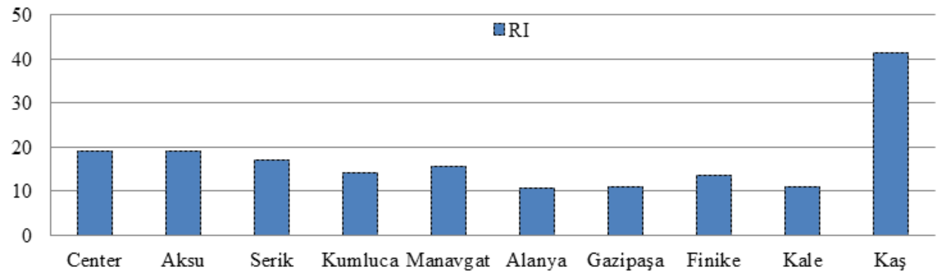

Fig. 6. Potential ecological risk indexes of metals in greenhouse regions

G. Plant Properties

1. Plant heavy metal content

Heavy metal concentrations of the leaves and fruits of greenhouse tomato plant were presented in Table 4 and Table 5, respectively. Lead, Ni and As concentrations of tomato leaves, and Zn, Cd, Pb and Ni concentrations of tomato fruits were varied depending on the regions. Mean Zn and Cd concentrations in tomato leaves were excess referenced background level limits [30]. Zinc concentration of tomato leaves in all greenhouse regions and Cd concentration in most of greenhouse regions were excessed plant background levels. But all heavy metal concentrations were found below the phytotoxic heavy metal limits of culture plants proposed by [31]. Tomato leaves contained higher concentrations of metals than fruits. The highest concentrations of Cd in polluted plants were always reported for roots and leaves [30]. Average heavy metal concentrations except Cu and Cd of tomato fruits were found below the permissible heavy metal limits for fresh vegetables [32]. Average Cd concentrations of tomato fruit in all greenhouse regions were excess reference limit (0,05 mg kg-1). In the study of heavy metal contamination in greenhouse vegetable production areas; It has been reported that metal concentrations of plants followed Zn> Cu> Cd> Pb order [21].

TABLE IV. TOTAL METAL CONTENTS (µG G-1 DRY WT) OF TOMATO LEAVES GROWN IN GREENHOUSE SOILS.

Site	Zn	Cu	Cd	Pb	Ni	As
1. Centre	107	38.9	0.765	3.05	0.861	0.470
2. Aksu	133	64.4	0.724	2.36	0.765	0.431
3. Serik	145	13.8	3.906	1.82	1.037	0.383
4. Kumluca	143	164.2	0.988	2.67	0.654	0.189
5. Manavgat	86	17.5	0.627	3.40	1.988	0.235
6. Alanya	183	83.2	0.280	2.61	0.970	0.198
7. Gazipasa	161	115.8	0.242	2.28	0.772	0.189
8. Finike	128	141.9	0.770	2.06	0.835	0.194
9. Kale	111	43.9	1.986	1.80	0.952	0.195
10. Kas	175	230.7	1.367	4.40	0.762	0.199
Mean	136	91,1	1,141	2,62	0,851	0,303
F degree and significancy	0,710 öd	1,675 öd	1,738 öd	4,492 **	11,886 **	4,503 **
Phytotoxic levels [1]	100-400	Ncs	5-30	30-300	10-100	1-20
Background levels [2]	40	35	<0,5	3	2	0,02-5

[1]: [31]; [2]: [30]; Ncs: No criteria set

This results show that plants cultivated in greenhouse soils were contaminated with the some of Cu and Cd by anthropogenic or natural sources. Due to large amount of consumption, and most of the production obtained by greenhouse culture, special attention should be given to Cd contents of tomato fruits, which have a major use in the kitchens. Because Cd is readily available to plants from both air and soil sources, its concentration rapidly increases in plants grown in polluted areas. Cadmium behaviour in soil and its accumulation by crops is complicated. Numerous factors (e.g. soil pH, organic matter content, salinity, macro and micronutrient fertilizers, crops species and cultivar, and tillage) influence the bioavailability and uptake of Cd by crops [33]. Both industrial and agronomic practices might create a significant Cd supply to plants. Especially that tomato greenhouses are highly fertilized with phosphates, and Cu-containing fungicides and bactericides are used extensively for disease control on staked tomatoes. Plants growing on Cu-polluted sites tend to accumulate increased amounts of this metal,especially near industrial areas, and in soils treated with Cu-bearing herbicides [34]. Phosphate fertilisers are identified as an important source of Cd in the soil. Cadmium is a natural contaminant of phosphate rocks and its final content in the fertiliser depends both on the type of raw material, as well as on the manufacturing method [35]. Thus fertilization increases the risk of Cd transfer to the food chain [33].

Although total Ni concentration of greenhouse soil was exceeded the pollutant limits (Table 2), Ni was largely (97,7 %) associated with residual phase (Figure 3) and metal mobility factor of Ni was recorded low (Figure 4), and also concentration of Ni in tomato fruit was found very low.

TABLE V. TOTAL METAL CONTENTS (µG G-1 DRY WT) OF TOMATO FRUITS GROWN IN GREENHOUSE SOILS.

Site	Zn	Cu	Cd	Pb	Ni	As
1. Centre	11.2	10.4	1.33	1.37	0.14	0.14
2. Aksu	12.9	10.8	1.20	1.65	0.16	0.11
3. Serik	14.6	13.8	1.24	1.51	0.23	0.17
4. Kumluca	12.7	13.4	1.44	1.43	0.18	0.09
5. Manavgat	8.6	5.4	0.48	0.97	0.22	0.09
6. Alanya	10.7	14.9	0.95	1.51	0.20	0.12
7. Gazipasa	12.0	14.3	1.04	2.21	0.23	0.10
8. Finike	12.1	21.6	1.65	4.42	0.23	0.11
9. Kale	10.1	9.0	1.98	1.18	0.18	0.15
10. Kas	12.9	10.5	1.96	3.11	0.33	0.12
Mean	12.1	12.2	1.36	1.75	0.19	0.12
F degree and significancy	2,122 *	1,337 öd	2,447 *	2,476 *	2,481 *	1,177 öd
Limit values for edible foods [1]	20	10	0,05	2	3	<0,5

[1]: [32]

2. Heavy metal transfer factor and Target Hazard Quotient of Tomato Fruit

Heavy metal transfer factor (TF) and target hazard quotient (THQ) values were presented in Figure 8. TF values for tomato leaf and tomato fruit were ranged as Cd>Cu>Zn>Pb>Ni>As and Cd>Cu>Ni>Pb>Zn>As, respectively. The highest average TF was found 3,72 for Cd in tomato fruits. TF values were recorded higher in the leaves than tomato fruit. High TF values of Cd metal might be due to higher mobility factor and relatively high enrichment factors of soil Cd in the greenhouse soil (Figure 4) and may be due to soluble metal participations by agricultural practices or anthropogenic factors. It has been reported that the high transfer factor of Cd and Pb metals originate from the high mobility of these metals [36]. 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 anthropogenic factors [37]. However, although As has the most metal mobility in greenhouse soils, its TF value was evaluated relatively lower.

Mean THQ values for all metals were found below the critical value 1. According to these results it could not be expected a health risk for heavy metals in the short or medium terms. THQ values were calculated based on data that an average adult consumes 80 g of water per day [38]. Average HI value of tomato fruit represent cumulative risk for all heavy metals in the Antalya greenhouses were below the critical value 1, and accepted none to low level of risk (Figure 8). However, in the regional size HI values were showed statistically differences. HI values of tomato fruit cultivated in Gazipaşa, Finike and Kaş regions were excess reference HI limits, are causing concern about the likelihood health hazard effect (Figure 9). In the study of heavy metal contamination in greenhouse vegetable production areas; The THQ values of metals were found to be below the critical limit value 1 in all sera products, but the THQ value of Cd element was found to be higher than other metals [21].

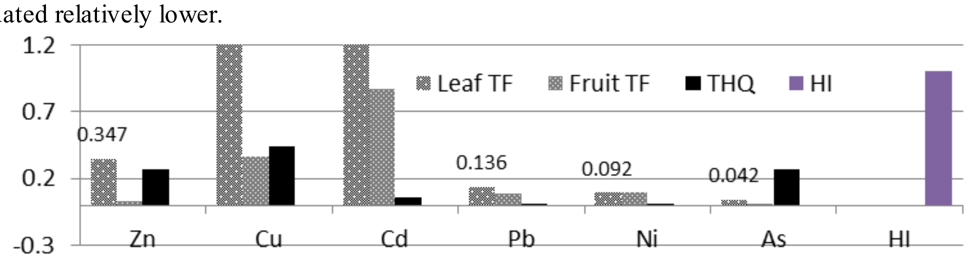

Fig. 7. Heavy metal transfer factor and Target Hazard Quotient (THQ) and HI of tomato (Copper TF values and Cd TF values in tomato leaves were recorded as 3.05 and 3.72, respectively).

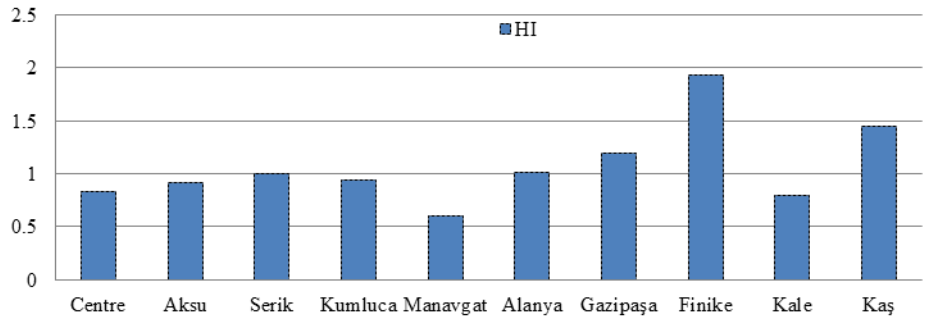

Fig. 8. Hazard index values of tomato fruit cultivated in the greenhouse regions

3. Soil-Plant metal correlations

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 6, Table 7 and Table 8, respectively. Correlations between for an element are crossing bold in its column and row, and other correlations matrices of elements are neglected in these Tables.

According to these results, significant correlations between soil total metal concentrations and leaf metal concentrations for an element were recorded for Cd, Pb and As; whereas significant correlation coefficient between soil DTPA-extractable metal concentrations and leaf metal concentrations were only recorded for Cu. However, significant correlations were recorded between soil metal mobility factor and plant metal transfer factor of all metals with the exception of Zn. It has been reported that total heavy metal concentrations can't accurately determine bioavailability and/or toxicity in heavy metal measurements on the soil [39].This results show that there were not a strictly relations between DTPA-extractable metals and plant metal content of all elements studied, and can be assumed that DTPA extraction procedure cannot be accepted solely an adequate method to determine bioavailable metals in greenhouse soils of studied region. Results also show that the importance of soil metal mobility and metal speciation studies on metal bioavailability and metal transfers to plants.

TABLE VI. PEARSON'S CORRELATION COFFICIENT SHOWING RELATIONSHIP BETWEEN SOIL TOTAL METAL CONCENTRATIONS AND TOMATO LEAF[1] METAL CONCENTRATIONS.

		Tomato Leaf Metals					
		Zn	Cu	Cd	Pb	Ni	As
Soil Total Metals	Zn	-0.028	0.039	-0.108	0.133	-0.102	-0.074
	Cu	-0.081	0.022	-0.126	-0.045	-0.112	-0.041
	Cd	-0.093	-0.136	**0.205***	-0.090	0.016	0.265**
	Pb	-0.184*	0.060	-0.096	**0.213****	-0.033	-0.132
	Ni	0.150	0.175*	-0.072	0.213**	-0.069	-0.068
	As	-0.102	-0.069	-0.055	-0.116	0.054	**0.283****

[1]: Total sample number is 148. *: Significant with P≤ 0.05; **: Significant with P≤ 0.01

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

		Tomato Fruit Metals					
		Zn	Cu	Cd	Pb	Ni	As
Soil DTPA-Ext. metals	Zn	0.090	0.063	0.100	-0.003	0.009	0.047
	Cu	0.162*	**0.182***	0.145	-0.064	-0.015	-0.099
	Cd	0.115	-0.104	-0.007	-0.057	-0.130	0.040
	Pb	0.142	0.179*	0.196*	-0.117	-0.054	0.092
	Ni	0.125	-0.012	0.204*	-0.141	-0.010	0.066
	As	0.009	-0.075	-0.127	-0.005	-0.089	-0.007

[1]: Total sample number is 148. *: Significant with P≤ 0.05; **: Significant with P≤ 0.01

TABLE VIII. PEARSON'S CORRELATION COFFICIENT SHOWING RELATIONSHIP BETWEEN SOIL METAL MOBILITY FACTOR AND PLANT METAL TRANSFER FACTOR OF TOMATO LEAF.

		Plant Metal Transfer Factor					
		Zn	Cu	Cd	Pb	Ni	As
Soil Metal Mobility Factor	Zn	0,095	0,023	-0,028	0,194*	0,112	-0,029
	Cu	0,097	**0,520****	-0,083	-0,023	-0,089	0,089
	Cd	-0,015	0,035	**0,390****	-0,009	-0,100	0,129
	Pb	0,010	-0,121	-0,072	**0,279****	0,153	0,076
	Ni	0,145	-0,032	-0,020	0,080	**0,845****	-0,023
	As	-0,054	-0,114	0,242**	0,335**	-0,012	**0,389****

[1]: Total sample number is 148. *: Significant with P≤ 0.05; **: Significant with P≤ 0.01

IV. CONCLUSION

According to limits referenced by the European Union 86/278/EEC directive to agricultural soils with pH >7, concentrations of heavy metals except Ni in the soils of Antalya greenhouses were recorded generally below. Ni concentrations in all soil samples examined were higher than limit values. However, soil metal speciation studies showed that the greatest percentage of all metals was present in the residual form and the mobility of metals declined by the following order: As>Cd>Zn>Pb>Ni. Thus, although Ni was the most important threatening metal as total concentration basis, its mobility in soil was recorded very low. 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. Also DTPA-extractable metal concentrations were not correlated with the plant metal concentrations for all metals.

In the greenhouse soils, single factor and composite pollution coefficient values of all metals except Ni were not exceeded critical limits. However, due to total concentration of Ni exceeding referenced limits greenhouse soils, composite pollution index of greenhouse soils in regional size was determined in heavy pollution risk group. Both anthropogenic and enrichment factor indexes of greenhouse soils indicate that there was 1 to 18 folds metal enrichment by anthropogenic inputs compared to uncontaminated soils at the same region. Single and potential ecological risk indexes of all soil metals were found below the threshold value that indicates these metals have none or low risk to surrounding environment.

Mean Zn and Cd concentrations in tomato leaves were exceeded reference limits. But none of heavy metal concentrations were exceeded phytotoxic heavy metal limits for culture plants. In reference to FAO/WHO limitations, average Cd concentrations were excessed limits in tomato fruits in all greenhouse regions. However, THQ of tomato fruits was recorded below the critical value and there cannot be expected a health risk for Cd metal in short or medium terms. Despite the fact that total concentration of Ni exceeded referenced limits in greenhouse soils, concentration of Ni in tomato fruit was recorded very low. Heavy metal TF of plants were mostly correlated with soil MF values of metals.

As can be seen, the results of evaluation of risk values based on different parameters concluded some inconsistencies. These paradoxes are mainly focused on the criterion based as total content of heavy metals for determining potential effect of metals on the environment. Results also show that the importance of metal speciation and soil metal mobility on metal transfers to plant, and determination of efficient extraction methods to estimating bioavailable metals.

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