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Determination and Evaluation of Heavy Metal Pollution in Greenhouse Regions of Antalya (Turkey)

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***Abstract*:** *To evaluate the heavy metal pollution of intensive greenhouse regions of Antalya, the relations among the soil, greenhouse plants and groundwater properties and heavy metal characteristics were determined. 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 and several environmental pollution indexes were used to evaluate the size of pollution and risks.*

Groundwaters of greenhouse area have low conductivity but high nitrate content. Heavy metal contents of groundwaters were below the permissible levels. Average total Cd, Ni, Pb and As contents of groundwaters were below the pollutant limits, but in sampling sites for Zn, Ni, Pb and As concentrations were exceeded permissible limits. However, the average heavy metal evaluation index (HEI) values for all metals in groundwaters were below the critical value.

The concentration of heavy metals with the exception of Ni in soils of greenhouses was 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. 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.

All heavy metal concentrations with the exception of Cd in tomato fruits were found below the permissible heavy metal limits. Although soil Ni concentration was excessed 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 and soil speciation studies may provide useful information for assessing metal bioavailability and environmental risk

Keywords: *Greenhouse Soils, Groundwater, Tomato, Metal Speciation, Metal Mobility, Pollution Indexes*

1. Introduction

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. Although greenhouse areas a have great impact on environment due to intensive use of agrochemicals, little attention has been paid to metal accumulation in greenhouse plants, metal contents of ground waters around greenhouses and heavy metal speciation and metal bioavailability and environmental pollution assessment in greenhouse soils with respect to comprehensive and integrated environmental evaluation.

The impact of agricultural activity on water sources has been widely acknowledged and its impact on surface water systems has been described in numerous studies [1]. Especially, the relationship between agricultural practices and the dissolution of nitrate in groundwater, as well as other pollutants have been studied in a number of case studies [2].

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. However, total concentrations of heavy metals provide inadequate information for assessing their bioavailability or toxicity [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. The aim of this study was to provide information on the metal accumulation in ground water and greenhouse plants, metal speciation and metal bioavailability in the greenhouse soils and also evaluate metal enrichments in ground waters, greenhouse soils and plants and paradoxes of soil metal establishments and soil pollution indexes versus to soil characteristics in greenhouse soils.

2. 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).

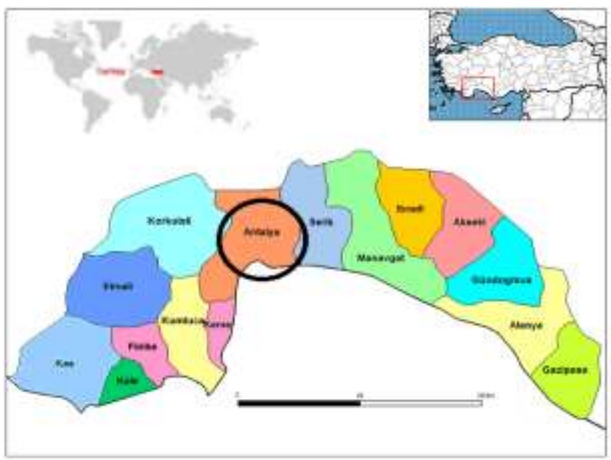

Fig. 1: Map of greenhouse regions of Antalya

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.

Groundwater samples were collected from eight greenhouse sites to analyze for heavy metals and other properties. 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, 10 ml of aqua regia and 1 ml of perchloric acid added to 100 ml 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.

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 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 [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 HNO3/HCl) and HCLO4 according to the international standard [5] Zn, Cd, Ni and Pb concentrations of water and 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 water samples 'Heavy Metal Evaluation Index (HEI) of the Groundwaters' [6], as 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

3. Result and Discussion

3.1 Ground Water Properties

Certain groundwater characteristics and total heavy metal contents of greenhouse areas are shown in Table 1. Groundwaters in greenhouse areas have generally slightly alkaline reaction, low electrical conductivity. Total nitrate content of groundwater has exceeded maximum permissible limits for drinking waters. High concentration of nitrate is of course may be due to highly intensive agricultural practices for all season. Average total Cd, Ni, Pb and As contents were below the permissible pollution limits, but in some sampling sites permissible limits for Zn, Ni, Pb and As were exceeded.

TABLE I: The analytical characteristics and heavy metal concentrations of the groundwaters

Site	pH	EC, µS cm^{-1}	NO_3, mg L^{-1}	Zn, µg L^{-1}	Cd, µg L^{-1}	Ni, µg L^{-1}	Pb, µg L^{-1}	As, µg L^{-1}
1	7,52	479	20,0	268	2,41	4,02	52,9	8,7
2	7,58	486	21,5	131	0,08	21,10	3,3	3,8
3	7,53	492	18,0	71	0,16	3,68	3,6	10,4
4	7,35	569	22,7	97	0,06	4,64	1,2	9,3
5	7,43	640	17,5	106	0,10	5,21	4,8	20,4
6	7,35	655	32,8	101	0,07	4,52	2,2	13,9
7	7,16	793	37,2	105	0,40	4,44	5,5	20,5
8	7,27	777	44,0	83	0,05	2,85	4,1	17,5
Mean	7,39	611	26,7	120	0,41	6,30	9,7	13,1
St.D.	0,14	127	9,9	62,2	0,81	6,01	17,5	6,0
Limits[12]			10	200	3	20	10	20

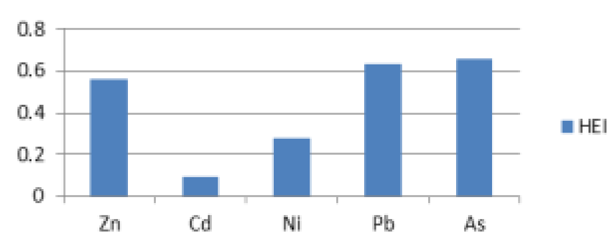

Fig. 2: Heavy metal evaluation index (HEI) of the groundwaters

The mean heavy metal evaluation index (HEI) values for all of metals in groundwaters were below the critical value 40. Thus, all of groundwater samples may be considered as less contaminated and may be acceptable clean.

3.2 Soil Properties

Certain soil characteristics and heavy metal contents of greenhouse areas are shown in Table 2 and Table 3. 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].

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 57 to 249 for zinc with a mean of 138; 0.23 to 0.78 for cadmium with a mean of 0.44; 56 to 215 for nickel with a mean of 122; 9,3 to 30,4 for lead with a mean of 19,4; and 4 to 34,3 for arsenic 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. Nickel 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 Ni>Zn> Pb>As>Cd.

TABLE II: The analytical characteristics of soils

Site	CaCO3, %	pH (H_2O)	EC, micS cm^{-1}	CEC, $meq^{-100\ g}$	Org. C., g^{-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

TABLE III: Total metal contents (µg 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	0.03-0.3	50	2-20	1-7

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 gives 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].

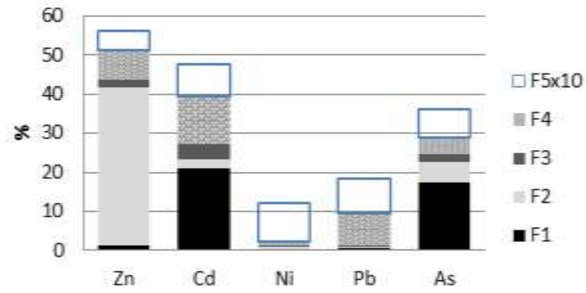

Fig. 3: Concentrations of Zn, Cd, Ni, Pb and As in soil fractions (F5 values are higher 10 fold than given values)

Mobility of metals

Due to some metal forms are strogly bound to soil components than those exracted 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:

$$MF :((F\_1+F\_2+F\_3))/((F\_1+F\_2+F\_3+F\_4+F\_5)) \text{ x100}$$

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).

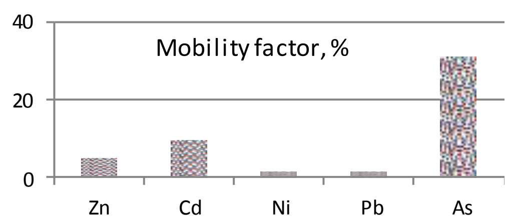

Fig. 4: Average metal mobility of greenhouse soils

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.

Altough 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 inferrerred that Ni abundancy of parent material of soil is very high and there are less Ni contaminant sources.

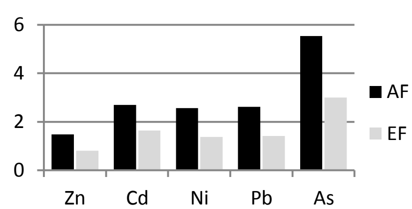

Fig. 5: Anthropogenic (AF) and enrichment factor (EF) indexes of the greenhouse soils

Single-factor (Pi), index composite pollution (PN) index and potential ecological risk factor index (Er)

Single-factor and composite pollution indexes and potential ecological risk indexes of heavy metals in greenhouse soils are summarized in Figure 6. It is clear that all contamination coefficients 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 was low, due to higher coefficient value of Ni, composite pollution index was determined in heavy pollution risk group.

The avarage monomial risk factors, Er of heavy metals in greenhouse soils were ranked in the following order Zn<Pb<As<Cd<Ni. The avarage monomial risk for heavy metals was 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. Avarage RI value were found 19, 17 and below the ecological risk level.

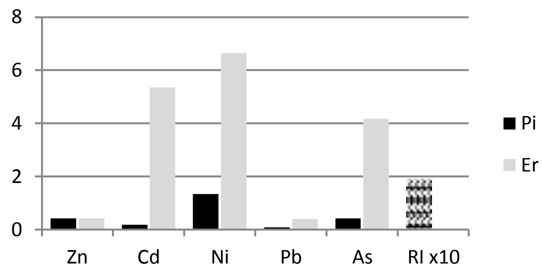

Fig. 6: Single factor index (Pi) of each metal, composite pollution index (PN) and and potential ecological risk indexes (Er) of metals

3.3 Plant Properties

Plant heavy metal content

Heavy metal concentration of fresh tomato fruits are shown in Figure 7.

All heavy metal concentrations with the exception of Cd were found below the permissible heavy metal limits for fresh vegetables [16]. Average Cd concentrations in tomato fruit were excessed referenced limit (0,02 mgkg-1) [16]. Although soil Ni concentration was excessed the pollutant limits, possibly due to low soil mobility factor of Ni, concentration of Ni in tomato fruit was found very low.

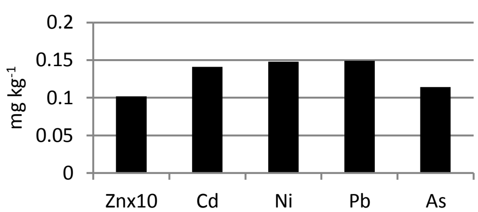

Fig 7: Heavy metal contents of tomato fruits grown in greenhouses (Zn element value is higher 10 fold than given values)

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 avarage 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 [17].

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.

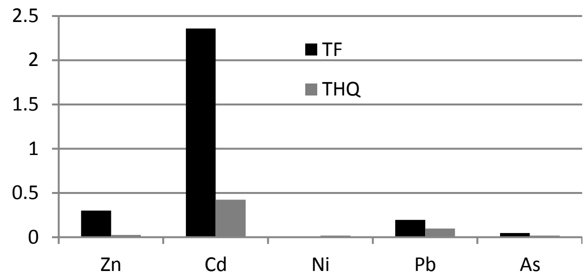

Fig 8: Heavy metal transfer factor and Target Hazard Quotient (THQ) of tomato

4. Conclusions

According to water analysis, groundwaters were not saline in nature but nitrate contents were exceeded maximum permissible limits for drinking waters. Average total Cd, Ni, Pb and As contents were below the permissible pollution limits, but in some sampling sites permissible limits for Zn, Ni, Pb and As were exceeded. However, the average heavy metal evaluation index (HEI) values for all metals in groundwaters were below the critical value. Thus generally, it can be concluded that all ground waters in regional size may be considered less contaminated, and in point of heavy metals and pollutants is in acceptable limits. High nitrate contents of groundwaters due to agricultural activities all season seem the main threats for public health.

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. 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.

All heavy metal concentrations with the exception of Cd in tomato fruits were found below the permissible heavy metal limits. Although soil Ni concentration was excessed 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 comparision 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.

5. Acknowledgements

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