

The Effect of Long-Term Municipal Solid Waste Compost Applications On Soil Metal Bioavailability and Environmental Risks

Bülent Topcuoğlu

Abstract: A greenhouse experiment was carried out to determine heavy metal loading capacity, metal mobility, bioavailability, metal-bound forms and pollution effects in the greenhouse soil and uptake of metals by cucumber plant following three cultivation years of municipal solid waste compost (MSWC) application. The effects of MSWC application on soil metals were compared with the same amount of manure application. Additional to routine soil analysis, several environmental pollution indexes were used to assess the size of possible environmental pollution risks.

Successive applications of MSWC increased both total and available (DTPA, EDTA and HCL extractable) concentrations of Zn, Cu, Ni, Pb and Cd in the greenhouse soil when compared with the manure application. However, the concentration of heavy metals in soil treated with MSWC were found below the referenced limits. Correlation values between soil metals and plant metal contents in MSWC and manure applications were considerably recorded higher in EDTA-extractable metals. Relative increases of total and bioavailable metal concentration were recorded higher in MSWC application than in manure application, and more than that, relative increases of bioavailable metals in MSWC application were more marked than those of manure application. The most mobile metal fraction in control soil was detected in Zn and the most immobile metal fractions were detected in Ni. Manure and MSWC incorporation into the greenhouse soil significantly increased the sum of metal concentrations in the mobile fractions. Manure and MSWC applications increased mobility factor values for all metals. MSWC application to greenhouse soil caused higher mobility factor values for all metals with the exception of Ni. Lead was detected as the most mobile metal in MSWC application.

'Single-factor pollution index' and 'composite pollution coefficient' of heavy metals in greenhouse soil were not exceeded critical value by the applications. Thus, all of soil samples may be considered as less contaminated by applications and may be acceptable clean. The average 'single-ecological risk index' and 'potential-ecological risk index' values for heavy metals were found below the limits that indicate all metals posed low risk to surrounding ecosystem in short or medium-term. MSWC application increased 'risk assessment code' values of metals except Ni and, MSWC has a medium size risk to ecosystem due to their higher toxicity and percentage in the exchangeable and carbonate fraction.

Heavy metal concentrations of cucumber leaves in MSWC application were higher than that of manure application, and Pb and Cd contents of cucumber fruits in MSWC application were exceeded the limit values for edible vegetables. But no phytotoxicity or no phytotoxic levels of metals were recorded by the application. MSWC application led to greater transfers of Ni, Pb and Cd metals in plant. However, 'target hazard quato' and 'hazard index' values representing health risks of cucumber fruit in all applications were found below the critical value.

Key words: MSW compost; Metals; Mobility, Bioavailability; Pollution risks

I. INTRODUCTION

Composting of municipal solid waste (MSW) and its subsequent application to agricultural land is gaining popularity because of environmental concerns associated with the disposal of this material in landfills.

However, there is a rising concern over MSWC often contains potentially toxic elements, that can cause soil contamination, phytotoxicity and undesirable residues in plant and animal products [2]. As a matter of fact, pollution problems may arise if toxic metals are mobilized into the soil solution and are either taken up by plants or transported in drainage waters. Risk for human health may then occur through consumption of such crops and intake of contaminated waters. This is particularly the case for heavy metals in MSWC due to their ubiquity and toxicity. Nevertheless, the main risks associated with the use of organic wastes in agriculture cannot be evaluated directly through determination of the total contents of metals in those materials, since the chemical or physicochemical forms of metals strongly affect their mobility, reactivity and availability to plants [3]. In the long term, the use of MSWC can also cause a significant accumulation of Zn, Cu, Pb, Ni and Cd in the soil and plants [4]

The maximum permissible concentrations of heavy metals in surface soils amended with sewage sludge or MSWC are normally based on total concentration, although it is the bioavailable metal fraction that poses environmental concern [5]. Nevertheless, these criteria are insufficient since mobility, environmental diffusion and bioavailability largely depend on soil physico-chemical characteristics and, likewise, on trace metal chemical forms [6]. From an environmental point of view, the evaluation and forecast of food contamination is related to the bioavailable fraction of heavy metals in soil.

Information on the fertilizing value of MSWC and their effects on the heavy metal loading potentials, metal mobility of greenhouse soil and environmental effects are scarce. The

aim of this study was to determine successive applications of MSWC on the total and bioavailable contents of Zn, Cu, Ni, Pb and Cd, metal mobility in the greenhouse soil, and heavy metal accumulation in cucumber plant and to assess environmental pollution risks.

II. MATERIAL AND METHODS

The experiment was conducted from 2011 to 2013 on the greenhouse representative of the major greenhouse vegetable growing area of Turkey Antalya Aksu. The site studied is intensively cultivated and is not industrialized area. 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. The analytical characteristics of the greenhouse soil and MSWC are shown in Table 1 which also shows the pollutant limits of soil and also organic materials used as soil amendments, permitted by EU legislation [7].

TABLE I: THE ANALYTICAL CHARACTERISTICS OF THE EXPERIMENTAL GREENHOUSE SOIL BEFORE APPLICATIONS					
Parameters		Available Metals ^{2,3,4} (mg kg ⁻¹ dry wt)			Metal limits in soil, (mg kg ⁻¹ dry wt) [7]
Texture	Loam				
pH- H ₂ O (1:5 w/v)	7.69				
CaCO ₃ , %	7.70				
Organic matter, %	2.04				
Clay,%	15,5				
CEC, cmol kg ⁻¹	9,5				
EC, dS m ⁻¹ 25°C	0,8				
Total N, %	0.12				
P (ex), mg kg ⁻¹	13.7				
K (ex), mg kg ⁻¹	96				
Ca (ex), mg kg ⁻¹	1716				
Mg (ex), mg kg ⁻¹	211				
Zn, mg kg ⁻¹	74.13 ¹	22	16.66	18.11	150-300
Cu, mg kg ⁻¹	22.44	3.4	6.89	5.78	50-140
Ni, mg kg ⁻¹	15.90	0.52	0.58	0.71	30-75
Pb, mg kg ⁻¹	42.11	7.95	7.12	9.22	50-300
Cd, mg kg ⁻¹	0,02	0,001	0,001	0.002	1-3

¹:Total concentrations, ²:DTPA-extractable concentrations, ³:EDTA-extractable concentrations, ⁴: HCl-extractable concentrations

The mean analytical characteristics of organic materials tested are given in Table 2, which also shows the of EU limits [7] for sewage sludge.

TABLE II. AVERAGE ANALYTICAL CHARACTERISTICS OF ORGANIC MATERIALS USED.

	Manure	MSWC	Limit values [6], (mg kg ⁻¹ dry wt)
Moisture, %	54	35.4	
pH- H ₂ O (1:5 w/v)	7.96	7.66	
Ash, %	26.2	48.5	
Total N, %	2.12	1.15	
P ₂ O ₅ , %	1.77	0.77	
K ₂ O, %	1.56	0.55	
Total Zn, mg kg ⁻¹	180	1220	2500-4000
Total Cu, mg kg ⁻¹	46	105	1000-1750
Total Ni, mg kg ⁻¹	15	43	300-400
Total Pb, mg kg ⁻¹	21	196	750-1200
Total Cd, mg kg ⁻¹	0,06	1.6	20-40

MSWC was obtained from municipal solid waste composting plant in Kemer, Antalya. Compost was produced by the composting of the organic fraction of unseparated municipal solid waste, selected mechanically at the plant. MSWC was applied from 2011 to 2013 to greenhouse soil as an oven-dry basis, totaly at 100 ton ha⁻¹ levels. MSWC was manually incorporated into the greenhouse soil and mixed throughout the upper 20 cm. Manure obtained from cattle farm were applied to greenhouse soil for the control application was used to compare the effectiveness of MSWC application in the same greenhouse with all agronomic practices with the same experimental design of MSWC applications.

The experimental plots have been cultivated in three consecutive years with cucumber (*Cucumis sativus* L.) at a density of 38200 plants ha⁻¹ and each plot (5.25 m²) consisted of 20 cucumber plants in a randomized block design with four replications. Basic fertilizer was applied with sprinkler irrigation in all plots at the rate of 300, 200 and 300 kg ha⁻¹ of N, P and K, respectively. Plant nutrient inequality by the manure and MSWC amendments were balanced by required amounts of additional N-P-K fertilizer applications to plots at the rate of basic fertilizer concentration level.

During the experiment, the plants were watered regularly and treated according to common agrotechnical principles. For the determination of heavy metals, both plant and soil samples were taken at the end of experiment, 2013. At the beginning of the flowering period leaf samples were collected from each application, and fruits were sampled at the full ripening stage. After the harvest of cucumber, soil samples were taken at a depth of 10-20 cm; and these were air-dried and sieved (< 2 mm). Leaves and fruits of cucumber were analysed separately. Plant samples were dried at 60 °C in a forced-air oven, ground and then digested in aqua regia (1:3 HNO₃/HCl).

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. For the determination of ‘total’ heavy metal concentrations, soil and plant samples were digested in aqua regia (1:3 HNO₃/HCl) according to the international standard [8]. To determine bioavailable fractions of metals, DTPA [9]; EDTA [10] and HCl [11] extraction procedures were used.

Sequential extraction method [12] was applied to soil samples to identify metal fractions. The heavy metal sequential extraction procedure had the following steps:

- F1. 1 M MgCl₂ (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 $\text{NH}_2\text{OH}/\text{HCl}$ 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.

Total, bioavailable and sequential extracted metal concentrations 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' (MF) [13], 'Risk assessment code' (RAC) [14], 'Single-Factor Pollution Index' (Pi) and 'Composite Pollution Index' (PN) [15], 'Potential Ecological Risk Factor Indexes' [16], as for plant samples 'Heavy Metal Transfer Factor' (TF) and 'Target Hazard Quotient of Food' (THQ) [17] were used for comprehensive and integrated evaluation of possible pollution risks of applications.

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

III. RESULT AND DISCUSSION

A. Total and bioavailable metal contents in the soil

The heavy metal contents of greenhouse soil and organic materials studied before the experiment (Table 1) are well within the accepted normal range of agronomic values. A comparison of metal contents of organic materials with that of untreated soil showed that the metals Zn, Cu, Ni, Pb and Cd were present in MSWC in greater concentrations than those of the manure and experimental soil. However, the heavy metal concentrations of MSWC are below the levels indicated by the EU [7] for the agricultural use of waste organic material (sewage sludge).

Successive applications of MSWC for 3-years period led to a far greater introduction of the heavy metals examined and brought about a significant increase in their 'total' and available metal forms in the soil when compared with the manure applications (Table 3).

The total Zn, Cu, Ni, Pb and Cd contents of soil at the beginning of the experiment were 74.13, 22.44, 15.9, 42.11 and 0.02 mg kg^{-1} , respectively (Table 1). During the trial period, these levels were increased by MSWC and manure application. But increase in metal contents was recorded higher in MSWC application. Increasing soil-metal concentrations with MSWC application have been reported [18]. Despite important increases in metal contents registered, the concentrations of metals in the soil remained below the EU legislation [7] for soils.

All amounts of MSWC brought about significant increases in extractable metal concentrations in comparison with the manure application (Table 3). HCl-extractable Zn, Cu, Pb, Ni and Cd contents of soil also registered significantly higher values than other extractable metals in manure and MSWC applications. However, Pearson's correlation coefficients between HCl-extractable metals and plant metal contents were not found high (Table 4.) Correlation values between soil metals and plant metal contents in MSWC and manure applications were considerably recorded higher in EDTA-extractable metals.

To compare the relative changes of different soil metal levels depending on the applications, 'treated soil's metals-to-untreated soil's metals ratio' is used to give metal changing values as a percentage of total and available soil metals. In this study, EDTA-extractable metals are considered the most representer of bioavailable metals to compare relative bioavailability of metals. The relative changes of Zn, Cu, Pb, Ni and Cd concentration in manure and MSWC applications are shown in Figure 1.

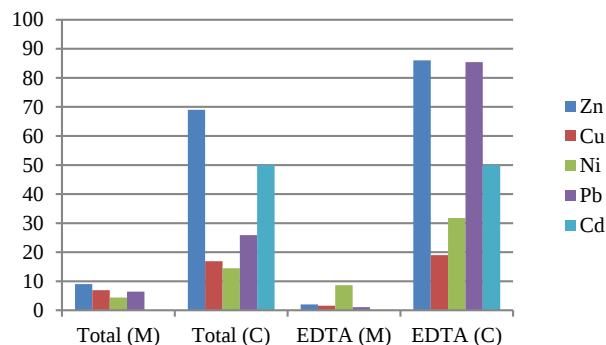


Fig. 1. Relative change of total and EDTA-extractable metal concentrations in Manure (M) and MSWC (C) applications.

As can be seen in Figure 1, all total and bioavailable metal concentrations were increased by the applications. Relative increases of total and bioavailable metal concentration were recorded higher in MSWC application than in manure application, and more than that, relative increases of bioavailable metal in MSWC application were more marked than those of manure application. Dominant relative increases of total and bioavailable metals in MSWC applications were generally belonged to Zn, Pb and Cd. Although total concentrations of all metals after applications were found below the pollutant limits, it might be seen that the increase in EDTA-extractable fraction was more marked than those of total concentrations. These results support the hypothesis [19] that metals added with sewage sludge or other organic wastes may be more mobile than native metals in soil.

B. Speciation and mobility of metals in the soil

Figure 2, Figure 3 and Figure 4 report the fractionation of heavy metals in greenhouse unapplied control soil and soil applied with manure and MSWC, respectively. For all metals, agreement between fractional total metal values and aqua regia extractable metal values are generally acceptable ($100 \pm 5\%$) rate. Concentrations of Zn, Cu, Ni, Pb and Cd in control soil fractions were given in Figure 2.

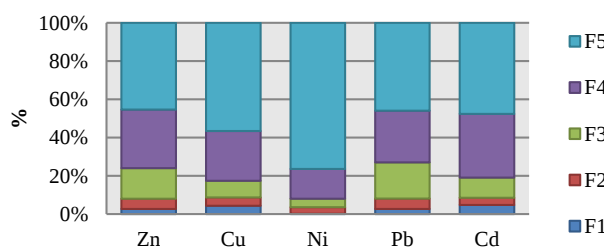


Fig. 2. Distribution of metals in the different fractions of pretreated (control) soil.

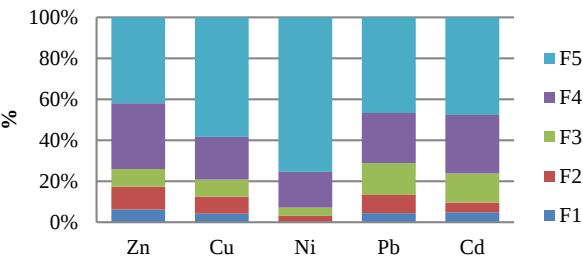


Fig. 3. Distrubution of metals in the different fractions of manure applied soil.

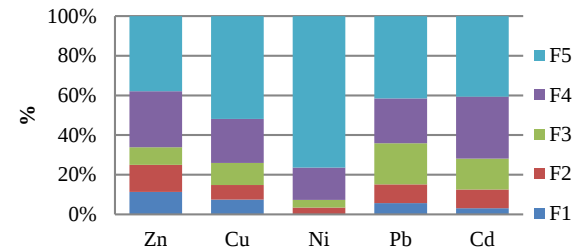


Fig. 4. Distrubution of metals in the different fractions of MSWC applied soil.

The distribution of metals in greenhouse control soil samples generally followed the order below for the metals studied:
Zn: F1<F2≤F3<F4<F5
Cu: F1≤F2<F3<F4<F5
Ni: F1<F2<F3<F4<F5
Pb: F1<F2<F3<F4<F5
Cd: F1≤F2<F3<F4<F5

TABLE III. Total and extractable concentrations of heavy metals in the greenhouse soil treated with manure and MSWC.																				
Applications	Zn				Cu				Ni				Pb				Cd			
	Total	DTPA	EDTA	HCL	Total	DTPA	EDTA	HCL	Total	DTPA	EDTA	HCL	Total	DTPA	EDTA	HCL	Total	DTPA	EDTA	HCL
Manure	81	24	17	19	24	3.5	7	6	16.6	0.55	0.63	0.77	45	8.1	7.2	9.40	0.02	0.001	0.001	0.002
MSWC	124	36	31	38	27	7.5	8.2	7.9	18.2	0.67	0.85	0.96	53	11.4	13.2	10.5	0.03	0.002	0.002	0.004
Significance	**	**	**	*	*	**	*	*	*	*	*	*	**	**	**	ns	*	*	*	*

All data are in mg kg⁻¹ as dry weight basis and average of 6 replicates. *: Significant with P≤ 0.05; **: Significant with P≤ 0.01; ns: not significant,

TABLE IV. Pearson's correlation coefficient showing relationship between soil metal contents and plant metal contents in manure and MSWC applications.

Plant metal contents		Total and extractable metals in manure applications				Total and extractable metals in MSWC applications			
		Total	DTPA	EDTA	HCL	Total	DTPA	EDTA	HCL
Leaf metals	Zn	0,126	-0,485	0,761**	0,531*	0,482	0,510	0,576*	0,511
	Cu	-0,564	0,519	0,894*	0,413	-0,608	0,820*	0,922**	0,603*
	Ni	1,000**	0,908*	0,943**	0,461	-0,074	-0,160	0,728*	-0,509
	Pb	0,904*	0,693*	0,786**	0,236	-0,220	0,677*	0,764*	0,331
	Cd	0,894*	0,159	0,810*	-0,231	0,245	0,438*	0,475*	-0,289
Fruit metals	Zn	0,700	-0,131	0,327*	0,327	-0,403	0,299	0,406*	-0,366
	Cu	-0,556	0,155	0,652*	-0,044	-0,760	0,810**	0,470*	0,339
	Ni	0,985**	0,872*	0,964**	0,356	1,000	-0,155	0,741*	-0,710
	Pb	0,653	0,693*	0,870*	0,585*	0,005	0,255	0,888**	0,882*
	Cd	0,673*	-0,171	0,525*	-0,781	0,015	0,504*	0,708**	-0,353

All data are in mg kg⁻¹ dry matter weight and average of 6 replicates. *: Significant with P≤ 0.05; **: Significant with P≤ 0.01

TABLE V. Heavy metal content in the leaves and fruits of cucumber grown in manure and MSWC applied soil.

Applications	Zn		Cu		Ni		Pb		Cd	
	Leaves	Fruit	Leaves	Fruit	Leaves	Fruit	Leaves	Fruit	Leaves	Fruit
Manure	38	7.1	9	6	1.4	0.5	2.1	0.2	0.1	0.01
MSWC	55	5.7	14	6	4.1	1.5	8.7	2.1	0.6	0.03
Significance	**	**	**	**	*	*	**	**	*	*
Background level [20]	40	-	8	-	2	-	3	-	<0,5	-
Limits for edible foods [21]	-	20	-	10	-	10	-	0,2	-	0,005
Phytotoxic level [22]	100-400	-	20-100	-	10-100	-	30-300	-	5-30	-

All data are in mg kg⁻¹ dry matter weight and average of 6 replicates. *: Significant with P≤ 0.05; **: Significant with P≤ 0.01

The study of the distribution of metals in control soil showed that the greatest percentage of all metals was present in the residual fraction (F5). F1, F2 and F3 fractions of Pb in control soil were higher than other metals. The most mobile metal fraction in control soil was detected in Zn and the most immobile metal fractions were detected in Ni. Nickel largely associated with residual phase. However, an important portion (19,05 %) of Cd was in labile form. These results indicate the higher percentages of metals in soluble, exchangeable and bound to Fe-Mn oxide fractions. 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 [13].

Manure and MSWC incorporation into the greenhouse soil significantly increased the sum of metal concentrations in the mobile fractions (Figure 3, Figure 4). Chemical forms of metals in manure and MSWC may vary, depending on the solid-phase components present and their ability to release the metal, pH, temperature, number and accessibility of adsorption sites, metal affinity for solid components and operational parameters of the extraction process [23].

The distribution trends of Zn, Cu, Ni, Pb and Cd metals in manure and MSWC applications were generally followed the $F1 < F3 < F2 < F4 < F5$ order. However, F1, F2 and F3 fractions of metals were considerably increased by the manure and MSWC applications. This increase was recorded as 33,87 % for Zn, 35,85 % for Pb and 28,13 % for Cd in MSWC applications. This property naturally gives these metals a high mobility. Despite the low total Pb and Cd concentrations in MSWC studied, the high solubilities of Pb and Cd in the exchangeable phase indicates that these elements could cause environmental damage and thus, the rate of MSWC application should be taken into account [24].

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) [25] 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 in control soil were considerably higher for Zn. Manure and MSWC applications increased MF values for all metals. MSWC application to greenhouse soil caused higher MF values for all metals with the exception of Ni (Figure 5). Lead was detected as the most mobile metal in MSWC application. The high MF values have been interpreted as symptoms of relatively high lability and biological availability of heavy metals in soils [24]. The results of the present study suggest that the increasing mobility order of the metals for control soil was $Ni < Pb < Cu < Cd < Zn$; and for both manure and MSWC applied soil was $Ni < Cu < Cd < Zn < Pb$ (Figure 5).

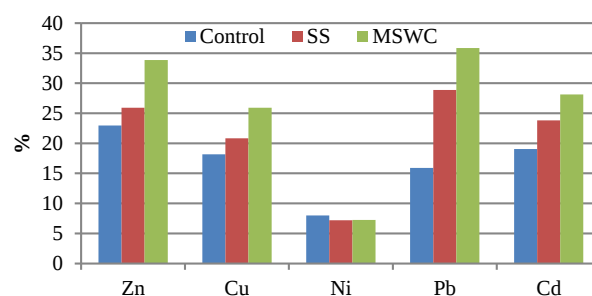


Fig. 5. Average metal mobilities of greenhouse soils treated with manure and MSWC

C. Plant properties and health risks

Plant Heavy Metal Content

Concentrations of Zn, Cu, Ni, Pb and Cd in the fruits of cucumber plant grown in the manure application were small and representative of background levels [22] (Table 2). As would be expected, heavy metal concentrations of cucumber leaves in MSWC applications were higher than that of manure application, but no phytotoxicity or no phytotoxic levels of metals were recorded by the applications. Limit values of Zn, Cu, Ni, Pb and Cd in edible vegetables were suggested as 20, 10, 10, 0,2 and 0,05, respectively [26]. According to results, Pb and Cd contents of cucumber fruits in MSWC application were exceeded the limit values for edible vegetables (Table II).

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

TF and THQ values are presented in Figure 6 and Figure 7, respectively. Metal transfer factors in all applications were higher in leaves than in fruits of cucumber. MSWC application led to greater transfers of Ni, Pb and Cd metals in plant. The highest average TF was found 20 for Cd in cucumber leaves. The second high TF was found for Cd in the fruit tissues of cucumber plant. These possibly might be due to higher mobility factor of Cd in the greenhouse soil (Figure 4 and Figure 5) and may be due to soluble metal participations by MSWC application. 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 [27]. High Cd accumulation in cucumber fruits may be possibly caused by high metal mobility and high solubility of Cd in the exchangeable phase of soil treated by MSWC. As might be expected, TF of Ni was the lowest due to its low solubility and MF.

As might be seen, mean THQ values of cucumber fruit in all applications were found below the critical value 1. An also hazard index (HI) value that represents sum of metal pollution hazards was below the critical value. Although transfer factor of Cd was detected very high especially in fruit tissue, no health risk can be proposed in short or medium term.

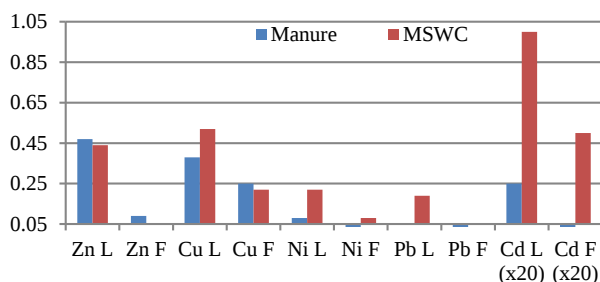


Fig. 6. Heavy metal transfer factor of cucumber tissues treated manure and MSWC (L: Leaf tissue, F: Fruit tissue).

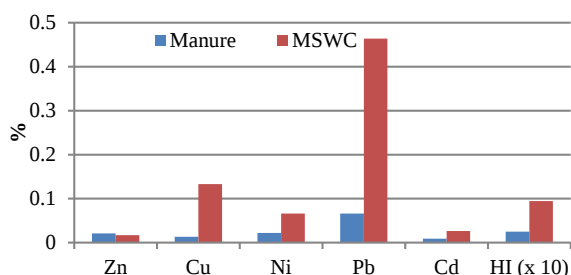


Fig. 7. Heavy metal Target Hazard Quotient (THQ) values and hazard index (HI) of cucumber fruit treated manure and MSWC.

D. Contamination evaluation of heavy metals

Single-factor and composite pollution indexes of soil: Single-factor pollution index (Pi) has been used to evaluate the degree of multi-element contamination. This is considered a better method of evaluation because heavy metals contamination in the surface environment is associated with a cocktail of contaminants rather than one element. Single indices are indicators used to calculate only one metal contamination:

$$P_i = C_i / S_i$$

where P_i is the single factor pollution index or contamination factor of heavy metal; C_i is the measured contamination value of heavy metal, S_i is the environmentally background contamination value of heavy metal.

Composite Pollution Index (PN) was applied to assess the quality of soil environment widely [15] and was defined as:

$$fPI_{Nemerow} = \sqrt{\frac{(\frac{1}{m} \sum_{i=1}^m P_i)^2 + P_{imax}^2}{2}}$$

where P_i is the single factor pollution index or contamination factor of heavy metal, P_{imax} is the maximum values of the single pollution indices of all heavy metals, m is the count of the heavy metals species.

Single-factor (Pi) and composite pollution coefficient (PN) of heavy metals are presented in Figure 8. It is clear that all contamination coefficients of metals in greenhouse soil were not exceeded critical value 0.7 (clean level) by the applications. Thus, all of soil samples may be considered as less contaminated by applications and may be acceptable clean. The average Pi of heavy metals in greenhouse soil for all applications were ranked in the following order: Zn < Ni < Cu < Pb > Cd.

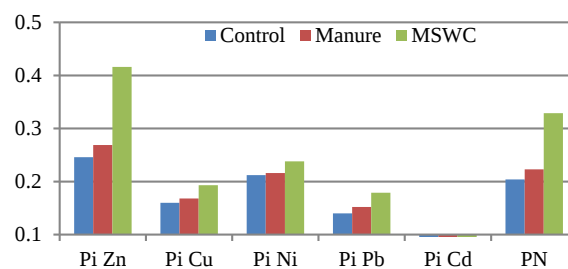


Fig. 8. Single-factor (Pi) and composite pollution coefficient (PN) of heavy metals in manure and MSWC applied soil.

Single and Potential ecological risk factor indexes: A single ecological risk factor (Er) to quantitatively express the potential ecological risk (RI) of a given contaminant [13] is:

$$RI = \sum_{i=1}^n E_r^i ; E_r^i = T_r^i \times C_f^i$$

where T_r is the toxic-response factor for a given substance, and C_f is the contamination factor, n is the count of the heavy metal species. Although the risk factor was originally used as a diagnostic tool for the purpose of controlling water pollution, it was successfully used for assessing the quality of sediments and soils in environment by heavy metals. In order to quantify the overall potential ecological risk of observed metals in the greenhouse soils, RI value was calculated as the sum of all the risk factors.

Er and RI risk assessment results of heavy metals in greenhouse soils are summarized in Figure 9. Er of heavy metals in greenhouse soils were ranked in the following order Cd < Zn < Pb < Cu < Ni. The average Er and RI values for heavy metals were found below the 40 and 150 limits, respectively that indicate all metals posed low risk to surrounding ecosystem in short or medium-term.

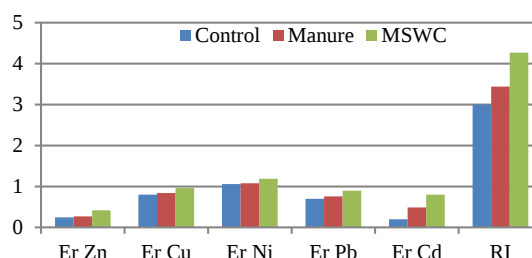


Fig. 9. Ecological risk index (Er) and Potential ecological indexes (RI) of metals in greenhouse soils treated manure and MSWC.

Risk Assessment Code (RAC): RAC classifies the risk levels based on the chemical speciation of heavy metals and reflects ecological risks. RAC determines the availability of heavy metals in sediments by applying a scale to the percentage of heavy metals in exchangeable and carbonate fraction [14]. In this study RAC parameter is modified to greenhouse soils. According to RAC guideline, classification of RAC is: <1%: no risk, 1-10 %: low risk; 11-30%: medium risk; 31-50%: high risk; >50 very high risk. RAC assessment results of heavy metals in greenhouse soils are summarized in Figure 10.

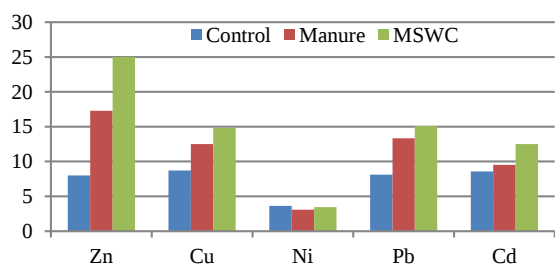


Fig. 10. RAC values of heavy metals in manure and MSWC applied soil.

According to RAC values of metals in unapplied control soil have low risk to ecosystem for all metals. However, manure and MSWC applications increased RAC values of metals except Ni and this increase was determined higher in MSWC application. RAC values of Zn, Cu and Pb in manure and MSWC applications and also RAC value of Cd in MSWC application were assessed in medium risk level. It was reported that the heavy metals accumulated to greater levels in the greenhouse topsoils with increasing cultivation periods [27]. These results show that MSWC has a medium size risk to ecosystem due to their higher toxicity and percentage in the exchangeable and carbonate fraction which are considered to be easily dissolved into water by acidity and possess an adverse impact on soil biota. The overall pollution degrees of heavy metals are in decreasing order of $Zn > Pb > Cu > Cd > Ni$.

IV. CONCLUSIONS

Repeated soil applications of manure and MSWC in three years experiment significantly increased total and extractable metals in the greenhouse soil compared to the untreated soil. Successive applications of MSWC led to a far greater introduction of the heavy metals examined and brought about a significant increase in their 'total' and available metal forms in the soil when compared with the manure applications. However, the concentration of heavy metals in greenhouse soils amended with MSWC were generally below the limits referenced by the 86/278/EEC directive to agricultural soils with $pH > 7$.

Correlation values between soil metals and plant metal contents in MSWC and manure applications were considerably recorded higher in EDTA-extractable metals. Relative increases total and bioavailable metal concentration were recorded higher in MSWC application than in manure application, and more than that, relative increases of bioavailable metals in MSWC application were more marked than that of manure application.

The most mobile metal fraction in control soil was detected in Zn and the most immobile metal fractions were detected in Ni. Manure and MSWC incorporation into the greenhouse soil significantly increased the sum of metal concentrations in the mobile fractions. Manure and MSWC applications increased MF values for all metals. MSWC applications to greenhouse soil caused higher MF values for all metals with the exception of Ni (Figure 5). Lead was detected as the most mobile metal in MSWC application. Single-factor (P_i) and composite pollution coefficient (P_N) of heavy metals in greenhouse soil were not exceeded critical value by the applications. Thus, all of soil samples may be

considered as less contaminated by applications and may be acceptable clean. The average Er and RI values for heavy metals were found below the limits that indicate all metals posed low risk to surrounding ecosystem in short or medium-term. MSWC application increased RAC values of metals except Ni and, MSWC has a medium size risk to ecosystem due to their higher toxicity and percentage in the exchangeable and carbonate fraction.

Heavy metal concentrations of cucumber leaves in MSWC application were higher than that of manure application, and Pb and Cd contents of cucumber fruits in MSWC application were exceeded the limit values for edible vegetables. But no phytotoxicity or no phytotoxic levels of metals were recorded by the applications. MSWC application led to greater transfers of Ni, Pb and Cd metals in plant. However, THQ and HI values representing health risks of cucumber fruit in all applications were found below the critical value.

In this three years study no detrimental effects on soil properties were detected and metals in applications were not higher than the allowed guideline level. However, taking into consideration the high potential bioavailability of heavy metals, repeated applications of MSWC would carry a risk of progressive build-up of available trace elements in the soil in the course of time. Results demonstrate the importance of measuring extractable as well as total concentrations and also metal mobility in topsoil when assessing likely effects on plant yields and metal uptakes, and settings soil quality criteria.

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