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Heavy metal contamination of municipal effluent in soil and plants

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Abstract

Using a plot study, this research aimed to assess the possible contamination of Tehran surface groundwater by heavy metals which lead to considerable effects on water, soil and plants. For this purpose, four experimental plots were spread with silty loamy soil collected from Varamin plain in the southern part of Tehran with an agricultural application. The plots were irrigated with four different types of regimes. In this study, two types of plants, including lettuce and spinach, were planted in four different plots and then regularly irrigated. After irrigation phases, the soil samples were taken from 0 up to 100 cm depth intervals from each plot and concentrations of four heavy metals, including cadmium, zinc, nickel and lead, were measured in each sampling by means of atomic absorption spectrophotometer. In order to find the relative concentrations of metals available to plants, three different reagents, such as deionized water, calcium chloride and diethylene triamine pentaacetic acid (DTPA), were selected and applied to the four proposed plots into three sections of the soil depths. Present metal mobility was determined by measuring the concentration of metals in the soil profile and leachate. Results showed that most accumulation of heavy metals was observed in the surface layer of the soil. However, through shrink-swell cracks heavy metals can penetrate into the subsoil layers and consequently contaminate the surface groundwater. The concentrations of metals are increased significantly in the soil and plants of plots compared with control plot. Long-term irrigation with effluent (Plot 3) and sludge (Plot 4) increased heavy metal contents in soil and plants and made this practice unsafe to be applied by man.

Key words: Heavy metals, accumulation, concentration, contamination, effluent, plant, soil.

Introduction

The application of sewage sludge in agricultural soils has been widespread in many countries around the world and also in Iran. This practice has been shown to improve soil properties such as organic matter, nutrients, porosity, aggregate stability, bulk density and water retention and as a result, to increase plant productivity. Heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic or industrial application [1]. One way of sludge disposal is its application on land. In the European Community, over 30% of sewage sludge is used as fertilizer in agriculture. For example, Gove *et al.* [3] reported increasing use of enhanced treated sewage sludge in agricultural lands. Heavy metals are very harmful because of their non-biodegradable nature, long biological half-life and their potential to accumulate in different body parts [4]. Even low concentrations of heavy metals are toxic because there is no good mechanism for their elimination from the body. Excessive accumulation of heavy metals in agricultural soils through wastewater irrigation may not only result in soil contamination but also leads to elevated heavy metal uptake by plants and thus affect food quality and safety [5]. In addition, there is also the possibility of transfer of these metals into environmental media, most especially shallow groundwater systems through leaching [6]. Metal transfer from sewage sludge to soil and subsequently to groundwater represents one of the most critical long-term hazards associated with the application of these wastes to soils [7]. With long-term use of sewage waste, heavy metals can accumulate to phytotoxic levels and, especially in low pH soils, results in reduced plant growth and/or enhanced metal concentrations, which enter the food chain when plants are consumed by animals [8]. Elevated concentrations of trace metals on land receiving sludge are of public concern because of possible phytotoxicity or increased movement of metals in the food chain. Another cause for concern is also pollution of surface and groundwater [9]. However, research carried out on the potential migration of heavy metals in sewage sludge-amended soils shows controversial results. Some studies showed that heavy metals migration in soils is practically insignificant as metals remain at the site of input [10-13]. This is consistent with the poorly soluble nature of heavy metals in most soils, especially basic soils [14],where the metals tend to accumulate at the soil surface and become part of the soil matrix. However, several field trials and column studies [15-22] have demonstrated migration of metals at depth and highlighted the concern regarding groundwater contamination by these pollutants.

Large land areas located in south of Tehran (approximately 6900ha) are irrigated with treated and untreated wastewater. Therefore, with attention to high water table in these areas, there is a need to assess the possible environmental impacts of groundwater pollution both in agricultural and environmental studies. The main objective of this study was to assess possible contamination of Tehran shallow groundwater system with heavy metals through plot study with 4 different irrigation regimes. This study has been conducted in Shush Treatment Plant located in the southern part of Tehran and the soil samplings were carried out in Varamin agricultural plain. The metals (Cd, Zn, Pb and Ni) were selected based on the origin of the polluted sources observed around the study area.

Materials and Methods

Soil sampling: Composite loamy soil samples were collected from upper horizon of Varamin plain in south of Tehran (51°38′ to 51°48′N, 35°14′ to 35°11′S). The samples were air-dried in the laboratory condition and passed through a 2-mm mesh sieve. Main soil properties such as pH, cation exchange capacity (CEC), phosphorus, total nitrogen, $CaCO_3$ equivalent, organic matter, saturated moisture and porosity were measured according to soil analysis methods [23].

Experimental design and soil sample preparation: Four experimental plots (2 m x 6 m) were filled with collected soils from Varamin plain area. A PVC drainage pipe was installed in one metre depth of each plot to collect the leached water. Plants such as lettuce and spinach were selected and cultivated in the plots. Then average concentrations of heavy metals in the effluent, drainages and sludge were measured [24]. The first and second plots were irrigated separately with pipe water as control plot and effluent from Shoush Wastewater Treatment Plant located in south of Tehran, respectively. The water for irrigation of the third plot was provided by simulated wastewater containing heavy metals (the concentration of each element in solution was 10 times higher than heavy metal concentration in drainages of south of Tehran and equal to several years irrigation). The fourth plot was watered with the mentioned plant sewage sludge and effluent. The sludge was incorporated into 0-20 cm plow layer before irrigation. After 6 months irrigation with three times per week, the soil samples were taken at 10 cm intervals up to 100 cm from each plot. Cd, Zn, Ni and Pb concentrations in each sample were measured by atomic absorption spectrophotometer (Varian Model-200) after the samples were digested and extracted with 2 N HNO_3 solution [24]. The average concentration of heavy metals in leached water was also measured [24]. Three different reagents, deionized water, 0.01 M calcium chloride and diethylene triamine pentaacetic acid (0.005 M DTPA), were applied to the four proposed plots into three sections (0-5, 30-35, 90-95 cm) of the soil depths. In addition, concentrated nitric acid was used as the total extractable solution in the experiment.

Digestion of the wastewater and leachates: Heavy metals of wastewater, drainages and leachate samples were determined according to water and wastewater standard methods [24]. For this purpose, 100 ml of wastewater or leachate was digested with concentrated nitric acid, passed through Whatman No. 42 and analysed using flame atomic absorption spectrophotometer (AAS, Varian Model 200).

Standard solutions: Standard solutions of heavy metals (1000 mg/L), including nickel (Ni), lead (Pb), zinc (Zn) and cadmium (Cd), were produced by Merck Company. Solutions of varying concentrations were prepared for all the metals by diluting the standards.

Preparation and digestion of plant samples: Plant samples were taken from each plot during September 2008. All the collected samples of various crops were washed carefully with deionized water to remove airborne pollutants. The above ground parts of the plants were weighed and air-dried for a day in order to reduce water content. All the samples were dried in a hot air oven at 70ºC for 24 h, to remove all moisture. Dried samples were powdered and sieved through muslin cloth. One g of each sample was accurately weighed and placed in crucibles. Then the samples were ashed in electrical muffle furnace at 450ºC and digested by HNO_3 [24]. Ni, Pb, Cd and Zn concentrations in the plant extracts were determined by a graphite furnace atomic absorption spectrophotometer (AAS;Varian Model-200).

Results and Discussion

Some physico-chemical properties of the soil measured before the sludge and effluent application are summarized in Table 1. Average concentrations of heavy metals in the wastewater, drainages, simulated solution and sludge are shown in Table 2 and extractability of heavy metals in soil through different reagents for various plots is shown in Tables 3-6. Table 7 shows the average heavy metal concentrations of leached water in different plots.

It is clear from Table 2 that nickel and lead have the highest concentrations of heavy metals in sludge and drainages in southern part of Tehran, because the presence of electroplating industries, car battery manufactures, dry cell manufactures and leather tanneries are located in the study region. In recent years, there has been great pressure on manufactures to reduce the metal concentrations in their effluents by introducing cleaner technology and recycling. From Tables 3 to 6 it can be observed that the greatest proportion of cadmium, lead, zinc and nickel in the soils were extracted with a strong chelating agent DTPA which seemed to be one of the superior reagents for extraction of these metals in the soil. DTPA extraction has frequently been found to correlate with amounts taken up by plants [25]. This implied that a greater proportion of metals in soils may be available to plants. Lindsay and Norvell [26] have also shown that the concentrations of some metals extracted with 0.005 DTPA are correlated with the concentrations in several types of crop plants growing in the soil. The distribution in depth of 4 elements (Ni, Pb, Cd and Zn) in plots is presented in Fig. 2. Heavy metals concentrations at the study plots were generally ordered as follows: Plot 4> Plot 3> Plot 2> Plot 1.

The concentrations of metals had increased significantly in the sampled plots compared with control plot. Also, Fig. 1 clearly indicates that in control plot (Plot 1) the highest concentrations were within the first 5 cm depth, while in other plots, the highest concentrations were consistently from the surface to within the top 35 cm of the profile. Lower migration of these pollutants in Plot 2, in comparison with other plots, is due to their low concentration in effluent of the study area used for irrigation of Plot 2.

The accumulation of the metals in the surface layer of the soil seems to be related to their high sorption capacity by soil resulted from chemical reaction between soil solid phases, including silicate clays, oxides and hydroxides of metals, especially Fe and Al, amorphous minerals and also lime, and organic matter and firm bonds with these compounds [27, 28]. This property associated with high adsorption rate of these elements by soil solid phases causes

Table 1. Some physico-chemical properties of the soil in the study area.

Plot #	pH	CEC (meq/L)	PO4-P (meq/L)	Nitrogen (meq/L)	CaCO3 (%)	Organic matter (%)	Soil moisture (%)	Soil porosity (%)
1	6.76	36.62	20	1.4	12.25	0.360	35.7934	0.52
2	6.94	44.25	20	1.3	11.25	0.375	40.9814	0.52
3	6.64	42.62	22	1.5	10.75	0.495	37.1495	0.51
4	6.57	41.5	19	1.4	10.50	0.420	38.9744	0.52

Table 2. Average concentrations of heavy metals in the various wastewaters (mg/L) and sludge (µg/g d.wt.).

Sample	Pb	Cd	Zn	Ni
Shoush Plant treated effluent	0.3± 0.05	0.01± 0.05	0.15± 0.05	0.1± 0.05
Drainages of south of Tehran	0.12± 0.05	0.02± 0.05	0.75± 0.05	2.98± 0.5
Simulated solution of heavy metals	1.2± 0.60	0.2± 0.5	7.5±1.5	29.8± 2.5
Shoush Plant sludge	185± 6.0	10± 2.0	40±10.0	190± 19.0

Table 3. Extractability of heavy metals average concentrations in soil through different reagents for Plot 1 (µg/g d.wt.)*.

Heavy metal	Depth cm	H_2O	$CaCl_2$	DTPA	HNO_3 (Conc.)
Cd	0-5	0.02	0.04	0.10	0.24
Zn		0.35	0.73	2.15	7.06
Pb		0.18	0.39	1.12	3.90
Ni		0.04	0.27	0.07	0.98
Cd	30-35	0.01	0.00	0.60	0.18
Zn		0.06	0.41	0.18	1.42
Pb		0.03	0.07	0.21	0.49
Ni		0.01	0.05	0.21	0.35
Cd	90-95	0.01	0.10	0.30	0.12
Zn		**ND	0.12	0.25	0.80
Pb		ND	ND	ND	ND
Ni		ND	ND	ND	ND

* The presented values are expressed as mean and standard error.
** Not detectable.

Table 4. Extractability of heavy metals average concentrations in soil through different reagents for Plot 2 (µg/g d.wt.)*.

Heavy metal	Depth cm	H_2O	$CaCl_2$	DTPA	HNO_3 (Conc.)
Cd	0-5	0.06	0.15	0.56	1.32
Zn		1.76	3.58	10.35	35.25
Pb		0.95	2.01	7.05	20.09
Ni		0.38	0.71	1.95	6.16
Cd	30-35	0.01	0.05	0.08	0.25
Zn		0.32	0.78	2.50	7.10
Pb		0.12	0.28	0.91	2.7
Ni		0.07	0.12	0.52	0.25
Cd	90-95	0.01	0.07	0.08	0.09
Zn		0.24	1.55	0.57	4.50
Pb		** ND	0.11	0.89	1.21
Ni		ND	ND	0.18	0.25

* The values presented are expressed as mean and standard error.
** Not detectable.

Table 5. Extractability of heavy metals average concentrations in soil through different reagents for Plot 3 (µg/g d.wt.).

Heavy metal	Depth cm	H_2O	$CaCl_2$	DTPA	HNO_3 (Conc.)
Cd	0-5	0.15	0.38	1.05	3.50
Zn		3.83	8.51	22.98	76.63
Pb		3.53	7.45	20.17	74.6
Ni		2.35	4.11	12.35	47.6
Cd	30-35	0.02	0.60	0.17	0.58
Zn		0.45	0.95	2.48	9.10
Pb		0.50	0.90	2.76	12.0
Ni		0.28	1.84	0.58	5.82
Cd	90-95	0.02	0.05	0.48	0.76
Zn		0.0	0.05	0.34	4.81
Pb		0.35	0.42	1.27	3.72
Ni		0.20	0.85	0.44	3.87

* The presented values are expressed as mean and standard error.

Table 6. Extractability of heavy metals average concentrations in soil through different reagents for Plot 4 (µg/g d.wt.).

Heavy metal	Depth cm	H_2O	$CaCl_2$	DTPA	HNO_3 (Conc.)
Cd	0-5	0.21	0.45	1.62	4.2
Zn		4.87	10.27	31.57	102.5
Pb		3.98	8.29	25.77	75.93
Ni		2.10	4.55	18.29	57.5
Cd	30-35	0.08	0.18	0.55	1.7
Zn		0.91	1.18	5.34	18.13
Pb		0.70	4.50	2.07	9
Ni		0.45	1.07	4.10	10.85
Cd	90-95	0.05	0.05	0.28	1.5
Zn		0.85	3.47	1.25	10.83
Pb		0.28	2.45	1.60	4.82
Ni		0.51	3.24	2.05	3.59

* The presented values are expressed as mean and standard error.

Table 7. The average concentrations of heavy metals in leached water (mg/L).

Plot #	Ni	Pb	Zn	Cd
1	*ND	ND	0.03	ND
2	0.05	0.15	0.44	0.01
3	0.78	0.18	0.78	0.02
4	0.58	0.11	0.15	0.01

* Not Detectable.

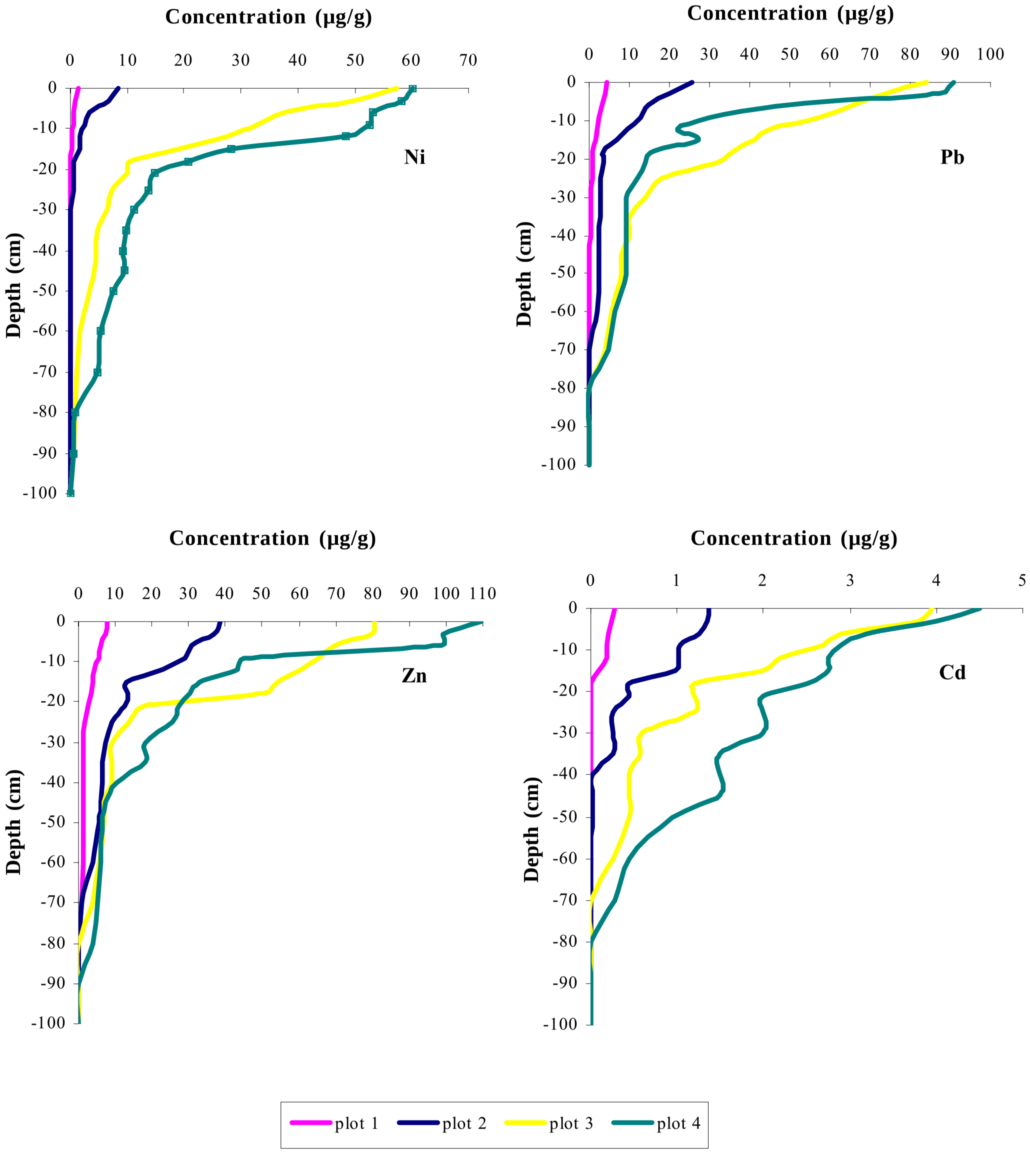

Figure 1. Depth distribution of heavy metals Ni, Pb,Zn and Cd in soil profiles (mean values µg/g).

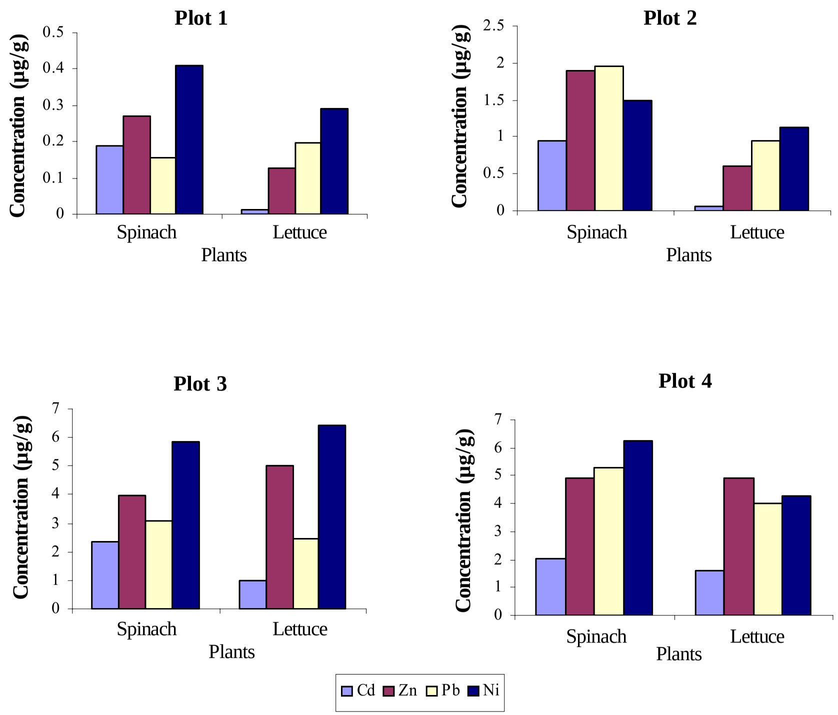

Figure 2. Heavy metals uptake in plants (Plots 1- 4).

their retention in surface layer of the soil. Soils, as filters of toxic chemicals, may adsorb and retain heavy metals from wastewater. However, when the capacity of soils is reduced due to continuous loading of pollutants or changes in pH to retain toxic metals, heavy metals can be released into groundwater or soil solution and are available for plant uptake [29]. Migration of the studied elements in soil is likely a product of some parameters including soil sorption capacity, reaction rate of these elements with solid phase, water movement rate in soil and their primary concentration.

The combined effect of the above mentioned parameters determined the distribution of these metals in soil profiles and depth of movement in soils. Soil acidity, light texture and structural features such as soil cracks can be considered as important factors[30-32]. Also, migration of these elements was observed in soils under lagoons where huge volume of sludge was disposed. Especially, if wastewater contains high chelating agents, they can form soluble complexes with Cd, Pb, Zn and Ni, thereby enhancing movement of metals in soil profile. As organically complexed ions or colloidal oxides, Pb and Ni can also move via diffusion or preferential flow through soil [33-35].

The uptake of heavy metals by plants in control plot was significantly lower than in other plots (Fig. 2). Ni had the greatest accumulation whereas the highest concentration of Ni for spinach was observed in Plot 4. Meanwhile, the concentration of heavy metals in spinach was higher than in lettuce. Long-term irrigation of plants by wastewater (Plot 3) and sludge (Plot 4) increased heavy metal contents in soil. Therefore, the plants grown on the polluted soils could absorb relatively high quantities of heavy metals. It seems that sludge application produced soluble organic complexes with the heavy metals. These complexes were more mobile, less readily adsorbed and possibly more readily taken up by plants than free metal ions [36, 37].

Table 7 shows that it was detected no concentration of heavy metals except Zn (low content) in leached water of control plot. In comparison, heavy metal concentrations of Plot 3 were higher than in the other plots. It is obvious that it was tried to control the pollution of wastewater with heavy metals. For this purpose, it is essential to recognize and study the pollution sources of wastewaters [38]. It can finally be concluded that once soil is polluted by treatment plant effluent or sewage sludge containing Pb, Cd, Zn and Ni in south of Tehran, these 4 elements tend to be accumulated in topsoil quickly and not easily desorbing from the soil, thus they will move downward to groundwater very slowly.

Conclusions

Iirrigation of agricultural lands by effluent and sewage sludge for several years increased heavy metals in soils and plants. The concentration of heavy metals increased significantly in the soil and plants of plots compared with control. Although the most accumulation of heavy metals was observed in the surface layers, preferential flow apparently allows leaching in the subsoil. Preferential flow can potentially increase the movement rate of water and solutions through soil profiles. It seems that groundwater contamination by these metals through shrink-swell cracks is likely. Control of wastewater and sewage sludge pollution with heavy metals is therefore of great concern. Thus, it is essential to study the pollution sources of wastewater. The results of this study can be used for the management of effluent and sludge application in agricultural lands and crop production. Also, the groundwater quality can be monitored and improved.

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