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Impact of untreated wastewater irrigation on soils and crops in Shiraz suburban area, SW Iran

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Abstract In this study an assessment is made of the negative impacts of wastewater irrigation on soils and crops sampled along the Khoshk River channel in suburban area of Shiraz City, SW Iran. For this purpose, samples of soil profiles (0–60 cm in depth) and crops were collected from two wastewater irrigated sites and a tube well-irrigated (control) site. Total concentrations of the five heavy metals (Ni, Pb, Cd, Zn and Cr) and their phytoavailable contents were determined. The Pollution Load Indexes (PLIs) and Contamination Factors (CFs) for soils and Hazard quotients (ΣHQ) for some vegetables were also calculated. The results showed the use of untreated wastewater has caused the following changes as compared to control site: (1) a 20–30% increase in organic matter content of soil; (2) increase in pH by 2–3 units; (3) significant concentration increase in Ex-Ca especially in top layers of soil resulting in high CEC; (4) build up of heavy metals (notably Pb and Ni) in topsoil above Maximum Permissible Limits (MPLs) indicating a moderate contamination (PLI>1, CF>2.5); (5) contamination of some vegetables (spinach and lettuce) with Cd due to its high phytoavailability in topsoil causing a HQ>1; (6) excessive accumulation of Ni and Pb in wheat due to continual addition of heavy metals through long-term wastewater application. The study concludes that strict protection measures, stringent guidelines and an integrated system for the treatment and recycling of wastewater are needed to minimize the negative impacts of wastewater irrigation in the study area.

Keywords Assessment · Crops · Heavy metals · Iran · Shiraz · Soil · Wastewater irrigation

Introduction

The use of industrial or municipal wastewater in agriculture is a common practice in many parts of the world (Urie 1986; Blumenthal et al. 2000; Ensink et al. 2002; Sharma et al. 2007; Feigin et al. 1991; WHO 2006). Rough estimates indicate that at least 20 million hectares in 50 countries are irrigated with raw or partially treated wastewater (Scott et al. 2004; Hussain et al. 2001). The major objectives of wastewater irrigation are that it provides a reliable source of water supply to farmers and has the beneficial aspects of adding valuable plant nutrients and organic matter to soil (Liu et al. 2005b; Horswell et al. 2003). With careful planning and management, the positive aspects of wastewater irrigation can be achieved (WHO 2006). Treatment of wastewater, as a segment of water management, usually produces a liquid effluent of suitable quality that can be used for irrigation purposes with minimum impacts on human

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health or the environment (Hussain et al. 2001; Blumenthal et al. 2000). In developed countries where environmental standards are applied, wastewater is treated prior to use for irrigation. However, in some developing countries where treatment costs can not yet be afforded, wastewater in its untreated form, is widely used in agriculture (Hussain et al. 2001; Friedel et al. 2000). Untreated or partially treated wastewater can introduce a huge amount of inorganic and organic contaminates, including heavy metals, into agricultural lands (Wang and Tao 1998). Hence, continual use of wastewater over extended periods can exert adverse impacts on quality of soil and plants grown on it (Madyiwa et al. 2002; Sinha et al. 2006). The indiscriminate use of untreated wastewater can then be considered as one of the most significant sources of environmental pollution that may directly affect the human health via crops and soil (Wang and Tao 1998; Butt et al. 2005).

It is predicted that many towns in developing countries will continue or expand the direct or indirect use of untreated wastewater despite the health and environmental risks associated with this practice (Scott et al. 2004; van der Hoek 2004). Some rapidly growing cities of Iran are experiencing such a trend. In these cities, large urban populations along with industrial activities generate a great volume of wastewater, some of which is discharged into surface waters (rivers) and applied to agricultural lands located in surrounding (suburban) areas. Shuval et al (1986) for the first time reported that raw wastewater from Tehran is used directly for crop irrigation in suburban areas.

Shiraz in southwest of Iran is another case which illustrates this problem. It is a growing city with widespread wheat and vegetable farms in its suburban area where untreated wastewater is used directly for irrigation of farms along the Khoshk River banks. During the dry season, these farms are frequently irrigated with wastewater streamed in the river channel. Concern for public health has been the most important aspect of wastewater application. The outbreak of cholera in 2004 in Shiraz was attributed to consumption of vegetables irrigated with wastewater. However, no study was conducted to assess the possible impacts of irrigation with untreated wastewater in Shiraz suburban area. Although Shiraz health organization prohibits the use of wastewater for irrigation of vegetables and other crops, the farmers along the Khoshk River banks continue to use wastewater for irrigation purposes. Protective measures taken by local and governmental authorities has recently led to a decrease in use of wastewater in Shiraz, nevertheless the health problems still have to be solved. One of these problems (risks) is accumulation and transfer of heavy metals in the soil–crop systems (Al-Nakshabandi et al. 1997; Qadir et al. 2000; Cui et al. 2004; Khouri et al. 1994). With repeated wastewater application, heavy metals can accumulate in soil to toxic levels (Sharma et al. 2007; Bohn et al. 1985). Crops raised on the metal contaminated soils also accumulate metals in quantities excessive enough to cause health problems to human beings consuming these metal rich plants (Tiller 1986; Rattan et al. 2005). Change in the basic physicochemical properties of soil (soil quality degradation) is another negative impact of wastewater application in agricultural lands (Chen et al. 2004; Aziz et al.1999). In view of the above stated problems the objectives of this paper are:

1. To evaluate the effects of wastewater irrigation on soil properties (pH, OM, CEC, exchangeable Ca).
2. To determine the total and phytoavailable contents of heavy metals (Ni, Pb, Cd, Zn and Cr) in soil profiles and their relationship with soil properties.
3. To determine the total concentration of heavy metals in crops and vegetables.
4. To appraise the extent of contamination in soils and crops.
5. To assess the human risk exposure posed by consumption of contaminated crops.

Materials and methods

Site description

The study area is located in east of Shiraz where the wheat and vegetable production sites along the Khoshk River are irrigated with water contaminated by domestic and industrial effluent from Shiraz. Abu-Nasr area, a suburban region (Fig. 1), has a surface area of 790 ha of which approximately 200 ha (30% of total area) is occupied by vegetable crops. Some agricultural lands in this area have been under wastewater irrigation for an unknown period of time

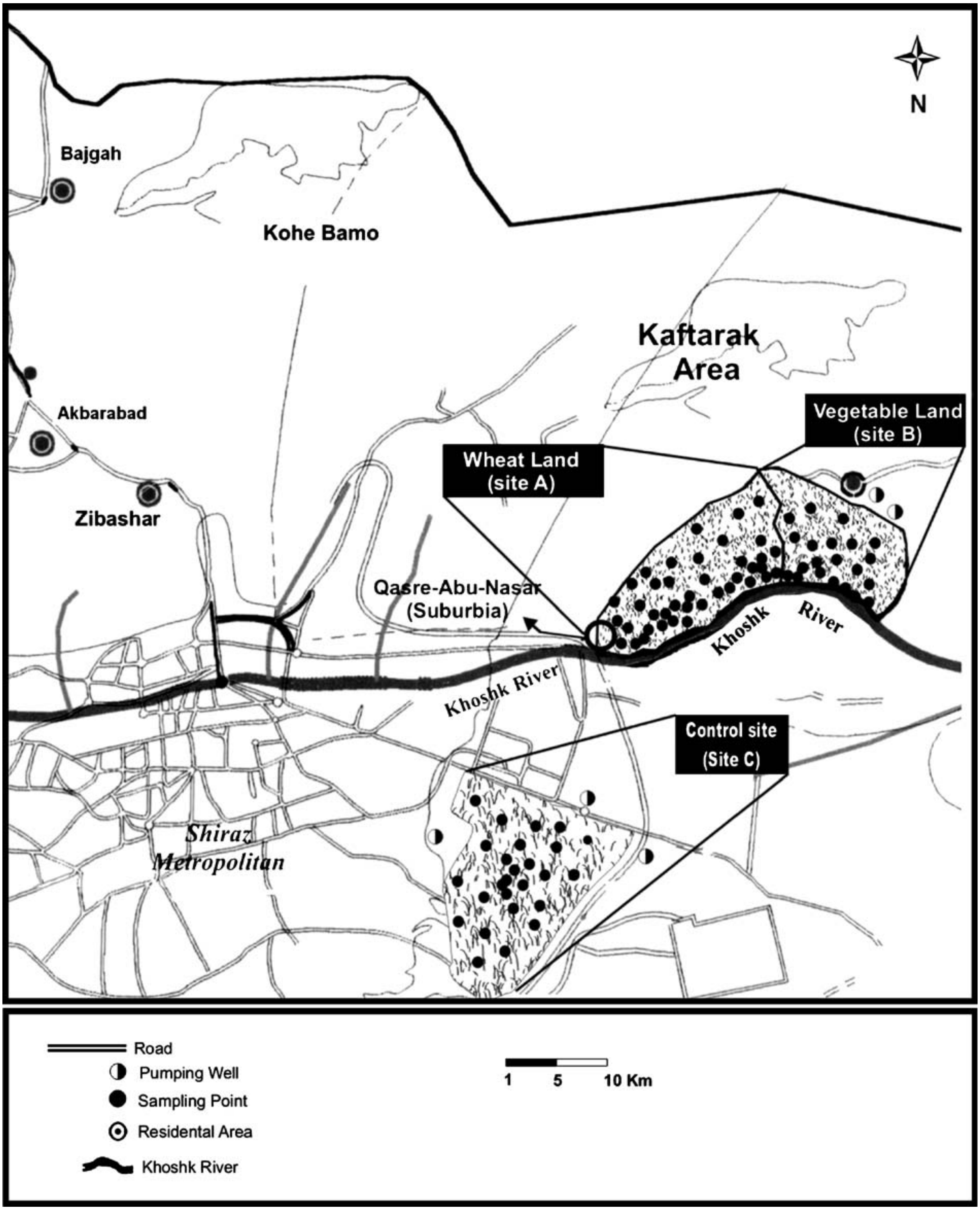

Fig. 1 Map of study sites in suburban Shiraz

(informally reported 20 years). Wheat, green vegetables, alfalfa and a variety of fruits are cultivated and locally consumed by residents or marketed in Shiraz City. This study is confined to two wheat farms and two vegetable cultivation sites scattered along the riverbanks (Fig. 1). In the wheat farms (site A), the wastewater and its sludge are used directly to irrigate the crops. In the vegetable farms (site B), both wastewater and tube well water are used periodically. Tube well water irrigated soils are also collected from a control location for comparison (site C). Many of the wheat and vegetable farms at this area are irrigated with pipes connected to pumps drawing the water directly from the river channel. In these sites, the use of untreated wastewater with its high BOD forms a thin layer of black residue on the soil surface.

There is no estimation of the volume of river water applied per unit area at these sites but it appears that the volume of applied wastewater is high in spite of the protective measures taken by Shiraz health organization. Khoshk River water is already reported to be polluted by heavy metals (Maddady and Ghasemi 2001). The major sources of these heavy metals are industrial and indiscriminate disposal of domestic waste or sewage drainage in the river (Irandoe 1997). In the study area (Abu-Nasr), additional local polluting sources such as car wash plants, garages and battery recharging units introduce a great amount of Ni, Pb and Cd and other heavy metals in the river channel. Table 1 gives the average concentration of heavy metals in the Khoshk River used for irrigation purposes.

Table 1 Chemical composition of wastewater used for irrigation in the study area

Element	Wastewater
P (mg l^{-1})	26–38 (35)
K (mg l^{-1})	20–39 (23)
Ca (mg l^{-1})	9.9–10.7 (9.3)
Fe (μg l^{-1})	1,200–2,700 (1,950)
Mn (μg l^{-1})	70–110 (84)
Ni (μg l^{-1})	169–220 (190)
Zn (μg l^{-1})	13–107 (65)
Cd (μg l^{-1})	4–12 (7)
Cu (μg l^{-1})	81–150 (113)
Pb (μg l^{-1})	89–585 (330)
Cr (μg l^{-1})	44–191 (110)
pH	8.4–9.8 (9)
BOD (mg l^{-1})	100–200 (135)

Figure in parenthesis indicate the mean value.

Crops and soil sampling

Crop sampling was made during mid-growing period (April–May 2006). Four crops were selected for this study: Wheat (*T. aestivum*), spinach (*Spinacia oleracea*), lettuce (*Lactuca sativa*) and celery (*Apium graveolens*) which representing the major species cultivated in this area in the sampling season. At each sampling site, 10 crop samples (n=30) were collected in the field by means of a random sampling method.

In wastewater irrigated farms (sites A and B), 15 profiles were dug. Soil samples were taken at the following depths: 0 to 20 cm for topsoil and 20 to 60 cm for subsoil. A total of 75 (15×5) samples were collected from wastewater irrigated sites. Topsoil samples (n=25) were also collected from a tube well water-irrigated site (site C; control site).

Sample pre-treatment and analytical methods

In the laboratory, the soil samples after air drying at room temperature, were sieved with nylon mesh (2 mm). The <2-mm fraction was ground in an agate mortar and pestle and passed through a 63 micron sieve. For heavy metal analysis, the soil samples were digested in aqua regia (1:3 HNO_3:HCl) and heated under reflux. After filtration, solutions were diluted with 2 M HNO_3.The heavy metals in resulting solutions were determined using atomic absorption spectrophotometry (Shimadzu AA-360).

Phytoavailable metals were extracted by 0.02 M EDTA and 1 N CH_3COONH_4 at pH 7.0. Ten grams of soil were mixed with 100 ml of extraction solution in 300 ml flask and the slurry was agitated for 1 h at 100 rpm. Following the filtration of slurry, the metals in filtrates were measured by AAS. Accuracy of the results was controlled by the use of reference material (GBW 07404 soil).

In order to measure concentration of exchangeable Ca (Ex-Ca), 5 g of soil samples were transferred to 100 ml flask, 40 ml of 1 mol l^{-1} KCl solution was added. pH was adjusted to 7 with NaOH solution. Then, the solution volume was diluted to 50 ml with 1 mol l^{-1} KCl and Ex-Ca was determined in solution by AAS.

Since soil properties play an important role in the retention/release characteristics of heavy metals, selected physicochemical properties of the soil such as pH, texture, CEC and organic matter were also investigated. Soil pH was measured in suspension (soil/water 1:2). Organic matter (OM) was analyzed by Walkley–Black method (Walkley and Black 1934). Clay content was determined using the hydrometer method. CEC was also determined by saturating the soil with 1 M CH_3COONH_4 buffering at pH 5.2.

The dry ashing method was used for analyzing the heavy metal contents in crop samples. Each determination was carried out by accurately measuring a sample of 1 g of a ground sample in a crucible. The crucible with its content was placed in a muffle furnace and ashed at 550C° for 7 h. The ash was digested with 5 ml of 20% (V/V) Analar HCl solution. The residue was filtered into 50-ml volumetric flask using Whatman filter paper No.41 and the solution was made to the mark with deionised water. Atomic absorption spectrophotometry was used for the heavy metal determination.

Assessment of human exposure risk

A full fledged risk assessment consists of several interactive and iterative steps. One of the essential steps of any chemical risk assessment process must be a means of determining or estimating levels of exposure (Weber et al. 2006). The exposure assessment identifies the pathways by which humans are potentially exposed to toxicants and estimates the magnitude, frequency and duration of these actual and or potential exposures (Lee et al. 2005). For irrigation of agricultural land with wastewater, four major anticipated pathways of exposure are shown in Table 2. In this study; we focus on the first pathway. It was narrowed down to the intake of potentially toxic elements through the leaf vegetable grown on wastewater irrigated soils. The average daily dose (ADD) of the contaminant via the first pathway indicates the quantity of heavy metal ingested per kilogram of body weight per day:

$$\mathrm{ADD} = \frac{\mathrm{mc} \times \mathrm{cf} \times \mathrm{di}}{\mathrm{bw}}$$

Where *mc* is the metal concentration in plants (mg kg^{-1}) on dry weight basis, *cf* the fresh to dry weight conversion factor (0.085), *di* the daily intake of green vegetable (kg) and *bw* the body weight (70 kg) (Rattan et al. 2005). Daily intake of green vegetable was considered 105 g/person/day (Maddady and Ghasemi 2001). Toxic risks refer to the non-carcinogenic harms incurred due to the exposure. The extent of harm is indicated in terms of hazard quotient (Vallero 2004):

$$\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfD}}$$

Where the RfD is the reference dose. The values of RfD for Cd and Ni are taken as 0.001 and 0.02 mg/kg bw/day respectively. These values are derived from The US EPA IRIS (Integrated Risk Information System) which is by far the most frequently cited RfD database.

If the sum of calculated HQs (ΣHQ_i or Hazard Index) is less than 1.0, the non-carcinogenic adverse effect due to this exposure pathway or chemical is assumed to be negligible and if this index is more than 1.0, the adverse health impacts are possible (Lee et al. 2005). The daily intake of metals (DIM) from

Table 2 Possible exposure pathways of heavy metals to human via wastewater irrigation

Pathway	Description
Wastewater irrigation → soil → plant uptake → food production → Human toxicity	Ingestion of food plants cultivated on land irrigated with waste water
Wastewater irrigation → soil → plant uptake → animal uptake → Human toxicity	Ingestion of metal/animal products from animals pasture on irrigated with wastewater
Wastewater irrigation → soil → vadoze zone → groundwater → Human toxicity	Ingestion of drinking water produced from groundwater polluted by wastewater
Wastewater irrigation → soil → direct ingestion → by human → human toxicity	Ingestion of soil caused by improper personal hygiene that transferred soils attached on hand to mouth

soil through vegetables was also calculated by the following method (Cui et al. 2004):

$$\mathrm{DIM} = \text{daily vegetable consumption (W)} \times \text{mean vegetable metal concentration} \quad \text{(mg/day fresh weight)}$$

It is evident that assessment of risk as computed here is not complete since metal accumulation in soil organisms, groundwater, surface water, direct uptake of soil by human and animals (other pathways in Table 2) are also risks which have not been considered here.

Quantification of the soil pollution

The degree and the extent of heavy metal pollution in the affected soils were measured and compared using the Pollution Load Index PLI of Tomlinson et al (1980). This index is based on the values of the Concentration Factors $\left(C_\mathrm{f}^i\right)$ of each metal in the soil. The C_f^i is the ratio obtained by dividing the mean concentration of each metal in the soil $\left(C_{0-1}^i\right)$ by the baseline or background value (concentration in unpolluted soil, C_n^i) (Liu et al. 2005b):

$$C_\mathrm{f}^i = \frac{C_{0-1}^i}{C_n^i}$$

In the present work, background values were estimated from the mean concentrations of the heavy metals in unaffected soils of the study area. C_f^i was defined according to four categories as follows (Liu et al. 2005b):

$C_\mathrm{f}^i < 1$	low concentration factor
$1 \leq C_\mathrm{f}^i < 3$	moderate contamination factor
$3 \leq C_\mathrm{f}^i < 6$	considerable contamination factor
$C_\mathrm{f}^i > 6$	very high contamination factor

The sum of the contamination factors for all the elements examined was represented as PLI. Values of PLI close to 1 indicate heavy metal loads near the background level, while values above 1 indicate soil pollution (Cabrera et al. 1999).

Statistical analysis

Simple correlation and linear regression analysis were carried out to assess the relationships of total and phytoavailable metal content (Pb, Ni, Cd) with soil physicochemical properties (pH, OM, Ex-Ca) and plant metal concentration(wheat and spinach). Statistical significance was also computed by analysis of variance. The level of significance was set at $p<0.05$ (two-tailed). Scatter diagrams of associated variables were drawn to check the uniform dispersion of plots and to help in the interpretation of significant and non-significant correlation coefficient. Only variables which resulted in clear correlated are reported and discussed in the text. All the statistical analyses were also performed using MS Excel 2003.

Results and discussion

Effects of wastewater irrigation on soil properties

The physical and chemical properties of soil profiles are given in Table 3. Variations of pH, OM and CEC with soil depth are graphically shown in Fig. 2. At site A, soil pH decreases with depth. The mean pH in wastewater irrigated soils is 8.6 in topsoil and 7.1 in subsoil. At site B where both wastewater and tube well water are used, soil pH also decreases from 8.1 in upper layers of soil to 6.1 in deeper layers. The mean pH values of control soil are nearly neutral. The

Table 3 Physicochemical properties of soils in the three investigated sites

	Depth (cm)	pH (H_2O)	OM (%)	CEC (cmol$^{(+)}$ kg^{-1})	Ex-Ca (mg/kg)	Clay content (%)
Site A	0–10	8.71	14.2	48.3	3,410	16.2
	10–20	8.13	17.5	43.4	2,240	13.1
	20–30	8.23	12.9	44.9	1,830	24.3
	30–40	6.56	5.6	20.1	1,050	30.9
	40–50	7.11	1.1	7.3	1,260	33.3
	50–60	7.09	0.3	2.2	980	33.0
Site B	0–10	8.13	10.5	44.5	2,360	8.7
	10–20	7.24	4.9	46.9	2,560	8.3
	20–30	6.15	4.4	39.1	1,540	7.5
	30–40	6.04	1.6	17.3	460	5.9
	40–50	6.19	1.6	11.4	420	5.3
	50–60	6.00	1.8	8.9	180	5.9
Site C	Mean	7.29	0.37	5.2	120	6.5
	Range	7.1–7.5	0.1–1.4	4.9–5.5	120–157	6.1–7.4

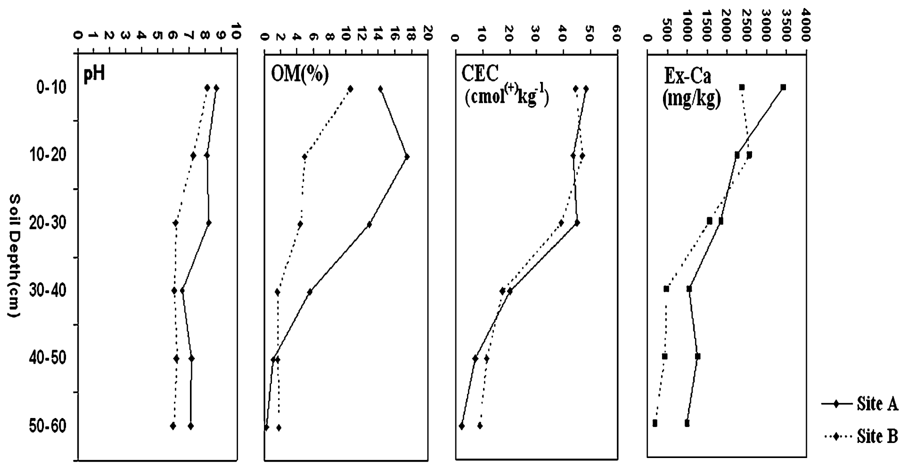

Fig. 2 Variation of some physicochemical properties of soil with depth in wastewater irrigated sites

higher pH in the upper layers of soils of sites A and B is attributed to alkalization effect of basic cations (especially Ca) contained in wastewater (Madyiwa et al. 2002).

After pH, soil organic matter (OM) is the most important indicator of soil quality and plays a major role in nutrient cycling. In this study, addition of organic matter through wastewater irrigation is comparable to those of sewage sludge application. In wastewater irrigated soils (site A), there is a decrease in organic matter content ranging from 18 wt% (for topsoil) to 0.3 wt% (for subsoil) as compared to tube well water-irrigated ones (0.1 to 1.4 wt%). In vegetable farm (site B), organic matter also decreases with soil depth but total OM content of these soils is generally lower than that of soils of site A. OM content in control soils is considered as NOM (natural organic matter). Thus the use of wastewater with high BOD (Table 1) has increased OM up to 22% to 30% as compared to tube well water-irrigated soils.

Cation exchange capacity (CEC) ranges from 48.3 to 2.3 (for site A), 44.5 to 11.4 (for site B) and 4.9 to 5.5 (for site C). In wastewater irrigated soils, a significant variation in CEC values is observed. This can be attributed to the high organic matter content and high loading of Ex-Ca rather than variability in clay content of soil. The concentration of Ex-Ca for these soils decreases sharply with depth (Fig. 2). This indicates that topsoil have received a large amount Ca during wastewater application. This trend is very similar to the decreasing trend of CEC in soil profile. Although the soil adsorption capacity of sandy soil is quite low, the wastewater irrigated soils (site A) can accumulate >2,500 mg kg^{-1} exchangeable Ca in topsoil. Apparently, a great increase in soil adsorption capacity induced by wastewater prompts the accumulation of certain heavy metals in the soil. In addition to OM content and pH, the exchangeable Ca may be a useful parameter for predicting the heavy metal accumulation in soil as this kind of Ca is water soluble and rapidly reacts with other elements (Hu et al. 2005).

Generally, it may be said that direct use of wastewater for irrigation has increased soil adsorption capacity through increase in pH, OM and Ex-Ca which in turn leads to accumulation of heavy metals in affected soils.

Heavy metal concentration in soils

Variations of total soil metal concentrations between wastewater irrigated and control sites

Table 4 summarizes the range, mean and standard deviation of heavy metal concentration in soil samples collected from the three investigated sites. The results show that concentrations of most heavy metals in wastewater-irrigated soils (sites A and B) are higher than those in control site. The obtained results also indicate site A and site B exhibit different concentrations of heavy metals. Greater concentrations after wastewater irrigation in site A compared to site B are probably due to greater amounts of wastewater used in site A. The control soils have relatively low concentration of all heavy metals. Zn and Cr do not show any significant change in both soils. On average, wastewater irrigation results in 4.5%, 7% and 4% increase in the Ni, Pb and Cd concentrations, respectively, in the soils of site A. The

Table 4 Heavy metal concentration in soils of the study area (all values in mg/kg)

Metals	Wastewater-irrigated soils (site A)			Wastewater+tube well water irrigated soil (site B)			Tube well-irrigated soil (site C)		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Ni	14.6–313.6	276.6[a]	25.4	12.6–198.2	181.3[a]	7.9	13.7–75.4	61.0	6.4
Zn	12.4–198.9	110.6[b]	8.7	15.9–139.5	79.7[b]	22.0	10.3–85.3	75.2[b]	7.8
Cd	0.09–3.30	0.35[b]	0.13	0.01–0.37	0.20[b]	0.01	0.02–0.06	0.21	0.19
Pb	16.7–465.2	441.7[a]	19.8	12.2–153.9	144.4[a]	8.8	2.2–73.3	63.2[a]	6.4
Cr	2.1–35.1	26.0	4.7	11.3–25.1	20.6	3.1	0.1–33.4	27.1	4.6

SD: standard deviation

[a] Indicate the differences between means of heavy metal concentrations in the three investigated sites that are significant at 0.01 (two-tailed).

[b] Indicate the differences between means of heavy metal concentrations in the three investigated sites that are significant at 0.05 (two-tailed).

concentration of heavy metals in tube well water-irrigated soils is generally very close to background level in non-polluted soils. Thus, taking into account the obtained data and concentration in non-polluted soils (site C), application of wastewater has seemingly enriched the soils in heavy metals.

Variation of total and phytoavailable metal content with soil depth in wastewater irrigates sites (A and B)

Table 5 represents the mean total and phytoavailable metal concentration for each soil horizon in wastewater irrigated sites. Variation of total and phytoavailable metal content with soil depth is also shown in Fig. 3a and b. At site A, there is a significantly decreasing trend of Pb and Ni concentrations in soil profile while their phytoavailable contents increase with depth. The relatively high metal concentration in the topsoil samples of site A can be attributed to high organic matter content of these layers rather than the clay content as the topsoil has got far less clay than subsoil. This indicates that Ni and Pb are less mobile than other heavy metals and hence accumulated in topsoil. The existing positive correlation between total concentrations of Pb and Ni and organic matter content in soil samples of site A confirms this conclusion (Fig. 4). This is in agreement with de Matos et al (2001) who found a high significance to the correlation between Pb–Ni adsorption and soil organic matter. Kachenko and Singh (2006) also observed positive linear correlations between soil Pb and organic matter, which may account for the

Table 5 Mean total and phytoavailable concentration of heavy metals in soil profiles at sites A and B

	Depth (cm)	Total concentration (mg/kg)					Phytoavailable content (mg/kg)				
		Pb	Ni	Zn	Cd	Cr	Pb	Ni	Zn	Cd	Cr
Site A	0–10	440.9	297.4	170.1	3.20	29.3	1.3	2.9	1.3	0.05	0.2
	10–20	418.7	275.3	175.2	3.29	30.7	1.7	2.3	1.3	0.06	0.3
	20–30	100.9	55.9	123.4	3.17	29.3	1.5	2.5	1.0	0.06	0.2
	30–40	28.71	17.7	27.1	2.20	12.1	1.7	0.3	0.5	0.08	0.4
	40–50	18.9	15.3	22.5	0.35	3.1	1.9	0.2	0.6	0.07	0.1
	50–60	16.7	15.0	15.9	ND	2.7	1.3	0.2	0.01	ND	0.1
Site B	0–10	147.3	180.9	110.3	0.25	20.3	0.4	0.2	0.02	0.1	0.02
	10–20	139.1	175.3	135.9	0.20	15.7	0.2	0.2	0.03	0.1	0.05
	20–30	77.4	20.9	95.1	0.25	13.9	0.1	0.7	0.05	0.04	0.01
	30–40	25.9	18.7	45.4	0.35	13.1	0.3	0.3	0.01	0.04	0.07
	40–50	13.3	17.9	25.3	0.32	13.7	0.2	0.5	0.02	0.03	0.09
	50–60	18.4	17.3	17.9	0.32	12.2	0.1	0.2	0.02	0.02	0.07

ND: not detectable

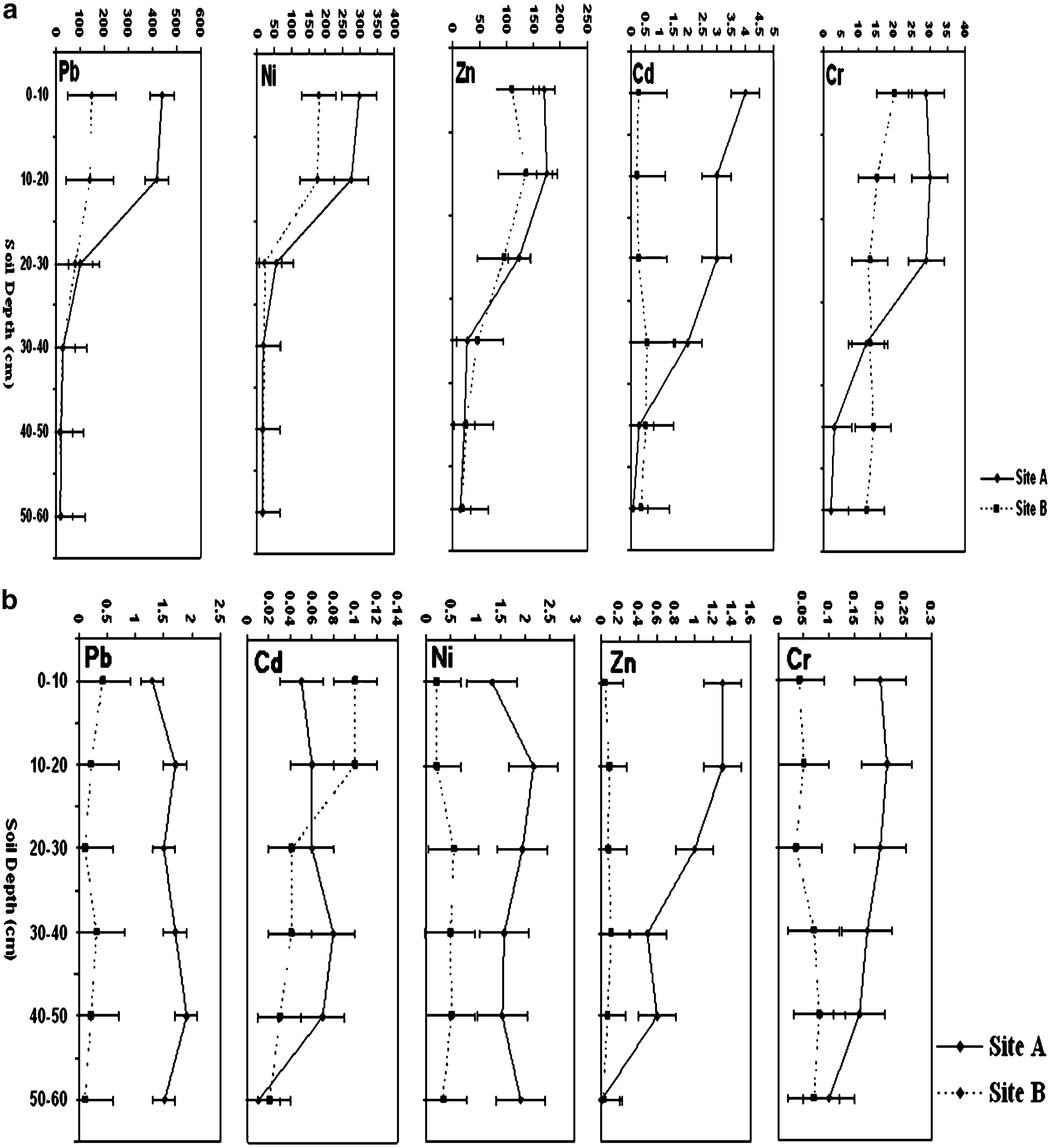

Fig. 3 **a** Variation of heavy metal concentration (mean values) in soil profiles of wastewater irrigated sites (all values in mg/kg). **b** Variation of phytoavailable metal content (mean values) in soil profiles of wastewater irrigated sites (all values in mg/kg)

elevated concentrations of Pb in topsoils collected from the Sydney basin. According to Alloway (1995), in soils which have received organic matter from wastewater or sludge, OM acts both as a source of several organic and inorganic pollutants (heavy metals) and also as the major adsorbent for them.

pH is another important factor that controls the accumulation, mobility and bioavailability of heavy metals in soils. The pH is, almost always, reported as soil characteristic to show good association to soil adsorption of heavy metals (Tyler and McBride 1982). A positive relationship ($p<0.01$) exists be-

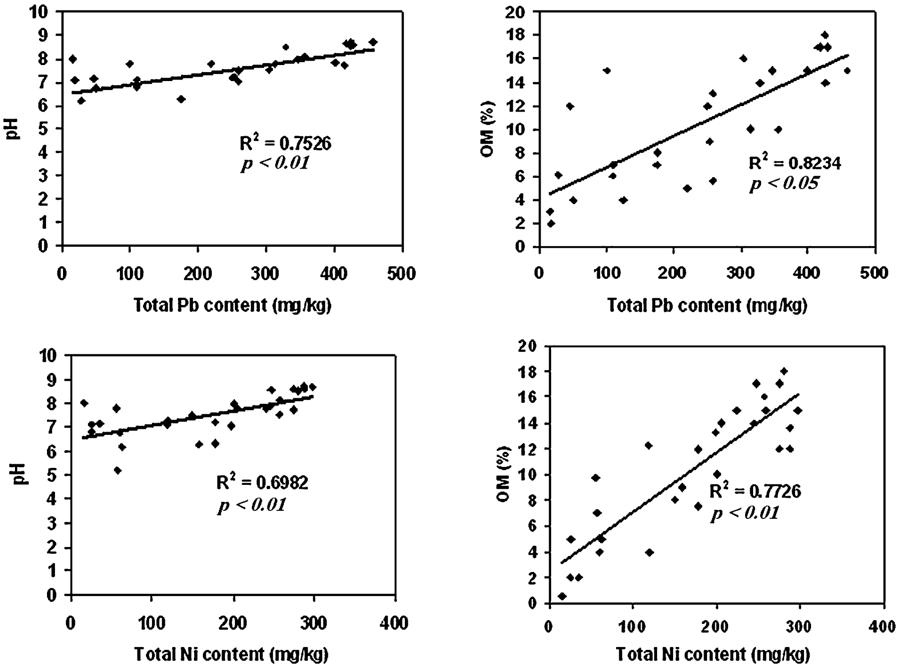

Fig. 4 Relationship between total concentration of Pb and Ni and soil pH and OM content in topsoil samples of site A

tween pH and total contents of Pb and Ni in soils sampled at site A (Fig. 4). Despite high total concentrations of Pb and Ni in soils of site A, only 1.3% to 7.7% and 0.07% to 1.69% of total content of these metals, respectively, are phytoavailable (Table 6). It seems that OM in soil with alkaline pH may chelate the metals and reduce their phytoavailability. This observation can be explained by negative relationship ($p<0.01$) between phytoavailable heavy metal contents and organic matter in wastewater irrigated soils. Thus, the high concentration of heavy metals in soil does not necessarily imply that they are phytoavailable (Chojnacka et al. 2005; Liu et al. 2005a).

As previously mentioned, the use of wastewater has elevated concentration of Ex-Ca in topsoil samples of affected sites (A and B). At site A, negative relationship is also observed between phytoavailable Pb content and concentration of Ex-Ca in soil. It may be suggested that Pb in soil solution probably replace Ca within carbonate fraction of soil resulting in the formation of insoluble complex of $PbCO_3$ in topsoil. Harter (1979) found a similar correlation, attributing it to hydrolysis $PbOH^+$ to Pb^{+2}, making possible more ionic adsorption in the exchangeable complex, as well as metal precipitation. Therefore, $PbCO_3$ precipitation may also influence the mobility and phytoavailability of Pb in these soils. Further studies, however, are needed to evaluate this implication.

At site B (vegetable production site) where both wastewater and tube well water are used, a marked decrease is observed in total concentrations of Pb, Zn, Ni and Cr with soil depth. On the contrary, total Cd content tends to increase in soil profile. It is also found that phytoavailability of Cd in soil decreases from topsoil to subsoil. This is confirmed by weak

Table 6 Proportion of heavy metal phytoavailability (%) in soil samples of wastewater irrigated sites

	Depth (cm)	Phytoavailable percent of heavy metals in soil				
		Pb	Ni	Zn	Cd	Cr
Site A	0–10	0.2	0.9	0.7	1.5	0.6
	10–20	0.4	0.8	0.7	1.8	0.9
	20–30	1.4	4.5	0.8	1.8	0.6
	30–40	4.7	1.6	1.8	3.6	3.3
	40–50	10.0	1.3	2.6	2.00	3.2
	50–60	7.7	1.3	0.06	–	3.7
Site B	0–10	0.2	0.1	0.01	40	0.09
	10–20	0.1	0.1	0.02	50	0.3
	20–30	0.1	3.3	0.05	16	0.07
	30–40	1.1	1.6	0.02	11	0.5
	40–50	1.5	2.7	0.07	9	0.6
	50–60	0.5	1.1	0.1	5	0.5

correlation between phytoavailable Cd content and pH and organic matter (Fig. 5). It is worth noticing that phytoavailable Cd content in soils of site B exhibits a linear correlation with Ex-Ca content (Fig. 6). However, of total Cr, Zn, Pb and Cd content of soils of site B, respectively, 0.09–0.6%, 0.01–0.1%, 0.1–1.5% and 5–50% are phytoavailable indicating that their availability depends upon physicochemical properties of soil rather than total contents in soil.

Assessment of soil contamination

In this study, a simplified approach to risk assessment based on comparing the measured level of contamination with established guidelines was adopted. Table 7 shows a comparison of mean concentrations in soil samples analyzed in this study and Maximum permitted limits (MPLs) prescribed by European Economic Community (EEC) Directive, world range of the regulated metals in unpolluted soils (Kabata-Pendias and Pendias 1992) and MAC in agricultural soils (Kabata-Pendias and Pendias 2001). These results and comparison with threshold of metal in natural background soil (site C) reveal some degree of heavy metal contamination. To evaluate the soil contamination extent, contamination factors (CF) and pollution load index (PLI) were calculated (Hakanson 1980; Tomlinson et al. 1980). Figure 7 shows the estimated CF for each element examined. PLI values calculated for C, B and A are 0.625, 1.208 and 1.573, respectively. As expected, contamination factor for Ni and Pb is moderate to slightly high in wheat and vegetable farms (sites A and B) due to continued irrigation with wastewater. The lowest CF is observed for Cd and Cr. Although concentrations of most heavy metals measured in soils are beneath or within critical levels, the severity of heavy metal accumulation in irrigation wastewater area is recognizable. The maximum permissible topsoil concentrations of Ni and Pb were reported to be 50 and 100 mg/kg respectively (Ross 1994). A comparison of the obtained results with these permissible limits reveals that topsoil has got metal levels (especially Ni and Pb) way above the permissible limits indicating significant contamination. Ni and Pb levels in wastewater-irrigated soils are 3.9 to 4.5 times more than the permissible limit. It is clear that long-term application of wastewater for irrigation will considerably elevate the concentration and accumulation of heavy metals in soils.

Heavy metal concentration in crops

Heavy metal concentrations found in crops sampled from site A, B and C are summarized in Table 8. It also gives maximum permitted limit of elements in vegetables and fruits. In general, the crops cultivated on wastewater irrigated soils show high level of heavy metals as compared to those grown on tube well water-irrigated soils. However, no significant variation in the levels of these metals among examined crops is found. At site A (wheat farm) where only wastewater is used, wheat have elevated contents of Ni and Pb (with mean values of 23.39 and 25.40 mg/kg, respectively) compared to those grown with tube well irrigation. At site B (vegetables land), spinach and lettuce accumulated relatively high content of Cd (with mean values of 3.59 and 2.17 mg/kg, respectively) which is five to eight times more than permissible limits. The same vegetables grown on the tube well-irrigated soils (site C) contain low levels of heavy

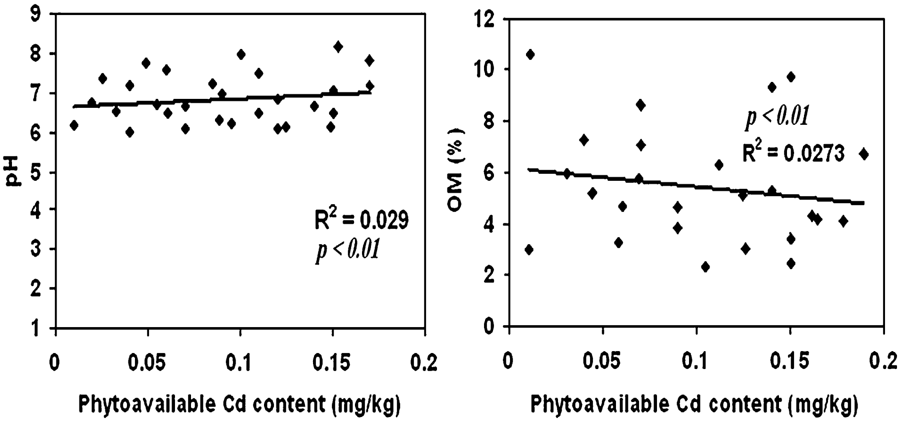

Fig. 5 Relationship between phytoavailable Cd content and soil pH and OM content in topsoil samples at site B

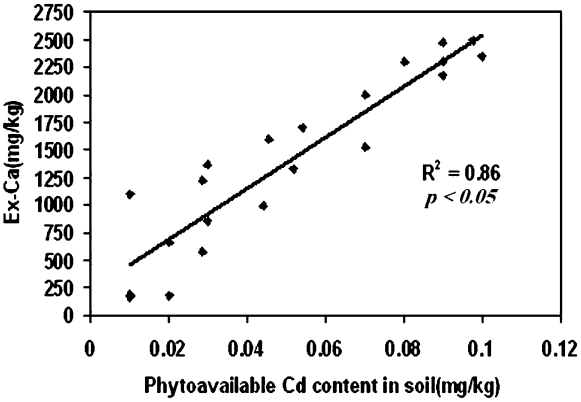

Fig. 6 Relationship between concentration of Ex-Ca and phytoavailable Cd content in soils of site B

metals (Table 7). A similar trend is also observed for celery. The mean concentration of heavy metals in the crops at sites A and B are decreased in following order when compared with relevant maximum permissible concentration: Ni > Cd > Pb > Zn > Cr.

The crops grown at sites A and B accumulated the heavy metals in the following decreasing order: wheat > spinach > lettuce > celery. From this study, it is difficult to elucidate the reasons for this trend. However, the accumulation effect strongly depends on the crop's physiological properties (Liu et al. 2005a). The data presented here show that wastewater has a clear effect on distribution and accumulation of heavy metals in the crops. It also indicates that crops grown along the banks of the Khoshk River are not free from heavy metal contamination. To appraise the extent of this contamination of crops grown on wastewater-irrigated soils, the observed concentration in the crop samples was compared with the corresponding maximum permitted limit (Turkdogan et al. 2003). The results are shown in Fig. 8. A ratio >1 indicates a certain extent of contamination. Among all analyzed crops, wheat is the most contaminated crop (for Ni and Pb) followed by spinach and lettuce (for Cd) confirming the above trend. Also, when the levels of some heavy metals in the crops are compared with the permissible levels required for safe food (set by FAO and WHO 1984), a strong divergence from these permissible limits will be observed (Table 9).Bahemuke and Mubofu (1999) and Kachenko and Singh (2006) reported high levels of Cd in spinach and lettuce above MPL, respectively, in Dar es Salaam (Tanzania) and Sydney basin (Australia). Alloway (1995) also showed that spinach, lettuce and celery can accumulate high level of Cd in their leaves.

Apart from physiological characteristics, the variations of the metal contents observed in the crops depend on the physical and chemical nature of the soil which in turn controls heavy metal bioavailability. It was known that high heavy metal contents in soils do not always imply high concentration in crops (Jones 1991). Inherent soil properties (such as pH, organic matter, texture, temperature, nutrient availability, etc) will determine the heavy metal uptake by plants (Sharma et al. 2007). Thus the occurrences of higher concentration of heavy metals in plants may be due to factors other than soil concentration. In this study, Cd content in spinach and lettuce were not related to its concentration level in corresponding soil. This indicates that even in the alkaline range, a significant proportion of heavy metals in soil appears in the

Table 7 Comparison of the mean concentration of heavy metals in wastewater-irrigated soils with MPLs and unpolluted soils

Heavy metal	Mean concentration of metals in soils of the study area (mg/kg DW)	World range of metals in non-polluted soils (mg/kg DW)[a]	MAC of heavy metals in agricultural soils (mg/kg DW)[b]	Limit values of heavy metals proposed by EEC sludge directive (mg/kg DW)[c]
Ni	275	1–200	20–100	15–70
Pb	441	10–70	20–300	70–100
Zn	177	17–125	100–300	60–200
Cd	0.4	0.07–1.10	1–5	0.5–1.5
Cr	25	5–120	50–150	30–100

MAC: maximum allowable concentration, *EEC*: European economic communities, *DW*: dry weight

[a] Kabata-Pendias and Pendias (1992)

[b] Kabata-Pendias and Pendias (2001)

[c] Stuczynski and Maliszewska-Kordybach (2001)

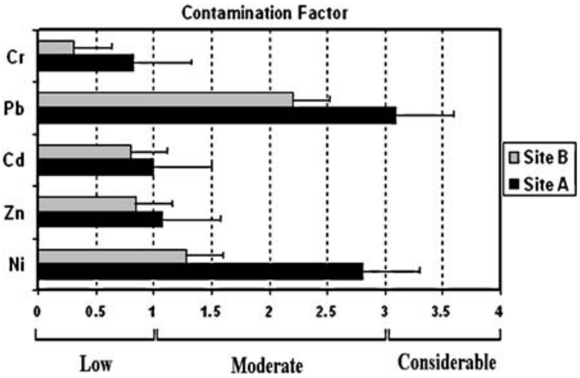

Fig. 7 Contamination factors for heavy metals at the two wastewater irrigated sites A and B

bioavailable fraction that is also easily available to plants as proposed by Xian 1987. Phytoavailable Cd content in topsoil samples is positively correlated with its content in plant (Fig. 9). It seems that high nutrient input (especially Ca) from wastewater at site B resulted in relatively high growth rates and hence high Cd uptake. High addition of calcium through long-term wastewater application has probably increased the availability of exchange sites in topsoil which are preferentially occupied by Cd and consequent uptake by plant. Due to complexity of the soil environment, however, the above interpretation needs further investigation.

There is a positive correlation between Pb and Ni concentrations in soil and their corresponding levels in wheat plant (Fig. 10a). This indicates that although phytoavailability of Pb and Ni is low at high pH, these metals are generally immobile at pH>7 and hence the risk of their absorption by plants will be highest at site A where there has been a long-term wastewater application. However, there is no correlation between phytoavailable Pb and Ni content in soil and their concentrations in wheat (Fig. 10b). This may be related to physiological characteristics of the plant and its different ability to take up and accumulate metals. In order to assess the transfer of metals from

Table 8 Mean concentration of heavy metals in crops cultivated in the study area (in mg/kg, dry weight)

	Ni		Pb		Zn		Cr		Cd	
	A	C	A	C	A	C	A	C	A	C
Wheat	20.33	0.53	25.45	0.09	41.96	35.53	0.93	ND	0.43	0.01
	27.19	0.14	26.23	0.02	44.91	44.14	0.73	ND	0.45	ND
	25.12	1.24	25.47	0.10	39.96	48.30	0.95	ND	0.43	0.02
	24.99	0.23	25.45	0.04	48.79	45.15	0.66	0.02	0.24	0.02
	20.20	0.15	24.45	0.09	48.38	42.97	0.72	0.01	0.49	ND
	B	C	B	C	B	C	B	C	B	C
Lettuce	0.03	0.01	0.65	0.03	3.75	2.17	0.17	ND	2.01	0.03
	0.01	0.01	0.12	0.10	1.59	3.33	0.01	ND	2.03	0.01
	ND	ND	0.97	0.02	3.67	2.47	0.05	0.01	2.17	0.06
	ND	ND	0.66	0.19	3.45	4.69	0.02	0.01	2.56	0.02
	ND	ND	0.12	0.05	3.29	3.12	0.05	0.02	2.13	0.01
	B	C	B	C	B	C	B	C	B	C
Spinach	0.05	0.01	1.93	0.05	2.73	1.95	ND	ND	3.42	0.01
	0.12	ND	2.14	0.02	2.19	1.17	ND	ND	4.12	ND
	0.13	0.01	2.93	0.03	1.75	1.03	ND	0.07	3.19	0.01
	0.09	0.03	1.15	0.05	3.19	1.33	0.01	0.01	3.33	0.05
	0.06	0.01	1.34	0.02	3.14	1.75	0.01	0.01	3.99	0.04
	B	C	B	C	B	C	B	C	B	C
Celery	0.21	0.01	0.05	0.09	2.97	1.11	0.01	0.05	2.19	0.01
	0.17	ND	0.01	0.08	4.19	1.34	0.05	0.03	1.77	0.03
	0.18	0.01	0.09	1.00	3.67	1.33	0.05	0.07	1.95	0.05
	0.14	0.06	0.07	0.07	2.33	2.75	0.03	0.04	1.11	0.15
	0.15	0.05	0.07	0.02	3.14	1.66	0.01	0.02	1.65	0.95
	10		*9*		*100*		*1*		*<0.5*	

Last row in italics indicates MPLs in vegetable and fruits (Turkdogan et al. 2003) The letters A, B and C are the three investigated sites. *ND*: not detectable

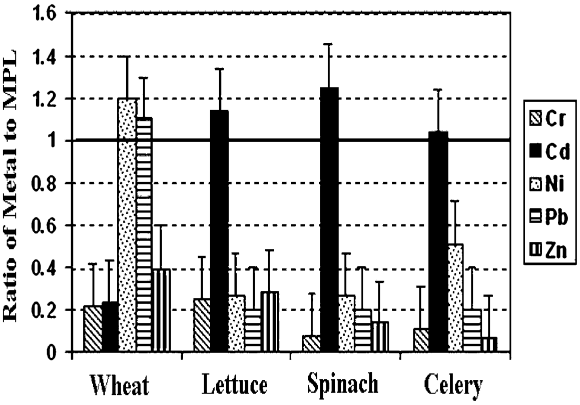

Fig. 8 Contamination extent in cultivated crops in the study area as compared to MPLs

soil to crop, the transfer factor (TF) values of the five analyzed metals were calculated. Soil–plant transfer factors are obtained by dividing the metal concentration in the crop (dry weight) by the EDTA-extractable metals in the soil (dry weight) from where the crop was grown (Cui et al. 2004). This is a convenient way of quantifying the relative differences in bioavailability of metals to plant. The results show that the highest transfer values belong to Cd (1.4–34.2), and Zn (0.21–0.28). The high TF values for Cd from soil to crop indicate a significant accumulation of this element by vegetables confirming its high phytoavailability in soils. This also indicates that as far as entry of these heavy metals to food chain is concerned, spinach and lettuce have the greatest potential for Cd.

Table 9 A comparison of heavy metal levels in cultivated crops of the study area and international limits

Heavy metal	Mean concentration of metals in vegetables and crops of the study area (mg/kg)	Permissible levels set by FAO/WHO[a] (mg/kg)	Maximum levels prescribed by other authorities (mg/kg)
Ni	23.39	NA	NA
Pb	25.40	0.30	0.30[b]
Zn	44.66	60.0	50.0[c]
Cd	2.36	0.20	0.20[b]
Cr	3.39	NA	NA

NA: not available

[a] Codex Alimentarius Commission (1984)

[b] Commission Regulation (No 466/2001)

[c] United Kingdom regulation (1989)

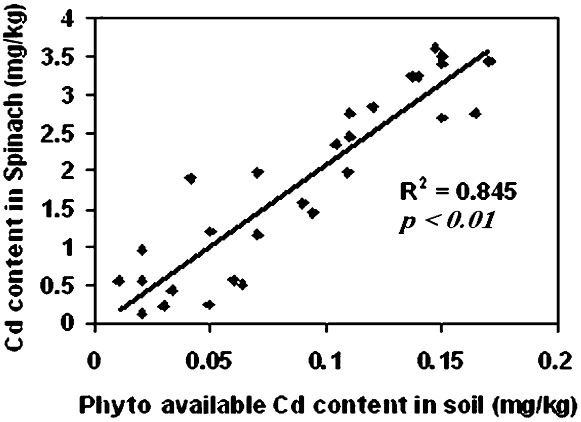

Fig. 9 Relationship between Cd content in spinach and phytoavailable Cd content in soils of site B

Human exposure risk assessment

In the study area, spinach, lettuce and celery are produced and marketed as leafy green vegetables. Hazard quotients (HQ) through the consumption of these leafy vegetables were calculated. The values (HQ) for lettuce range from 0.95 to 2.52 for Cd and from 0.001 to 0.003 for Ni. In the case of spinach, HQ varies from 0.08 to 4.35 for Cd and from 0.005 to 0.01 for Ni. HQ of celery ranges between 0.01 and 0.95 for Cd and 0.03 and 0.11 for Ni. It can be observed that sum of HQ values of lettuce and spinach are more than 1 for Cd. Hence, these green vegetables are likely to induce some health hazard to consumers as far as their metal contents are concerned.

Estimates made in Shiraz region, show that the average consumption of leafy vegetables per person per day is about 105 g (Maddady and Ghasemi 2001). Estimated daily intake in relation to each heavy metal show that by consuming these green vegetables grown at site B, an adult will intake 24 mg Cd, 0.98 mg Ni, 7 mg Pb, 10 mg Zn and 0.2 mg Cr. For Cd, DIM value is 20 times more than the oral reference dose (0.001 mg Cd/kg/day) recommended by Integrated Risk Information System (USEPA 2003). For other analyzed metals, DIM values are within the critical levels. Furthermore, if the mean level of cadmium is consumed daily, then the contribution of the green vegetables to dietary intake of an individual for this metal will be 356 mg per day which is above 10–30 mg per day reported from other countries (Reilly 1991). It is evident that excessive accumulation of heavy metals in vegetables and crops may pose serious threat to the residence, which rely on crops

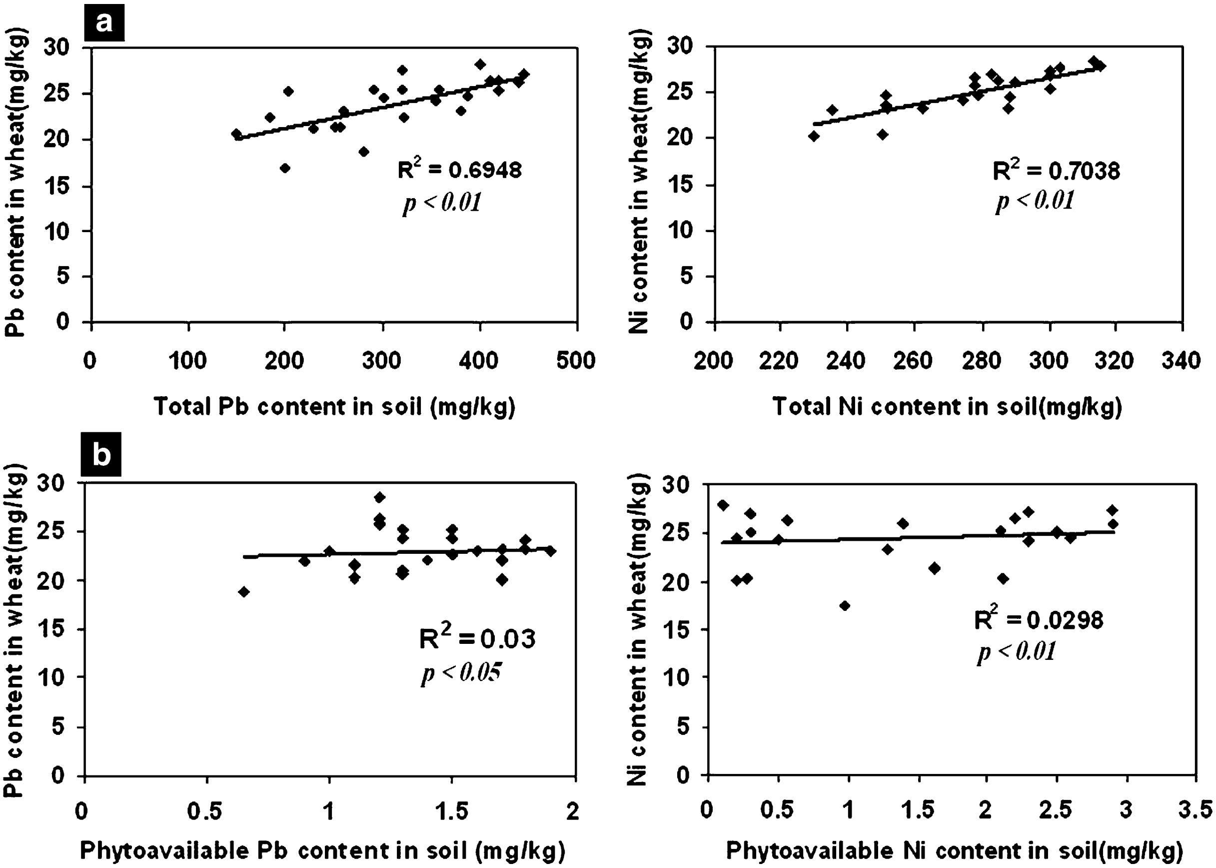

Fig. 10 **a** and **b** Relationship between Pb and Ni content in wheat and their total and phytoavailable contents in soils of site A

grown in suburban lands. Some systemic health problems such as hepatic damaging, renal system damaging, mental retardation and CNS breakdown can develop as a result of accumulation of dietary heavy metals in the human body (Misra and Dinesh 1991).

Concluding remarks

This is the first study on the potential impacts of wastewater irrigation on soil properties and heavy metal contents in soils and crops in suburban area of Shiraz. The results obtained from this preliminary study show that use of wastewater for irrigation purposes in the study area lead to change in soil quality (pH, OM, Ex-Ca), increase in heavy metal concentration in soil (notably Ni and Pb) and crops (Cd and Ni) and probably pose potential health risk through consumption of affected vegetables (HQ>1). Although the present severity of this situation is moderate, long-term application of wastewater will maximize the rate and extent of future contamination problems. Each of these problems is a matter of concern and needed to alleviate. In order to minimize the negative impacts of wastewater irrigation in the study area, the following approaches are proposed:

1. Strict legislation and stringent standards must be enforced to prevent the use of wastewater for irrigation purposes.
2. An integrated system for the treatment and recycling of wastewater needs to be developed in the study area. For this purpose, governmental authorities should provide prompting or supporting mechanisms. Loans with low interest rate and long term bank credits are proper options. Also, state and local governmental agencies should make legal constraints easy to any person desiring to dig a tube-well.
3. In order to terminate irrigation with wastewater, the farmers are obligated to remove all pump installation along Khoshk River banks. It is also

proposed that through a general education program, they become aware of the negative impacts of wastewater irrigation.

4. With respect to long term application of wastewater in affected sites, operational monitoring should be conducted to verify the build up of heavy metals in view of their significant accumulation in phytoavailable fraction associated with changes in soil properties.

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