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Evaluation of heavy metals pollution in groundwater, soil and some vegetables irrigated with wastewater in the Skhirat region "Morocco"

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Abstract

A field survey was conducted from April to June 2013 in region of Skhirat-Rabat -Morocco to evaluate the heavy metals contamination in shallow well, soils and vegetables, where wastewater are used. The evaluation was done by chemical characterization by measure of contamination levels with Iron (Fe), Copper (Cu), zinc (Zn), Manganese (Mn), Nickel (Ni), Chromium (Cr), Cadmium (Cd) and lead (Pb). Results showed that both shallow wells within line of Food and Agriculture Organization (FAO) and World Health Organization (WHO) recommendations to irrigate with the mean of 0.520, 0.014, 0.051, 0.435, 0.251, 0.286, 0.0017 and 0.062 mg/L. On the other hand, results indicate that there is a substantial buildup of heavy metals concentrations in canal wastewater above FAO and WHO recommendations with respectively mean of 1.32, 0.043, 0.230, 0.70, 0.67, 0.41, 0.01, and 0.093 mg/l. And when soil was analyzed results for most of the elements were observed ordinary value except for Cr, and Pb with respectively average of 276.67, and 107.19 mg/kg. Data Statistical analysis indicated that canal wastewater obtained values were in high significance amount relatively to elements P, K, S, Zn, Cu, Fe, Mn and Ni compared to shallow well. Also sludge was found in high significance concentrations above normal soil. It is noticed that when vegetables were analyzed; Fe, Cu, Zn, Mn, Ni and Cd showed normal value within the prescribed safety limits at all tested samples, with an average of 456.55, 16.41, 40.11, 81.76, 44.61, and 0 mg/kg. While, concentrations of Cr and Pb in all tested samples have crossed the safe limits for the prescribed safety limits with respectively mean of 14.36 and 13.78 mg/kg. Mint and leek registered maximum content of Cr, whereas high amount of Pb in Parsley and cabbage was recorded the highest value for Ni. Thus we expect that consumption of Cd and Pb through vegetables poses substantial health risk to consumers and for this reason perhaps these products are unfit consumption. Therefore, this emphasizes the need for proper method to manage using wastewater to reduce the health risk and the extent of heavy metals contamination.

Keywords: Heavy metals • Wastewater• Vegetables • Soil

Introduction

The implications associated with heavy metals contamination have considered one of a serious environmental pollutant. It was said that heavy metals in most cases are accumulated in the crop, and could adversely affect consumers feeding on these crops especially group of heavy metals which have been shown to create clear health hazards when taken up by plants [1,2]. Also vegetables are known to be good absorber of heavy metals from the soil [3,4]. The danger lies in its ability to accumulate in the bodies of local residents. [5].Human and animal need a certain percentage of these elements that might happen on the part of the plant through the food chain [6]. The accumulation of heavy metals and metalloids in agricultural soils is of increasing concern due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems [7]. The increase in concentration is a result of vegetables growth in soil contaminated with these elements, owing to geological weathering factors to the soil or as a result of excessive use of fertilizers. Agricultural chemicals, laboratories and factories residues and sewage are often the pollutant source of irrigation water [6]. Currently, there are more area of agricultural land in the world are using untreated wastewater for irrigation due to lack of water [5]. Also Pescod [1] reported that surveys of wastewater use have shown that more than 85% of the applied heavy metals are likely to accumulate in the soil, most at the surface. Consequently, wastewater treatment plants will pose additional risks to public health. Research and studies conducted on vegetable farms irrigated with wastewater and contaminated water demonstrated that this vegetable contains substantial concentrations of heavy elements that make them unfit for consumption [8]. Skhirat area with a total surface of 485 km^2, 393262 inhabitants and extends in western Rabat city. It's considered one of the important agriculture areas to vegetables and cereal production in Morocco. There are major vegetables grown in this district for own consumption of the farmers and for supply to retail and wholesale markets of nearby cities. In where, treated wastewater and wells are the main irrigation source for farmland. Moreover they apply sludge as fertilizer. Therefore, we expect that wells and soil suffers from a significant change in physical-chemical properties as a result of contamination with canal wastewater across Skhirat district [9,10].The accumulation of heavy metals in agricultural soils is of increasing concern due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems [7].There is no assessment conducted in this area in the region. So, the aim of this current research conducted from April to June 2013, was to assess the concentrations of heavy metals in order to gain a better understanding of its source used in vegetables production, their behavior in the field environment: water, soil and vegetables which watered by this sources-fed from wastewater's canal.

2. Material and Methods

2.1. Sampling

Water, Soil and plant samples which irrigated with contaminated water were collected from 3 sites across Skhirat district. The sites were a commercial vegetable farms and they are considered one of the most important site to supply vegetable markets in nearby cities. 54 samples of different vegetables**,** 27 samples of soil and 24 samples from water sources were collected randomly from Skhirat district (Production sites) between April and June 2013. The treated vegetables are tomato, parsley, mint, coriander, leek, and cabbage. Samples were then taken from the water sources which are 3 sites from wastewater channel C and 5 shallow wells (W1,W2,W3, W4 and W5) from which we took the above-mentioned samples of plants and the soil samples are divided between sludge, soil/sludge mixtures (mixed sludge & soil at a rate of 50 to 50) and normal soil depth of 20 cm. It is noticed that the sampling points were statistically distributed all over the study area to ensure appropriate spatial coverage of the zone. The considered sites were of commercial vegetable farms. The importance of the study is that the Skhirat regions were within close proximity to wastewater station site. Therefore, the cultivation of some vegetables uses mostly sludge as type of organic amendment in addition to chemical fertilizer.

2.2. Water analysis

In this step of the research, wastewater samples (Nine separate liters from thee points of wastewater channel and fifteen litres from shallow wells, three separate liter from every well) were carefully taken and filtered through Whatman number 0,42 µm filter paper and were stored at less than 4°C until analysis.

2.3. Soil analysis

Nine separate kg from sludge samples. Also with dimensions of about $50m^2$, 5 points at depth of 20 cm in all farms were chosen to take mixed sludge & soil and normal soil samples. Samples were mixed individually then analyzed sample was taken from the mixture. 1kg from every sample was air-dried, mechanically ground using a stainless steel roller and sieved to obtain 2 mm fraction. A 20–30 g subsample was drawn from the bulk soil (2 mm fraction) and reground to obtain 200 μm fraction using a mortar and pestle. Soil samples were digested in an aqua reguia mixture of concentrated nitric acid (HNO3), concentrated hydrochloric acid (HCl) and according to Pint [11].

2.4. Plant analysis

To carry out the operation, 500g from every plant samples were dried at 70^oC in hot air oven, and then incinerated at 500^oC in a muffle furnace. The ashes were then solubilized in concentrated HCl [11].

2.5. Heavy metals analysis

These transparent solutions of water, soil and vegetables samples were then filtered through Whatman number 42 µm filter paper and diluted to 100 mL with distilled water. The concentrations of Fe, Cu, Zn, Mn, Ni, Cr, Cd, Pb in the filtrate were determined by using atomic absorption spectrophotometer [11]. Fitted with a specific lamp of particular metal using appropriate drift blanks in laboratory of research of environment and conservation of natural resources *INRA, RCAR-Rabat.*

Statistical analysis

The data of the present research were statistically analyzed by SAS Institute Inc.,Cary copy right © 2002. NC, USA. Software version 9.00 (TS MO).

3. Results and Discussion

3.1. Water samples

Results summarized in Table 1, indicate that concentrations (mg/L) of heavy metals in wastewater channel were highest relatively for the Fe, followed by Mn, Ni, Cr, Zn, Pb, Cu and Cd. However, heavy metals concentrations in groundwater meet the permissible limits of FAO [1,12],Pint [11] Row and Abdel-Majid [13]. Same detection was also obtained by Rattan *et al*., [14] and Singh *et al.*, [15] who have found higher concentrations of heavy metals in sewage effluents when compared to the ground water. Overall concentrations of heavy metals in the different types of used water samples over the study area did not exceed the permissible limits except for Chromium, and Manganese with the main average, respectively, 0.286 and 0.435 mg/L and these exceeds the allowable 0.01 mg /L of FAO [12],As well Ni showed slightly high in W1, and W2. It's known that Chromium element is a toxic and has been considered one of a noxious elements carcinogens which cause lung carcinoma when is exposed to substantial concentrations [12].Then, it is often found in waste plants dyes, plastic and rubber factories, electrical panels and batteries [13]. The concentration increase of this element in the water sources happened as a result of contamination with canal wastewater across the region. This result indicates that the use of this water for irrigation purposes could expose population to dangerous healthy risks and could damage the environment [17].

Table 1: Heavy metals concentrations (mg/L) in water samples collected from the study area compared to the limited standards

Sites	N.S.	Fe	Cu	Zn	Mn	Ni	Cr	Cd	Pb
C	9	1.32	0.043	0.230	0.70	0.67	0.41	0.01	0.093
W1	3	0.23	nil	0.027	0.37	0.52	0.17	nil	0.083
W2	3	0.31	nil	0.009	0.40	0.28	0.12	nil	0.060
W3	3	0.38	nil	0.0003	0.44	0.02	0.41	nil	0.033
W4	3	0.47	nil	0.027	0.38	0.02	0.44	nil	0.030
W5	3	0.42	nil	0.014	0.32	nil	0.17	nil	0.070
St. limited		5.0	0.2	2.0	0.2	0.2	0.1	0.01	5
Total/Av.	24	0.520	0.014	0.051	0.435	0.251	0.286	0.0017	0.062
significance		P>.0001	P>.0001	P>.0001	P>.0001	P>.0001	P=0.0146	P>0.0001	P=0.0001

N.S= Number of samples, C= canal wastewater, w1-w5= shallow wells and St. Stander limited

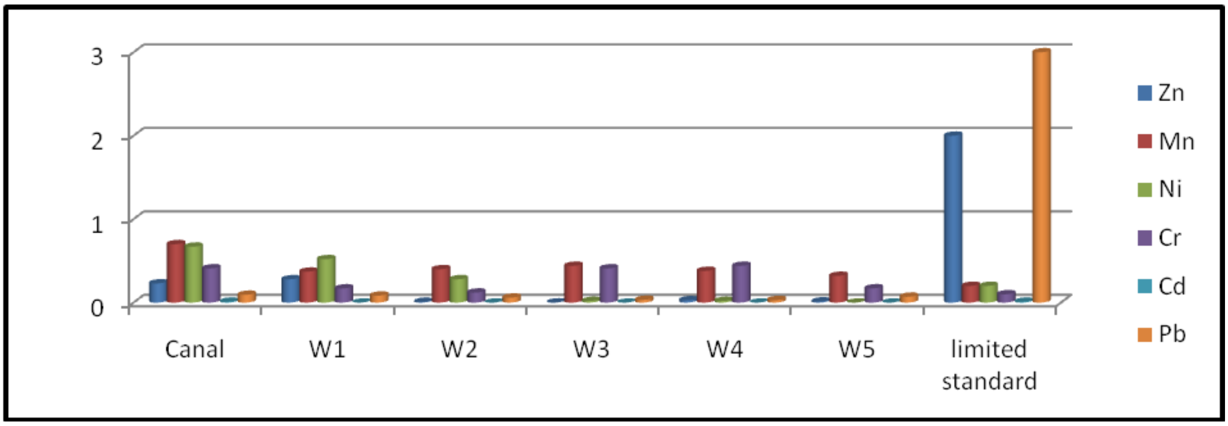

Figure 1: Heavy metals concentrations (mg/L) in water samples

Therefore, higher Cr concentration in W3 and W4 perhaps due to short distance from main wastewater canal which considered as potential source of heavy metals thus this is obvious indication that wastewater canal is the main source of contamination of these shallow wells [18].The distribution of metals in wells at each site was mainly affected by the location of the wells. Investigation in West-Africa proved that elements migrate into the deep soil layers and can be hazardous for shallow groundwater [19]. Also similar result was showed in Haiti by Emmanuel *et al*., [20] and in Australia by Hanjra *et al*., [21]. However, all concentrations of heavy metals in municipal wastewater still low due to low heavy industry activities in the region.

3.2. Soil samples

Data presented in (Table 2) demonstrated that concentrations of heavy metals in normal soil samples are low. We observe a clear increase of heavy metals in sludge and soil/sludge mixtures for all tested elements except Zn and Cr have reached extremely high concentration in each of these samples compared to 300 and 100 mg/kg of WHO [12], FAO [1] maximum allowable in soil. A study done by Catherine [22] in Nairobi has shown that Cr accumulation in the soils could be attributed to long term continuous application of waste water that indeed passes through paints, lubricants, leather and textile . The soil concentration of Fe, Ni, Pb, Cd and Mn were mostly normal except at sludge and soil/sludge mixtures. A Pb content in soil amended with contaminated sludge**,** was slightly higher compared to normal soil. Those farmlands use sludge as fertilizer in rate 50/50 sludge-soil. There is a confirmed relation between the use of sludge and contaminated water on buildup of heavy metals in soil [23,24]. Heavy metals reported constitute a major problem in agricultural land receiving wastes such as sewage sludge [17,25]. Also, it was reported in Australia that irrigation with wastewater may lead to accumulate heavy metals in soils, which can affect soil flora. This effect was attributed to the toxic metals present in wastewater and sludge on soil microbes [26,27] and may therefore result in crop contamination [21]. We noted in all dates of sampling, that the heavy metal concentrations decreased in sludge when mixed with soil but remained much higher than the normal soil.

Table 2: Heavy metals concentrations (mg/kg) in selected sludge and soil samples collected from farmers in the study area compared to limited standards

Varieties	N.S.	Fe	Cu	Zn	Mn	Ni	Cr	Cd	Pb
Sludge	9	573.9	520.67	1500	64	54.67	430	2	205
soil/sludge	9	495.1	185.67	555	85.67	46.83	271	1	75
Normal soil	9	145.16	78.38	193.33	88.91	34.22	129	0	41.67
Total/Av.	27	404.7	261.72	749.44	79.53	45.24	276.67	1.17	107.19
St. limited		-	100	300	2000	50	100	3	100
significance		P<0.0001	P=.0001	P<0.0001	P=.0057	P=.0010	P=.2458	P=.0001	P<0.0001

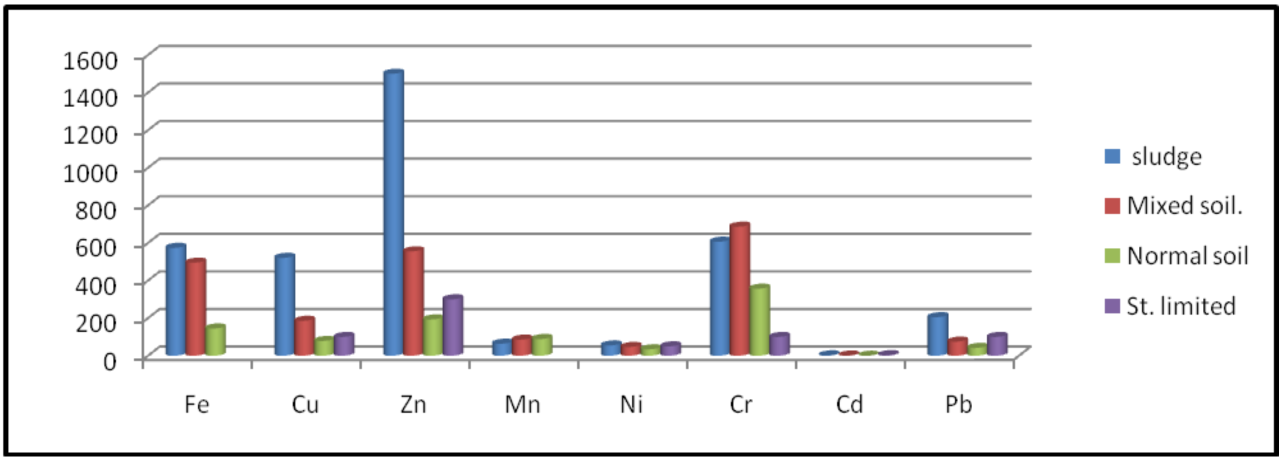

Figure 2: Heavy metal concentrations (mg/kg) in selected sludge and soil samples

It was inferred from the study that sludge of wastewater constitutes potential source of heavy metals contamination. Hence may constitute an environmental and health challenges in the long-term. Therefore, enrichment the soil with heavy metals confirms the sanitary risk related to sludge application in agricultural lands [6]. Then, using of sludge as a fertilizer source or as a mixed with soil at 50/50 is not suitability to produce quality vegetables nor to protect the environment which is necessary for a sustainable life of animals and humans.

3.3. Vegetables samples
Heavy metals present in edible portions of studied vegetables are in table 3. The vegetables concentration of Fe, Cu, Zn, Mn, Ni and Cd and Pb were mostly observed normal in every tested sample with respectively average of 456.6, 16.41, 40.11, 81.76, 44.61 and 0 mg/kg except Cr and Pb were in high concentrations with average 14.36, and 13.78 mg/kg which imply that Cr and Pb concentration was in real increase above 0.5 mg / kg of FAO/ WHO [28] and Pint [11] recommendations. These two elements were likely to be a health hazard to human consumers. They may further lead to toxicity not only to plants and animals but also to consumers through the food chain [29]. In fact the highest concentration of lead was recorded in the Parsley plant equal to 16.67 mg/kg. Whereas, Mint had the highest concentration of Chromium among all tested samples, and evaluated to 28.73 mg/kg. Lead can be absorbed through

ingestion into the body. It is reported that young children absorb from 40% to 53% of lead ingested from food. It enters either a "rapid turnover" biological pool with distribution to the soft tissues (blood, liver, lung, spleen, kidney, and bone marrow) or a "slow turnover" pool with distribution mainly to the skeleton. This causes brittle bones and weakness in the wrists and fingers [30]. The seriousness of this issue lies in their capacity of accumulation in human body that these elements are very dangerous and considered as toxic and lung carcinogens in highly exposed cohorts [16,31]. Also, they can cause physiological damage, such as mental retardation and a lack of vital functions [32]. Highest accumulation of Pb has been reported in other contaminated sites in some vegetables in Nebal such as in Kathmandu Valley [33] in China, such as in Nanning province [10]. On the other hand, Cr was found in mean concentration which was a proximately 45.93 times higher than 0.3 mg/kg value set by FAO/WHO [28]. According to Gupta *et al*. [34] among the heavy metals aforementioned, Cr is of greatest concern due to its high uptake rates in plants, its accumulation in vegetal's tissue and the possibility of implicating in a health hazard associated with the consumption of these heavy metal-contaminated vegetables over a long period. A correlation has been found between exposure to Cr by the inhalation route and lung cancer [34]. Several species of vegetables have the tendency to hyperaccumulate certain of heavy metals if they are present in soil and water resources. [34-36]. The concentrations of Pb, and Cr that were obtained in every samples from this area are alarming therefore, we conclude that both Cd and Pb in vegetables pose a real risk to consumers according to Cuia *et al.* [10] and Sheldon [37].

Table2. Heavy metals concentrations (mg/kg) in some vegetable samples collected from farmers in the study area compared to limited standards

Varieties	N.S	Fe	Cu	Zn	Mn	Ni	Cr	Cd	Pb
Tomato	9	145.8	7.97	26.07	62.93	56.93	10.77	nil	11
Coriander	9	492.1	19.47	55.27	85.23	31.00	10.10	nil	14.67
Parsley	9	524.5	28.47	46.70	89.83	26.43	10.83	nil	16.67
Mint	9	596.1	20.27	58.77	97.90	49.47	28.73	nil	13.67
leek	9	601.9	16.17	37.73	79	18.83	19.87	nil	11.33
Cabbage	9	378.4	6.1	16.13	75.67	85.00	5.83	nil	15.33
St. limited		1000	73	100	200	67	0.5	0.1	0.3
Total/Av.	54	456.55	16.41	40.11	81.76	44.61	14.36	0	13.78
significance		P=0.0038	P=0.0110	P=.0017	P=0.0565	P=0.0239	P=0.4901		P=0.0139

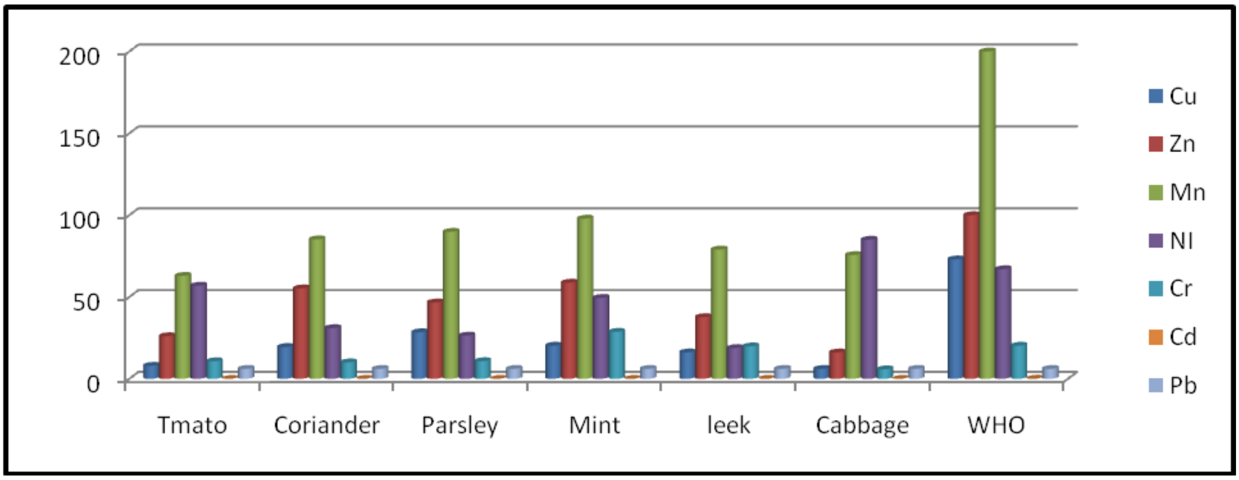

Figure 3: Heavy metal concentrations (mg/kg) in some vegetable samples

We believe think that using pesticide and chemical fertilizer alongside sludge in the farms is an additional reason for transferring Cr, Ni and Pb from soil to edible parts of the crops [38,39].Therefore, the increase concentrations are seen as a result of a root uptake from soil to the vegetables [21]. The mean concentration of Ni in tomato, coriander, parsley, mint, and leek was lower than those reported in Food Standards Program of FAO/WHO [28].Although that Ni concentration in the soil did not exceed the allowable limit cabbage has about 85 mg/kg above of 0.267 mg/kg set by FAO/ WHO [28]. This phenomenon is explained by the large capacity of this plant to concentrate the metal while it is low in the soil [2,32].

Conclusion

In all the heavy metals cadmium and lead are common air pollutants being emitted mainly as result of various industrial activities. Although the atmospheric levels are low, they contribute to the deposition and build-up in the soils. Heavy metals are persistent in the environment and subject to bioaccumulation in foods chain and therefore constitute real dangerous healthy risks for human and animal. These important sources of these elements can increase the levels of these heavy metals in wastewater which is a real health risk if these waters are used for irrigation. Because of these risks, our team research have drawn as future goal to go on the study on heavy metals and concentrate its technological idea around the efficient way in order to develop efficient and sensitive process for removing heavy metals from certain interesting matrices related to foods chain.

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