Uptake and distribution of heavy metals in agricultural production irrigated by raw wastewater

Mohamed SBAA¹, Hassan CHERGUI ², Mohamed MELHAOUI ¹ & Abderrahime BOUALI ³

(Received  05/10/1999 ; Revised 08/07/2000 ; Accepted  08/09/2000)

¹ Laboratoire d’Hydrobiologie et Écologie Générale. Fac. Sc. Université Mohamed Premier, Oujda
² Laboratoire d’Hydrobiologie et Écologie Générale. Fac. Sc. Dhar Elmahraz. Université Mohamed Ben Abdellah, Fès
³ Laboratoire de Génétique et Biotechnologie Végétale. Fac. Sc. Université Mohamed Premier, Oujda

A field experiment was carried out to determine iron, copper, zinc, nickel, cadmium and lead concentrations in a soil irrigated by raw wastewater and in the tissues of various plants of great economic importance: broad bean (Aphis fabae L.), carrot (Daucus carota L.), pea (Pisum sativum L.), lettuce (Lactuca sativa L.) and oats (Avena sativa L.). The plots irrigated with raw wastewater have a higher rate of organic matter than the control plot. The concentrations of Cu, Zn, Pb and Cd in the plots irrigated by wastewater are higher than those of the control plot (P) and the soils polluted by heavy metals. In the tissues of plants irrigated by wastewater, the content of metals are higher than those of normal values recorded in vegetable species.

Key words: Wastewater - Contamination - Soil - Vegetables - Bioaccumulation - Heavy metals

Bio-accumulation des métaux lourds dans la production agricole irriguée par des eaux usées brutes

Une expérience au champ a été réalisée pour déterminer les concentrations en fer, cuivre, zinc, nickel, cadmium et plomb dans le sol du champ d’épandage d’eaux usées et dans les tissus de divers plantes de grande importance économique : fève (Aphis fabae L.), carotte (Daucus carota L.), petit pois (Pisum sativum L.), laitue (Lactuca sativa L.), blé tendre (Triticum vulgare L.) et avoine (Avena sativa L.). Les parcelles irriguées par les eaux usées présentent des taux de matière organique largement supérieurs à celui de la parcelle témoin. Les concentrations en métal (cuivre, zinc, plomb et cadmium) dans les parcelles irriguées par eaux usées sont supérieures à celles de la parcelle témoin (P) et des sols pollués par métaux lourds. Dans les tissus des plantes irriguées par ces eaux usées, le teneur en métal est élevée par rapport aux valeurs normales rencontrées chez les espèces végétales.

Mots clés : Eaux usées - Contamination - Sol - Végétaux - Bioaccumulation - Métaux lourds
INTRODUCTION

The soil naturally contain essential elements for plants such as Zn, Cu, Co, Fe, Mo, Cr, Mn and undesirable elements such as Cd, Pb, Hg. To this natural level can be added contaminations of varied origin:
- proximity to the mining deposit (Bonnefoy & Bourg, 1983; Mouvet et al., 1982; Nourisson et al., 1986),
- agrochemicals: water of irrigation, agroalimentary wastewater, urban compost, sludge of the stations wastewater purification with splay of Cd, Pb, Hg and in less great quantity, Zn, Cu, Cr, Ni (Department of the Environment, 1982),
- phytosanitary processing, (iv) impurities contained in some fertilizers (Cd) (Department of the Environment, 1982), (v) atmospheric pollution and road axes (Department of the Environment, 1982).

The soils pollution, hidden for a long time or been ignored, settles in the receiving medium for long years. It is discovered only too late in certain situations, which presents a real and immediate threat for man. The most significant properties influencing the contamination of the soil as well as the mobility and the solubility of the contaminants are: the composition of soil matrix (organic and mineral matter contents), the heterogeneity of soil, pH, redox potential and variations of concentration of dissolved organic matter (Hesterberg, 1998).

Moreover Serpaud et al. (1994) underline the particular role of the reducible fractions (iron oxides and manganese) and organic matter (particularly humic substances) of which respective properties of ions exchange and complexation were often verified.

The plants bio-accumulation is one of the most significant mechanisms by which heavy metals enter the food chain. Indeed the transfer of Cd in the food chain was found: such as the Itaï-itai disease which resulted from the consumption of rice (Oryza sativa) growing on soil contaminated by Cd.

The accumulation of heavy metals in the plants concerns their fundamental physiological activity. According to Baker (1981), the plants can be indicative of the soil on which they develop. The symptoms, when they exist, can be symptoms of deficiency or toxicity which can be superposed (Bussler, 1981). Some species of plants appeared to be very good indicators of metal contamination, such as Artemis artemisia (Greffard et al., 1983), lettuce and radish (Gomez et al., 1983).

The wastewater could bring some toxic metals to the plant, such as lead, mercury, cadmium, aluminium, chromium and other. In the absence of industrial dismissals, the Moroccan domestic wastewater are characterised by some weak contents in trace metals. They are present in quantity below the level fixed by the FAO for the quality of the water used in the irrigation (Ratel et al., 1986).

The yearly volume of raw wastewater rejected by Oujda city (East of Morocco) is 6307 $10^3$ m$^3$/year. The impact study carried out in the Marrakech area irrigated by raw wastewater, have shown that the human population of this zone have the rate of Cd and Pb exceeding the recommended threshold by OMS (Sedki & Lekouch, 1996).

The objective of this research is to quantify the accumulation of heavy metals which are drained by domestic wastewater of the town of Oujda, in the soil and in the plants tissues. What would make it possible to draw up the ecotoxicological assessment of the irrational re-use of raw wastewater of Oujda city in agriculture.

MATERIALS AND METHODS

The samples of domestic wastewater of Oujda city were taking at the source of rejection, at different times in order to follow the rates of heavy metals (Cd, Cu, Pb, Ni, Zn).

Concerning the receiving medium (sewage field), the soil is calcimagnesic type, having a significant amount of organic matter. The depth of soil varies between 30 to 50 cm in the studied plots. The geological substratum is made of a calcareous crust. The cultivated crops are: fodder crops, cereals, arboriculture and market gardening.

Three plots ($P_1$, $P_2$, $P_3$) of 200 m$^2$ were established in the sewage field of domestic wastewater. They are irrigated by raw wastewater, in continuous manner during several years (approximately 30 years). The plot $P_1$ is excessively irrigated by wastewater, because of its proximity to the source of water rejection. Moreover, the crops grown on this plot such as oats, require a continuous water
contribution. For the plots P₂ and P₃, the wastewater is applied generally twice per week during the year. The type of crops applied in the latter plots are either lettuce, broad bean, pea, carrot or common wheat.

A fourth agricultural plot of 200 m², showing the same soil characteristics and is not irrigated by raw wastewater, was used as a control plot in the experimental design.

Six others plots were selected from the sewage field in order to take plant samples. The species considered are: broad bean (*Aphis fabae* L.) (4 months after seedling), pea (*Pisum sativum* L.) (4 months after seedling), carrot (*Daucus carota* L.) (3 months after seedling), Laituce (*Lactuca sativa* L.) (2 months after seedling), tender wheat (*Triticum vulgare* L.) (5 months after seedling) and oats (*Avena sativa* L.) (6 months after seedling). Each type of culture corresponds to one of the six plots of land.

The samples correspond to the shoot system of various types of culture except for the carrot where the taking away were carried out in both shoot and root systems.

The sampling procedure used is that of the composite sample: for the soil, twelve samples were taken on each plot then mixed to constitute only one composite sample.

For each plants, an average composite sample is taken from each plot. The soil samples are strained with 2 mm mesh and then dried in oven at 105°C during 24 hours. The plant samples are dried at 65°C during 3 days.

In order to analyse oxides (SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, SO₃, K₂O), the soil was crushed, mixed with triethanolamine and then melted to obtain pearls. The pearls of each soil were analysed with X-Ray spectrometry fluorescence (Simultaneous XRF, ARL 8460 S).

The organic matter was determined by calcination method: The soil samples were dried at 105°C during 24 hours and calcined at 800°C during four hours.

The soil digestion and plant samples is carried out by a mixture of nitric and hydrochloric acids (25% HCl and 75% HNO₃). The samples are then filtered through Wathman paper 0,45 µm.

Iron, copper, zinc, nickel, cadmium, and lead concentrations were carried out by atomic absorption (Varian type).

**RESULTS AND DISCUSSION**

The analysis of heavy metals in wastewater of Oujda city showed the presence of Zn, with rate reached 0.58 mg/l (Figure 1). About the others metals, the rates are very low, they reached 0.03 mg/l for Cd, 0.16 mg/l for Pb and 0.07 mg/l for Ni. Cu is absent. Those rates dont pass the recommended concentrations by the FAO for water irrigation (Mazlani & Maarouf, 1999).

The order of importance of heavy metals in domestic wastewater of Oujda city is: Zn > Pb > Ni > Cd. These concentrations are below the indicative values of the maximal tolerable metals contents in the irrigation waters used in continuous or discontinuous manner (Mustin, 1987).

![Figure 1. Amount of heavy metals in raw wastewater of Oujda city](image-url)

The control plot presented the lowest amount of organic matter compared to that of the studied plots. Indeed as shown in table 1, the plot excessively irrigated with raw wastewater (P₁) contains the highest amount of organic matter (22.5%).

Because the plots (P₁, P₂, P₃) did not receive any organic manure, the highest amount of organic matter can be explained by deposition of domestic sludge carried by the raw wastewater during irrigation. The organic matter and suspended matter containing in the wastewater can reach 3,10 t/ha . year and 5.6 t/ha . year respectively (Sbaa et al., 1999).
Table 1. Organic and mineral composition (in %) of the plots irrigated with raw wastewater and the control plot

<table>
<thead>
<tr>
<th>Plots</th>
<th>Organic matter</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>K$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_0$</td>
<td></td>
<td>11.6</td>
<td>59.54</td>
<td>8.21</td>
<td>4.68</td>
<td>2.82</td>
<td>0.1</td>
<td>1.81</td>
</tr>
<tr>
<td>P$_1$</td>
<td></td>
<td>22.5</td>
<td>51.81</td>
<td>8.4</td>
<td>4.93</td>
<td>12.06</td>
<td>3.23</td>
<td>0.16</td>
</tr>
<tr>
<td>P$_2$</td>
<td></td>
<td>14.66</td>
<td>52.45</td>
<td>9.61</td>
<td>5.38</td>
<td>10.06</td>
<td>2.25</td>
<td>0.17</td>
</tr>
<tr>
<td>P$_3$</td>
<td></td>
<td>18.52</td>
<td>49</td>
<td>6.71</td>
<td>4.32</td>
<td>13.82</td>
<td>2.19</td>
<td>0.15</td>
</tr>
</tbody>
</table>

It is worth to note that the mineral composition of the four plots (The rate of insoluble oxides can reach 9.61 % for Al$_2$O$_3$, 5.38 % for Fe$_2$O$_3$ and 59.54 for SiO$_2$) is homogenous as reported in the literature (Kodama, 1979).

The studied heavy metals presented variable contents in a soil plots irrigated by raw wastewater of Oujda city. The average of Fe in the soil, varies between 92.25 g/kg to 121.3 g/kg (Figure 2). For Cu, its range varies between 214 mg/kg to 537 mg/kg (Figure 3). For zinc, the average rate can reach 3.54 g/kg in the plot P$_1$ (Figure 4).

Lead is absent in the control plot. Its maximum concentration which is 1.091g/kg, was found in the plot excessively irrigated by wastewater : P$_1$ (Figure 5). The Ni content is close to that of the control plot. It can reach an average value of 184 mg/kg (Figure 6). Finally, the highest rate of cadmium was noticed in the plot P$_1$. It is about 22.8 mg/kg (Figure 7).
The contents of Cu, Zn, Cd and Pb in the plots irrigated by wastewater (P1, P2, P3) are higher than both of the control plot and of the extreme average values of the soil (Mustin, 1987): the concentrations limits were 25 g/kg, 300 mg/kg, 100 mg/kg, 1 g/kg, 200 mg/kg and 0.7 mg/kg for Fe, Zn, Cu, Ni, Pb and Cd respectively.

This difference is significant in the plot excessively irrigated by raw wastewater (P1). The rates of iron and nickel are almost similar in the four plots. These results show well that heavy metals, particularly Cu, Zn, Cd and Pb, can be accumulated in significant quantity in the soil of the sewage field. For cadmium, the content of 22.8 mg/kg in the plot P1, exceeds to that found in the soil of the sewage field of Marrakech city (Elgharmali et al., 1998). Moreover, the Cu, Zn, Pb and Cd contents found in the soil of the sewage field and particularly in the plot P1, largely exceed those reported for the soils polluted by heavy metals (Boularbah et al., 1998).

If the amounts of heavy metals dissolved in wastewater of Oujda city are low, these high heavy metal concentrations in the soil can originate from the domestic sludge accumulated during years of continuous irrigation. This fact was proven in domestic sludge in France and in the United States, these sludge are true sources of panoply of a heavy metal (Zn, Cu, Ni, Cd, Pb,...) (Mustin, 1987). Moreover domestic sludge often play the role of manure in the exploited field by farmers. These sludge could generate during their degradation a significant quantities of heavy metals. To this can be added the cumulative effect of low dose of soluble heavy metal drained by domestic wastewater.

This accumulation is favoured by the presence in the soil of a significant quantity of organic matter (dissolved or in domestic sludge) brought by domestic wastewater of Oujda city, which would result in the formation of organometallic complexes. Moreover the soil of the sewage field which is a calcimagnesic type on carbonated substratum, takes part in the formation of heavy metals carbonate complexes, as well as the cation exchange between heavy metals of wastewater and the reducible phases (manganese and iron oxides). These three forms of heavy metal complexation belong to the categories defined by Forstner (1985). The availability of these heavy metals in plants varies with soil depth. This has been confirmed by Krishnamutri et al. (1997), which stipulates that the index of availability of the Cd in soil decreases in general, in inverse function of depth. This point highlights the importance of the organometallic complexes for the availability of Cd in plants.

The studied plants showed considerable contents of Cu, Zn, Cd and Ni. Pb is missing. Concerning broad bean (Aphis fabae), copper is present primarily in the leaves with an average content of 1.775 g/kg. Zinc is mainly present in the stem with an average rate of 1.4 g/kg. Cadmium is primarily present in the stem with an average rate of 93.4 mg/kg. Nickel is only present in leaves with an average value of 8.25 mg/kg (Figure 8).

The storage of copper and zinc in the shoot system of pea (Pisum sativum) is variable in stems, leaves and in the reproductive apparatus. The average copper rates are about 426 mg/kg in leaves, 523 mg/kg in stem and 811 mg/kg in the reproductive apparatus. The zinc is better stored in the reproductive apparatus, with an average rate of 1.319 g/kg. For stem and leaves, the respective average contents are of 1.013 g/kg and 720 mg/kg (Figure 9).

![Figure 8](image1.png)

**Figure 8.** Amount of heavy metals in the shoot system of broad bean irrigated with domestic raw wastewater

![Figure 9](image2.png)

**Figure 9.** Amount of heavy metals in the shoot system of pea irrigated with domestic raw wastewater
Cadmium is present in average quantity of 50 mg/kg in the reproductive apparatus, 32 mg/kg in stem and 26 mg/kg in leaves. Lead and nickel are absent.

Concerning tender wheat, the shoot system present an average contents of 1.106 g/kg of copper and 1.422 g/kg of zinc (Figure 10), nickel and cadmium present an average contents of 105 mg/kg and 52 mg/kg respectively.

In the same way for lettuce, Cu and Zn appear among the metals best stored in the shoot system. Whereas The average rates of Cu, Zn and Cd are about 468 mg/kg 820 mg/kg and 23 mg/kg respectively. Nickel and lead are absent (Figure 11).

This bio-accumulation of cadmium in the shoot system of lettuce was also reported by Davies et al. (1981). For the oats, the shoot system shows an average rate of 1.061 g/kg of Cu and 1.433 g/kg of Zn. Ni and Cd can reach an average values of 159 mg/kg and 53 mg/kg respectively (Figure 12). Lead is always missing.

Finally, for carrot, zinc and copper seem to be accumulated in both shoot and root systems With a contents of 440.5 mg/kg of copper and 474.5 mg/kg of zinc. The average concentration of cadmium is about 33.5 mg/kg and it is accumulated in the leaves (Figure 13). Similar result were reported by Davies et al. (1981). Nickel and cadmium were absent.

The micronutrients (Cu and Zn) are bio-accumulated in significant quantity in plant tissues (broad bean, pea, common wheat, lettuce, oats and carrot) in comparison with the extreme values found in plants (Melsted, 1973). This accumulation of copper and zinc was observed by Lerch et al. (1990) in wheat leaves when is cultivated on a soil having received a waste sludge.

Cadmium and nickel are present in higher quantities compared to the normal level met in plant species (Page et al., 1981 ; Chaney, 1989). Lead is absent in all analysed plants tissues. Indeed Right et al. (1979) showed that copper, zinc, nickel and cadmium are easily absorbed, whereas lead penetrates little. In the same way, Lee et al. (1981) confirmed the concentration of lead in the plants root, with on the other hand some transfers for zinc, cadmium and nickel. This explains the abundant presence of copper, zinc, cadmium and sometimes nickel in the shoot system of all the analysed plants. As well as the absence of lead in the shoot system of these plants. Indeed the root
CONCLUSION

In spite of the presence of low contents of heavy metals soluble in domestic wastewater of Oujda city, the soil of the sewage field accumulated significant amounts of heavy metals year after year. Indeed the domestic sludge present in wastewater of Oujda city, which settled in soil during many years of continuous irrigation, are probably the major source of heavy metal contribution.

This accumulation is supported by the presence in soil, of organic matter, carbonate and both iron and manganese oxide, which take an active part in metal retention in the active horizons of soil and consequently their availability for the plant.

For the six types of plants cited above, copper and zinc seem to be best accumulated. Indeed, these two metals form a part of the plants micro-nutrients. Their presence in high concentration compared to the others, concerns the normal physiological activity of these plants. However the stored quantities are higher than the average extreme values found in plants.

Cadmium and nickel are incorporated in vegetable tissue with rates exceeding the normal values found in vegetable species. Lead is missed practically in all tissues of analysed plants.

On ecotoxicological plan, the heavy metals listed in “the red list” such as cadmium, copper, nickel and lead are present in significant amounts in the two receiving medium compartment: soil and plant, which presents a real threat for pubic health.

With the demographic growth and economic development of the eastern part of Morocco and within the framework of the respect of the environmental standards, domestic and industrial wastewater must be treated before any re-use in agriculture. Moreover any industrial activity will be seen in the obligation to treat its wastewater before their rejection in the domestic wastewater. A heavy metal pollution is primarily of industrial origin. The current situation in the receiving medium is alarming as far as ecotoxicology is concerned. Taken into consideration of the cumulative and invisible nature of the chemical pollution of the soil, encourages environmental installation of a continuous audit to supervise the hidden face of this pollution.

ACKNOWLEDGMENTS

We thank Dr F. Atmani, N. El-Mtili for critical reading of the manuscript, and the laboratories of “Zeliga Oued Elhimer” and “CIOR Laâyoune” for the support to this project.

REFERENCES


