ASSESSMENT OF CADMIUM CONTAMINATION AND ACCUMULATION IN MAIZE (ZEA MAYS L.*)* AND AGRICULTURAL SOILS

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Abstract

Accumulation of heavy metals in soils from different sources (atmospheric deposition, industrial activities and urban, agricultural practices ...) should be studied and followed because of persistent and potentially toxic to these chemical compounds. Determining the bioavailability of heavy metals the chemical form in which they find themselves is a necessary step to determine the ecotoxicological risks for organisms in contaminated soil.
Soil pollution by cadmium (Cd), a metal which is potentially toxic to humans because of its high mobility in soil, bioavailability through the food chain, and its impact on kidney in case of chronic exposure through the diet.
In this study an assessment is done concerning the impact of soils on heavy metals contamination of maize.
In this work, we have studied the distribution and migration of cadmium in different soil horizons it was applied on a site widely cultivated with maize in Algeria.
The soil was subjected to chemical characterisation, total metal quantification (Cd) sequential extraction as well metal speciation in 2011. Cadmium concentrations exceeded the acceptable limits in soils, with strong surface accumulations and a rapid decrease of the pollution with depth.
However, in the edible portion of maize, the cadmium concentrations were higher than the permitted limits of the european standard.
As for the plants grown, the study indicates a potential ecological risk of maize contamination by cadmium.

Keywords: Maize, cadmium, soil contamination, sequential extraction.

1-Introduction

Contamination of soils with heavy metals is a common problem throughout the world.

The presence of heavy metals can lead to risks of water contamination, soil, transfers in the chain food, or reduce the biological activity of the soil (Sterckeman and al., 2008).

It is known that serious systemic health problems can be developed as a result of excessive accumulation of dietary heavy metals such as Cd, Cr, and Pb in the human body (Oliver, 1997). Heavy metals are extremely persistent in the environment; they are nonbio-degradable and nonthermo-degradable and thus readily accumulate at toxic levels (Goulding and al., 1998).

Heavy metals can be accumulated in the soil at toxic levels due to the long-term application of wastewater (Bohn et al., 1985). One important dietary uptake pathway could be irrigated through crops with contaminated wastewater.

Soils irrigated by wastewater accumulate heavy metals such as Cd, Zn, Cr, Ni, Pb, and Mn in surface soil (Baize et al., 2002).

Zinc and cadmium are generally considered as mobile metals, migrating to depth in soil as free ions solution (Citeau and al., 2003) but easily intercepted in subsurface horizons by clay-iron fabrics (van Oort and al., 2006). Lead is considered as a low- or non-mobile element (Semlali and al., 2004), strongly accumulating at the soil's surface due to complexation with organic matter.

For these reasons, it is necessary to understand the impact of cadmium in soils and develop techniques to determine the potential risks related to contaminated soils.

Thus it is proposed in the present work to evaluate both the contamination and the risk of metal contamination by cadmium in agriculture in different soil horizons near urban areas, road and river Tafna city of Hammam Boughrara and a food plant of maize **(**Zea mays L.) in according to the reference values. for a better understanding of the sensitivity of soil related to deposits of cadmium pollutants.

Whether these soils will play a capital role of cadmium or they will transfer these metals to plants and animals (bioavailability) then to man. Then to highlight the role of vegetation in the interception, distribution and accumulation of cadmium and finally confirm or deny the negative impact of irrigated land in the region by such wastewater.

2- Materials And Methods

2.1- Soil and plant samples

Soil samples: different soils horizons (S) [0-30cm, 30-60cm and 60-80cm] (were collected in triplicate two sampling stations in Hammam-Boughrara, 100 m far from Tlemcen (Algeria). The samples were air-dried, crushed, passed through 2-mm sieve and stored at ambient temperature.

Afterwards, the soil properties and the concentrations of the heavy metals were determined (Allison and al, 1986).

Wheat samples: Plant samples (maize) were taken in triplicate from the same field simultaneously. Replicate samples were washed using distilled water and then separately oven-dried at 80°C till constant weight was achieved. The samples were then crushed separately through a steel grinder and the crushed material was passed through 2-mm sieve (Allen and al, 1986).

2.2- Chemical characterization of the soils

Three replicates of each sample (S) were analysed. The pH was measured in water (1:2,5 w/v) using a pH meter (Allison,1986) (HM-50V, Toadkk, Tokyo, Japan). The organic carbon has been determined using the Allison (1986) method, cation exchange capacity by cobaltihexamine chloride the Orsini and Remy's method (1976). The total concentration of $CaCO_3$ was measured in an acidic medium using a Bernard calcimeter (Allison and al, 1986).

2.3- Metal analysis

The concentrations of cadmium in both soil (S1) and plant (maize) were determined by using the atomic absorption spectrometry (Aurora Instruments Ltd-AI 1200).

2.4- Metal speciation

The sequential extraction previously described (Tessier and al, 1979) was followed. This method is based on the partitioning of particular metal traces of samples with 8mL magnesium chloride solution (1 mol L^{-1}, pH = 7) in order to liberate exchangeable/acid- extractable metals (Step 1). Metals associated and bound to carbonates phases were sollubilised using 8 mL of 1M NaOAc adjusted to pH 5 with acetic acid (HOAc) (Step 2). The residue from step 2 was extracted with 20 mL 0. 04 M $NH_2OH.HCl$ in 25% (v/v) HOAc in order to release the metals bound to Fe-Mn oxides phases (Step 3). The residue from step 3 was added to 3 mL of 0,02 M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3 to liberate the metals associated with organic matter phases (Step 4). Finally, the contaminants were released by HF-$HClO_4$ mixture (Step 5). The extracts were analysed to assess the metal (Cd) concentrations. Analyses were performed on independent triplicates samples of the soils and blanks were measured in parallel for each set.

Maize samples weighing approximately 10 g were carbonized on an electrothermal plate and ashed at 500°C in a furnace for 3 h. A 0,1 g of ash was digested with 2 mL of a mixture of concentrated HCl (37,5%) and HNO_3 (65%) in 3:1 ratio at 80°C until a transparent solution was obtained **(**Allen and al, 1986). The solution was filtered through Whatman No. 42 filter paper and diluted to 50 mL with distilled water to estimate the amount of metals absorbed from the soil.

The results of the analysis of total concentrations of cadmium by the method of sequential different soil horizons extraction in the different seasons of 2011 are listed in table 5**.** To verify the accumulation of cadmium in the maize, extraction of cadmium by aqua regia in the roots and aerial parts was performed. This assay was performed on these samples of plants collected in 2011. The results of these extractions are listed in table 6.

3-Results

A table 1, 2 and 3 summarizes the results of the different physico-chemical parameters of the soil (S).

Table 1: Physico-chemical properties of soil horizon (0-30cm) Supporting maize at different seasons of the year 2011.

Seasons / Properties	Autumn	Spring	Summer
pH	8,25 ± 0,2	8,70 ± 0,2	8,76 ± 0,2
CEC(cmol^{+} kg^{-1})	9,70	10,75	11,33
Total amount of calcium	38,35 ± 2	38,81 ± 2	38,88 ± 2
Organics Matter (%)	3,63	3,45	3,28
Total carbon	2,10	2	1,90

Table 2: Physico-chemical properties of soil horizon (30-60cm) supporting maize at different seasons and of the year 2011.

Seasons / Properties	Autumn	Spring	Summer
pH	8,54 ± 0,2	8,81 ± 0,2	8,85 ± 0,2
CEC(cmol^{+} kg^{-1})	9,68	10,70	11,05
Total amount of calcium	37,24 ± 2	37,50 ± 2	37,63 ± 2
Organics Matter (%)	3,04	2,97	2,82
Total carbon	1,76	1,72	1,63

Table 3: Physico-chemical properties of soil horizon (60-90cm) supporting maize at different seasons of the year 2011.

Seasons / Properties	Autumn	Spring	Summer
pH	8,61 ± 0,2	8,84 ± 0,2	8,93 ± 0,2
CEC(cmol^{+} kg^{-1})	9,64	10,68	11
Total amount of calcium	37,20 ± 2	37,46 ± 2	37,57 ± 2
Organics Matter (%)	2,20	2,07	1,93
Total carbon	1,27	1,19	1,11

The results of the analysis of total concentrations of cadmium by the method of sequential extraction of different soil horizons in the different seasons of 2011 are listed in table 5**.**

Table 4: The total concentrations of cadmium (mg Kg^{-1} dry weight) in different soil horizons after fractionation by sequential extraction in different seasons of the year 2011.

Seasons / ETM	Autumn	Spring	Summer
0-30cm	12,51	9,10	10,23
30-60cm	6,38	4,55	5,22
60-90cm	3,10	2,27	2,64

To verify the accumulation of cadmium in the maize, extraction of cadmium by aqua regia in the roots and aerial parts was performed. This assay was performed on these samples of plants collected in 2011. The results of these extractions are listed in table 5.

Table 5: Concentrations of cadmium (mg Kg^{-1} dry weight) in the different parts of maize during the different seasons of the year 2011.

Seasons / Different parts of The plant	Autumn	Spring	Summer
Roots	1,15 ± 0,09	2,07 ± 0,17	1,87 ± 0,13
Stems	1,57 ± 0,1	1,96 ± 0,14	1,50 ± 0,10
Leaves	1,45 ± 0,10	2,71 ± 0,30	1,60 ± 0,20
Grains	5,10 ± 0,12	5,94 ± 0,21	5,20 ± 0,13

4-Discussion

4.1- Chemical characterization

We note from these results that all soils were alkaline and there were no significant changes in pH different soils horizons.

The soil showed an average CEC (soil sandy loam) and would transfer more heavy metals to plants than the heavier soils (with more clay). The uptake of heavy metals by plants tends to increase when the sunlight rises (in our case in the seasons of spring and summer). The results show that soils of maize are calcareous soils.

The organic matter contented by soils was relatively stable over time and variations were possibly due to contributions from manure or compost, but were noticeable after 10 or 20 years of regular additions.

4.2- Sequential extraction

In the absence of standards relating to Algerian reference levels in the soil, we adopted a comparative approach identified by references to reports in the literature and supplemented by European standards (Alloway, 1990) (Table 6).

Table 6: Maximum authorized concentrations of heavy metals in sludges used in agriculture and in soils amended by sludges (Baize and Sterckeman, 2002).

ETM	Content limits of heavy metals in soils (mg kg^{-1} dry weight)
Cadmium	2
Lead	100

Cadmium was mainly bound to carbonates with a maximum of 40%. This represents more than 50% of the total content of all five fractions**,** cadmium is therefore potentially mobilized**.**

Numerous reports in the literature associate preferentially to Cadmium carbonate fraction (Salomon and al., 1978) and the exchangeable fraction (Dong and al., 2000).

The total concentrations of cadmium content after fractionation by sequential extraction in different soil horizons 0-30cm, 30-60cm and 60-80cm between 9,10 and 12,51mg/kg, 4,55 and 6,38mg/kg and 2,27 and 3,10mg/kg respectively. The total cadmium content in the different phases slightly exceeded the limits defined in Table 3 in different soil horizons, so there is possibility of cadmium contamination, with strong surface accumulations and a rapid decrease of the pollution with depth and it appears that a significant proportion of this pollution is theoretically releasable because it is not associated with the residual phase.

Thus, following these results, the soil may be contaminated by cadmium, this contamination varied with seasons.

4.3- Metal content in the plant

4.3.1-Roots

Therefore the values of cadmium were within the range of normal levels (Fageria and al, 2002) and (Prasad and al., 2003) for heavy metals in plants defined in Table 7. This shows accumulation by cadmium in the roots of maize.

Table 7: Critical and normal levels (mg Kg^{-1} dry weight) of heavy metals in plants (Fageria and al, 2002).

ETM	Deficiency	Toxicity	Normal Content
Cd	-	5	0,05
Pb	-	12-300	1,0

4.3.2-Shoot

Cadmium concentrated more in shoots than roots of maize. In contrast, cadmium, levels were higher in roots than the aerial part of maize.

Levels of cadmium measured in spring in the shoots were higher than in autumn and summer. There was a seasonal effect on the levels of cadmium.

-The levels of cadmium was higher in grains than in stems and leaves, with a maximum respectively range of (1,96 ± 0,14)mg/kg in stems, (2,71 ± 0,30)mg/kg in leaves and (5,94 ± 0,21)mg/kg in grains. Thus, cadmium concentration in grains was slightly above the threshold of toxicity in plant.

-By comparing the results between the roots and aerial parts, it seems that cadmium is absorbed by the roots and transported and enrich the aerial parts.

However, some chemical elements showed a similarity in behavior either at the plant or in their distribution and penetration into tissues. In our case, this similarity in behavior was observed for cadmium (are translocated in different plant organs). This result confirms that the type of plants is a key determinant of the transfer and accumulation of heavy metals.

Several studies have shown similar Ni accumulation in roots and aerial parts for different species such as clover, ryegrass, wheat and pea (Ye and al., 2001) and (Souza and al., 2003).

5-Conclusion

The sequential extraction performed on soil showed that the source of contamination by cadmium is not a potential threat to the environment despite high levels because they are very mobile.

From eco toxicological point of view, the transfer of metals to the aerial parts of a plant is not desirable since heavy metals can accumulate in the food chain passing through herbivores. And in maize, though translocation of cadmium to the aerial parts appears to be limited, it may contaminate the animals fed by its forage or grain especially with cadmium.

At the end, the study of the localization of cadmium has also to follow the evolution of this metal as a function of depth. This could inform us about the potential risks associated with the contamination of the soil and the food chain in Hammam Boughrara.

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List of symbols and Abbreviations

cm = centimeter
m = meter
mm= millimeter
S1=soil 1
W= water
V= bulk
°C= degree(s) CelsiusC
h=hours
ml= milliliter
mol L^{-1}=mole $liter^{-1}$
M= mole $liter^{-1}$
%=percentage
g= gram
No=numero
mg Kg^{-1}= milligram $kilogram^{-1}$
Fig=figure