

Evaluation of the Speciation of Heavy Metals (Cd, Pb, Zn, Cr and As) in the Different Horizons of an Agricultural Soil

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Abstract: This research has enabled the assessment of environmental risk related to potential transfers of metal trace elements such as lead, cadmium, zinc, chromium and arsenic in agricultural soils whose cultivation is nearby barley. From the industrial discharge of the technical discharge center (CET) of the municipality of Oued El Djemaa is located in the Wilaya de Relizane-Algeria and close to solid domestic waste from industrial discharges. To meet this main objective, several analyzes were carried out, based on the first place on the chemical extraction of heavy metals by treating water. This extraction has highlighted a fairly strong accumulation of cadmium, arsenic and zinc in the soil. If the total levels of heavy metal by lawy water allow for a first state of fixtures, it is more specified according to the method of Tessier which has allowed an estimate of the future of pollutants and a risk approach. The sequential extraction on the ground showed a significant source of pollution by cadmium which is mainly related to the carbonates that makes it mobile and which constitutes a potential threat to the environment. On the other hand, arsenic and zinc are mainly related to the residual phase and the reducible phase respectively so they are little mobile in the soil and do not show threat. This research work has made it possible to access fine knowledge of the fate of metal pollutants

(Cd, Pb, Zn, Cr and As) in agricultural soil. He also highlighted shadow points requiring multidisciplinary research.

Key-Words: - sequential extraction, lead, soil, cadmium, chromium, Arsenic

I. INTRODUCTION

Good soil management remains a crucial issue of protecting natural resources and the prevention of environmental pollution. Soils can be degraded in various ways: storage of waste, different spreads, etc.).

The emissions of the metal particles in the environment induced by many anthropogenic activities pose questions in the field of health, but also the environment (Goix et al., 2015, Lévêque et al., 2015, Austruy et al. 2016). [1-3]

These metal particle emissions generate accumulations of heavy metals in soils and the nearby environment and even more distant impacts according to climate, soil or relief factors. Lead, cadmium, copper, arsenic are metal pollutants commonly found in ecosystems (Wu et al. 2015) [4].

All persistent, some are (eco) toxic even at low concentration (WongsaSuluk et al., 2014) as has been demonstrated for example in the case of rich lead particles issued in the environment by various companies (JARUP 2003, Hernández-Ochoa and al. 2005). [5-7]

It is in this context that several studies (Baize et al., 2006, Bur, 2008, Aduayi-Akue and Grandi, 2014, Yehouenou Azehoun Pazou et al., 2020) have been carried out in the world on concentrations and mobility Metal trace elements in the soil and in vegetable products. [8-11]

The speciation, that is, the chemical forms of a metal trace element, is thus intimately linked to its bioavailability and therefore is of fundamental importance in estimating environmental risks associated with its presence. In the solid phase, determining the distribution of a metal trace element between the different reactive phases makes it possible to evaluate their ability to release the metal trace elements in the soil solution. The determination of the chemical forms of the metal trace elements in the soil solution makes it possible to evaluate the fractions likely to be directly assimilated by the living organisms, the free form of the metal trace elements being a priori the most assimilable form. It is therefore essential to determine the speciation of metal trace elements both within the solid phase and the liquid phase (Mulligan et al., 2001).[12]

If elsewhere data on the concentrations and dispersion of metal trace elements are quite well-supported, in Algeria, the question of metal trace elements in soils in general, and in particular peri-urban agricultural soils, remains still asked. And yet, most agricultural products for consumption come from these soils.

The main objective of this work was to understand the behavior of the metal trace elements and more particularly that of lead, cadmium, arsenic, chromium and zinc in the solution of the selected ground whose cultivation is barley to Proximity to industrial discharge from the technical discharge center (CET) in the municipality of Oued El Djemaa is located in the wilaya of Rélizane-Algeria and also close to solid waste domestic waste.

To meet this main objective, several intermediate objectives have been defined:

- Determine the physico-chemical soil settings.
- Determine the total content of the metal trace elements in the ground by extracting with a treat.
- Determine the speciation of metal trace elements in the soil solution by sequential extraction.

II. MATERIALS AND METHODS

A. Description of CET in Oued el Djemaa zone

The samples selected for this study are soil from an agricultural site located near industrial discharges from the technical landfill center (CET) in Oued el

Djemaa and also near domestic solid waste. For this, a plot whose crop is barley (figure.1) was chosen.

- Sample I (ground O): an area of about 2ha; of which barley is like crop.



Soil O

Fig. 1: Study area: sample collection plots.

The CET of Oued El-Djemaa considered as one of the most important projects falling within the framework of the program of the preservation of the environment stopped by the wilaya of Relizane, the (CET) is operational today.

This infrastructure aims, in fact, to process household waste from 9 municipalities Located in a site far from the urban fabric. (figure.2).



Fig. 2: CET of oued el Djemaa-Rélizane

B. Soil samples

Surface soils (S1) were sampled in triplicate from the different horizontals (0-30 cm) and (30-60cm) of an agricultural site located near industrial waste from the technical landfill center (CET) of Oued el Djemaa, wilaya of Rélizane-Algeria and 100 m apart. The samples were air-dried, ground, passed through a 2 mm sieve and stored at room temperature. Next, soil properties and heavy metal concentrations were determined.

C. Chemical characterization of the soil

Three replicates of each sample (S1) have been analysed: the pH was measured in water (1:2,5 w/v) using the pH meter [13]. The organic carbon has been determined using the Walkley and Black's method [13], Cation exchange

capacity by cobaltihexamine chloride the Orsini and Remy’s method [14] and the total concentration of CaCO₃ was measured in an acidic medium by a Bernard calcimeter [13]. The water-holding capacity has been determined gravimetrically, after draining the water-saturated soil. [15].

D. Extraction of heavy metals by aqua regia

The samples are mineralized by acid digestion with aqua regia. Each sample is the subject of 3 test portions of 0.5g ± 5mg. Each catch is placed in a glass Erlenmeyer flask where it receives 2-3ml of demineralized water to obtain a boat product, then addition of 7.5ml of hydrochloric acid (37% (m/m), density 1.19g/ml, Merck Supra pure max Hg 0.005ppm) and 2.5ml of nitric acid (65% (m/m), ρ=1.38 g/ml, Merck Supra pure max Hg 0.005ppm). The mixture is sealed and left at room temperature for 12 hours. The mineralizate is then concentrated by boiling for 2 hours. After cooling, filter on ashless filter paper, the volume obtained is adjusted to 25ml with distilled water. [16]

E. Metal speciation

The sequential extraction described previously has been followed. This method is based on the partitioning of particular metal traces of samples with 8 mL 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 have been solubilised using 8 mL of 1M NaOAc adjusted to pH 5 with acetic acid (HOAc) (Step 2). [17]

The residue from step 2 has been extracted with 20 mL 0,04 M NH₂OH.HCl in 25% (v/v) HOAc in order to release the metals associated with the bound to Fe-Mn oxides phases (Step 3). The residue from step 3 has been added to 3 mL of 0,02 M HNO₃ and 5 mL of 30% H₂O₂ adjusted to pH 2 with HNO₃ to liberate the metals associated with the bound to organic matter phases (Step 4). Finally, the contaminants have been released by HF-HClO₄ mixture (Step 5).

The extracts were analysed in order to assess the metal (Cd, Pb, Zn, As and Cr) concentrations. Analyses were performed on independent triplicates samples of the soil (S1) and blanks were measured in parallel for each set. [17]

F. Metal analysis

The concentrations of Cd, Pb, Zn, As and Cr in both soils (S1) have been determined by using the atomic absorption spectrometry (Aurora Instruments Ltd-AI 1200).

The expression of the results in mg/kg relative to the dry matter (Ms) is given by the following formula:

$$C = C_1 \cdot V \cdot D / T$$

C : C (sample) (mg/kg) ; V : V (mineralization) (L) ;

D : dilution ; T : Test sample mass (Kg)

III.RESULTS

The results of the physico-chemical properties are listed in table 1.

Table 1: Physico-chemical characteristics of the soil

Identification of the land	Residual humidity	Layers (cm)	pH (eau)	CEC (C+mole/litre)	Carbonates (g/kg)	MO (%)
Soil R	17,50	0 – 30	8,43	35,44	4,97	3,29
	20,66	30-60	8,85	37,75	5,95	3,78

Note that: CEC: Cation exchange capacity, expressed in (C+mole/litre)*, MO: Organic matter, expressed in % relative to the raw sample, CaCO₃: Carbon carbonate, expressed in % relative to the raw sample.

The results obtained from the analysis of the total contents of heavy metals by extraction with aqua regia of the soil are given in table 2 and represented in the form of histogram in the figure 3.

Table 2: Heavy metal contents (mg/kg) in the different soil horizons.

	Pb	Cd	Zn	Cr	As
0-30cm	50,27	5,51	325,33	70,66	50,46
30-60cm	44,81	4,30	326,55	58,63	62,11

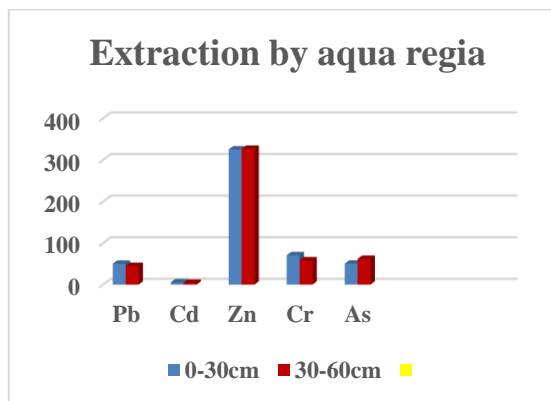


Fig 3 : Heavy metal contents (mg/Kg) extracted by aqua regia.

After the dissolution, it was determined the total concentration of nine heavy metals: cadmium, lead, copper, zinc, nickel, cobalt, iron, manganese and chromium using atomic absorption spectroscopy with flame and furnace. Results of the analysis of total concentrations by the sequential extraction protocol of S1 are listed in the tables (3-6). Relative distribution of metals as a percentage of the total

metal (sum of all five fractions), are shown in figure 4, 5.

Table 3: Contents of heavy metals in mg/Kg in the different fractions of the soil depth (0-30cm).

	Pb	Cd	Zn	Cr	As
F1	0,077	1,80	3	1,76	0,024
F2	1,01	0,57	26,10	3,62	0,15
F3	7,46	0,61	429,54	106,20	0,26
F4	1,85	5,50	1,98	22,84	0,16
F5	49,27	0,84	139,38	1,31	59,40

Table 4 : Mass percentage of heavy metals in the soil - depth (0-30cm).

	Pb	Cd	Zn	Cr	As
F1%	0,13	19,31	0,50	1,30	0,04
F2%	1,70	6,11	4,35	2,67	0,25
F3%	12,50	6,54	71,59	78,24	0,43
F4%	3,10	59,01	0,33	16,82	0,27
F5%	82,57	9,01	23,23	0,97	99,01

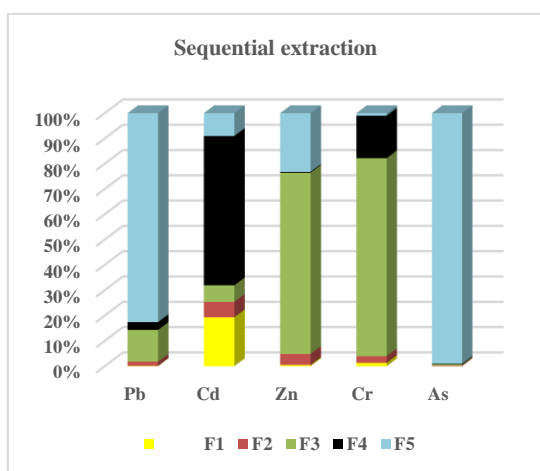


Fig 4 : Metals as a percent of the total content after fractionation through the sequential extraction in spring season- depth (0-30cm).

Table 5 : Contents of heavy metals in mg/Kg in the different soil fractions - depth (30-60cm).

	Pb	Cd	Zn	Cr	As
F1	0,13	1,30	2,50	1,54	0,021
F2	0,92	0,38	24,53	3,05	0,20
F3	5,57	0,51	426,42	93,05	0,37

F4	2,07	4,40	2,37	19,17	0,25
F5	41,67	0,61	154,38	3,76	71,52

Table 6: Mass percentage of heavy metals in the soil - depth (30-60cm).

	Pb	Cd	Zn	Cr	As
F1%	0,26	18,07	0,41	1,28	0,03
F2%	1,83	5,38	4,02	2,53	0,28
F3%	11,06	7,16	69,88	77,17	0,52
F4%	4,12	60,84	0,39	15,90	0,35
F5%	82,73	8,55	25,30	3,12	98,82

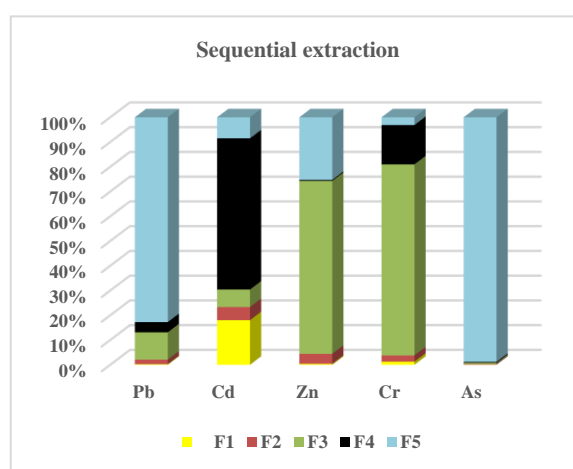


Fig 4: Metals as a percent of the total content after fractionation through the sequential extraction in spring season- depth (30-60cm).

IV. DISCUSSION

A. Physico-chemical parameter

-We notice a fairly average residual humidity, but it increases in depth (30-60cm). The uptake of ETM by plants mainly increases with an increase in the residual moisture value.

-The pH is another important factor influencing the solubility and the speciation of the metal and therefore its toxicity, [18] when the pH decreases by one unit, the concentration of free metal cations increases by about a factor of 2 in the soil solution and hence enhances phytoextraction [19, 20].

-The soil collected has a remarkable basicity. Changes in pH could in particular result from biological activity and an increase in the CO₂ content.

Carbonates are found in large quantities, which explains the basicity of the soils studied, depth but

in depth increases (30-60cm).-The percentage of organic matter (OM) seems very low.

-The cation exchange capacity is also an important characteristic of a solid matrix, it corresponds to the quantity of saturating cations fixed by the soil in a buffered medium. Our soil is highly ion exchanger, the estimated CEC is higher compared to the average values announced by the literature [21]: 0.6 meq/g (60meq/100g) for a mineral soil and 2 meq/g (200meq/100) for organic soil.

Indeed, humic compounds have a particular affinity for this Ca^{+2} cation, the adsorption of Ca^{+2} in the presence of organic matter is favored [21].

B. Heavy metals in agricultural soil extracted by aqua regia

The heavy metal contents obtained by aqua regia extraction are given in Table 2. In the absence of standards relating to the Algerian reference levels in the soil, we adopted a comparative approach identified by references to reports in the literature and supplemented by European standards [22-24].

The total contents of arsenic, cadmium and zinc exceed the limit values tolerated in agricultural soil in both horizons and There is a kind of very clear "pollution" by arsenic, by cadmium and by zinc ,There is a "nature of the pollutant" effect, with " $\text{Cd} > \text{As} > \text{Zn}$ ".

On the other hand, the total contents of lead and chromium are below the limit values tolerated in agricultural soil in the depths [0-30cm] and [30-60cm], so these total contents are within the standards.

-Knowing the total levels of heavy metals is necessary, but not sufficient to assess their mobility and the resulting environmental risks. The prediction of these risks is closely linked to the physico-chemical forms in which the metals are present, i.e. say to their speciation, knowledge of speciation can make it possible to predict the conditions of current or future mobility of metallic elements. The speciation of heavy metals is obtained thanks to sequential extractions carried out in triplicate according to the protocol described by Tessier.

C. Sequential extraction of Heavy metals in agricultural soil

Note that the five heavy metals have the same distribution in the five fractions for the two soil horizons [0-30cm] and [30-60cm].

-The lead

Lead is mainly bound to the residual fraction followed by the reducible fraction (iron and manganese oxides). This distribution is consistent with numerous studies reported in the literature which preferentially associate lead with the residual

fraction and with the reducible fraction [25, 26], lead appearing to be very little present in the exchangeable phase. This is explained by the fact that lead is not mobile. Lead is listed in descending order: $\text{F5} > \text{F3} > \text{F4} > \text{F2} > \text{F1}$.

-Cadmium

Cadmium is mainly present in carbonates. Many studies reported in the literature preferentially associate the cadmium carbonate fraction [27], the exchangeable fraction and the residual phase [28].

The affinity of cadmium for the five fractions follows the following order: $\text{F4} > \text{F1} > \text{F5} > \text{F2} \approx \text{F3}$.

The presence of carbonates is a cadmium trap by precipitation. The dominant presence of Cd in this fraction makes this soil unstable and the free mobility and migration of cadmium ions on the surface little caused a danger either vegetation for animal and subsequently on human health may the levels of cadmium exceed the limit values tolerated in agricultural soil considering the fractions F4 and F2.

-Zinc

Zinc are mainly associated with manganese and iron oxides followed by the residual phase. Similar associations have been highlighted by several works including those of Aboubaker and Algan et al [29, 30]. The affinity of zinc for the reducible and residual phases shows that zinc is not very mobile.

These results show that Zinc is stable in the soil because all of the Zinc is found in the reducible fraction and the residual fraction.

-Chromium

Chromium is mainly bound by iron and manganese oxides followed by carbonates. This association with iron and manganese oxides, organic matter, has been underlined by several authors [31]. The results show that chromium is toxic, but is quite stable in soil.

-Arsenic

Arsenic is predominant in the residual fraction, which means that it is included in the primary and secondary ores and is therefore poorly soluble and this is explained by the fact that arsenic is not mobile. The levels of arsenic exceed the threshold limit tolerated in agricultural soil, so it is one of the most stable toxic elements among those we have analyzed. This poses no problem in the food chain.

-In the soil, heavy metal content varies with depth. Because of their very strong bond with the different solid phases listed above.

Microelements from external inputs will accumulate on the surface, their concentration will therefore decrease with depth and mark, in the case of

cultivated soils, a clear discontinuity below the worked layer according to [32].

In the case of soils that were formed from source rocks particularly rich in metallic elements, we can see an increase in the content of the latter with depth.

Arsenic and zinc evolve in deep growth, we know that arsenic is a very dangerous metal for humans or plants, which poses a very great danger, for plants and subsequently for humans.

V. CONCLUSION

Metals have two origins, one endogenous and one exogenous. This is due in our case mainly to the activities of peri-urban industries, industrial discharges from the technical landfill center (CET) of Oued el Djema and also near solid household waste and atmospheric discharges. Soil contamination occurs mostly near surface horizons. This accumulation is the result of several factors including exposure to atmospheric deposition, the physico-chemical properties of the soil and climatic conditions. Indeed, the soil studied is calcareous and has a pH greater than 7 in two seasons. At these pH values, the mobility of heavy metals by accumulating causes a decrease in surface levels. In addition, this region is a bioclimatic characterized by erratic precipitation which reduces the continuous renewal of the soil, the winds are the wind causing pollution by the metallic elements of the soil and the plants surrounding the source of pollution.

The toxicity of a metal depends on its speciation (chemical form) as much as environmental factors. The sequential extraction results show that the metal element found shows the influence, in order of importance, of the reducible fraction of the carbonate fraction of the residual fraction of the organic fraction and of the exchangeable fraction of the soil on the retention. heavy metals. There is a kind of very clear "pollution" for Cadmium, arsenic and zinc in the S1 soil.

However, a metal is only toxic to living organisms if it is in free form; it is then bioavailable. Like any positively charged element, metal cations can interact in the soil with any negatively charged organic or mineral particle. The balance between the free and fixed forms of the ion will determine its bioavailability, directly linked to its toxicity. In our case cadmium.

During this work, we studied a real case of the fate of heavy metals in the agricultural soil of the wilaya of Rélizane.

It is difficult for us (for lack of data on the geochemical background of Algerian soils) to

differentiate with certainty the share of metals of endogenous nature from that of anthropic origin. Nevertheless, the high levels found on the surface would probably be an argument in favor of anthropogenic input. Whereas for the intersoil distribution, the levels detected in soil O are indeed always the highest compared to other soils.

VI. RECOMMENDATIONS

Furthermore, it is interesting to be able to compare the results relating to these sites with those obtained on other sites in order to consider a generalization of the trends observed and also to be able to propose practical measures to control or attenuate the effects of this pollution.

It would also be interesting to continue this study with a phenomenon modeling approach, which would make it possible to estimate the risks of migration of pollutants or the accumulation capacities within the different phases according to variations in multiple conditions (mixture of reagents, ...etc) and on a larger time scale, by limiting experiments to the laboratory. The use of methods allowing the monitoring of the evolution of speciation, in conjunction with these experiments, would make it possible to better support the conclusions.

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