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ICP analysis of heavy metals in corn and soil irrigated by Berrechide waste water (Morocco)

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Abstract

The study is devoted to agricultural use of waste water released into the environment and its impacts on soil and agricultural products that are irrigated with. Mixed domestic and industrial sewage, from an industrial city, are charged on heavy metals, and produce same foods including maize. We have done samples at two soils levels and corn fragments, taken with technical regulations. ICP analyzes have revealed doses of 8 metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn), with disparities between the elements themselves and within the components of each matrix. Some high concentrations are noted, especially in surface soil and maize roots, particularly the iron metal.

1. Introduction

Wastewater irrigation, contamination of soils, plants in general and foodstuffs in particular by heavy metals has been widely described in the literature [1-6]. The phenomenon is universal but it is more acute in underdeveloped countries. It must be recognized that this problem is quite complex and that the results present enormous disparities from one study to another. This requires, in our opinion, great multidisciplinary effort for a more elaborate elucidation of transition mechanisms or metal uptake in plants and their adsorption by substrates. For example, some authors speak of bioconcentration of elements in the roots [7,8].

This phenomenon has long existed in the vicinity of several Moroccan cities. Berrechide is one such case. It is located in the back country of the great megalopolis of Casablanca. The saturation of the latter in terms of homes and factory installations have resulted in many industrial investments being relocated to this city.

The industrial district of this agglomeration includes some 120 industrial companies (brake plates, cable industries, battery and radiator manufacturing, valves, sawmills, diapers, textiles), agri-food (canned goods, packaged juice, ...) and other conventional activities such as brick factories and ceramics. The city is located on a very low slope plain, which hinders the flow of domestic and industrial sewage that have been mixed. As a result, the plants have created open-pit storage tanks on the outskirts of the factories, which causes observable flooding of different colored waste water depending on the basins as well as foul odors at the southern entrance of the city

While some metals are essential for physiological processes at very low doses (trace elements), they become very toxic at non-physiological doses, particularly Arsenic (As), cadmium (Cd), chromium (Cr), Mercury (Hg) and lead (Pb). The ways of bioaccessibility to these metals are numerous and have been of growing concern because of their effect on human health. A major source of this contribution is food (seafood, fruits and vegetables ...). Living beings have developed a system of immune defense or chemo-defense to protect themselves against toxic substances -natural or synthetic- with which they are in contact, including metallic elements [9]. For example, ecosystems of deep hydrothermal sources (abyssal fossae) have developed effective defense mechanisms to protect themselves against excess toxic hydrogen sulfide (H_2S) molecules and heavy metals (Pb, Cd, Hg, Zn ...), present in high concentrations in the effluents of their environment [10]. According to the same author: there are naturally occurring proteins in numerous organisms, metallothionein, whose ability to complex the metals have been demonstrated [11, 12]. It is also recognized that these proteins play an important role in the detoxification mechanisms of metals [13]. They are therefore a means of protecting against the effects of toxic or non-essential metals (cadmium, mercury, etc.) in the hope of ensuring the survival of species, or many of them would have disappeared, including humans, who have used these metals since the dawn of time.

Industries generate toxic metal wastes and other emerging substances with harmful effects on ecosystems: fauna, flora, water, soil and human health. Many of these substances are known to bioaccumulate with dangerous effects for a long time. Some have characteristics of acting in physiological processes as biochemical blockers or as endocrine disrupters [14]. These elements, especially Pb, Ni, Fe, Zn, Cu, Ch, C ... are recognized as carcinogens [15-19], mutagens [20] Cytotoxic [14,22,23] and genotoxic [3,21]. Even in traces, they are likely to cause dysfunctions in biological and physiological processes for both fauna and flora. By way of example, some metals in excess, compared to a natural threshold, decrease the yield in certain plants [24]. Some are recognized as endocrine disruptors, including heavy metals [25], antibiotics and pesticides. Thus lead, for example, negatively affects fertility in humans [26] and prenatal exposure to doses of mercury disrupts newborn size [27].

The objective of this study is to contribute to the identification of problems of insalubrity that are harmful to human health. In this sense we identified and quantified eight trace metallic elements (Pb, Ni, Fe, Mn, Zn, Cu, Cr, Cd) in soil and maize irrigated by wastewater in the town of Berrechide.

2. Materials and methods:

The analyses were carried out by plasma atomic emission spectrometry at the ICP-AES laboratories, in the Technical Assistance Unit for Scientific Research (UTARS), at the National Center for Scientific and Technical Research (Rabat). This laboratory has developed analytical techniques which obey quality standards recognized by a label. It uses standards and is ISO 9001 certified: thanks to an accurate 1000 ppm Ain ICS device model Ultima 2 from JobinYvon. It analyzes major - minor - trace - ultra trace in all types of matrices (rocks, floors, slags, glasses, ceramics ...). An ICP V5 analyst / windows 98 / NT software is designed to optimize productivity by automatically rolling out the sequence of tasks required for a given operation. Finally, a calibration equation (equations of the first grade) is used to differentiate one element from another and one calibration from another. Calibration of the instrument is carried out systematically before each analysis.

The analysis involved eight trace elements in soil samples and corn fragments, namely: Cadmium, Chromium, Copper, Iron, Manganese, Nickel, Lead, and Zinc.

2.1. Sampling:

2.1.1. Soil:

Sampling of soil is done at each station by means of a manual auger. Only two horizons were surveyed (0 cm and 20 cm) due to limestone slab that creates a barrier at a low depth and prevents from going further. Each sample is immediately placed in a new referenced plastic bag.

An uncontaminated control soil sample of identical structure is also removed from the same area.

2.1.2. Corn:

Fragments of the root system, shreds of leaves and pieces of corn were taken on each occasion and placed in new referenced plastic bags

3. Chemical analysis procedure:

3.1. Soils:

The samples were dried at 100° C in an oven for 24 hours before grinding and sifting. 150 mg of soil was placed in a 30 ml Teflon beaker and2 ml of concentrated HNO3 (70%) were added, as it is known that the reaction can be effervescent on samples containing carbonates or sulfides. The beakers were left open to dry on a hot plate at about 100 - 110 ° C. Finally, two other acid etching procedures are carried out first with nitric acid, then with hydrochloric acid, with 2 ml of HNO 3 added each time and the heating plate at 110 ° C.

3.2. Corn:

Procedure: Flakes of roots, blade and cobs are dried for 16 hours at 80 ° C. The plant is then ground. 2 g of sample were measured into a platinum capsule. This is placed in a cold oven and the temperature raised to 450° Cfor two hours. The ash is moistened with 2 to 3 ml of water and 1 ml of concentrated hydrochloric acid is added slowly. The sample is then heated until the first vapors appear, then a few ml of water are added. The solution is filtered through a 100 ml volumetric flask, rinsed 3 or 4 times with lukewarm water. The filter paper is then incinerated for half an hour at a maximum of 500 ° C. It is taken up in 5 ml HF and dried on a hot plate or a water bath without exceeding 1000 ° C.

Repeat with 1 ml of concentrated HCl, wash with lukewarm water and filter. Bring to 100 ml, make up to the gauge mark after cooling and pass to the dosage of the elements by atomic absorption spectrometry.

4. Results and discussion:

4.1. Analysis of MTEs in soil matrices:

The values in the control soil are reported in Table 1 below. The results of the analyze of contaminated soils are grouped in Tables 2 and 3, those of the corn parts in Tables 4, 5, 6 and 7.

Table 1: Concentrations of MTEs in the control soil matrix (mg / Kg):

Elements :	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Mn**	**Ni**	**Zn**
Control soil matrix	0.01	0.06	0.13	8.30	0.05	0.23	0.23	1.04

A first overview (Table 2) shows values that are already clearly too high, particularly as they are expressed in mg / kg. Concentrations of Iron are especially high, closely followed by Zinc. We believe this is normal with regard to the high frequencies of sewage irrigation by gravity during hot seasons over several years (more concentrated by low water). Indeed, several decades of drought have "legitimized" the use of unsafe water. This will have caused higher concentrations every year. In addition, the multiple uses of these minerals both in industries and in drug therapy are numerous. Iron being the most widely used of all metals (scrap iron, boilerworks, surface treatments, medicines, ...). The iron concentrations are followed by those of lead, zinc, chromium and nickel, cadmium being the least represented of the range.

Table 2: Trace elements in the surface soil (horizon A1, mg/kg):

Eléments : / Station :	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
St1	0.25	42.67	0.25	18688.77	356.35	19.06	61.85	30.67
St2	2.68	29.10	0.22	12482.75	289.36	10.04	45.16	32.89
St3	0.34	69.55	0.34	25281.28	530.56	26.49	97.74	53.65
St4	0.42	40.71	0.42	16770.99	307.95	21.33	57.43	28.72
St5	0.27	32.41	0.27	14034.04	273.55	27.74	54.68	47.61
St6	0.33	24.01	2.30	9374.09	186.48	23.35	35.61	48.52
St7	0.30	29.46	5.48	11210.92	248.14	14.51	39.09	30.94
St8	0.25	44.64	3.71	18078.46	315.81	24.36	70.98	69.12
St9	0.46	42.92	0.31	16082.55	370.80	25.88	54.39	35.02
St10	0.22	31.73	0.22	13523.51	262.45	14.13	46.64	22.76

As for the adsorption of these elements by the soil (Table 3), there is a marked increase in quantities in depth rather than at the surface. This is compatible with the bibliographies in the field [28, 29], due to the mobility of the elements, in particular as a result of precipitation which drains them down to the water table. In addition, clay soils are known to be relatively acidic and very absorbent. The exchange and adsorption of metals are elevated at low pH values [30]. Additionally, at the same pH, metal concentrations can vary from one soil to another [5]. These concentrations reflect the degree of use of each metal in everyday life, and the activities associated with the metal treatments that cause the discharge. Some concentrations, such as those of Fe and Mn, are significantly higher than other elements. The most abundant metals are in fact those produced by surface treatments, boiler works, plumbing (Fe, Pb, Zn) and scrap metal in the city or are likely of chemical and pharmaceutical origin (Fe, Mn, Zn, Cr, Or). Concentrations of metals in soils may also be affected by the presence of fertilizers, which contribute to increasing the concentration of a given element (Case of the Cd) [31].

Table 3: Trace elements in the A2 horizon at 20 cm depth (mg/kg) :

Eléments : Station :	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
St1	0.23	54.96	11.74	24277.86	362.67	20.22	80.18	45.44
St2	0.24	47.12	0.28	20000.37	359.07	18.26	73.51	29.92
St3	0.24	46.42	0.24	19085.07	300.11	20.31	69.45	26.93
St4	0.34	53.68	11.63	21323.63	410.83	28.72	72.32	44.79
St5	0.32	40.78	0.32	16557.59	340.86	23.17	59.03	43.48
St6	0.33	31.26	3.84	12910.35	273.30	15.04	43.96	41.29
St7	6.58	54.17	0.35	22199.57	473.99	20.94	75.97	39.98
St8	0.78	49.10	0.26	19765.42	353.36	20.06	74.37	75.41
St9	0.34	48.07	0.34	17411.54	411.17	25.74	62.39	42.28
St10	0.39	52.36	8.14	18254.81	367.92	29.60	62.05	46.80

We see a trend towards mild accumulation in depth in most cases. In fact, although metals are generally more or less permanently trapped by a large number of constituents (adsorption by organic matter, oxides and hydroxides of iron and manganese, phyllosilicates, phosphates, carbonates, etc.), a non-negligible fraction may be mobilized and migrate vertically in soluble or colloidal form [32, 33, 34] or integrate the plant by its rhizosphere to end up in the biomass and present a threat to human and animal health.
The difference in temperature between the surface of the soil and that of the less warm depth should not be overlooked. It has an influence favoring chemical reactions and the retention of metals especially in very hot weather, which is the case here. Clay soils are acidic, which has an effect on availability and absorption in general and on heavy metals in particular [35]. Similarly, the plastic character of clay soils, which once saturated with water become impermeable. This promotes evapotranspiration rather than infiltration, which results in concentrated metal pellets at bedsoil level.

4.2. Analysis of MTEs in Corn Matrices

4.2.1 Corn Leaves

In a context of accentuated drought where crops are practically linked to irrigation (here by wastewater), it is difficult to find control plans in the immediate vicinity of crops. The corn taken as a witness was taken from a garden. This corn is lagging in vegetation compared to the others and has not reached the heading stage: only the leaf and the root have been analyzed.

Table 4: Concentrations of MTEs in the control maize matrix (mg/Kg) :

	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Feuille	0.006	0.018	0.16	9.23	0.24	0.040	0.008	1.5
Racine	0.014	0.042	0.20	19.35	0.60	0.080	0.012	3.1

These concentrations (Table 5) are high compared to similar cases for other vegetation types and in other countries [33,34]. By comparing leaf concentrations with other organs of the plant, there is generally an increase in the concentrations of the elements (exception for Fe and Ni). The same case has been found elsewhere for other species and other plants [35]. The accumulation of metals in the roots and tops of a plant is a reflection of the concentrations of these metals in the soil and the genome of the plant [36]. The fixation mechanism of heavy metals and other minerals is based on the coordination and availability of the functional molecular groups present in the biological membrane surfaces [37]. Several of these groups are identified and known, including the PO4, COO and NH2 radicals and are used to subtract these metals from wastewater (biological purification). The phenomenon is in fact quite complex due to other parameters, including pH.

Table 5: Concentration of trace elements in corn leaves (mg /kg) :

Elément : / Station :	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
St1	0 .34	17.37	0.34	6879.96	144.41	13.62	20.44	22.65
St2	0.32	13.92	0.32	1425.67	193.02	20.73	12.18	30.38
St3	0.30	7.83	6.62	750.73	80.24	4.22	5.12	39.74
St4	0.31	9.62	29.46	2939.75	61.97	9.16	9.77	89.59
St5	0.34	9.99	9.48	2483.38	167.84	21.51	5.42	41.66
St6	0.32	9.93	49.65	369.16	34.59	40.20	10.41	93.69
St7	0.33	9.69	188.88	351.04	96.53	85.67	7.18	183.04
St8	0.27	4.50	24.29	413.35	51.86	6.00	4.50	61.00
St9	0.29	13.78	15.64	404.66	123.41	11.91	8.04	56.82
St10	0.31	2.63	0.31	112.58	32.74	1.70	3.40	53.74

In regards to physiological assimilation, metals by the different tissues of plants, in our case the corn plant, there are disparities in absorption within the same element and between the elements compared to each other. This is also normal from a physiological assimilation point of view and the need for different tissue ions. Only cadmium seems to have close and stable values both with respect to soil horizons and plant tissues. It is one of the few elements used in everyday life and its presence here is unquestionably of industrial origin

The corn plants in question appear to be normal, with no symptoms of chlorosis or any abnormality, contrary to what has been cited in some cases [38]. On the contrary, these corn plants are of a normal size, dark green color, and fairly developed stalk. The metal levels accumulated by the plants are probably not directly toxic: a part is evacuated by the detoxification system specific to each species, the rest is metabolized [39].

On the other hand, the "management of metals" in general within a plant follows a double logic: that of absorption which is a function of the state of availability or saturation of the transmembrane transfer pumps as well as the redistribution of the cations from the leaves following the development of what's known as "elaborated" sap [40]. As a result, there is likely to be bioaccumulation of metals at the root level. This concentration of elements is not analogous to that known in animals where there is always an element-organ or element-tissue specificity. This would translate in our case by a simple "congestion" following a saturation of the transmembrane ion exchange pumps of reinforced by the physiological contribution descending from the leaves

4.2.2. Corn Cobs

Concentrations at the cobs (Table 6 below) are often less than at the leaf level (except Cr and Cu). There is more Cu in the cobs, reminiscent of a bioconcentration. Indeed, the cobs being the last tissues formed before maturation suggests a double hypothesis: either there is really concentration by predilection of the fruit tissues (cobs), or that the plant reaches maturation when the sap is enriched in concentration by the simple evapotranspiration of plant tissues. This is all the more accurate in our case as the growth of maize does this per season of high heat (stronglyheliophile plant). The heavy metals are known to be non-biodegradable. They accumulate in the various plant tissues (and animals) and can cause disorders, deformities or even mortality [41]. This is not the case in our study: the corn plants are large and healthy, with no malformations or necrosis.

4.2.3 Corn Roots

At root level (Table 7), there are disparities in concentrations from one mineral to another. The elements (Cd and Cu) are approximately equally present on both sides of the root walls (soil side and intracellular side).

Table 6: Concentrations of trace elements in corn cobs (mg/kg):

Elément : / Station :	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
St1	0.34	40.96	9.95	570.76	248.63	47.70	7.25	68.27
St2	0.25	35.56	31.05	133.86	9.54	5.47	6.87	60.57
St3	0.23	29.15	78.11	392.16	61.18	15.12	5.03	59.22
St4	0.29	30.14	70.30	300.14	62.32	21.14	6.30	44.96
St5	0.27	31.11	86.43	250.51	27.66	16.22	2.13	41.69
St6	0.28	5.50	18.29	472.83	52.67	29.43	6.60	55.29
St7	0.30	8.24	0.45	1298.35	182.12	18.29	10.64	32.68
St8	0.30	12.65	0.15	508.32	52.10	14.00	8.13	44.57
St9	0.31	5.38	8.92	590.31	289.16	3.84	4.00	48.58
St10	0.31	2.63	0.31	112.58	32.74	1.70	3.40	53.74

Table 7: Concentration of trace elements in the maize root matrix (mg/kg) :

Elément : / Station :	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
St1	1.99	75.84	0.33	30585.18	510.83	37.84	104.06	44.81
St2	0.29	5.01	0.29	1191.48	74.55	10.02	5.44	17.60
St3	0.25	6.03	0.22	1081.48	64.35	9.15	4.31	15.50
St4	0.26	6.24	0.26	475.34	9.62	4.94	0.65	17.68
St5	0.28	6.91	0.28	2177.78	63.27	9.67	5.94	20.03
St6	0.29	3.34	0.29	1734.20	21.94	4.65	3.92	28.19
St7	0.25	5.80	0.25	1614.73	46.29	10.09	4.67	29.77
St8	0.29	9.88	0.29	2345.05	43.30	5.23	5.38	47.66
St9	0.33	11.39	0.31	2131.65	66.32	16.38	6.87	34.48
St10	0.30	3.62	0.30	1127.30	94.97	4.83	4.38	57.23

Other elements (Fe, Mn, Ni and Pb) are more present in the surface soil where corn roots grow than in the root tissue. In all cases, the concentration of an element in the roots is never higher than in the surrounding soil [42]. These latter authors report that roots generally contain more metals than stems and leaves: the available concentrations of metals in the soil do not necessarily influence the rates of their uptake by the plant. The same phenomenon has been reported in the experimentation with tomato plants [43]. It should be kept in mind that the roots are the only part of the plant buried in the soil and sheltered from high temperatures which would favor the absorption of the metallic elements during and long after irrigation. This can make (locally), When temperatures are biologically favorable, the very easy transmembrane transfer leading to high concentrations.

Conclusion

This study proved to be interesting because it revealed a case of distribution of the doses of the MTEs in "soil" and "plant" matrices. The values are sometimes quite high as is the case for iron, but in other cases in concordance with similar studies. Indeed, it has been found that the metallic traces obey the absorption rules which correspond to the physicochemical parameters mentioned above, mainly the adsorption by the surface of the roots, but also physiological phenomena of redistribution of the elements, in particular towards the roots, after the development of the sap at the leaves, which explains this hyperconcentration at the roots level.

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