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EVALUATION OF PHYSICO-CHEMICAL PARAMETERS OF AGRICULTURAL SOILS IRRIGATED BY THE WATERS OF THE HYDROLIC BASIN OF SEBOU RIVER AND THEIR INFLUENCES ON THE TRANSFER OF TRACE ELEMENTS INTO SUGAR CROPS (THE CASE OF SUGAR CANE)

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ABSTRACT

This research was conducted in Kenitra (northwestern Morocco) to determine the physicochemical parameters and metallic concentrations at three levels: surface water of Sebou and Beht intended for irrigation, agricultural soils and sugarcane. The spectrometric analysis of source plasma emission (ICP) has identified eight trace elements contained in the materials taken from zone 1 (As, Cd, Co, Zn, Ni, Pb, Cu and Cr). The obtained results showed that the interaction between the different physicochemical parameters of agricultural soils decides the transfer of the metal elements to the plants. Indeed, for the soil which is used in this agriculture (for sugar cane), its irrigation water, and the contents of Cr, Cd and As exceeds the accepted standards.

Keywords: heavy metals; ACP; sugar cane; agricultural soils; Oued Sebou; Oued Beht; Kenitra.

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1. INTRODUCTION

Moroccan agriculture has known a remarkable progress that has affected virtually all productions, whether animal or vegetable. The overall production has nearly tripled in real terms. Agriculture, despite the strong urbanization, still represents 15% of national wealth produced each year [1]. It is therefore absolutely essential to assess the risks related to the presence of heavy metals (trace elements) in the waters of irrigation, agricultural soils and crops since food is a major route of human exposure to trace elements [2].

The use of the waters of the river basin of Sebou area (Sebou Ouergha, Beht, low Sebou) for irrigation, which receives a load of 142 t / year of metallic elements [3] coming from cottage industries and which is estimated by 2000 units [4], can generate a metal pollution drained along these rivers that will be transferred to the soil through irrigation waters and subsequently into the crops.

This work lists the physicochemical parameters of evaluation of agricultural soils in the city of Kenitra (Sidi Allal Tazi and Mograne) and the environmental impact induced by irrigation from a water pumping station coming from Sebou in the various environmental media including: the waters of irrigation, agricultural land and sugar cane.

2. RESULTS AND DISCUSSION

2.1. Physico-chemical parameters of water and soil

a- physicochemical parameters of irrigation water

The parameters of waters shown in Table 2 are below the national standards of irrigation water with the exception of Sodium.

The high sodium content is likely to be harmful to agricultural soils because it replaces the calcium and the magnesium adsorbed on the clay particles and causes the dispersion of soil particles. So, there is this burst of soil aggregates causing a hard and compact ground when it is dry and excessively waterproof [5]. The concentration of sodium in the irrigation water is estimated by the sodium absorption ratio (SAR). This ratio describes the amount of sodium in excess of the calcium and magnesium cations, that they can be tolerated in relatively large amounts of irrigation water in [5].

$$SAR = Na + / \sqrt{(Ca 2 + Mg 2 +) / 2}$$

Sodium, calcium, and magnesium are given in meq / l.

Concerning this study, irrigation waters were characterized by a RAS between 0 and 6 so that they can generally be used on any type of ground with little problems of sodium accumulation.

The water neutralization potency is attributed mainly to the presence of calcium and magnesium bicarbonates dissolved in water. The weakly basic pH of the analyzed irrigation water promotes the imprisonment of calcium and magnesium in this carbonate, making them unavailable to the plant medium [5].

	Zone 1		Zone 2		Zone 3		Zone 4		Standard
Parameters	meq/l	mg /l	meq/l	mg /l	meq/l	mg /l	meq/l	mg /l	(mg/l)
nH	7.95	7.95	7.22	7.22	7.76	7.76	7.91	7.91	6.5 à 8.4
Flootrical	1.07	1.27	1.7	1.7	1.92	1.92	1.00	1.00	2
Electrical	1,27	1,27	1,/	1,/	1,05	1,05	1,22	1,22	3
conductivity									
(mmhos/cm)									
Calcium	3,8	76	6,21	124,2	5,96	119,2	3,98	79,6	-
Magnesium	1,7	20,4	3,75	45	3,98	47,76	1,32	15,84	-
Sodium	7	161	7,35	169,05	8,50	195,5	7,20	165,6	69
Potassium	0,23	8,97	0,52	20,28	0,50	19,5	0,23	8,97	-
Ammonium	0,03	0,612	0,078	1,404	0,03	0,468	0,17	3,096	-
Chlorides	5,66	198,1	6,18	216,3	6,32	221,2	5,34	186,9	350
Sulfates	2,35	112,8	4,199	201,55	4,13	198,2	2,95	141,8	250
Carbonates	-	-	-	-	-	-	-	-	-
Bicarbonate	4,3	262,3	6,12	373,32	7,62	464,8	3,88	236,6	518
Nitrate	0,35	36,9	0,596	21,7	0,69	24,97	0,31	11,35	-

Table 2. Physico-chemical parameters of irrigation waters

b- Physicochemical parameters of agricultural soils

The results shown in Table 3 show that the particle size of the studied soils corresponds to a clay loam texture.

The studied soils are characterized by a slightly basic pH, which moderately impedes the mineralization and dissolution of nutrients to make them available to plant roots and low organic content which requires the input of organic manure necessary for the photosynthesis

<u>_</u>	Zone 1	Zone 2	Zone 3	Zone 4
Fine ground %	-	-	-	-
Clay %	40,26	48,20	41,18	48,68
Fine silt %	31,02	27,95	35,64	28,73
Coarse silt %	16,46	16,98	22,26	25,03
Sandy %	12,89	4,55	0,90	0,72
Coarse sand %	1,93	0,81	0,63	0,41
рН	8,07	8,52	8,21	8,23
Electrical conductivity	0,18	0,47	0,22	0,24
in the extract 1/5				
(mmhos / cm)				
Limestone total %	19,40	15,20	16,60	15,20
Organic matter (%)	1,25	2,10	1,67	2,10
Organic carbon %	0,72	1,22	0,97	1,22
Ammonia nitrogen	23,40	17,28	21,24	20,16
(ppm)				
Ammonia nitrogen	74,40	23,04	100,44	68,20
(ppm)				
Mineral nitrogen (ppm)	98,52	40,32	121,68	88,36
- Calcium (meq / 100)	13,90	13,60	15,20	18,10
- Magnesium (meq/100)	15,00	15,60	14,60	14,50
- Sodium (méq/100)	1,00	3,75	1,58	1,83
- Potassium (méq/100)	0,59	1,55	0,99	0,85
Are	30,49	34,50	32,36	35,28
CEC	30,50	35,50	32,50	35,50
Available phosphorus	50	33	49	14
(ppm)				
Potassium echangeble	252	481	423	434
(ppm)				

of plants and the development of some micro-organisms necessary for the plant [6].

Table 3. Physico-chemical parameters of agricultural soils

Nitrogen (N) is an element for living organisms, assimilated by plants mostly as nitrate (NO3) or ammonium (NH4 +) from the soil solution [6], is contained in the soil in the area 2 at low

concentrations, which involves the contribution of nitrogen fertilizers.

In contrast, the concentration of assimilable phosphorus, which is a nutrient and necessary element for the growth of cultures in the zone 4 of soil, is less important compared to other areas.

Regarding the rest of the nutritious and the consitutive elements for plants, they are concentrated in the soil of all areas to tolerable and suitable levels for plant growth according to the interpretations of the ORMVAG.

c- Influence of physicochemical parameters of the studied agricultural soils on the transfer of trace elements to the crops

The physicochemical parameters affect the concentration of the metallic elements and decide their transfer from one environmental medium to another. Indeed, the weakly basic pH of irrigation water and alkali of the studied agricultural soils limit the mobility of metal and promotes their retention by the clay soil particles. Thus the clay structure for maintaining the metallic trace elements is carried out by adsorption in two modes [7]:

Adsorption by formating a covalent bond between the metal and the terminal -OH groups of the solid surface according to the following mechanism: X-O-H + $M^{n+} \rightarrow XO-M^{n-1} + H^+$.

Adsorption By exchanging ions based on the ionic substitution at the lamellar space of the clay. This mechanism depends on the load and the relative size of the exchanged metal elements. However, it is the second mode (adsorption at the solid surface) that predominates in the clay structure.

The values of cationic exchange capacity (CEC) vary between 30.5 and 35.5 meq/100 g. These values are quite low compared to the average values reported by [8] (60 meq/100 g for mineral soil), following the low organic matter of the studied soils where the metal elements are less complex by the latter and more available for root crops. However, there was an increase of the cationic exchange capacity with an increase in pH.

The rate of the total limestone soils in the different areas are average (15.2% to 19.4%). Limestone provides the plant with the necessary calcium. Among others, limestone blocks some elements which are indispensable to plants such as trace elements (Zn and Cu) [9].

2.2. Metallic fractions contained in the irrigation water, agricultural soil, bagasse and sugar cane juice (Zone 1)

The metallic contents in the supports of zone 1 represented by Table 4 show concentrations that exceed the thresholds set by the Moroccan standard of irrigation water (As and Cd), the AFNOR standards (NFU 44-041) for agricultural soils (Cr and Cd) and the Codex Alimentarius standards for sugar cane juice (As).

 Table 4. Results of nutrient trace elements in the irrigation water, agricultural soil, bagasse

 and sugar cane juice taken from Zone 1

	Irrigation	Standards Agricultural soils		Standards
	water (mg/l)		(mg/kg)	
As	0,247	0,1	30,43	-
Cd	0,042	0,01	10,6	2
Со	0,034	0,5	19,75	30
Cr	0,218	1	487,09	150
Cu	0,117	2	48,66	100
Ni	0,132	2	41	50
Pb	0,296	5	13,19	100
Zn	0,556	2	125,07	300
	Bagasse	Standards	Sugar cane juice	Standards
	(mg/kg)	(EC	(mg/l)	Codex
		directive)		Alimentarius
As	≤LQ	4	0,495	0,2
Cd	0,64	1	0,051	-
Со	0,204	-	0,012	-
Cr	1,034	-	0,236	-
Cu	4,19	-	0,274	5
Ni	3,591	-	0,208	-
Pb	1,619	10	0,142	0,2-0,3
Zn	7,075	-	0,711	5

Only a small fraction of the total contents of metallic trace elements in soil is available for plant roots (More bass from 1 to 3 orders of magnitude) [10]. Indeed, the metal enrichment for sugar cane juice and bagasse is respected in the following descending order:

- Bagasse: Zn> Cu> Ni> Pb> Cd> Cr> Co> As.

- Sugarcane juice: Zn> As> Cr Ni ~ Cu> Pb> Cd> Co.

Moreover, the passage from one organ to another of heavy metals is performed through the carriers that regulate the migration of the element through the chemical mechanisms (complexation with: organic acids, sugars, phenols and peptides and precipitation) that facilitate the movement or reduce it [11]. This explains the fluctuation in the range of metallic enrichment between sweet juice of the cane and bagasse.

Analyse globale des concentrations métalliques

The global analysis by the method of PCA (principal component analysis) is combined with the different levels of trace elements in a limited number of factors in order to facilitate the detection of independence relations between different metal concentrations.

Figure 2 illustrates the degree of information (proper value %) that each factor represents (number of compounds). Indeed, it is found that the first factor represents 99% of the overall total of the information of variables (As, Cr, Cd, Co, Cu, Ni, Pb and Zn) while the second factor represents 0.15% of variables. Therefore, the factor 1 and 2, which restore 99.15% of the variable, will be adopted to explain the correlation between the various metal contents.



Fig.2. Diagram of the proper values of each component

The correlations on the axis of factors 1 and 2 (component 1 and component 2) are displayed on the factorial map after rotation (Fig.3). However, it is noted that all the metallic elements are positively correlated in both axes. Thus we have:

- A high correlation of variables: Zn, Pb, Cu, Ni and Cd on the axis 1 (correlation>0.7)
- A good correlation of variables: As, Cr and Co on axis 2 (correlation> 0.7).



Fig.3. Correlation of metallic trace elements on the axes of Component 1 and Component 2 Where the factor 1 includes more and more variables (Zn, Cu, Ni, Pb, Cd) which are strongly accumulated in the bagasse with respect to Co, Cr and As, compiled by the factor 2. Thus, for the metallic elements of the factor 1 which restores 99% of the variable, the increase in the content of a metal induces an increase of the other in all the combined supports.

3. EXPERIMENTAL

3.1. Areas of Study

Surface water for irrigation in the region of Gharb-Chrarda-Beni Hssen (northwestern Morocco) consists mainly of the hydraulic basin of Sebou and its tributaries. The areas of study which are part of the complaint of Gharb, are two rural towns are named Sidi Allal Tazi and Mogran belonging to the city of KENITRA. These areas that develop various crops including cereals, fodder and sugar crops have pumping stations of irrigation waters of the Oued Sebou installed on and Oued Beht under the direction of the Regional Office of Setting Agricultural Value of Gharb (ORMVAG).

The agricultural lands Irrigated by the pumping stations of irrigation waters of Sebou and Beht (Fig.1) were identified through the pipes that supply their hydraulic needs.



Fig.4. Location of the study areas of Oued Sebou and Oued Beht

Agricultural areas, which are located through topographic coordinates of the four pumping stations of surface water coming from Oued Sebou and Oued Beht (Table 5), are located at 27 Km (Mograne rural commune) and 44 Km (rural commune of Sidi Allal Tazi) of the province of Kenitra. Thus, two surfaces were selected in each rural district:

- Zone 1: Agricultural area irrigated by pumping station of Sebou surface water at Sidi Allal Tazi.
- Zone 2: Agricultural area irrigated by a pumping station developed at a channel for diverting the flow of water of the Oued Beht to meet the needs of farmers in irrigation of their crops at Sidi Allal Tazi.
- Zone 3: Agricultural area irrigated by pumping station of Beht surface water at Mograne.

• Zone 4: Agricultural area located at Mograne and irrigated by the water of the dam that has the function of limiting losses in the sea waters of SEBOU river and maintenance of the water that will serve as a source of hydraulic irrigation.

Zones	Latitude (N)	Longitude (W)
Zone 1	34°30'22"	6°17'13"
Zone 2	34°29'37"	6°14'04"
Zone 3	34°24'36''	6°25'48"
Zone 4	34°28'59"	6°24'08''

Table 5.	Topographic	coordinates	of sam	pling sites
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3.2. The used materials

The samples were taken on 04/20/2014, which is the harvest period of sugarcane.

a- Sampling of irrigation water

Irrigation water were removed from the pumping stations in polyethylene sterile bottles of 500 ml and rinsed beforehand with the sample before being transported to the laboratory and stored at 4 $^{\circ}$ C.

b- Sampling of agricultural soils

The soil was taken in a zigzag way from five points on average of each site using a helical auger. The soils (Layer: 0-15 cm) from the same area were mixed, put into a clean plastic bag and labeled for transport to the laboratory.

c- Sugarcane Sampling

The sugar canes collected from the five points of zone 1 were put into a clean plastic bag and labeled to be sent to the laboratory where they were washed with tap water and then rinsed by distilled water to remove dirt and dust.

d- Extraction of sugar cane juice

The sugar cane juice was obtained by grinding the rods in a press comprising two rollers which provide the crushing allowing the recovery of juice (sugar juice) and bagasse (fibrous residue of sugarcane).

3.3 Treatment of samples and methods of analysis

a- mineralization of irrigation water and sugarcane juice [12]

A 10 ml sample of water was taken up in 10 ml of 50% hydrofluoric acid and dried with a sand bath in a Teflon beaker. Dissolving the obtained residue was effected by adding 7.5 ml of

hydrochloric acid and 2.5 ml of nitric acid. The beaker was covered with a watch glass and placed on a hotplate until the disappearance of red vapors synonymously with a complete mineralization. The solution obtained after filtration was completed to 50 ml with distilled water.

b- Mineralization of soil [13]

An amount of 1 g of the soil of the same depth was sieved by a sieve of 1 mm and dried at 70°C for 48 hours and was calcined in a muffle furnace at 450 ° C for 2 hours. The sample was then taken up in 10 ml of 50% hydrofluoric acid to be dried again in a Teflon beaker on a sand bath. The dissolving the residue is performed by a mixture of hydrochloric and nitric acid (7.5 and 2.5 mL). The suspension of the solution obtained after the filtration was completed to 50 ml with distilled water.

c- Mineralization of plant material [12]

A test sample of 1 to 2 g of vegetable, dried at 70 $^{\circ}$ C for 48 hours and then crushed, was calcined in a muffle furnace at 450 $^{\circ}$ C for 4 hours. The obtained ash was mineralized by aqua regia (HNO3 25% and 75% HCl) then reduced to dryness on a sand bath until the discoloration of the solution. The resulting residue was solved in 10 ml of HCl (5%), then filtered to 0.45 microns, before being diluted with HCl (5%) to the final volume of 20 ml.

d- The physicochemical analysis and the determination of trace metals

The analyzes of the physico-chemical parameters of soil and irrigation water were conducted in the laboratory of ORMVAG and the determination of metal fractions (Chromium, Cobalt, Copper, Zinc, Arsenic, Lead, Cadmium and Nickel) developed at the media, were read in ICP-AES (Ultima 2) by the National Scientific and Technical Research Centre (Rabat). The analytical laboratory uses the standards (1000 ppm precise Jobin Yvon) which are certified by ISO 9001 quality assurance system.

The metal concentrations conversion formula of mg/l to mg/kg for solid supports is as flows:

Cech (mg/kg) = Cech (mg/l)*VMineralization (l) / Mass sec taking (kg)

With Cech (mg/kg) the metal final concentration in mg/kg, Cech (mg/l) the metal concentration in mg/l, Vmineralization the volume of the sample after the mineralization in L and Mass sec prise d'essai (kg) the mass of the dried sample before calcinations in kg.

The principal component analysis of the average heavy metal content of irrigation water,

agricultural lands and sugar cane was produced by IBM SPSS STATISTICS software according to the procedure published by several authors [14, 15].

4. CONCLUSION

In this study, we studied the influence of the physicochemical parameters of agricultural soils irrigated by the waters of the Sebou hydraulic basin on the transfer of metals to crops and the bioaccumulation of trace elements in sugar cane sown in the ground of Zone 1.

Indeed, the weakly basic pH of the irrigation water and the clay texture of soil particles inhibit the bioavailability of heavy metals to the crop roots. This limited mobility following the physicochemical factors can be mitigated by the physiology of the plant. The nature of culture and the chemical form of this metal in the soil solution can be favorably absorbed by plant roots.

On zone 1, the average concentrations of As and Cd in irrigation waters are above the standards required by the national norms of waters intended for irrigation. In contrast, the average contents of Cr and Cd in agricultural soils exceed the limits recommended by the French standard AFNOR. Regarding plant supports, the As in the sugar cane juice exceeds the levels recommended by the Codex Alimentarius Standard.

Furthermore, the bagasse is able to accumulate the divalent ions (trace elements) in the following descending order: Zn>Cu>Ni>Pb>Cd>Cr>Co>As.

For the global analysis (PCA), the correlation between the different metals is positive in both the developed axes, so the contents of trace elements in all supports are proportional to each other.

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