Bioaccumulation of trace elements in agricultural crops and soils irrigated by the surface waters of Sebou and Beht rivers

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Received: 17/08/2021
Revised: 06/03/2022
Accepted: 28/03/2022

Abstract

Purpose: This study assessed the bioaccumulation of metallic elements in agricultural crops which is irrigated by the surface waters of Beht and Sebou rivers.

Method: The study focused on two plants. Seven metal elements (Cd, Co, Cr, Cu, Ni, Pb and Zn) were analyzed by spectrometry emission coupled plasma (ICP).

Results: The obtained results showed that the levels of Cd in irrigating water exceed the thresholds set by Moroccan standards. The concentrations of Cd and Cr in soil (0-15, 15-30 cm) are higher than those set by the AFNOR and the contents of Cd, Cr, Cu and Ni in the supports of the plants exceed normal levels which are established by Kabata-Pendias and Mukherjee. Indeed, the high absorption of certain trace elements by the tissues of the plants studied can be associated with the chemical forms of the metal in the soil matrix, the physicochemical characteristics of the soil and the nature of the plant species.

Conclusion: The bioaccumulation of identified metallic elements in plants is caused using surface waters of Sebou and Beht rivers as a source of irrigation.

Keywords: Morocco, Sebou and Beht River, metallic elements, irrigation water, soils, Plants.

Introduction

The cultivation of sugar beet is mainly localized in the irrigated areas of Lokkos, Doukkala, Tadla, Moulouya and Gharb. The latter, located northwest of Morocco has about 30% of sugar beet surfaces and provides 25.5% of the whole production which is 763.712 tons. However, in recent years, a reduction was observed in yields. The latter went from 49.5 tonsper hectare in 1999 to 45.5 tons in 2002 while the area under cultivation increased from 13 679 to 16 963 hectare.

The cultivation of Bersim is very widespread in the Mediterranean basin. In Morocco, it is very much used for the food of the dairy bovines (rich in nitrogenous matter). Adapted well to the climate it allows several cuts in the year, with important outputs, it has thus a vocation as principal fodder crops to bring a protein supplement in green.

Among the water resources which are threatened is the Sebou basin and Beht (rushes of the left bank of the Sebou River). Sebou is the most important river(watershed) in Morocco which measures 6.6.109 m3/year. It is a source of irrigation water supplying the national agricultural area of nearly 267.600 hectares and containing 30% of the national total resources that are currently and highly threatened **(Agence du Bassin Hydraulique du Sebou,2006)**. Beht is a course of sustainable and relatively powerful water; it originates from the Middle Atlas and its average annual inflows are of the order of 410 million m3 **(Administration de l'Hydraulique, 1991)**.

The two basins are given a load of metal elements exceeding 140 tons/year originating mainly from artisanal industries estimated at no less than 2000 units **(Agence du Bassin Hydraulique du Sebou,2010)**; therefore, any pollution drained along this stream is transferred to the soil through irrigation water and subsequently in cultures and finally to man. The aim of this study is to evaluate the average contents of seven metallic elements (Cd, Co, Cr, Cu, Ni, Pb and Zn) in the two plants (sugar beet and Bersim) cultivated in soils irrigated by the surface waters of Sebou and Beht Rivers.

Materials and methods

Study site

The two rural communes (Mograne and Sidi Allal Tazi) develop various cultures, mainly based on sugar crops, forage crops and cereals **(ORMVAG d'ELGHARB, 2012/2013)**. The samples (water, soil and crops) were collected from four areas located at 27 Km (rural commune of Mograne) and 44 Km (rural commune of Sidi Allal Tazi) of the province of Kenitra (Figure 1). The sampling points are located on figure 1:

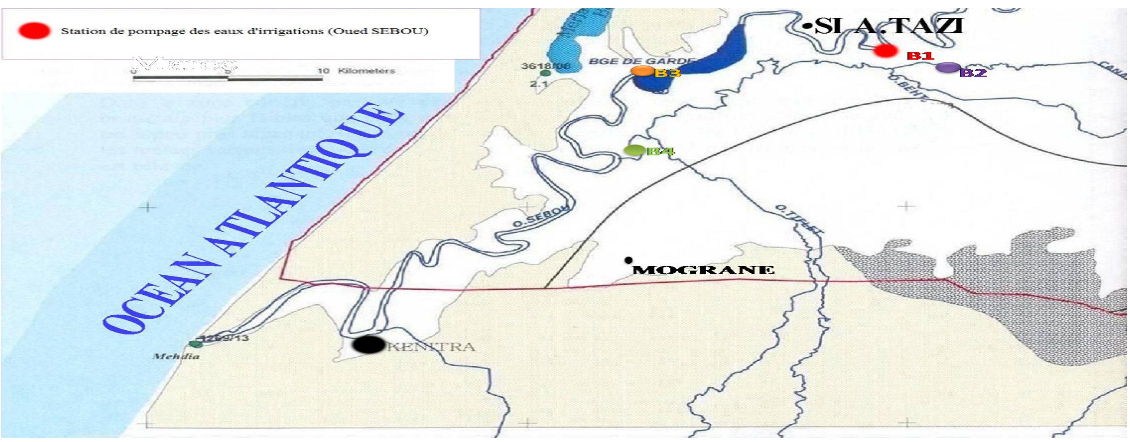

Figure 1. Location of study sites on Sebou and Beht rivers.

Table1. Topographic coordinates of the sampling sites.

Areas	Latitude (N)	Longitude (W)
B1	30°34 minutes 22seconds	17°6 minutes 13 seconds
B2	29°34 minutes 37seconds	14°6 minutes 04 se seconds
B3	34°28 minutes 59 seconds	6°24 minutes 08 seconds
B4	34°24 minutes 36 seconds	6°25 minutes 48 seconds

Soil sampling

The floor is collected through 5 sampling points with the aid of a helical auger, at two different depths (0 - 15 and 15 - 30 cm). The same soil of the two different depths is mixed, put into a plastic bag, and then transported to the laboratory. The sol was dried in the open air and sieved to 2 mm to remove unwanted materials such as rocks and stones.

Collection of cultures

The Agricultural plants collected (Five points on average in a zone) of each sampling zone **(B1, B2, B3, B4)** was put into a clean plastic bag and labeled to be conveyed to the laboratory where they are washed and rinsed with tap water. The supports of the same kind belonging to a similar area were mixed and subdivided to obtain four test samples from each sampling point.

Soil mineralization

An amount of 0.5 to 1g of soil was calcined in a muffle furnace at 450 °C for 2 hours. Each sample, previously ground, was placed in a Teflon beaker, and added to 10ml of hydrofluoric acid (HF) to 50% to be re-dried on a sand bath to dryness. The obtained residue is taken up by a hot mixture of hydrochloric and nitric acid (7.5 and 2.5 ml) to be concentrated until its complete dissolution. The suspension obtained after the decantation is transferred to a 50 ml vial. It is then calibrated with distilled water and then homogenized. In the presence of refractory compounds and / or high concentrations of silica, a residue will always remain. The silica can be eliminated by repeating the first step for a second time (HF-HCl) **(Tauzin et Juste, 1986)**.

Mineralization of water

A sample of 10 ml of water, without any prior calcination, has been taken up by 10 ml of hydrofluoric acid (HF) to 50% and dried again in a Teflon beaker in a sand bath. Dissolving the obtained residue is affected by the addition of 7.5 ml of hydrochloric acid and 2.5 ml of pure nitric acid. The beaker is covered with a watch glass and placed on a hotplate until disappearance of red vapors synonymous with a complete mineralization. The resulting solution is made up to 10ml with distilled water. Whites of mineralization were conducted jointly **(Tauzin et Juste, 1986)**.

Mineralization of plant material

A test sample of 1 to 2 g of vegetable, which are dried at 70 °C for 48 hours and crushed, was calcined in a muffle oven at 450 °C for 4 hours. The obtained ash is mineralized by aqua regia (HNO_3 25% and 75% HCl) then reduced to dryness on a sand bath until the complete discoloration of the solution. The obtained residue is redissolved in 10 ml of HCl (5%), and then filtered to 0.45 microns, before diluted with HCl (5%) to the final volume of 20 ml (Tauzin et Juste, 1986).

The analyzes of the physico-chemical parameters of soil and irrigation water were conducted in the laboratory of the regional office of agricultural development of Gharb and the determination of metal fractions (Chromium, Cobalt, Copper, Zinc, Lead, Cadmium and Nickel) were read in ICP-MS (Ultima 2) at the National Center of Scientific and Technical Research (Rabat).

The metal concentrations of the conversion formula from mg/l to mg/kg for solid materials is given as follows:

$$C_{ech}\ (mg/kg) = C_{ech}\ (mg/l) \times V_{minéralisation}\ (l)\ /\ \text{dry mass of the test portion (kg)}$$

With:

C_{ech} (mg / kg): The final concentration of metal in mg/kg.
C_{ech} (mg / l): The final concentration of metal in mg/l.
$V_{minéralisation}$: The volume of the sample after the mineralization in liters.
Dry test sample mass: The mass of the sample dried before calcination.

Results and discussion:

Analysis of irrigation water

The results of the pH measures and contents of the obtained metal fractions are shown in **Table 2.**

Table 2. pH and metallic characteristics (mg/l) of irrigation water

Parameters	B_1	B_2	B_3	B_4	Averages	Moroccan standards for irrigation
pH	7.95	7.22	7.91	7.76	7.71	6.5-8.5
Cd	0.042	0.037	0.058	0.049	0.042	0.01
Co	0.034	0.032	0.066	0.076	0.052	0.5
Cr	0.218	0.232	0.411	0.698	0.389	1
Cu	0.117	0.088	0.211	0.184	0.150	2
Ni	0.132	0.088	0.214	0.323	0.189	2
Pb	0.296	0.175	0.438	0.389	0.324	5
Zn	0.556	0.119	0.311	0.410	0.349	2

The results of analyzes show that metal contents in Cd exceeds the thresholds of irrigation water set by Moroccan standards, this contamination originates from urban waste. The physico-chemical parameters of irrigation water decide the transfer of the metallic micropolluant towards agricultural crops **(Anne Tremelo-Schaub et Isabelle Feix, 2005)**. Indeed, the neutral and the weakly-basic pH of irrigation water hinder the passage of the trace elements to the plants **(Godin, 1982)**.

Soil analysis

Table 3 shows the physicochemical characteristics of the metal and solid supports of soil.

Table 3. The physico-chemical and metallic characteristics (mg/kg) of soil from different study areas.

Parameters	B_1	B_2	B_3	B_4	Averages	Standards	
pH	8.07	8.52	8.23	8.21	8.25	-	
Clay (%)	40.26	48.2	48.68	41.18	44.58	-	
Fine silt%	31.02	27.95	28.73	35.64	30.83	-	
Coarse silt%	16.46	16.98	25.03	22.26	20.18	-	
Fine sand %	12.89	4.55	0.72	0.90	4.76	-	
Coarse sand%	1.93	0.81	0.41	0.63	0.94	-	
CEC	30.5	35.5	35.5	32.5	33.5	-	
O.M rate (%)	1.25	2.10	2.10	1.67	1.78	-	
Depth (15-0):						AFNOR	Agricultural soils
Cd	10.76	7.87	8.9	7.2	9.31	2	1-300
Co	20.12	17.4	27.2	13.5	19.55	30	20-50
Cr	450	321.2	366.85	391.7	382.43	150	50-200
Cu	40.3	24.4	42.25	48.5	38.86	100	60-150
Ni	42.79	33.77	46.65	38.05	40.31	50	20-60
Pb	16.39	20.87	36.25	36.55	27.51	100	20-300
Zn	114.4	86.93	133.3	91.7	106.58	300	1-300
Depth (30-15):							
Cd	9.34	9.2	8 .55	8.15	8.89	2	1-300
Co	21.93	20.61	29.25	18.1	22.47	30	20-50
Cr	604.3	523	190.3	364.35	420.48	150	50-200
Cu	47.7	46.74	46.7	44.8	46.48	100	60-150
Ni	43.6	46.25	45.5	37.25	43.15	50	20-60
Pb	13.95	9.66	34.65	20.25	19.62	100	20-300
Zn	130.2	103.64	104.78	108.6	111.80	300	1-300

The study areas are characterized by a basic pH soil, low organic matter content, a high cationic exchange capacity (CEC) and a grain size of salty clay with variations of clay percentages of a sampling point to another. The results of the analyzes show that metallic contents of Cd and Cr in soil (0-15 and 15-30 cm) exceeds the thresholds set by AFNOR, which is explained by the excess in urban wastes (industrial, craft activities), the agricultural activities, the chemical forms of metal in the soil matrix, and the physico-chemical characteristics of the soil.

Plant analyzes

The results of the metal fractions contained in the various samples of the plants collected through surfaces studied, were summarized in **table 4**.

Table 4. Metal levels (mg/kg) in the supports of the plants

Supports	B_1	B_2	B_3	B_4	Medium	Kabata et Pendias* **(2007)**	FAO/WHO limits **(2001)**
Beet							
Cd	0,581	0,584	0,494	0,564	0,555	0.005–0.04	0,02-0 ,2-
Co	0,295	0,303	0,272	0,245	0,270	0.005–0.27	-
Cr	1,438	0,82	0,454	0,907	0,904	0.01–0.41	-
Cu	4,867	4,946	7,111	7,926	6,212	3–8	5
Ni	4,479	3,091	3,636	4,159	3,841	0.06–1.3	0,2
Pb	2,897	3,946	3,353	2,159	3,088	0.2–2.4	0,5-1
Zn	19,234	14,041	14,535	9,791	14,400	1.2–27	100
Bersim							
Cd	0 ,28	0 ,80	0,66	0,65	0 ,60	0.005–0.04	0,02-0 ,2
Co	0,25	0,46	0,35	0,50	0 ,39	0.005–0.27	-
Cr	0,34	1,71	1,13	1,00	1,05	0.01–0.41	-
Cu	7,38	14,77	11,07	13,67	11,72	3–8	5
Ni	4,00	1,17	1,99	1,96	2,28	0.06–1.3	0,2
Pb	1,29	5,57	2,40	4,08	3,33	0.2–2.4	0,5-1
Zn	8,79	26,90	15,23	31,01	20,48	1.2–27	100

(*): Average levels of the metallic elements in agricultural crops sown in normal soil.

The results represented by the figure2 which illustrates the variation of the metal contents within the edible part of the Bersim, show that thanks to its high content of cellulose and proteins, the Bersim is able to accumulate the divalent ions (metal elements), in the order of specificity according to: $Zn^{2+} >> Cu^{2+} >> Pb^{2+} > Ni^{2+} \approx Cr^{2+} > Cd^{2+} \approx Co^{2+}$.

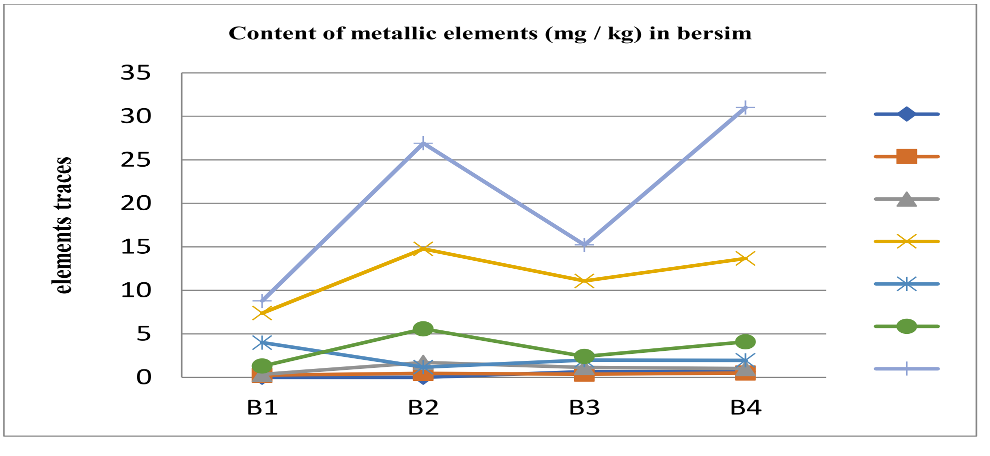

Figure 2. Content of metallic elements (mg / kg) in Bersim

The results represented by figure 3 which illustrates the variation of the metal contents within the beet leaves (edible part by the cattle), show that, thanks to its high content pectin, the leaves of beet is able to accumulate the divalent ions (metal elements) in the order of specificity according to: $Zn^{2+} >> Cu^{2+} >> Ni^{2+} > Pb^{2+} > Cr^{2+} > Cd^{2+} \approx Co^{2+}$.

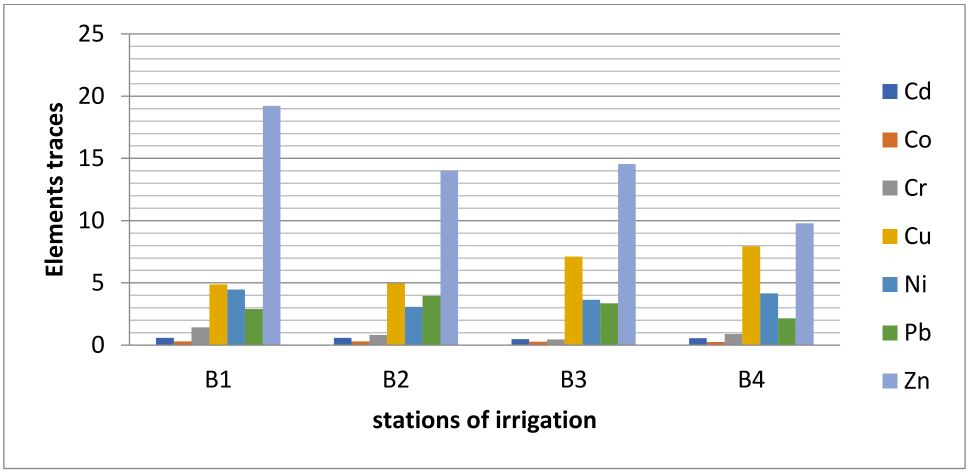

Figure 3. Content of metallic elements (mg / kg) in sugar beet

Calculation of the transfer factor TF:

The absorption of metallic elements from the growth medium is evaluated by the ratio of the concentrations of these elements in plants and in the soil. The transfer factor (FT) is a primary factor controlling the exposure of consumers (humans) to metal risks **(Kabata-Pendias, A., Mukherjee, A.B., 2007, Zhuang, P. et al, 2009)**. It is calculated by the following relation:

$$TF = C_{plant}/C_{soil}$$

With:

C_{plant}: The concentrations of metallic elements in the plant (consumable part).

C_{soil}: The concentrations of metallic elements in the soil.

Table 6. Transfer factor of metallic elements from the soil (0-15 cm) to the edible part of plants

Supports	Cd	Co	Cr	Cu	Ni	Pb	Zn
B1(bersim)	0,034	0,010	0,0007	0,185	0,089	0,102	0,077
B2(bersim)	0,108	0,026	0,0065	0,600	0,046	0,320	0,387
B3(bersim)	0,088	0,013	0,0030	0,274	0,042	0,070	0,106
B4(bersim)	0,072	0,031	0,0025	0,271	0,048	0,106	0,354
B1(beet)	0,053	0,014	0,0031	0,120	0,104	0,176	0,168
B2(beet)	0,074	0,017	0,0025	0,202	0,091	0,189	0,161
B3(beet)	0,055	0,01	0,0012	0,168	0,077	0,092	0,109
B4(beet)	0.078	0,018	0,0023	0,163	0,109	0.59	0,106

The results of Table 5 show that the transfer factors of Zn, Cu and Pb are high compared to other metallic elements (Co, Cd, Ni, and Cr), this is explained by the interactions between phosphorus, zinc, calcium and copper in soil and plants which may play a role in improving the absorption of both elements. Low organic matter content (1.25 to 2.10%) can encourage greater mobility and improve uptake by plant tissues. The trace elements (Zn, Cu…) are essential, in small quantities, with the growth of the plants, in order to avoid the risks related to their deficiency.

Treatment of irrigation water with sugar cane bagasse (SCB)

The results of analyzes of trace elements in irrigation water treated with **SCB** are presented in **Table 6**.

Table 6. Levels of trace elements (mg/kg) in irrigation water after treatment with **SCB**

Trace elements	Cd	Co	Cr	Cu	Ni	Pb	Zn
B3	0,01	0,005	0,09	0,01	0,005	0,005	0,005
R% (B3)	%83	%92	%78	%95	%98	%99	%98

R%: yield

The results of this table show that there is a significant decrease in the levels of trace elements for most of these elements (Co, Cu, Ni, Pb and Zn). For the other elements (Cd and Cr), we observe that that purification is not complete, this is explained by the presence of other elements which are not characterized, and which enter in competition with these elements on the level of the SCB **(Elanza, S, et al, 2014)**.

Conclusion

In this study, we studied the bioaccumulation of metallic elements in sugar beet leaves and Bersim irrigated by water from pumping stations in the Sebou and Beht rivers. The obtained results showed that the levels of Cd of irrigation water exceed the thresholds set by Moroccan standards, the concentrations of Cd and Cr in soil (0-15, 15-30 cm) are higher than those set by the **AFNOR** and contents of Cd, Cr, Cu and Ni in the supports of the plants exceed normal levels established by **Kabata-Pendias and Mukherjee**. The high uptake of some trace elements by the plants studied may be associated with the chemical form of the metal in the soil matrix, the physicochemical characteristics of the soil and the nature of the plant species. Thanks to its high content pectin, the leaves of beet is able to accumulate the divalent ions (metal elements) in the order of specificity according to: $Zn^{2+} >> Cu^{2+} >> Ni^{2+} > Pb^{2+} > Cr^{2+} > Cd^{2+} \approx Co^{2+}$. Thanks to its high content of cellulose and proteins, the Bersim is able to accumulate the divalent ions (metal elements), in the order of specificity according to: $Zn^{2+} >> Cu^{2+} >> Pb^{2+} > Ni^{2+} \approx Cr^{2+} > Cd^{2+} \approx Co^{2+}$.

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التراكم الإحيائي للعناصر المعدنية (المعادن الثقيلة) في المحاصيل الزراعية التي تروى بالمياه السطحية لنهري سبو وبهت

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تاريخ استلام البحث: 2021/08/17
تاريخ تعديل البحث: 2022/03/06
تاريخ قبول البحث: 2022/03/28

المُستَخلَص

الهدف قيمت هذه الدراسة التراكم الإحيائي للعناصر المعدنية(المعادن الثقيلة) في المحاصيل الزراعية التي تروى بالمياه السطحية لنهري سبو وبهت(غرب المملكة المغربية).

الطريقة: ركزت هده الدراسة على نبتتين مختلفتين وتم تحليل سبعة عناصر معدنية (الكادميوم والكربون والكروم والنحاس والنيكل والرصاص والزنك) بواسطة البلازما المقترنة بانبعاث الطيف (ICP).

النتائج: المحصل عليها أظهرت أن مستويات معدن الكادميوم في مياه الري تتجاوز العتبات التي حددتها المواصفات المغربية و تركيزات الكادميوم والكروم في التربة (0-15 و 15-30 سم) أعلى من تلك التي حددتها AFNOR بينما محتويات الكادميوم والكروم والنحاس والنيكل في دعامات النباتات تتجاوز المستويات الطبيعية التي تم تحديدها بواسطة Kabata-Pendias and Mukherjee. في الواقع، يمكن أن يرتبط الامتصاص العالي لبعض العناصر المعدنية في أنسجة النباتات المدروسة بالأشكال الكيميائية للمعدن في مصفوفة التربة وبعض الخصائص الفيزيائية والكيميائية للتربة وطبيعة الأنواع النباتية.

مفاتيح الكلمات: التراكم البيولوجي للعناصر المعدنية (الثقيلة) المدروسة في النباتات ينتج عن استخدام المياه السطحية لنهري سبو وبهت كمصدر للري.