Evaluation Of The Heavy Metals Accumulate In Samples Of The Sediments, Soils And Plants By Icp-oes With The Average Sebou

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The urban, industrial and artisanal wastes liquid of the town of Fez have a very remarkable impact in the valley of Sebou. For that, various samples of sediments, agricultural grounds and plants were collected upstream like downstream from the junction Oued Fez- Oued Sebou along about thirty the kilometers; and analyzed by the method of the optical spectrometry of emission to source of plasma in inductive coupling (ICP-OES). These analyses enabled us to evaluate the contents of heavy metals such as: Ba, Zn, Cr, Ni, Co, Cd, Pb, Cu and others. All the results record a high degree of contamination of the metal elements to the state of trace in samples of sediments, grounds and plants irrigated with worn water containing of the particles of suspended materials. We could establish significant correlations of each metal for the various compartments of the ecosystem.

Keywords: heavy metals, sediment, soil, plant, Sebou River, Fez River

I. INTRODUCTION

The metallic pollution threatens our globe more and more and often results mostly from a high degree of development (Industry,.....). Indeed, the creation of big production capacities in the industry and in agriculture, as well as the apparition of massive concentrations of the urban populations, generate damages and give vise to an unbalance of the environment in general and of the aquatic surroundings in particular.

Besides, Sebou river represents a resource in important water for the flight of the region of the Sebou basin; this important aquatic system has become the unique receiver of waste water of the city of Fez valued to a volume of 110000 m^3 / day, rejected in Sebou river without any treatment. However, these waste water, are used - until our days - for the irrigation of several types of cultures in the region, which is consequently is associated to non negligible risks. This survey has for object to value the contents in accumulated heavy metals in the different samples taken from different chosen sites, upstream as well as downstream, at the junction Fez river - Sebou river, in order to show the obvious impact of the waters of Fez river on the waters of Sebou river and on the neighbouring fields.

II. EXPERIMENTAL SURVEY

II.1. Sampling

Urban, industrial and agricultural discharge of the city of Fez in the valley of Sebou river, have a great impact on the wildlife downstream the confluence Fez river - Sebou river. To explore this impact, seven sites have been selected to take samples from water, sediments, soil and plants, to get information about the nature and the composition of the discharges

Site of withdrawal	Point of withdrawal
S1	Fez River downstream (situated before the confluence)
S2	5 km after the confluence
S3	10 km after the confluence
S4	15 km after the confluence
S5	20 km after the confluence
S6	25 km after the confluence

Geographical situation of the different sites and points of withdrawal

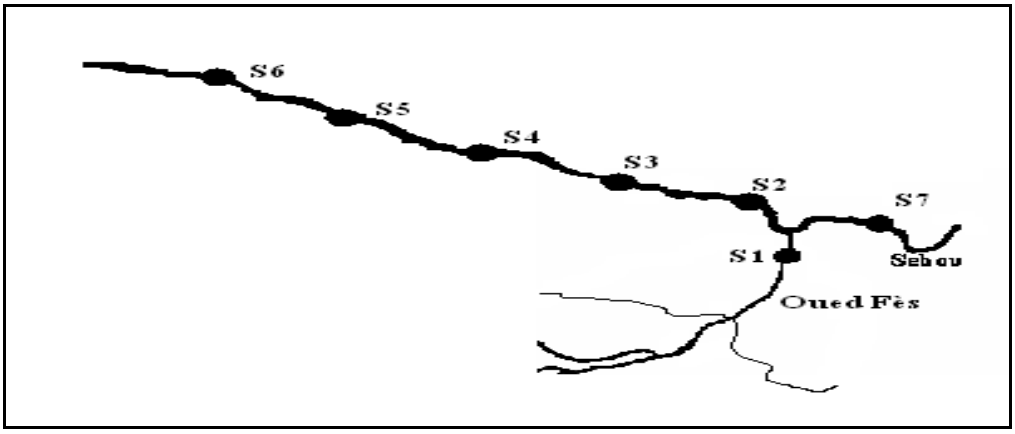


Figure 1: Various sites of taking away and river

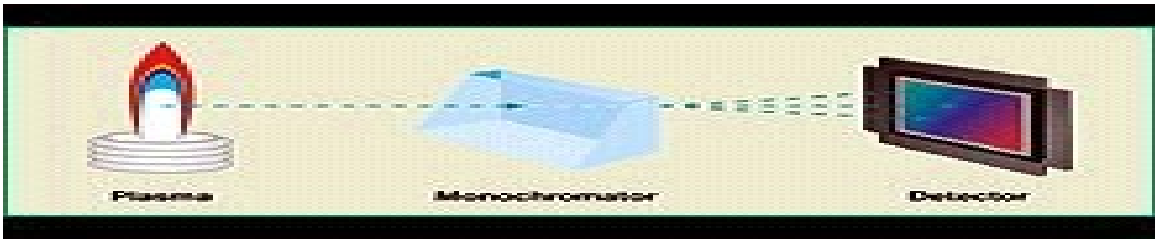
Metals and the major elements considered have therefore been measured out in samples of sediments, withdrown below 10 cm of depth [1-a] to avoid all accidental contamination. These samples have been dried at 80°C during 24 hours, ground and sifted to 250 µm. Other withdrawals of samples of soil in the same sites, have been taken near the root of plants and submitted to the same procedure of preparation [1-b].

Samples of plants have been calcined at 405°C during 4 hours in order to eliminate the organic matter and to value the bio-availability of some undesirable or toxic elements in the plant and to determine the risk of contamination that can occur within perishable produces. Analysis of the samples revealed that these samples constitute a very good indicator of the metallic contamination [2]; they also know a fast growth and a big consumption in the region.

The samples of all compartments (sediment, soil, plant) have been analyzed by Optical Emission Spectrometry equipped with an Inductive Coupling Plasma source (ICP-OES).

II.2. ANALYSIS TECHNIQUE

THE **ICP-OES** is a major technique for a preliminary analysis. It consists in introducing the sample in the plasma torch. The atoms in the plasma emit light (photons) with characteristic wavelengths for every element having a proportional intensity to its concentration. This light is recorded by one or several optic spectrometers and is calibrated; the technique provides a quantitative analysis of the original sample (fig. 2). The samples are dissolved by acid attacks before their passage in the spectrometer [3].



Torche ICP Monochromateur Détecteur

Figure 2: General outline of an optical spectrometer of emission

Site / Elément	S1	S2	S3	S4	S5	S6	S7	Norme (b)
Fe	26700	26120	26200	27200	17700	17700	31700	
Mn	350	440	400	420	540	500	490	
Mg	12200	22700	19800	19500	8900	9300	23900	
Ca	168000	171000	163000	167000	217000	211000	152000	
Ba	130	120	130	180	240	290	180	**445**
Zn	150	180	220	190	80	70	100	**140**
Cr	50	90	170	170	30	30	80	**100**
Ni	30	30	40	40	30	30	40	**35**
Co	6.2	9.1	9.0	11.1	6.4	6.7	4.0	**20**
Cd	0.25	0.27	0.39	0.57	0.11	0.09	0.08	
Pb	167	57	73	82	15	14	21	**85**
Cu	**75**	**101**	**112**	**97**	**43**	**35**	**72**	**36**

Table 1: Contents of the metal elements traces (in ppm) accumulated in the samples of the sediments analyzed by ICP-OES

II.2.1 / Factor of contamination (FC):

If (S_i) represents the concentration of a metal of a sediment sample in the site (i) and S7 the reference value of this concentration at the reference site upstream of Sebou river before its confluence with the discharges of the city of Fez, then FC = S_i/ S7.

II.2.2 / Factor of pollution (FP):

This factor is calculated in relation with a standard reference value of general use « norms: geological service. Alsace, 1982, Martin, 1979 », then FP = S_i / Norm. So, there is contamination or pollution if FC or FP > 1.

II.2.3 / Factor of concentration (FC):

This factor is defined as the ratio of the metal concentration of a sample at the plant root to its concentration at the soil, then FC = Cv / Cs

Site / Paramètre	S1	S2	S3	S4	S5	S6	S7
PH	7.5	7.2	7.8	7.2	7	7.5	7
H_2O %	5.4	3.4	5.22	5.96	6.11	7.3	7.4
M.O %	0.44	0.2	3.24	1.5	2.6	0.75	0.58
Perte au feu %	0.76	0.3	0.16	0.3	0.3	0.75	1.12
$CaCO_3$ %	39.13	18.47	19.56	27.17	26.17	41.3	28.26

Table 2: Contents of the metal elements traces (in ppm) accumulated in the samples of the Soils analyzed by ICP-OES

Site	S1	S2	S3	S4	S5	S6	S7	Nor
Fe	26500	26300	31900	29700	27300	20600	27900	20000
Mn	3420	4200	3400	3600	3600	5000	4100	
Mg	15300	18300	20300	20000	19900	15400	26800	
Ca	159000	153000	126000	140000	143000	153000	132000	

Ba	190	130	150	210	170	290	80	
Zn	920	210	320	280	260	100	80	**88**
Cr	540	90	920	700	590	120	100	**45**
Ni	50	30	40	40	40	30	30	**22**
Co	6.6	9.1	7.9	7.8	6.6	6.8	7.3	
Cd	1.68	0.44	0.43	0.45	0.27	0.10	0.04	
Pb	510	106	93	83	77	38	15	**22**
Cu	**518**	**157**	**160**	**133**	**117**	**47**	**35**	**26**

Table 3: Contents of the metal elements traces in (ppm) accumulated in the samples of the plants analyzed by ICP-OES

Site / Elément	S1	S2	S3	S4	S5	S6	S7	Norme (c)
Fe	2300	500	2400	4200	1000	2900	1400	
Mn	40	20	50	80	60	80	40	
Mg	5000	2100	6000	4800	3200	2600	3600	
Ca	22000	11000	22000	37000	30000	29000	26000	
Ba	30	20	30	100	100	110	20	
Zn	50	60	70	260	50	60	230	**100**
Cr	10	<10	10	40	<10	10	10	**0.3**
Ni	10	<10	10	10	10	10	10	**1**
Co	<0.1	<0.1	1.0	<0.1	<0.1	1.6	0.3	**0.5**
Cd	0.07	0.02	0.08	0.35	<0.01	<0.01	0.31	
Pb	24	1.5	2.5	9.9	1.2	3.9	13	**8**
Cu	**41**	**79**	**75**	**134**	**45**	**73**	**229**	**15**

Table 4: Results of the physicochemical parameters of the water samples taken in various sites

Site / Paramètre	S1	S2	S3	S4	S5	S6	S7	Norme (d)
T (°C)	17	18	16	14	13	13.5	15	15
pH	7.2	7.1	7.2	7.1	7.1	7.2	7.7	6.5-7.5
C (µs/cm)	2214	1754.3	1606	1882	1943	2256	1169	500
OD (mg d'O_2/l)	0	2.439	8.38	2.579	2.821	3.465	6.367	6.1
MES (g/l)	0.15	0.13	0.1	0.07	0.02	0.02	0.01	0.03
DCO (mg d'O_2/l)	252.2	127.36	47..91	56.74	153.84	117.27	37.83	30
Cl^- (mg/l)	305.3	262.7	241.4	284	305.3	326.6	191.7	
SO_4^{2-} (mg/l)	39.25	87.25	18	32	26.25	9.25	2.65	0.48
PO_4^{3-} (mg/l)	4.88	3.55	0.84	1.35	2.43	2.29	0.043	
NO_3^- (mg/l)	5.33	13.34	0	0	0	0	2.66	0.05
NH_4^+ (mg/l)	23.9	14.22	2.43	8.5	11.14	10.74	0.032	

Table 5: Physicochemical parameters of the sediments

FC / Elément	*FC1*	*FC2*	*FC3*	*FC4*	*FC5*	*FC6*	*FC7*
Cr	*0.2*	*0.11*	*0.058*	*0.235*	*0.33*	*0.33*	*0.125*
Zn	*0.33*	*0.33*	*0.318*	*1.36*	*0.625*	*0.85*	*2.3*
Pb	*0.14*	*0.026*	*0.034*	*0.12*	*0.08*	*0.27*	*0.61*
Cu	*0.54*	*0.78*	*0.67*	*1.38*	*1.046*	*2.08*	*3.18*

Table 6: Factor of concentration of the elements Cr, Zn, Pb and Cu in various sites

III. RESULTS AND DISCUSSIONS

To appreciate the impact of the waters of Fez river on the quality of the waters of Sebou river, it is necessary to value the mineral composition of these waters widely used in the domain of agriculture. Several indicatory parameters of pollution are used.

The study of the physico-chemical parameters has been done according to the spatial dimension that consists of the assessment of the pollution along about thirty kilometers downstream the junction Fez river - Sebou river. The concentration of the OD at the S1 site is null; which is imputed to the strong loads in organic matters poured by Fez river in the river of Sebou. Weak contents in OD were recorded for S2, S4, S5 and S6 sites traducing a serious insufficiency of the capacity of the receiving environment to accomplish an auto-purification.

The DCO has recorded high values at all sites, which is due to big loads in organic matter. (high DCO low OD). The electric conductivity shows high values for all

sites without exception. It could be of natural origin or due to salty polluting discharges.

- The MES recorded at the different sites, decreases progressively along the river; until it reaches the acceptable values 0.02g/l at S5, S6 sites and 0.01g/l at the S7 site (taken as reference). This can be explained, essentially, by the auto-purification.

Indeed, by comparison of our results with the international norms, we note that the average values of the quasi-totality of the studied parameters exceed the limits of pollution.

This preliminary physico-chemical characterization of the sediments (Tab.5) permitted us to note that the different studied sediments have a middle fluidity, that they are neutral or slightly alkali traducing the sedimentary nature of the chalky lands rich in organic matter and in carbonates.

III.1 / TOXIC METALS IN THE SEDIMENTS:

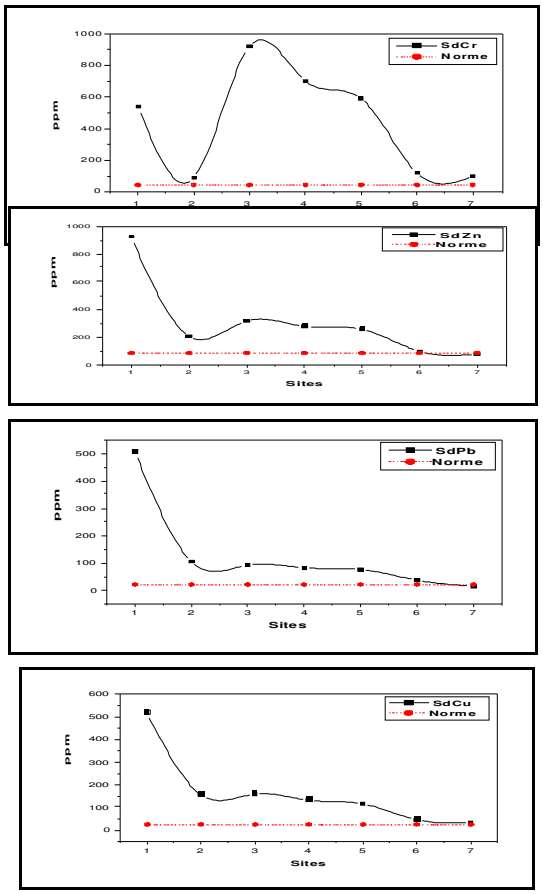


Figure 3: Concentrations in ppm, of the elements Cr, Zn, Pb and Cu in the sediments taken in various sites

From figure 3, except for the S7 site which has been taken as reference, one notes that all elements: Cr, Zn, Pb and Cu present high contents that exceed extensively the norm recommended by the geological service of Alsace. The Cr records high values [10] in the S3, S4 and S5 sites; which is due to the dripping of contaminated agricultural soils, and to the use of the chromium, that represents an impurity in fertilizers, is a source of considerable contribution to soils [11].

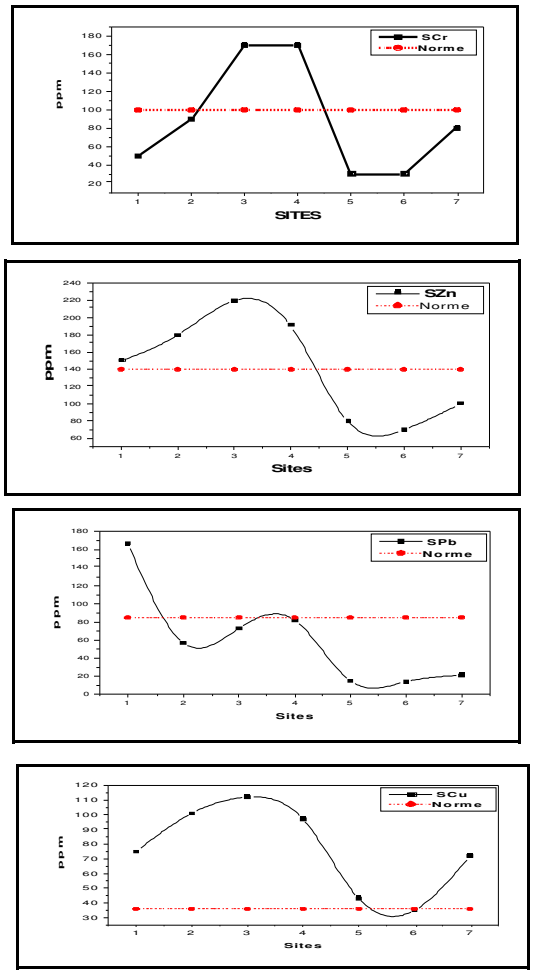


Figure 4: Concentrations in ppm, of the elements Cr, Zn, Pb and Cu in the samples of the soil taken in various sites

III.2/ Toxic metals in soil:

According to figure 4, one notices that the concentration of the Cr, in all sites, is lower than the

natural content; with the exception of S3 and S4 sites, for which high values were recorded due to the granulometry and the type of soil, as well as to the geology of the region consisting of the two sites.
However, recorded concentrations of Cu at all sites, except the S6 site, are superior to the norms and especially for the S3 and S4 sites. This high concentration in copper is due to the use of the sulphate and the acetate of copper as insecticides in this zone [12].
For the Pb, all contents are lower than the natural ones.

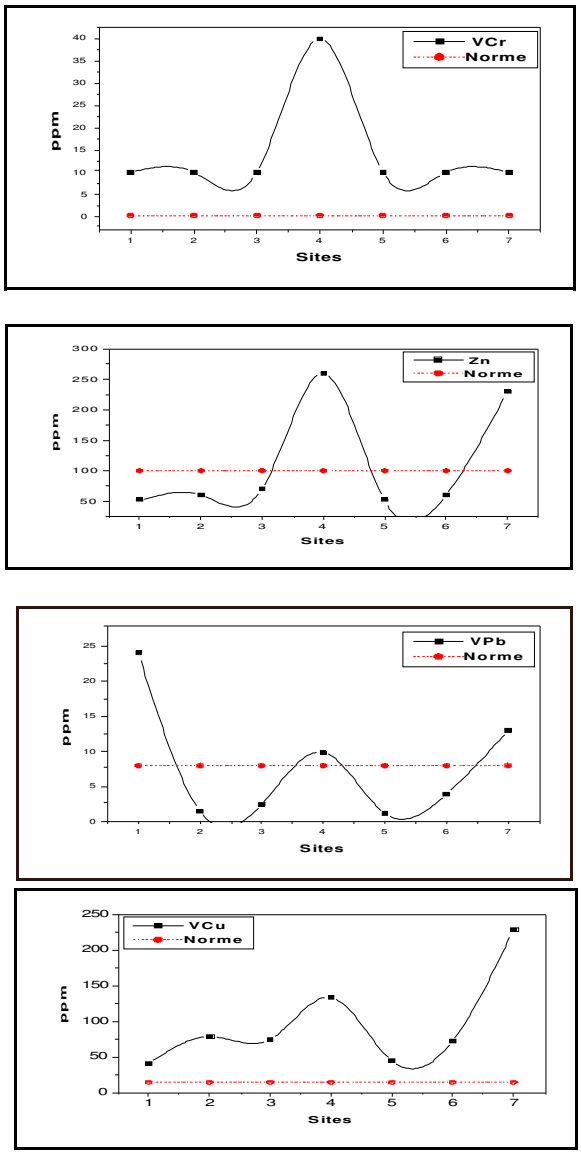


Figure 5: Concentrations in ppm, of the elements Cr, Zn, Pb and Cu in the samples of the plants taken in various sites

Indeed, soil plays the role of an epurative system that could keep these metals in these different phases. Some of these metals, once incorporated in soils, can be absorbed by vegetation.

III.3/ Toxic metals in the root of plants:

According to figure 5, concentrations of Cr and Cu, in the root of the plants taken from different sites, exceed the norms recommended by the O.M.S, especially in the S4 site. This is illustrated by the strong accumulation of chromium as well as copper in the plant, while Zn and Pb elements which contents are lower than the norm, except the S1 and S4 sites, are less absorbed by the root of the plant.
The anomaly present at the S7 site, consisting in very high concentrations for Cr, Zn, Pb and Cu elements, is probably due to the nature of the plant and to its duration of production.

III.4/ FACTOR OF CONCENTRATION:

To confirm our results, we have calculated the factor of concentration [13].
The results presented in table 6, show that only the Cu element that is more accumulated in the vacuoles of the root in the S4, S5, S6 and S7 sites. The Zn element presents a case, in the S4 site, where it is more absorbed by the root than by the soil. The other toxic metals have a FC < 1, which traduces their strong accumulation in soils than in the plants.
And the variations of metallic accumulation especially observed between the roots due to the capacities of exchanges of the root and their radicular device to absorb a metal.

IV/ CONCLUSION

The behavior of the heavy metals in soil and their bio-availability to the plants is linked to the physico-chemical factors of soil including granulometry, the organic matter present in soil, the pH and the cationic exchange capacity; as well as the process that control the speciations of the

heavy metals: precipitation, adsorption and the formation of complexes.

The contents in heavy metals in the sediments are higher in relation to the admissible norms and so are the concentrations of Cr, Cu and Zn taking into account the natural contents present in the non polluted soils and in the root of the plant.

All results indicate a degree of high pollution of all compartments (waste water, sediment, soil and plant) belonging to the downstream of the middle Sebou, and show the obvious impact of the reuse of the waste water and/or their discharge in the natural environment; what constitutes a threat for the quality of the surface waters, the underground water, soils, the edible plants and therefore important sanitary risks for the public health.

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