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The Metal Elements Traces Dregs with the Unstable Fraction of the Sediment of Sebou Which Risk?

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Abstract
In forms dissolved and/or fixed at the particles the metal elements traces can accumulate in the sedimentary zones and constitute important stocks of pollutants. These contaminants can be remaining in the dissolved phase and become biodisponible under the effect of the physicochemical conditions and could act as a long-term source of pollution. To understand the mobility and the reactivity of these stocks is an important issue for the management of the quality of the hydrosystèmes. The exchangeable or unstable fraction of the sediment corresponds to the metal ions being adsorbed on the surface of the particles constituting the sediment (clays, oxide iron…), or mobility and the biodisponibility are high in this fraction because of the weak electrostatic interactions. The goal of this study and to characterize the sediments of Sebou and Fès Rivers and to evaluate the risk of toxicity of the elements metal traces related to the particulate phase by the method of spared digestion. Metals in these fractions are assumed to be more available than metals associated with residual fractions.
The results obtained show a strong mobilization of the elements related to the unstable fraction which reaches 100% for Pb and 70% for Cr. The sediments are composed of two mineralogical phases and they are also very rich in organic matter.

Keywords: Sebou, Fes, Sediment, Pollution, Metal Elements Traces, Unstable fraction, characterization.

1. Introduction
The Sebou River is the biggest river in Morocco. 600 km is the distance between its source in the Middle Atlas and the Atlantic. It plays a vital role in supplying water for drinking, irrigation and industrial purposes in all over its watershed. It can be divided into three distinct geomorphic catchments: the upper, middle, and lower Sebou. The sampling sites are located on the middle Sebou, where the river is facing a very strong pollution flows of water surface [1] and sediments [2].
Fès city (alone) generates 40% of the total impact of water quality on the Sebou River [3]. The city accounts for 400 industrial units, employing more than 22,000 persons and a huge variety of craft industries [4].

These rejections contain important concentrations of micropolluants organic, toxic nutrients and elements metal traces, and thus involve a considerable degradation of the water quality of Sebou [5].
The agricultural use of waste water of the Fès and Sebou Rivers on the level of the area of Fès is more intense and aims primarily the market gardening's [7]. This use is accompanied by health hazards for the man and his environment [7].

The metal elements traces are most dreaded of the polluting substances owing to the fact that they are no biodegradable and the phenomenon of car purification proves generally unable to solve the problem [8].
And even if the sediments are quasi ultimate traps for the EMT, nevertheless that this fixing is not final because of the change of the physic-chemical conditions [9]

However, the majority of the legislations governing the acceptable levels of an element trace metal in a compartment of the environment (water, the biocoenosis, the sediment or ground) refer to the total concentration rather than with the chemical shape of this element and the substrate in which it is [10]. This data does not provide any information about becoming element traces metal concerning its interaction in deposits, its biodisponibility or its toxicity. The abundance of an element traces metal in a fraction of the sediment compared to another determines the impacts on a given medium [11].

In general, five mineral fractions are differentiated by Tessier [12] and Kribi, 2005 [13]:
Exchangeable fraction: This exchangeable fraction corresponds to the metal ions which being adsorbed on the surface of the particles constituting the sediment (clays, oxide iron…) Mobility and the biodisponibility are high in this fraction because of the weak electrostatic interactions.
Fraction related to carbonates: This fraction corresponds to (Co) the metal precipitation of ion with carbonates. A dissolution with acid pH (between 6 and 8) of carbonates causes a release of heavy metals.
Reducible fraction: the fraction related to manganese and iron oxides this very unstable thermodynamically in a reducing medium and/or anoxic fraction can contain metal ions associated with (oxy-) hydroxides with iron, manganese….
Oxydable fraction: the fraction related on MO and sulfides, it corresponds to the ETM related to the humic, acid …. This fraction strongly reacts in medium oxidizing or under the activity of the micro-organism.
Residual fraction: This part represents the metal ions trapped in the crystalline mineral matrix which thus has a low reactivity.

Heavy metals exist mainly in six different geochemical forms in sediment
These are water soluble, exchangeable, carbonate bound, Fe–Mn oxide bound, organic matter bound and residual. The sum of the fractions with the exception of residual is termed non-residual fraction (Hickey and Kittrick, 1984). Metals in the non-residual fractions are assumed to be more available than metals associated with residual fractions.

Our study is interested especially in the unstable fraction (exchangeable) which indicates the elements adsorbed on mineral surfaces by nonspecific connections of electrostatic attractions type. This fraction is environnementalement very important insofar as it represents the fraction of the elements which interact quickly with the solution of the medium and are thus most easily mobilizable [14].

2. **Materials and methods**

2.1. *Study area:*

The studied area has a continental semi-arid climate with cold winter and hot summer. The winter period, between October and April, is the rainy season; while the remaining months are mainly dry [4]. The base flow of the river is around 17 m3 [15].
The geological characteristic of Sebou watershed includes clays and calcareous formations of the middle Atlas Mountains.
Samples were selected along the Sebou River and its junction with Fès River, where the principal vector of pollution is noted (Fig1):

Station N°1, "FES AMONT": located on the Fès River before its entry to the city, considered as a reference station,
Station N°2, "AIN NOKBI": The station is located downstream of Fès city (Fig. 1), representing the converging area of all the effluents from Fès city before joining the Sebou Rive
Station N° 3, "CONFLUENCE": in the confluence of Fès river with Sebou River.
Station N°4, "AMONT ONEP": located on the Sebou River upstream of the confluence with Fès River, this reference station is not influenced by the pollutant emissions.
Station N°5, "SEBOU BORD ROUTE": located on the Sebou Rivers at approximately two kilometers downstream of the junction with Fès River.

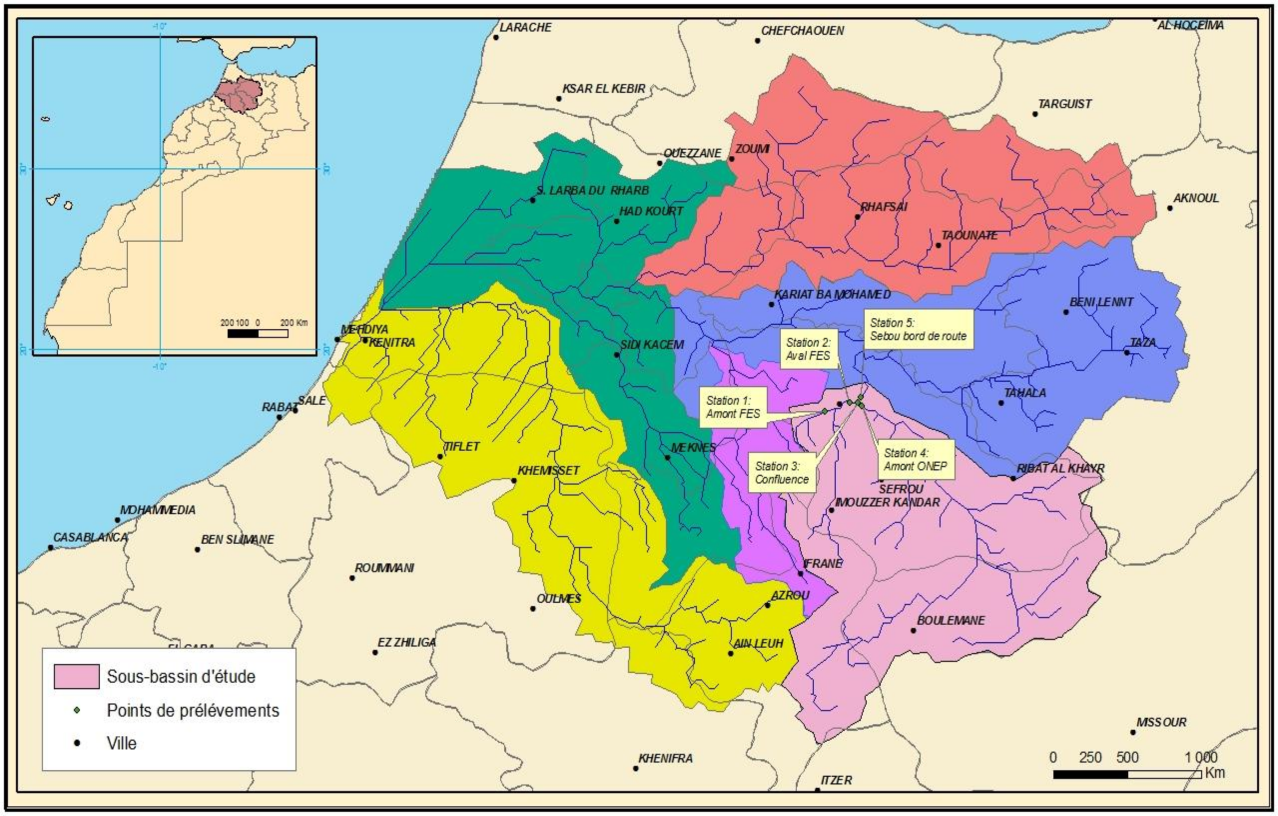

Figure 1: Chart of distribution of the intake points in the basin.

2.2 *Measurement in situ*
Silver All materials in contact with the samples were with polypropylene which has been carefully decontaminated (24 hours in HNO3) [16]. Samples were manually collected from approximately 10 cm underneath the surface and transported in a refrigerator to the laboratory in a bottle decontaminated. Measurements of the physicochemical parameters (temperature, pH, dissolved oxygen (DO), electric conductivity (EC)) were performed in situ with a multi-probe (Probe Holder, Standard, portable hach) calibrated before each campaign
2.3 *Diffraction x-ray*
The diffraction of x-rays is a method universally used to identify the nature and (or) the structure of the crystallized products. Indeed, this method applies only to crystalline mediums (rocks, crystals, minerals,

pigments, clays…) showing the characteristics of the crystalline state, i.e. an ordered and periodic arrangement of the atoms on a three-dimensional scale. The atoms of a crystal are organized in more or less dense reticular plans indicated by their coordinates (hkl) in a system of location of space (these coordinates are called indices of the reticular plans). Certain plans contain much more atoms than others according to the chemical formula of the crystal and are separated by characteristic distances (inter-reticular distances d) depending on the internal symmetry of the crystal. These are the plans which are at the origin of the diffraction of x-rays by a crystal (in the same manner that the luminous rays are refracted by plane mirrors). This diffraction is all the more intense as the plan is dense (rich in atoms). The analyses which we carried out were carried out on a D 5000 diffractometer of Siemens (30 mA, 40 KV) with a radiation source of Cu Kα (1,543 Å), a nickel filter removes the Kβ line of Cu. The diffractograms were recorded between 20° and 60° in 2θ with a step of counting of 0,02° and a time of counting by steps of 2 S. the slits before and back are respectively of 1 mm and 1mm.

2.4. Organic Matter determination

Organic matter influences many of the physical, chemical and biological properties of sediment. Organic matter content in the sediments was determined by the calcination technique according to Byers et al. (1978) the results were expressed as percentage of total organic matter in each sample. One weighs 0,25 g of sample prepared for test in a quartz capsule, one places it in a furnace then one calcined with 450°C during 3 hours, then one withdraws the capsule and one lets cool. The percentage of loss of mass generated by the calcination represents the percentage out of organic matter.

Data Analysis:

(1) Determine the mass of the dry sediment. MD=MPDS-MP

(2) Determine the mass of the ashed (burned) sediment. MA=MPA-MP

(3) Determine the mass of organic matter MO = MD – MA

(4) Determine the organic matter (content).

$$OM = \frac{\mathrm{MO}}{\mathrm{MD}} \times 100$$

2.5. Attacks with aqua regia

For the determination of the total metal elements traces, the samples of all the sampling stations were dried at 80°C. Then they were crushed and sieved. After an attack by the method of aqua regia, the extracted liquid fraction was the subject of the later analysis; 10 ml of aqua regia (mixture of HNO_3 and HCl, in a 1 /3 ratio) were added to 2 g of fresh sediments, wetted with a few ml of ultrapure water in a 100 ml round bottom flask. This solution is heated under backward flow during 2 hours. After cooling and filtration, the solution is analyzed by ICP-MS (Inductively Coupled Plasma Mass-Spectrometer).

2.6. Provided digestion

The exchangeable fraction is removed by changing the ionic composition of water allowing metals sorbed to the exposed surfaces of sediment to be removed easily. A salt solution is commonly used to remove the exchangeable fraction. [14]. It possible to evaluate the concentration in element related to the unstable fraction in the particulate phase of the sediments by provided digestion. The method of spared digestion is thus, very practical for the fast evaluation of the reactivity and biodisponibility of certain mineral phases of the sediments. The method consists in attacking dried sediment with 80°C using 50 mL of acetic acid 5%. On 2g of dried crushed and filtered sediment one adds 50ml of acid in a balloon to round bottom. The balloon is heated during 15 min with a system has backward flow then the samples and filtered is analyzed with ICP [18]. Sample used is that of the N°5 station has two the most representative kilometer of the junction.

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3. **Results and discussion**

3.1. ***Results of the measurements «in situ»***

The temperature and the pH of water are two factors important in the aquatic environment owing to the fact that they intervene almost in the totality of the physical, chemical and biological reactions [23].

The variations of the measured parameters in the Fez and Sebou Rivers are displayed in figure 2. Results indicated global changes from the upstream Sebou River S4 to downstream (S5) or water parameters (pH, and DO) Fig 2. The mixing of the Fez and Sebou Rivers leads to an increase in EC values (values always higher than 700 µS/cm) and a decrease in DO values in S5. Oxygen depletion in S3 and S5 indicates that water quality has been seriously degraded by anaerobic conditions, most probably due to the decomposition of organic material from Fez's untreated wastewaters [24].

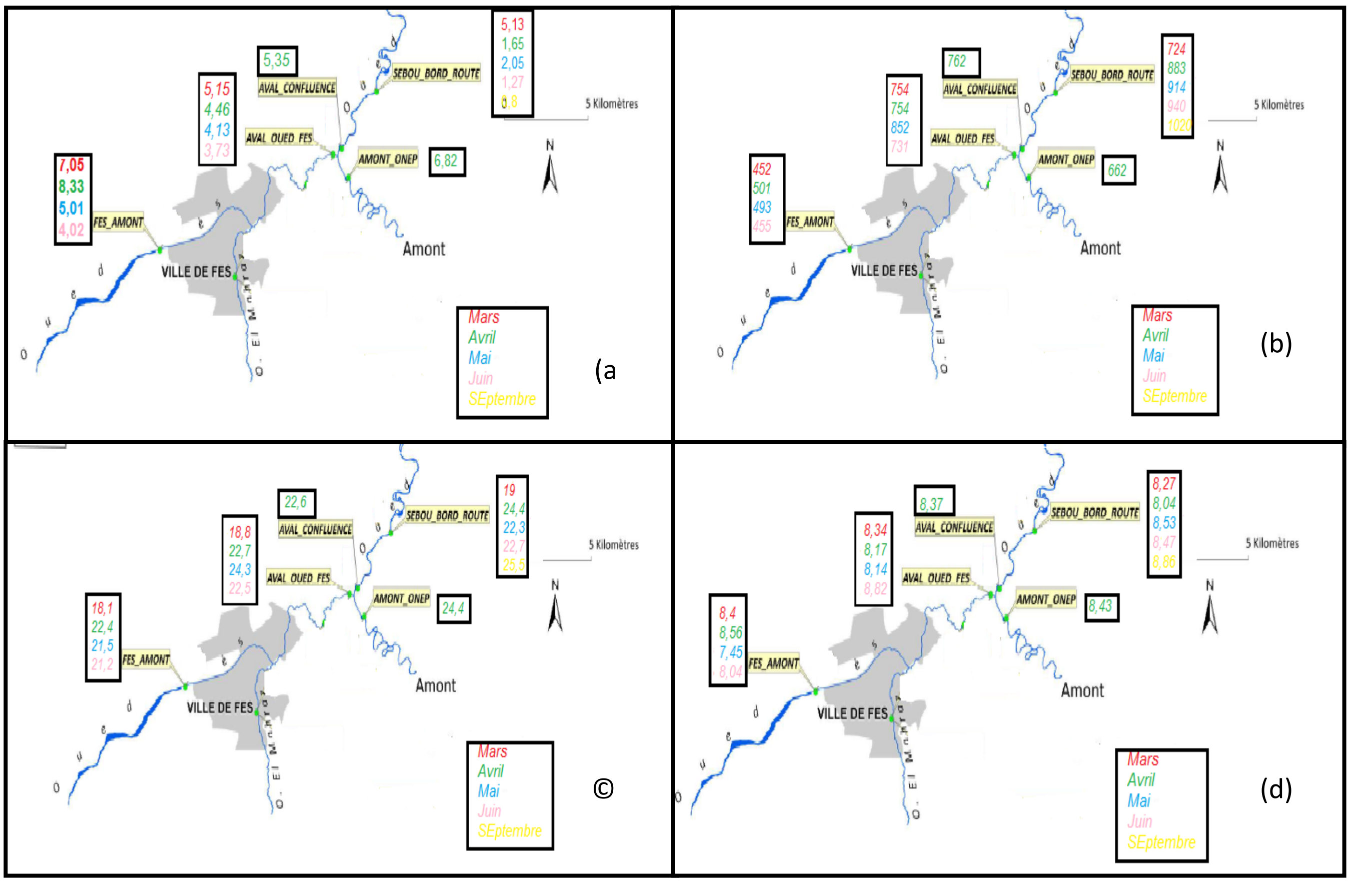

Figure 2: Physicochemical chart of follow-up of the parameters for 5 months. (a)The oxygen follow-up dissolved in mg/l, (b) Followed conductivity in µS/cm, (c) Followed temperature in °C, (d) Followed pH.

3.2. ***Result of the Diffraction x-ray***

The mineralogical characterization of the sediments is a complement essential to the physicochemical analyzes. It makes it possible to characterize various minerals or materials supports of pollution. The information obtained starting from the diffractogram of x-rays of the sediments allows the description of two distinct crystalline phases: calcite and quartz. It will be noticed that the intensity of the peaks of the various phases is more important for the sediment of the N°4 station what represents a stronger concentration of these phases in this sediment. This analysis enables us to conclude that part of carbonates present in the sediments is calcite ($CaCO_3$) (fig3). The mineralogy of the sediments is consistent with the descriptions mineralogical region; the Sebou River originates in the Atlas medium chain characterized by essentially calcareous dolomitic [25]. It is noted that heavy metals are not detectable directly by the means of this method for the reason which they present in amorphous forms. The identification of compounds on the curves of XRD remains quite difficult, and it is not obvious to find other compounds that the majority (quartz, calcite) (figure3).

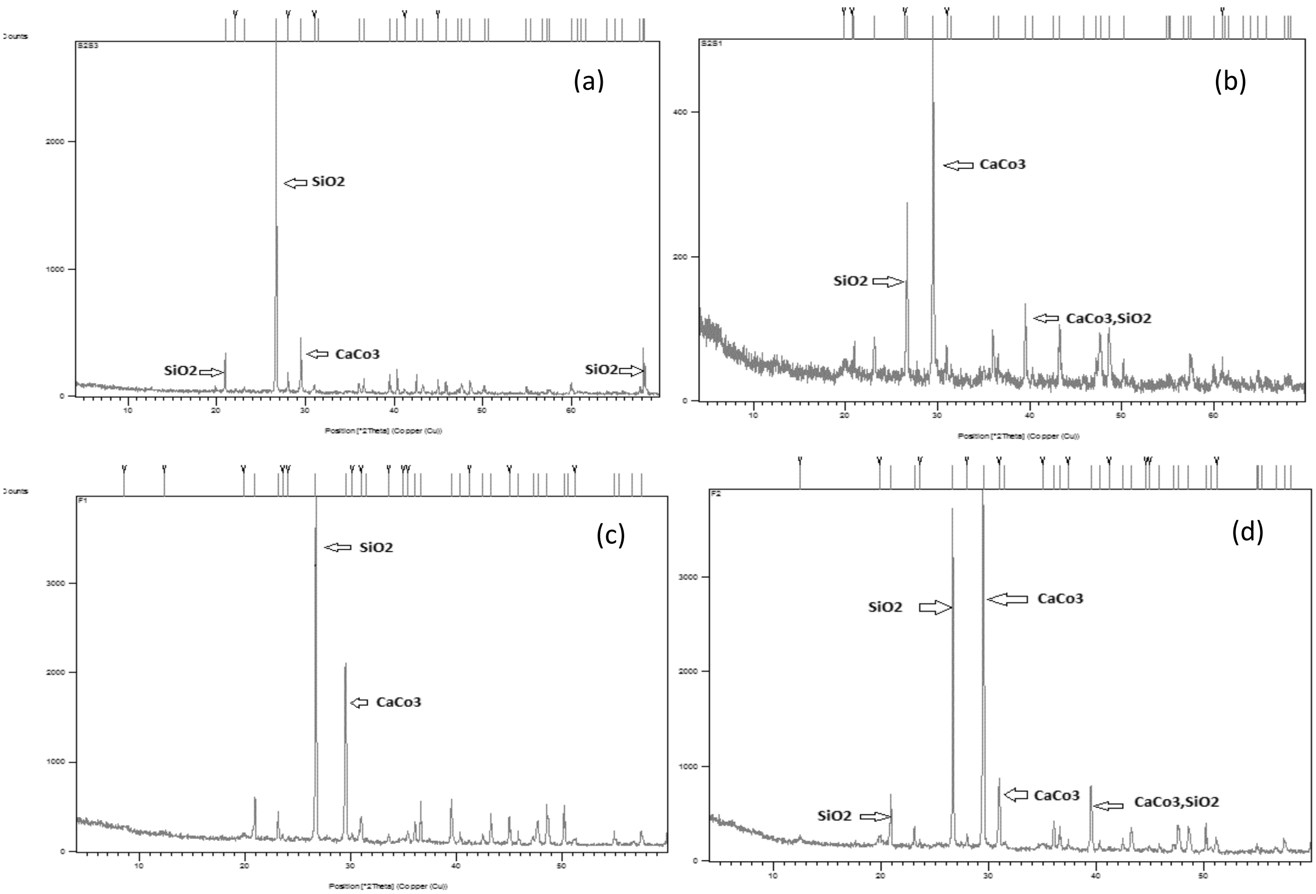

Figure 3: Mineralogical analysis by diffraction of x-rays of the sediments of various stations (a)sample of the station N°1(Amont Oued Fes), (b)sample of the station N°4 (Amont ONEP), (c) sample of the station N°2(Ain Nokbi),(d) sample of the station N5(Sebou Bord de la route).

The table 1 presents the organic matter content in surficial sediments in the study area. The calculation of the percentage of the organic matter of the samples by calcination shows also the presence of an important Organic Matter mass in different the stations except for both station from refers. This would be in relation to the strong polluting load of the Fès city and development of phytoplankton in rivers.

Table 1: % of the organic matter in the various stations.

Stations	MD(g)	MO(g)	OM (%)
SN°1	4.79	1,49	31,10
SN°2	4,92	4,61	93,69

SN°4	**4.80**	**2,56**	**53,3**
SN°5	**4,92**	**4,41**	**89,63**

3.4. *Results of the attacks to water levels*

The ETM settle with the solids in suspension, tend to accumulate in the surface sediments. They are used not only like vector of transport but also stock room and accumulations; it presents a better analytical determination due to the important total contents like with an integration in time.

The metals mobilized by the attack with aqua regia sediments of Sebou and of its affluent Fès river show a progressive enrichment of the sediments in several metals, (chromium exceed 1404µg/g, Pb 431, 2µg/g, Ni 120, 25µg/g… at the station 5. contrary to the station n°4 (station of refers) an almost total of Cr and Pb. This enrichment is related and also dependent to the property of the sediments to trap the elements metal traces [9], thus with the rejection of the effluents of the artisanal activities ² (tannery and dinandery) of the Fes city, the annual flow of particulate Cr (86 T) transported by the Fès river and which is introduced thereafter into Sebou, is only 5 times lower than that transported by large rivers like Saint Laurent, in spite of flow 4500 times lower than this last and such a related to the property of the sediments to trap the elements metal traces [26].The measured concentrations of metals in S3 and S9 surface sediments (0–10 cm) were compared with those recorded in other rivers from various countries, including Morocco (Table 2). The metal concentrations measured in the Fès River were superior to those recorded in heavily polluted rivers such as the Deûle [23], which received direct discharges from metallurgical industry in the area. However, the Fès river concentrations appeared to be significantly higher than environments receiving comparable urban inputs, particularly with respect to Cr concentrations. Nevertheless that this fixing can be transformed into a source of pollution related to the changes of the physicochemical conditions [27].

Table 2: Comparison of maximal trace metal contents in Sebou and Fès Rivers surface sediments in the present study and other studies of other Moroccan and international rivers.

Authors	River, location	Layer (cm)	Pb (µg/g)	Zn (µg/g)	Cr (µg/g)	Ni (µg/g)	Cu (µg/g)
Barakat et al(2012) [19]	**Day, Morocco**	**0-10**	**135.3**	**145.5**	**311.7**	**-**	**740.8**
Singh et al (2005) [20]	**Gomti, India**	**Surface**	**40.3**	**41.7**	**8.15**	**15.7**	**5.0**
Mohiuddin et al (2010) [21]	**Tsurumi,Japon**	**0-10**	**41**	**381**	**103**	**37**	**133**
Suresh et al (2011) [22]	**Ponnaiyar,India**	**Surface**	**85.2**	**182.9**	**87.3**	**29.5**	**81.8**
Lesven et al (2010) [23]	**Deule, French**	**0-6**	**2.490**	**5**	**-**	**28.333**	**179**
Hayzoun et al (2014) [4]	**Sebou (Downstream of Fes city, Morocco**	**0-6**	**100**	**236**	**115**	**46**	**171**
Hayzoun et al (2014) [4]	**Fes, Morocco**	**0-6**	**184**	**365**	**881**	**84**	**244**
Present study	**Sebou (Downstream f Fes city, Morocco**	**0-10**	**431.2**	**157.7**	**1404**	**24.59**	**137.5**

Present study	**Fes, Morocco**	**0-10**	**284.4**	**136.5**	**1376**	**120.25**	**81.9**

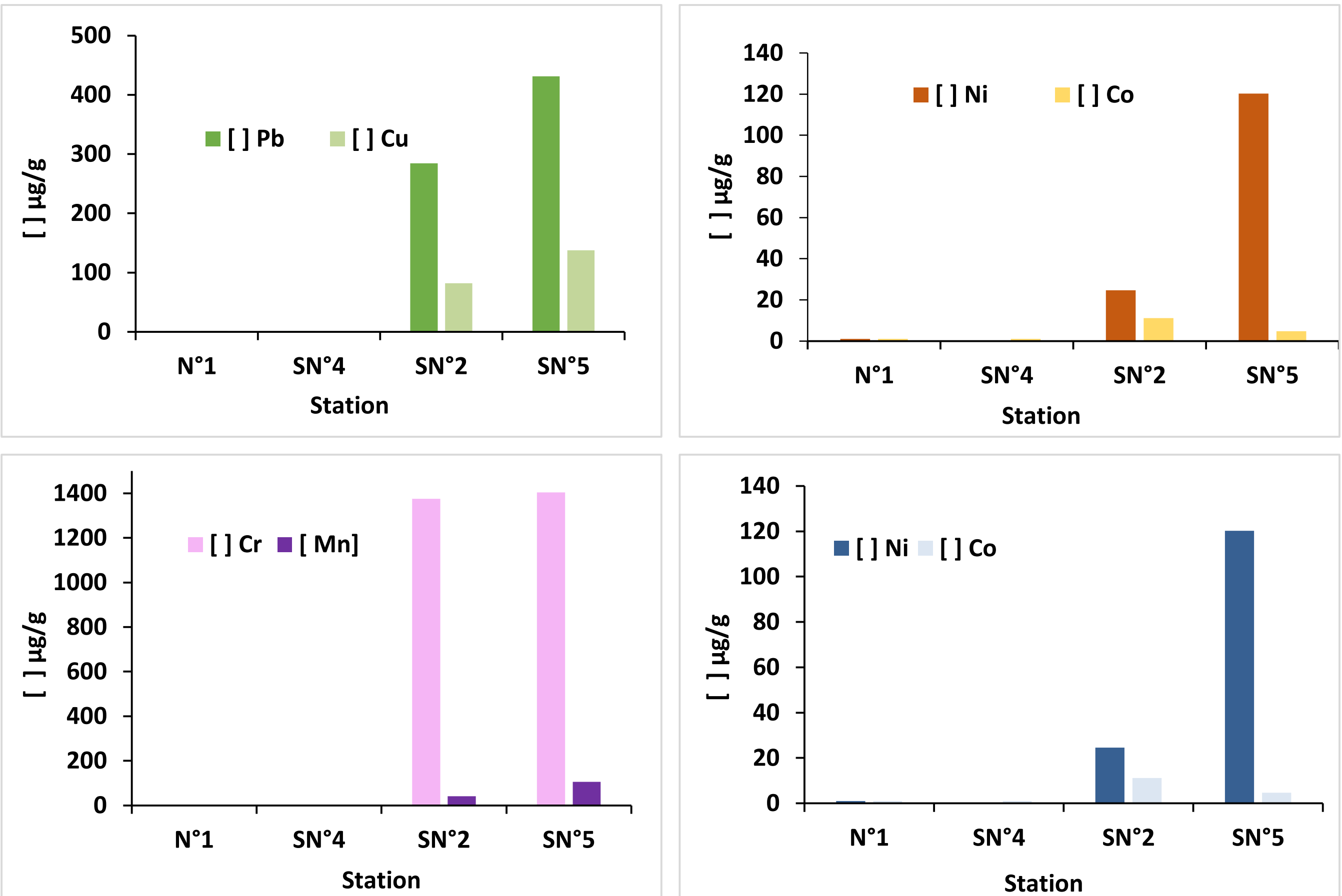

Figure 4: Concentrations of the ETM (Ni, As, Co, Cr, Mn, Pb, Zn and Cu) in 3 stations in 2014.

3.5. Results of spared digestion

Exchangeable fraction was extracted at room temperature cations exchangeable this is mainly an adsorption – desorption process. Metals extracted in the exchangeable fraction include weakly adsorbed metals and can be released by ion-exchange process. Changes in the ionic composition of the water would strongly influence the ionic exchange process of metal ions with the major constituents of the samples like clays, hydrated oxides of iron and manganese [28].

The percentages of metals in the fractions are represented graphically in Figure 4 as percentage total concentrations.

The mobile fraction extracted by this method is very variable from one element to another, and of a station has another and it is by order ascending according to: Co= 0.04% < Mg= 0, 75 %< Zn=7, 93% <Mn = 10, 49% < Pb= 11, 17% < < Cr= 15, 45%

However, Cr (15, 45%) Mn (23.73%) and Pb (11, 17%), were also very abundant in the Exchangeable fraction.

These indicate that Mn, Cr, Pb, Mn and Zn had higher bioavailability in sediment than other metals such as Cd, Co, Ni which were mainly available in the Residual or Inert fraction.

This shows that Cr was more available and mobile, followed by Pb, Mn and Zn, which constitutes a true danger of contamination of the natural environment by these metals and in particular Cr especially that water of Fes and Sebou rivers is very loaded in chromium and it used for the irrigation. On the other hand, other elements are relatively more difficult to mobilize solid phase like Mg and Co. However, if the anthropogenic fraction is very reactive in general, there could be the shapes of very stable pollutants.

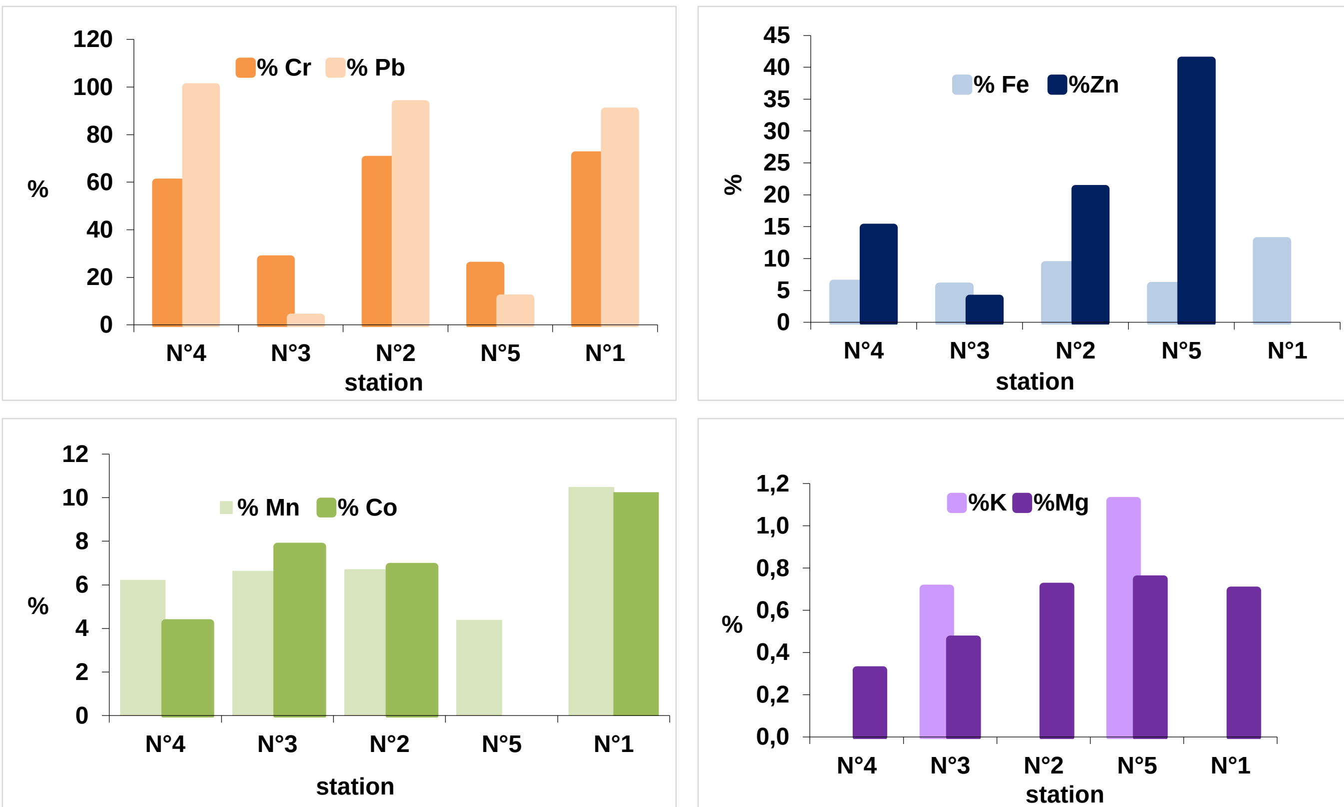

Figure 5: % released of the elements traces metal related to the exchangeable fraction.

Conclusion:

In this study, we determined the physicochemical parameters of waste water of river Fès and Sebou, thus we characterized these sediments by determining the percentage of the organic matter, the mineralogy and the total concentration of the metal elements traces trapped in the sediments of river Fès and Sebou. The results obtained indicate that the sampling stations located downstream from Fès city and the confluence between Fès and Sebou Rivers are polluted, low oxygen contents, high percentage of the organic matter and high rates in ETM especially Cr, Pb and Mn. In order to evaluate the environmental impacts and the health hazards knowing that water of Sebou is used in market-gardening agriculture the sediments is composed primarily of two phase mineralogical.

The salting out of certain metals traces is very easy like Cr, Pb and Mn. What constitutes a true danger of contamination of the natural environment.

The protection of this water of metal pollution is necessary and imperative so that this water is still useful in agriculture without risk of contamination.

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