Carpathian Journal of Earth and Environmental Sciences, May 2015, Vol. 10, No. 2, p. 189 - 198

EVALUATION OF THE PHYSICOCHEMICAL AND SOME TRACE ELEMENTS OF THE SURFACE WATERS OF THE MOROCCAN ATLANTIC ESTUARY: CASE OF THE ESTUARY OF THE RIVER BOUREGREG

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Abstract: Concentrations of heavy metals in water and sediment samples of Bouregreg River in the capital city Rabat, Morocco, were studied to understand the level of heavy metals and their source apportionment. The results showed that the mean concentrations of heavy metals both in water and sediment samples were very high and, in most cases, exceeded the permissible limits recommended by the Morocco government and other international organizations. Significantly higher concentrations of Pb, Cr, Cd and Hg were found in sediment samples. However, above the maximum values registered for heavy metals Cr, Cd, Hg and Pb are respectively 32.12; 0.34; 14.12 and 12.21 mg / L. Moreover, downstream are respectively 82.14; 0.15; 16.91 and 18.17 mg/L. The results illustrated that the environment has been polluted by industrial and urban activities.

Keywords: Bouregreg River, Trace element, Physicochemical parameters, Atlantic estuary, Morocco.

1. INTRODUCTION

Estuaries are a unique class of coastal forms. They correspond to the terminal portions of river ecosystems. The encounter between salt water and freshwater ensue particular hydrological dynamics and specific sedimentary mechanisms. Estuaries appear as places of exchange of energy and matter very important among the marine area and the continental area. This crossroads that estuaries are privileged spaces for human activities. They are also very favorable for crop and livestock because they are places of contact, protected, but dynamic, in which the nutrients are abundant life. Many fish and birds breed (Pirazzoli, 1993).

In Moroccan estuaries, several authors have shown contamination (Cheggour et al., 2005; Zerki et al., 2011; Bounakhla et al., 2011) which are due to domestic and industrial businesses along the Moroccan coast. Indeed, the physicochemical characteristics of sediments such as pH, temperature and conductivity, are among the main factors that govern the exchange of heavy metals in the sediment-water interface (Förstner & Salomons, 1980). In addition, these characteristics are among the factors that govern the exchange of phosphorus and nitrogen ions in water - sediment interface (He et al., 2005).

Today and worldwide, there has been an intensification of industrial and agricultural as well as a rapid increase in population and the growth of living things. These activities brought in hydro (estuaries, groundwater, rivers, lakes, lagoons, oceans) pollutants that adversely impact on the environment and consequently on human health. Indeed, some chemicals can cause the disappearance of certain animal and / or plant species and therefore, cause dysfunction of the food chain (Gold, 2002). Among these pollutants are the heavy metals that can be harmful or even fatal, some anions and some nutrients such as nitrogen and phosphorus when they exceed the recommended limits. A high grade, they accentuate the algal development, water is then deprived of oxygen, causes the death of fish and other marine life. Morocco does not escape this reality.

The Oued Bouregreg main river through the two cities Rabat and Sale and opening of the Atlantic Ocean known for several years a significant degradation caused by several factors. These factors appear:

- The construction of all residential complexes, commercial and tourism which has upset the balance of the Oued.
- Quarrying.
- Releases special pottery waste, rubble and demolition products.
- Discharge of domestic and industrial wastewater (sewage several emissaries in the estuary such as the port, Oudaya, discharge Akreuch, marina).

In this paper we present the results of the study of physico-chemical parameters of the water of the estuary of the Bouregreg could inquire about the possibilities of distribution of heavy metals and nutrients in the two compartments: water and sediment.

2. PRESENTATION OF THE STUDY AREA

2.1. Bouregreg estuary

The Bouregreg river took its source in the Middle Atlas, after a long and winding path, swollen swelled by its tributaries, is extended by a large estuary on the Atlantic coast. It is known in ancient times by the name of the wadi SALA. It was not until the thirteenth century he appeared under the name of "ABIRAKRAK", its name Berber was "ASIF URGRAZ" Arabized in "BURGRAG." The latter means in Berber "gravel" and applies to a Berber Tribe "RGRAGA" who have stayed long on the banks of the river (Chastel, 1994).

This river has become famous because of its intimate connection with the history of towns on both sides Rabat and Sale. It will be privileged to witness, through his story, a bigger story and that exceeds that of Morocco since the earliest times to the present day.

The region of the mouth of Bouregreg has been inhabited since prehistoric times, as the man of Rabat was dated Pre-Neanderthal. Thus, the valley of Bouregreg length was chosen as the location. According to some historians, the Phoenicians and the Carthaginians would have done well to install a countertop edge of Bouregreg. After the arrival of Islam in the late 7th century under the dynasty of Idrissids the mouth of Bouregreg was the scene of ongoing battles between Muslims (left bank) and Bourghonates (right bank). These rivalries led to two cities on either side of the estuary (Chastel, 1994).

The Bouregreg estuary is located on the Atlantic between the two cities Rabat and Sale 34° N and 6° 50 'west. It has a length of 23 km, limited by the dam of Sidi Mohammed Ben Abdellah and an average width of 150 m. It is generally facing south-east and north-west, except in the area ranging from kilometer point (pk) 13.5 to the confluence of Wadi Akrech where it is oriented sud-ouest/north – East.

Upstream and up the river Akrach (18 km), the estuary has an appearance of deep valley surrounded by highlands; Downstream of pk 14.5 (Both islands), the collection disappears and the estuary through an alluvial plain in which he describes many meanders. This terrace, called Oulja disappears, about 4 km from the ocean where marshes are observed. Near its mouth are two sandy beaches of Rabat and Sale which constitute the terminal portion of the estuary (Fig. 1).

3. SAMPLING AND ANALYSIS METHODS

The water sample was taken using a Van Dorn bottle 1 liter in PVC. Sampling was conducted at two scales: a spatial and temporal scale during the 2013-2014 hydrological cycle and a vertical scale from the surface to the bottom every 2 m. The temperature measurements (°C), pH (unit), and conductivity (μSiemens / cm) are formed by a multi parameter Loviband.

As regards nutrients, Nitrate (mg / L) were measured by photometric determination of a phosphomolybdic complex after reduction with ascorbic acid. The determination of the ammonium content (mg / L) is produced by digestion with sulfuric acid, then distilling the indophenol blue colorimetry. The concentrations of orthophosphate are determined by colorimetry reactive sulfomolybdique (Rodier, 1984; Salama et al, 2013).

Before analyzing different nutrients (P, N) and heavy metals (Cd, Cr, Hg, Pb) in natural waters, the samples were acidified upon collection by addition of nitric acid with pH ~ 1 to retain them until the chemical analysis (Henney et al., 1980; Bchitou et al., 2003).

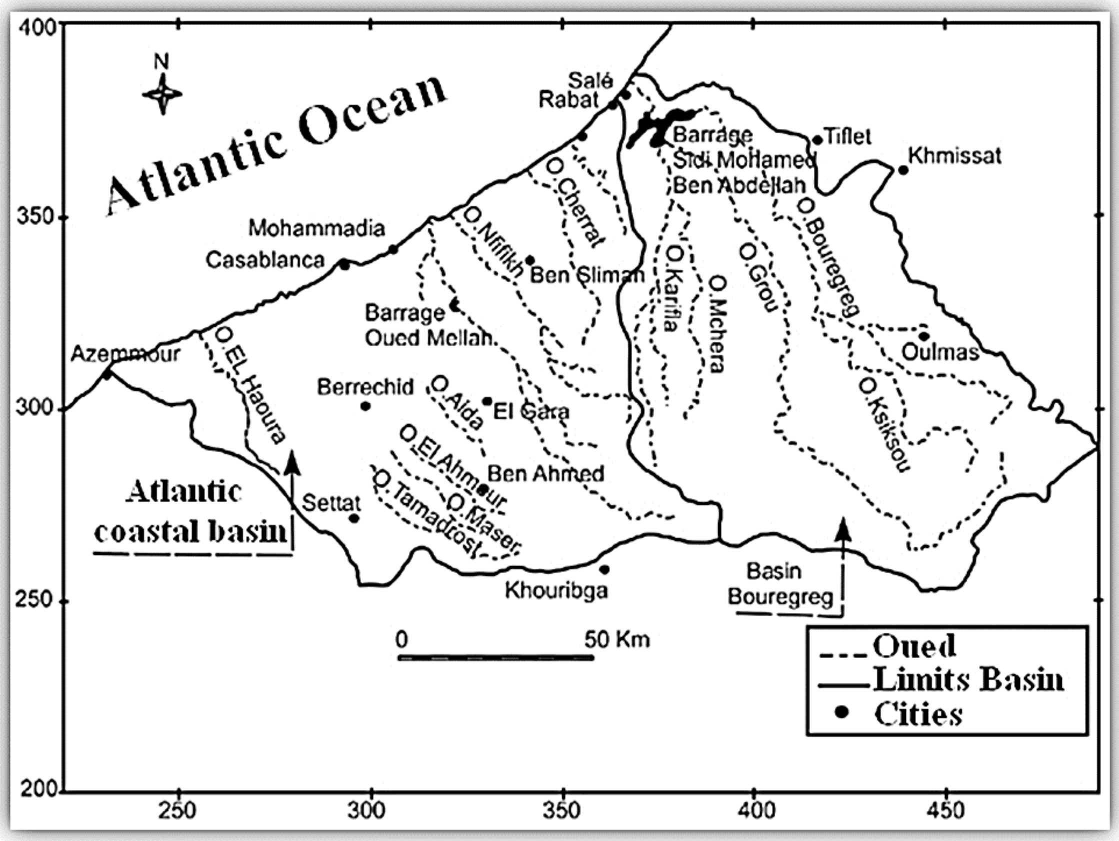

Figure 1. Location of the study area (Becking, 1998).

The samples were analyzed by ICP-AES (Atomic Emission Spectrometry Coupled with Induced Plasma) in the laboratory of the National Center for Scientific and Technical Research (CNRST) in Rabat, Morocco.

4. MATERIALS AND METHODS

4.1. Choice of stations

The physico-chemical and bacteriological parameters were determined upstream and downstream of the estuary Bouregreg. Samples of water and sediment samples for this study, transport and conservation have been made so as to be closest to the optimum conditions for the analysis of water and sediment. All samplings were performed for subsurface waters and along the river sediments. The samples were taken downstream site (S4, S5 and S6) side of Moulay Al Hassan bridge, and the bridge of Al Fida, and upstream (S1, S2 and S3), in the vicinity of Sidi Mohamed Ben Abdellah dam (around about 5 km) (Fig. 2). Upstream sites are characterized by stagnant waters where maritime influence and very weak. By against downstream sites are located at the mouth of the ocean, this is a crossing area between Rabat and Sale. This area receives polluted effluents mainly from the city of Sale which are paid directly into the ocean without treatment, and the work of the development of the Bouregreg Valley Project.

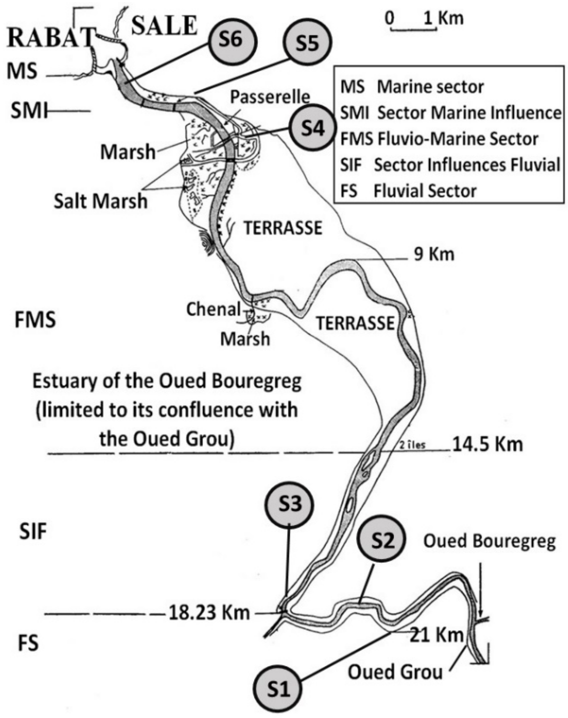

Figure 2. Location of study sites in the estuary of the Bouregreg.

Upstream sites are characterized by stagnant waters where maritime influence and very weak. By against downstream sites are located at the mouth of the ocean, this is a crossing area between Rabat and Sale. This area receives polluted effluents mainly from the city of Sale which are paid directly into the ocean without treatment, and the work of the development of the Bouregreg Valley Project.

4.2. Methods of analysis

The physico-chemical parameters such as temperature, pH and conductivity were determined in the field (AFNOR, 2001).

- ***Choice of nutrients and heavy metals***

We chose to study the distribution of nitrogen, phosphorus and heavy metals (Cd, Cr, Pb, Hg). These elements were analyzed in natural waters and sediments.

These nutrients and heavy metals in the context of this work, were chosen for their uses in industrial units installed downstream and agricultural activities in the two banks of Bouregreg, and also because they are characterized by toxicity vis-à-vis human and aquatic organisms (ONEP, 1994; Thiery, 1976).

Before analyzing the different nutrients (P, N) and heavy metals (Cd, Cr, Hg, Pb) in natural waters, samples were acidified upon collection by adding nitric acid whose pH ~ 1 to hold to the achievement of chemical analysis (Bchitou et al, 2003; Henney et al., 1980).

5. RESULTS AND DISCUSSION

5.1. Temperature variation

The temperature is generally governed by the seasonal weather conditions. Thus, one can distinguish four main periods relating to thermal characteristics of the four seasons Mediterranean climate:

- A cold period which lasts from December to February. Mean monthly temperatures are around 14°C, extreme temperatures never fall below zero. The maximum average for this period is around 16°C and minimum of 8°C (Fig. 3).

- A warm period that runs from June to September with monthly averages of around 20°C. The highest temperatures are recorded in the month of August, while extreme temperatures can reach 45°C.

- A transition period between the cold and warm periods.

- A transition period between the hot and the cold period.

Our study period, falling in the month of May 2013, coincides with the second transition between the cold and warm periods.

In general, water temperature Bouregreg decreases from upstream to downstream in the dry season while in wet period, this gradient is reversed. This reversal is due to the fact that cold period, the air temperature is higher upstream and downstream. Upstream shallow depths on the one hand and the collection of the valley on the other hand make the water under the direct influence of temperature of the air where a decrease in those waters. Downstream, slightly warmer waters from seaward entering the estuary causing a rise in temperature of the water in this area.

In fact, the temperature varies between 17°C (Site S4) and 19°C (site S3) with an average of 18.1°C. This average increases gradually as one moves downstream sites to the upstream sites. The temperature rise at site S3 is due to the discharge of water from the Oued Akrech.

The measuring instrument is the mercury thermometer accurate 1/10.

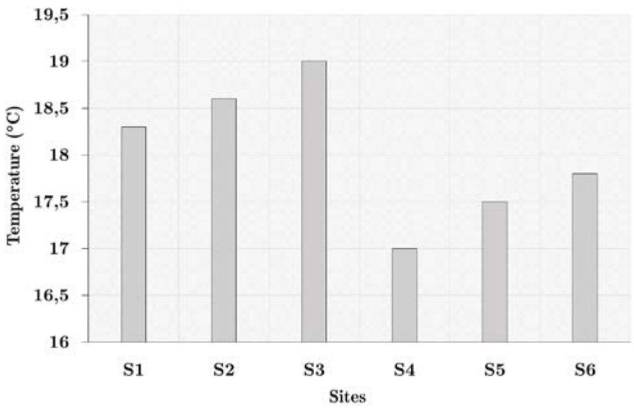

Figure 3. Variation of temperature as a function of study sites.

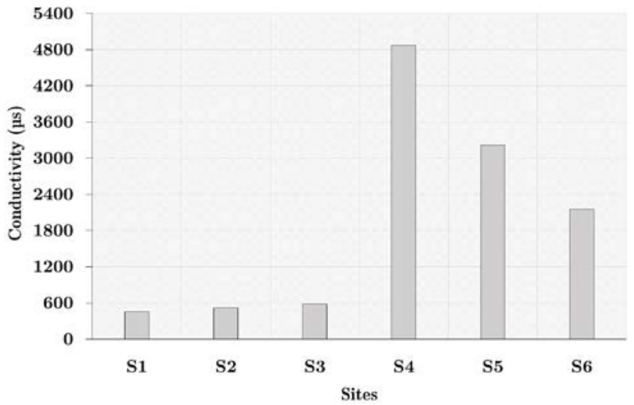

Figure 4. Variation of conductivity as a function of study sites.

5.2. Variation of the conductivity

The results of measurements of the conductivity in the sampling sites are shown in figure 4.

Indeed, as shown in figure 4, the value of the conductivity increases from upstream to downstream. This is mainly due to the concentration of salt water from the ocean. S4 site that is the closest to the ocean has the maximum value of the conductivity.

5.3. Variation of pH

The pH affects a large number of physico-chemical equilibrium, it depends on the source of water, the geological nature of the watershed. Given their character buffer, pH changes do not affect the natural water with difficulty.

The study of the spatial variation of the pH level in the estuary Bouregreg showing the existence of a spatial change characterized by the presence of two areas, one upstream and the other downstream. The upstream zone is characterized by relatively basic pH with pH values are between 7.4 and 9.6 (Fig. 5).

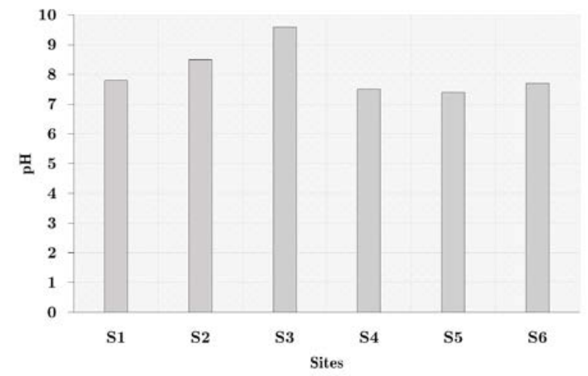

Figure 5. Evolution of pH as a function of study sites.

The downstream area is characterized by a pH ranging from 7.4 to 7.7. The constancy of pH values at the mouth reflects the alkalizing effect of seawater Between these two areas, domestic waste and neutral or slightly basic characters give the water of the estuary values intermediate pH. We notice a more basic pH at the site S3 this is due to a temperature increase which causes increased dissolved CO_2 who will lead to an increase of pH.

The gaseous carbon dioxide is easily dissolved in water to form the aqueous CO_2. The aqueous CO_2 reacts with water (hydrolysis) to then form carbonic acid which is a weak acid can dissociate in bicarbonate, which is in turn dissociated into carbonate according to the reaction:

$$CO_2\,(g) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$$

The relative proportion of each of carbonate species is determined solely by the pH of the medium.

5.4. Variation in nitrogen and phosphorus in water and sediments Bouregreg

Several studies have shown that the sediment can act as a reservoir with a storage of nutrients during winter and release of these items when the rise in temperature allows increased biological activity (Hahn & Sorn, 1995; Mouvet et al., 1982).

The results of the variation of the levels of total nitrogen and total phosphorus are studied for each site shown in figures 6 and 7. We mean concentrations recorded for each analyzed nutrient in water and sediment in the corresponding.

- **Variation of the total nitrogen content in the water**

The figure 6 shows the variation of the total nitrogen content in the water of different sampling sites.

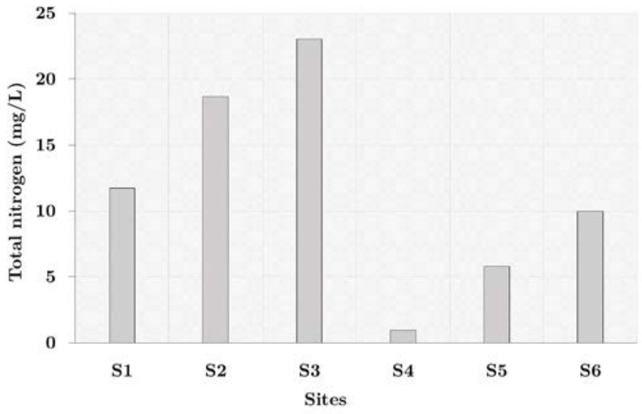

Figure 6. Variation of the total nitrogen content based sites.

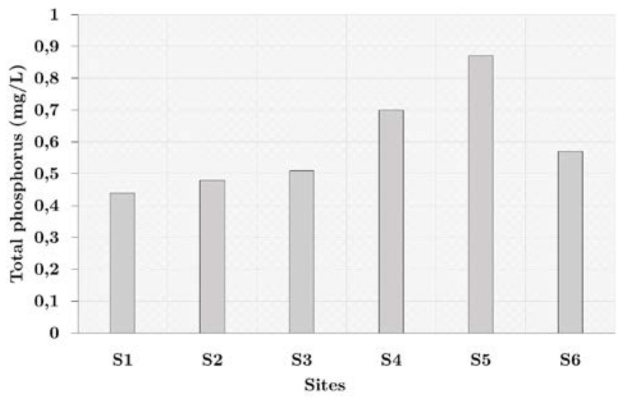

Figure 7. Variation of the total phosphorus content based sites.

Indeed, as shown in this figure, the site S3 in the most loaded nitrogen. This is mainly due to the use of fertilizers and pesticides in the crop of the upstream region.

- **Variation of the total phosphorus in the water**

The figure 7 shows the variation of the total phosphorus content in natural water samples taken from different sites. From Figure 7, we note that the total phosphorus content has a maximum at the site S5. Concentrations in the downstream sites are relatively more important than the upstream site, this is probably due to the discharge of sewage.

- **Variation of the total phosphorus in sediments**

The figure 8 shows the variation of the total phosphorus content in different sediment samples taken from different sites.

From figure 8, the total phosphorus content has a maximum in the downstream site that S5 is 1521.142 mg / kg. The total phosphorus content in the upstream sites is almost the same. On the other hand, downstream the total phosphorus content presents a wide difference between the sampling sites. The high phosphorus content in the S5 site is due to the discharge of wastewater (Cherkaoui et al., 2013).

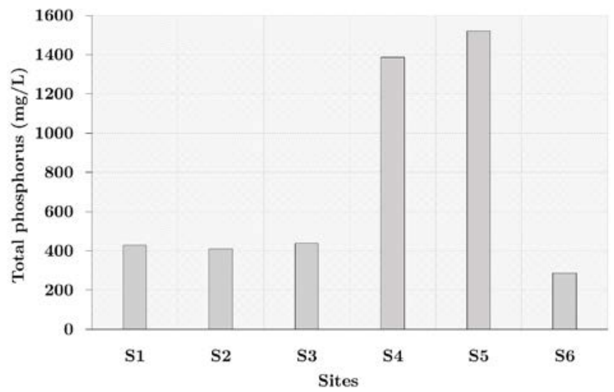

Figure 8. Variation of the total phosphorus content based sites.

5.5. Variation in heavy metals in water and sediment

Heavy metals from anthropogenic inputs are present in significantly more reactive, entailing much higher natural metals which are usually fixed in relatively inert chemical forms (Billen et al., 1995; Gibbs, 1973; Lietz & Galling, 1989).

Furthermore, it is known that the physico-chemical characteristics of sediments are among the main factors that govern the exchange of heavy metals in the sediment-water (Bchitou et al., 2006; Fendorf et al., 2000; Purves, 1985; Sigg et al., 1994). The results of the variation of the levels of metals studied are presented for each site. We increased the mean concentrations recorded for each metal analysis in water and sediment in the corresponding.

- **Variation of the chromium content in the water**

The figure 9 below shows the variation in the chromium content in different sites upstream and downstream.

The longitudinal profile of the total chromium has a high content of this metal in the downstream Site S5, which has the characteristics of a medium that promotes aerobic oxidation (Karg, 2001) organic compounds.

However, the maximum Cr content recorded during this period (0.8917 x10^{-3} mg / L) does not reach the maximum value is 0.05 mg / L.

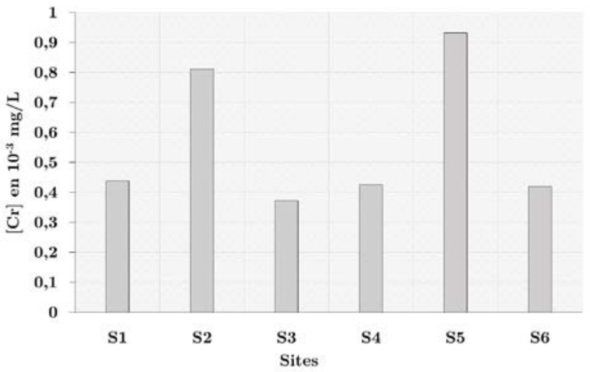

Figure 9. Variation of the chromium content in water based sites.

The spatial distribution of metals in different sampling sites shows that the site downstream S5 has the highest chromium and lead in water and sediments. These high levels are probably due to significant human activities in the area characterized by a permanent pollution due to domestic sewage of the industrial city of Takaddoum and Maadid that flow directly into the estuary without treatment.

This reflects that the process of accumulation of chromium and lead in water and sediments of the estuary Bouregreg are the result of wastewater discharges from the cities of Rabat and Sale.

The industries dischargers of these metals are mainly those manufacturing of surface treatment products (paints). The colored pigments such as chrome yellow or orange chromium components the paints are constituted of chromate of lead (II) and lead hydroxydochromate (II).

The chromate yellow for example is obtained by the action of the ion chromate CrO_4^{2-} on the Lead (II) salt. By precipitation in water is obtained lead chromate $PbCrO_4$(s) according to the reaction:

$Pb^{2+} + CrO_4^{2-} \rightarrow PbCrO_4$ (s)

- **Variation of cadmium in water**

The figure 10 shows the variation of the content of cadmium in the different upstream and downstream locations.

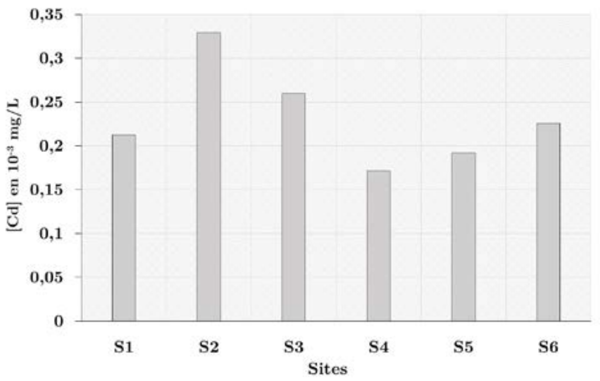

Figure 10. Variation of cadmium depending on the upstream and downstream locations

The Concentrations of cadmium in the waters of the estuary Bouregreg are generally very low. The maximum concentration is about 0.3291 x 10^{-3} mg / L for total metal. This value is recorded at the upstream S2 site and lower the standard of cadmium in natural waters is fixed at 0.005 mg / L.

We also note that the downstream sites for this metal have low and below the limit of detection is 0.1917 x 10^{-3} mg / L, except for S6 concentrations website. In addition, this site presents a high nitrogen content, low conductivity and high temperature during sampling. This shows that the larger the salinity decreases as the cadmium concentration increases. Coastal zone during mixing of freshwater with seawater, cadmium form very stable complexes with anions especially chlorides and nitrates (Karg, 2001).

- **Variation in the content of mercury in water**

The figure 11 shows the variation of the mercury content in the different sampling sites. The mercury concentrations in the waters of the estuary of the Bouregreg not show very significant variations between sites. The high content in metal recorded at site S1. The mercury concentrations in the waters of the river Bouregreg exceed the standard is set at 0.001 mg / L.

Mercury tends to concentrate and sediment in drainage basins due to erosion in sediments and deposition of atmospheric dust ore.

Mercury and especially its organic compounds such as methyl mercury, are toxic and can attack cells and nerves when absorbed doses exceed certain values (El Himri, 2012).

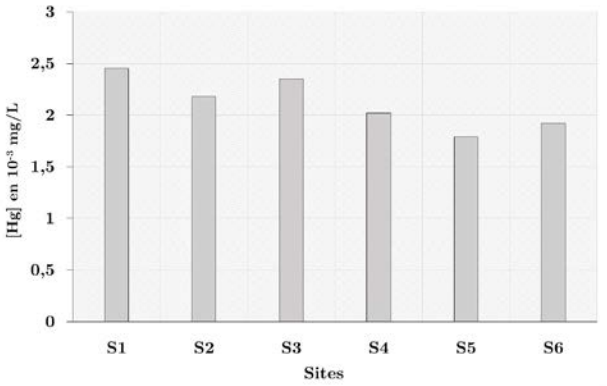

Figure 11. Variation of the mercury content based sites.

- **Variation of the lead content in water**

The figure 12 below shows the variation of the lead content in the collected different water upstream and downstream locations.

The Pb content of the downstream sites is higher than in the upstream site but does not exceed the standard which is set at 0.05 mg / L. The high lead content below is due to wastewater discharges and roads linking the two cities Rabat and Sale (Cherkaoui et al., 2013).

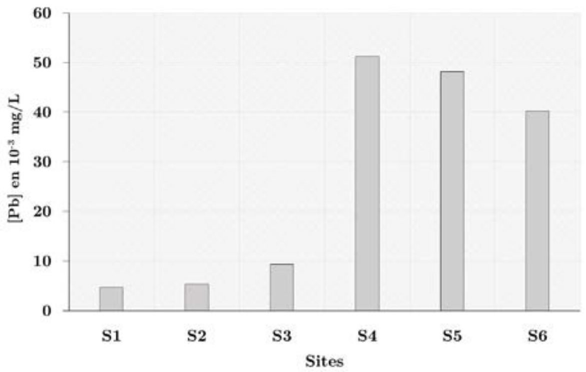

Figure 12. Variation of the lead content based sites.

- **Variation of the chromium content in the sediment**

The figure 13 shows the change in the chromium content in different sampling sites.

The longitudinal profile of the chromium content in the sediment shows relatively low concentrations in the upstream sites. All times at downstream sites, levels are high (82.1421 mg / kg S4). This leads us to assume that some industrial discharges cities of Rabat and Sale contribute to the enrichment of estuarine sediment chromium.

- **Variation of cadmium in sediments**

The figure 14 shows the variation of the cadmium content in different sites.

The longitudinal profile of cadmium in

sediments has a maximum upstream S1 site. As for water, the Cd concentration is also high in the upstream sites. Levels in upstream sites are relatively high.

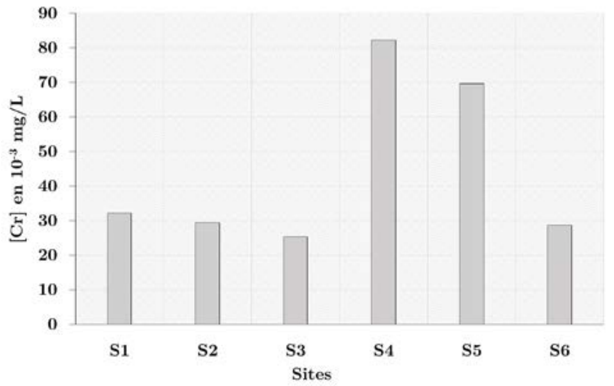

Figure 13. Variation of the content of chromium in sediments based sites.

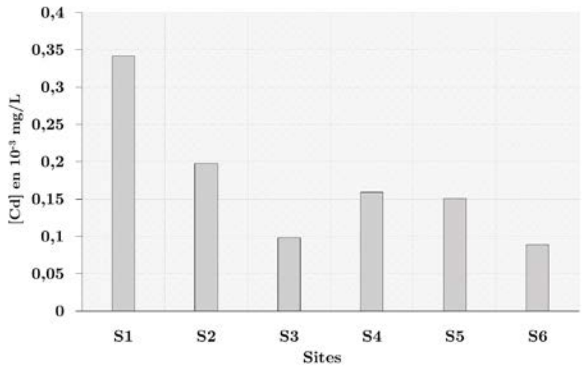

Figure 14. Variation of cadmium in sediments based sites.

- **Variation of the Pb content in sediments**

The figure 15 shows the variation of the Pb content in the different sampling sites.

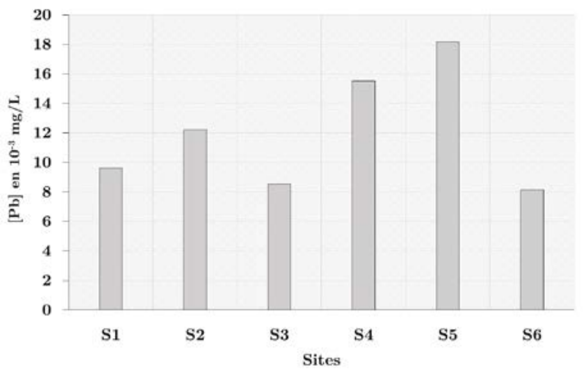

Figure 15. Variation of the Pb content in sediments based sites.

The profile shows elevated Pb in the downstream site (S4 and S5) with up to 18.1721 mg / kg at the site contents S5.

High concentrations of Pb at S4 and S5 sites appear to be related in part to the large traffic (main roads and motorway) connecting Rabat Sale. The lead, used as an octane fuels in vehicle engines, is released directly into the atmosphere through the exhaust pipes. Contamination is directly or indirectly by atmospheric fallout after leaching by rainwater roads.

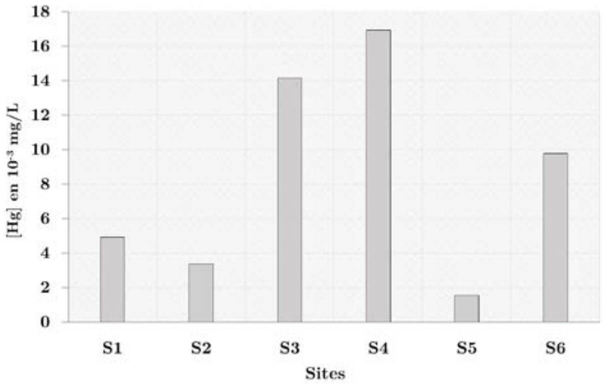

Figure 16. Variation of mercury in sediments based sites.

- **Variation of the mercury in sediments**

The figure 16 shows the variation of the mercury content in the different sampling sites.

The longitudinal profile of the mercury in the sediment has a maximum of 16.918 ppm at the site downstream S4.

6. CONCLUSIONS

The temperature is highest in the S3 site, this can be explained by the contribution of water from the Oued Akreuch. The conductivity increases from upstream to downstream. This can be explained both by the removal of marine influences and dilution by freshwater inputs.

The study of the spatial variation of the pH level in the estuary Bouregreg showing the existence of a spatial change characterized by the presence of two areas, one upstream and the other downstream.

The contents of chemical elements analyzed in the water and sediments show that the classification of the levels in the water are respectively Cd <Cr <Hg <Pb and sediments are respectively Cd <Hg <Pb <Cr.

The spatial distribution of metals in the different sampling sites showed that the downstream Site S5 has a high content of chromium and lead in water and in. These high levels are probably due to significant anthropogenic activities in the area characterized by a permanent pollution due to domestic sewage flowing directly into the estuary without treatment.

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Received at: 30. 07. 2014

Revised at: 26. 02. 2015
Accepted for publication at: 08. 04. 2015
Published online at: 21. 04. 2015