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RESEARCH ARTICLE

Monitoring of heavy metals in the sediments of the Inaouene River, Morocco

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Abstract

The watercourse of the Inaouène River carries all the solid waste disposals from the urban areas (City of Taza, Bab marzouka, oued Amlil, Bouhlou). It also receives wastewater which is not treated at the sources. This wastewater contains various types of heavy metals. The study of heavy metal contents in the sediments was carried out at 11 sampling sites alongside the Inaouène River and some of its principal tributaries in May 2008 and October 2009. The results can be classified into three series: the series 1: including the metals (Fe, Sr, Mn, Zn, Rb, Pb) detected on all the sampled sites, the series 2: including the metals (Cu, Ni, Cr, As, Co, Pt, Sn) detected only some sites, the series 3: including hazardous metals (Ag, Cd, Hg) which were under the limit of detection. The correlation analyses of heavy metal contents of two study periods indicated that a large part of examined heavy metals had common sources and behaved similarly during the transportation.

Keywords: sediments, heavy metals, pollution, Inaouene River

Introduction

In the aquatic natural ecosystems, heavy metals are in weak concentrations, generally on the order of the nanogram or microgram per litre. These metals are accumulated slowly attaining toxic thresholds in the end. After reaching the water environment from different sources, the metals are adsorbed on the inorganic and organic particles and incorporated in the accumulated sediments, and it results in an elevation of their concentrations in the bottom sediments (Jeon *et al*. 2003). In fact, the sediments act as reservoirs of the metallic elements that can be transferred in part towards water. In other words, the metals there are not fixed in a permanent manner and can be realeased back into the water column at the time of an environmental change, such as the pH, the potential redox (PE) the presence of the micro organisms and hydrodynamics (James 1978; Fôrstner 1987).

This study concerns a part of the Inaouene watershed situated upstream of the Dam Idriss1er. It covers an area of 2720 km^2 and a perimeter of 268 km (Figure 1); which constitutes 52.46% of this watershed that has an area of 5184 km^2. Situated between the latitudes (33°84'-34°58'N) and the longitudes (3°78'-4°91'W), the study area is limited to the east by the watershed of the Middle Moulouya, to the northwest by those of the Upper Ouergha watershed, and to the southwest by the Upper Sebou. The water quality of the Inaouene River change along the course. While taking its source between the Middles Atlas and the Rif Mountains, the water is of an excellent quality, which becomes afterward very bad while crossing the city of Taza and the succeeding towns, because of the uncontrolled disposals of domestic solid wastes and the discharging of waste waters by the domestic and industrial activities.

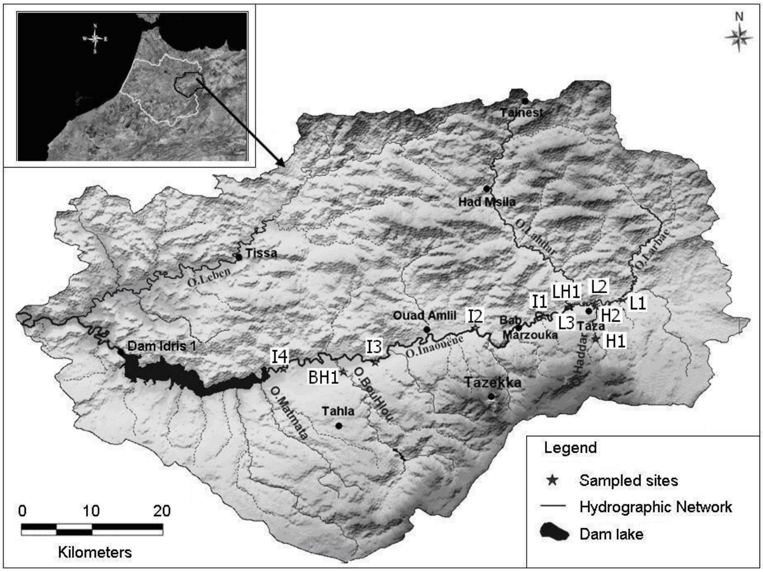


Figure 1. Map of the Inaouene watershed.

Materials and Methods

The sampling of the superficial sediments (depth of 0-10 cm) was carried out in May 2008 on 10 sites and in March 2009 on 11 sites. One sampling site (BH1) was added to the survey in 2009 due to its importance as a tributary of the Inaouene River (Figure 1). This choice of sampling sites based on various factors, such as the establishment of industrial zones, urbanization, and confluences with other watercourses.

The sampled sediments were collected in plastic bags, from the moistened layer, not submerged in water. The weight of each sample was 500g. The sediment samples were kept in these plastic bags until they were transferred to the laboratory, where they were quickly washed and dried at 40° C. The sediments were then crushed in an agate mortar. We proceeded first to a partial acid reaction (HNO_3). During this reaction, the metallic ions absorbed on the surface of the particles were released into the solution. The diluted acid solution was analyzed in continuation by ICP-MS (Inductively Coulped Plasma Mass Spectrometry). It is a technique that uses the mass spectrometry after ionization in inductive plasma. The analyzed metals were Fe, Sr, Mn, Zn, Rb, Pb, Cu, Ni, Cr, Co, Pt, Ag, Cd by ICP-MS and As, Hg, Sn by hydride generation system, with a limit of detection of 0.5 mg/kg, except for Hg 0.02 mg/kg. The calibration of the ICP-MS was carried out with dilutions of the analytical standard in an acid solution of same type which was for the reactions.

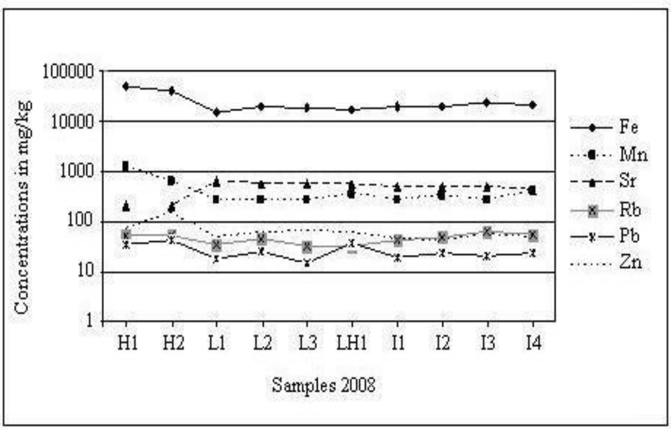
Results and Discussion

The results of analysis of the sediments sampled along the Inaouene River and some of its tributaries in 2008 and 2009 can be classified in three series: The series 1: Including the metals (Fe, Sr, Mn, Zn, Rb, Pb) detected on all the sampled sites, The series 2: Including the metals (Cu, Ni, Cr, As, Co, Pt, Sn) detected only on certain sites, The series 3: Including some hazardous metals (Ag, Cd, Hg), which were under the limit of detection.

For the series 1 (Fe, Sr, Mn, Zn, Rb, Pb) (Figure 2); the fluctuations of concentrations of these elements during two years were almost sama, with the exception of the fluctuations at BH1, that was integrated in the survey in 2009, due to the importance of this tributary of the Inaouene River. The high concentrations were noticed for Fe, medium for Mn and Sr, on the other hand weak for Rb, Pb and Zn. Concentrations above the norms were noticed for Fe at H1 and H2 during 2008 and at H1 during 2009, Mn at H1 for the two years, Sr in all the sites with the exception of H1 and H2 during 2008 and at H1, H2, and BH1 during 2009, Zn only for H1, Pb in all the sites with the exception of L3 during 2008, H1, H2, L1, LH1, BH1, and I4 during 2009. The Rb concentrations were in accordance with the norm.

These high concentrations of Fe, Mn, and Zn, at H1, resulted from a natural cause. This site is located in the neighbourhood of the carbonated lands and laterites rich in iron, which explains the presence of the former mines of Fe of Chekka. On the other hand, at H2, there could also have been a natural cause or some source of pollution.

The high concentrations of Pb revealed the existence of pollution sources: irrigation, batteries, paints, additives for the gasoline, dirty water running from the traffic ways; pharmaceutical and steel-manufacturing industries (Baize and Janiec 1994). The variability of lead concentration reflects the existence of sources of contamination that could be related to urban wastes (Bouasria *et al.* 2007). Also for Sr, the high concentration of the concerned sites is explained by polluting agents.



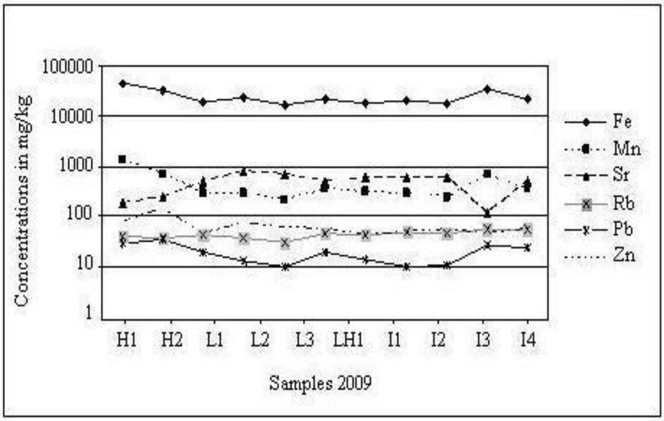


Figure 2. Spatial variations of Series 1 heavy metals in 2008 and 2009.

Concerning the series 2 (Figure 3), the most common element was the copper, with remarkable concentrations at H1, BH1, LH1, which owes the cause in natural sources. The copper is generated by the effect of reactions between the hydrothermal solutions and iron ores in the porous zones of basaltic outcrops at the level of the carbonated and silicate lands (Dean *et al*. 1972; Fôrstner andWittmann 1979; Chabert 1980; Blanchard 1982; Nriagu and Pacyna 1988). In the study zone these natural conditions are favourable by the existence of the quaternary basaltic lands.The copper is generated also by pollution, such as irrigation, electric wires, radiators, heaters, according to Baize and Janiec (1994). At L2, H2, and I1, the high concentration of Cu can be explained by these pollution sources, since these sites are at the vicinity of the solid rubbish dump or wastewaters. At I2, I 3, and I4, the concentration in copper may be due to a natural origin, as it can have an origin issued from on other sources of pollution.

The natural origin of Ni it is the iron oxides or laterites rich in iron, which explains its high concentration in 2009 at H1, which is located in Liassic carbonated lands with Triassic red clay outcrops. This site is in the vicinity of a former iron mine (mine Chekka). Since the same site in 2008 does not show a trace of Ni, we assume the remobilisation by natural factors as:

- The change of redox conditions, usually, underneath the surface of the sediment and that principally leads to the reduction of Fe and Mn oxides, and consequently to the placement in solution of these oxides and of their associated metals that can migrate, thus, towards the surface (Morgan and Stumm 1964).

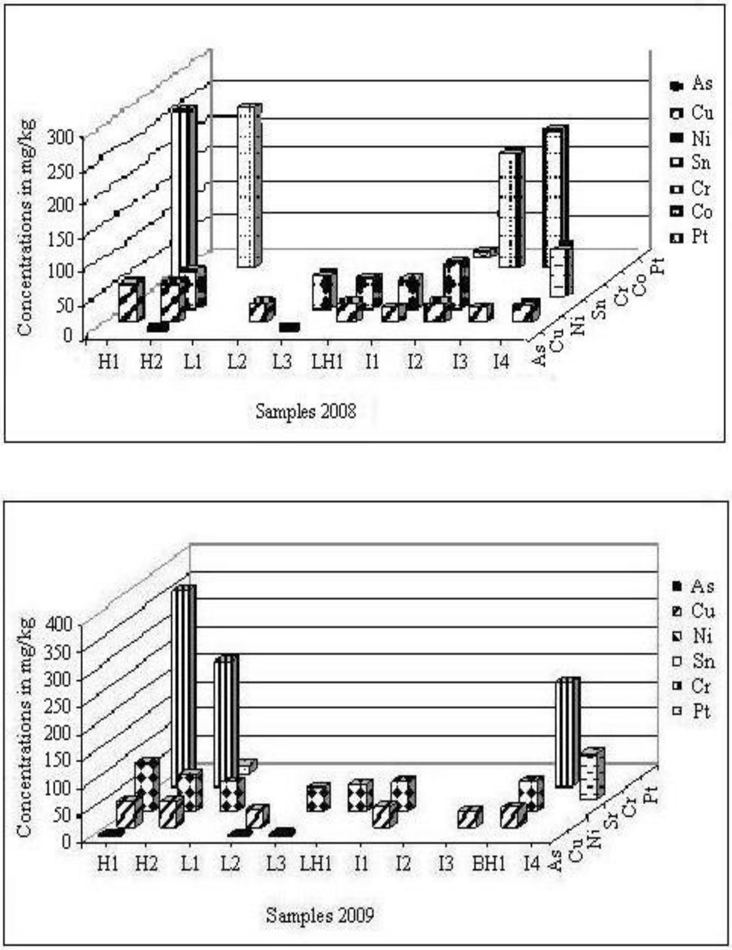


Figure 3. Spatial variations of Series 2 heavy metals in 2008 and 2009.

- The decrease of pH that can provoke a dissolution of the carbonates, hydroxydes and of their associated metals, and/or to a desorption of metallic cations, by competition between the protons H^+ and metallic cations for the surface sites (Bouasria 2008). For the pollution sources, their impact is well marked, especially at H2, L 3, and I2, situated in the vicinity of a public rubbish dump or wastewater canals. The only exception is the absence of Ni at L2, despite its proximal position to these sources of pollution.

The arsenic presents high concentrations at H2, L2, and L3, exposed to a strong pollution, but these concentrations remain below the WHO standards. The site H1 represents an exception, since its concentration was remarkable although it is far from the sources of pollution, which implies the possibility of contamination by the used pesticides and/or bullets in rifles, because this element is used as an additive to the lead of these bullets.

Chromium was present especially at H1 and BH1, not polluted, thus probably the natural origin of this metal as chromate ore ($FeCr2O_4$).

The matrix and the correlation circle below (Tables 1 and 2), obtained by software XLSTAT, between the analyzed heavy metals for 2008 and 2009, indicate that the large part of the examined heavy metals had common sources, dependence and showed an identical behaviour during the transportation.

Table 1. Matrix of correlation between metallic trace elements in samples sites in 2008.

Variables	Fe	Mn	Sr	Rb	Pb	Zn	As	Cu	Ni	Co
Fe	1									
Mn	0.936	1								
Sr	-0.947	-0.845	1							
Rb	0.443	0.310	-0.523	1						
Pb	0.647	0.600	-0.701	0.128	1					
Zn	0.653	0.423	-0.701	0.138	0.703	1				
As	0.302	0.079	-0.356	-0.140	0.235	0.787	1			
Cu	0.822	0.729	-0.900	0.528	0.844	0.619	0.129	1		
Ni	-0.097	-0.192	-0.070	-0.316	0.171	0.237	0.470	0.065	1	
Co	0.282	-0.002	-0.385	0.570	0.273	0.521	0.382	0.389	0.331	1

Table 2. Matrix of correlation between metallic trace elements in samples sites in 2009.

Variables	Fe	Mn	Sr	Rb	Pb	Zn	As	Cu	Ni	Cr
Fe	1									
Mn	0.966	1								
Sr	-0.846	-0.786	1							
Rb	0.035	-0.044	-0.316	1						
Pb	0.795	0.712	-0.893	0.209	1					
Zn	0.458	0.377	-0.360	-0.376	0.602	1				
As	0.198	0.261	0.214	-0.685	-0.187	0.095	1			
Cu	0.663	0.623	-0.503	-0.167	0.487	0.521	0.100	1		
Ni	0.634	0.680	-0.689	-0.329	0.628	0.318	0.152	0.450	1	
Cr	0.972	0.956	-0.853	-0.076	0.782	0.536	0.211	0.716	0.705	1

According to the results in 2008, all the variables, except strontium, were correlated negatively with F1 factorial axis and occupied a rather restricted zone inside the circle of the correlations. On the other hand, the 2009 survey revealed a positive correlation of Fe, Mn, Cr, Pb, Ni, Cu and Zn, with the F1 axis; while it was negative for Sr. However, the correlation with the F2 axis was positive for Rb but negative for As (Figure 4).

The square cosines obtained by the PCA (Principal Component Analysis) for 2008, shows that the variables Sr, Fe, Cu, Zn, Pb and Mn, were strongly linked to the F1 axis. On the other hand Ni and As were linked to the axis F2. During the 2009 survey, the link was strong between the axis F1 and the elements Cr, Fe, Mn, Sr, Pb, Cu and Ni on one hand and on the other hand between F2 and Rb and As.

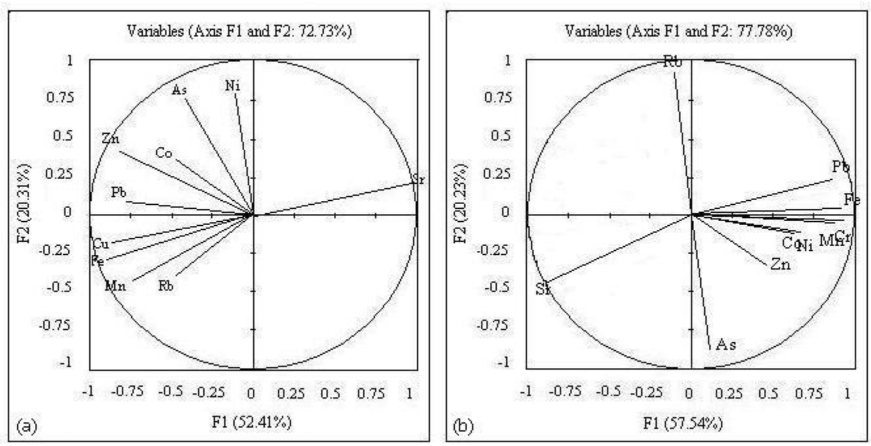


Figure 4. Correlation circles between heavy metals in samples of (a) 2008 and (b) 2009.

The angle between two variables as well as the distance between the centre of the circle and the point representative of the variable constitutes two essential parameters of correlation. More variable elements were projected towards the edge of the circle. The angle between two elements shows the correlation. If it is smaller, the correlation is positively strong. In the opposite case, this correlation is negative. Thus, during the 2008 survey, positive correlations were concluded for example for the pairs of Fe-Mn, Fe-Cu, Mn-Cu, Pb-Cu, and negative for F-Sr, Cu-Sr, M-Sr. For the 2009 survey, the strong correlations were observed positively between Fe-Cr, Fe-Mn, Mn-Cr, and negatively between Fe-Sr, S-Pb, S-Cr.

Figure 5 corresponds to the one of the objectives of the PCA. It allows representing the individuals on a two dimensional map, and thus to identify tendencies.

During the 2008 survey, we noticed that the factorial axis F1 reflected the sites that differ greatly, regarding the content of trace elements, which constituted the following two groups (Ni, As, Zn, Pb and Co) and (Fe, Cu, Mn and Rb). The axis F2, however, reflected the rich sites in Sr and those poor in this element.

For the 2009 survey, the sites were divided globally following four groups, according to the extent of the elements that were strongly linked with the factorials axes. The site BH1, for example, was located at the quotation of the Fe and Pb, meanwhile the sites H1 and H2 were located at the quotation of the Mn, Cr, Cu, Ni and Zn.

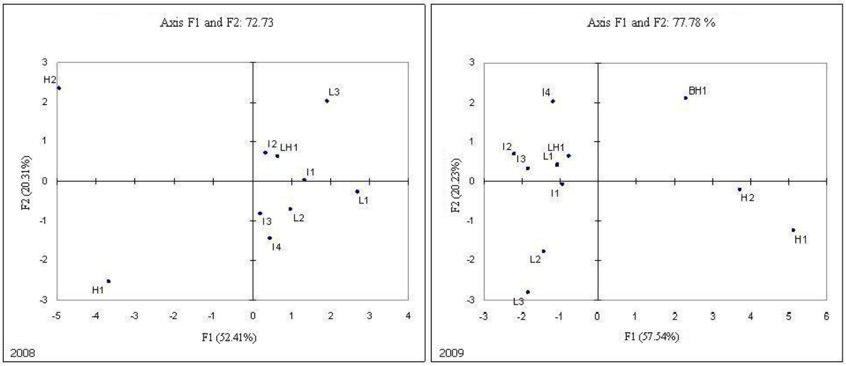


Figure 5. Representation of samples sites vs factorial axes as results of PCAs

The correlation results showed that certain elements kept the characteristics of originality and/or chemical similarities, as Mn –Fe, during the two sampling surveys. Furthermore, a large part of the examined metals had different characteristics, which reflected the impact of the chemical processes controlling their behaviours.

Conclusion

The watercourse of the Inaouene River crosses the solid rubbish dump and collects all wastewaters relatives to the urban zones of the city of Taza and the localities of Bab Marzouka, Oued Amlil, Bou Hlou. Despite this situation, the present study concluded a low level of anthropogenic pollution. The high concentration in certain heavy metals (Fe, Mn, Sr, Or, Cu), had an origin more natural than anthropogenic. Furthermore, the concentration of hazardous heavy metals for public health such as Ag, Cd, and Hg, was at under the limit of detection, in spite of the variety of pollution sources in the study zone. The metal concentrations in the sediments of the Inaouène River and of its main tributaries have not given rise, therefore, to the original state of their ecological condtions.

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