Study of the spatiotemporal variation of iron and manganese ions content in the Oued Moulouya water (North-East of Morocco)

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Abstract. Oued Moulouya is one of the most important water resources, not only for water supply, but also for the agro-industrial development of the North-East region of Morocco. However, the remarkable modification in terms of physico-chemical quality of this water resource which is constantly expressed by high concentrations of various mineralogical and organic components. This calls for the necessary measures to be taken to remedy this pollution. To understand the contribution of each source of this imbalance, whether geological and/or anthropogenic, we conducted a study to monitor, during the both wet and dry periods, the spatiotemporal variations of iron and manganese ions at eight stations along the Oued Moulouya. The water samples collected were therefore analysed to determine their pH (in situ) and their contents in these two ions following the method of Inductive Coupled Plasma spectrometry. The results obtained showed disparities in the concentrations of various components between the two periods of the year: wet and dry periods. Thus, the two elements monitored (Fe and Mn), expressed their maximum levels during the dry period, with values of 21.75 mg/l and 4.9 mg/l. These values were recorded at the station near the city of Guercif. While the minimum concentrations of these elements were recorded upstream of the Oued during the rainy months with values of 0.047 mg/l for iron and 0.016 mg/l for manganese. Hence, it is concluded, that the variation of the content of these two elements Fe and Mn is influenced by the geochemical contribution, which occurs during the dry periods and decreases by the physical dilution during the rainy periods. **Key words**: Iron, Manganese, physicochemical quality, Moulouya, Pollution.

1 Introduction

The Moulouya, which originates in the High and Middle Atlas Mountains, with a highly variable flow that extends over more than 500 km [1], is one of the main rivers in North Africa that empties into the Mediterranean Sea. In addition, this Oued is considered the main source of irrigation of the plains in its watershed [2], hence its socio-economic importance for Morocco in general and in particular, for the Oriental region [3]. However, the Moulouya, which is the field of this research, is subject to several threats of pollution of agro-industrial origin, as it borders on both sides several agricultural plots and settlements, including the cities of Tounfite, Boumia, Zaida, Missour, Outat El Haj, Tendit and Guercif, generating an important flow of liquid discharges [4]. In addition, with an average water flow of 1 billion m^3/year [5], this fluvial course is subject to a considerable pressure of pollution threatening its quality while compromising its various uses [3]. Moreover, in spite of the agricultural activities practiced in the small plots of land located on the banks of this Oued, the anthropic pollution that influences this watercourse is manifested by different activities related to the agglomerations settled alongside the said river [6]. On the one hand, the exposure of river waters to these polluting sources is widely and previously studied. Indeed, [7] have reported that the water quality of river Ramganga in Bareilly, Uttar Pradesh is unfit for drinking purposes

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because of the discharging of domestic and industrial wastewater into the river and other anthropogenic activities around the river. On the other hand, the pollution due to metallic elements is considered of alarming importance that indicates a toxicity risk for the consumers. Besides being the fourth most abundant metal, constituting 5.6% of the earth's crust, Iron is also essential for the production of many enzymes, myoglobin and hemoglobin, and its deficiency can cause anemia and other health problems [8]. Furthermore, the specific degradation by erosion activity estimated at 214 m^3/km^2/year in the Moulouya watershed leads to the change of the ions concentrations and affects the Oued water quality [8]. These phenomena affect consequently the quality of this water by provoking remarkable alterations that can harm the living communities [9]. This fact is also coupled with the load of several metallic elements draining from the old mining sites in the upstream part of the Oued, where several mining districts are abandoned, namely those of Aouli, Zaida and Mibladen [10]. As for the excessive quantities of this metallic load contained in the aquatic system, it is often linked mainly to past and present mining activities [11-15]. These metallic substances are also considered among the most feared pollutants due to their non-biodegradable character and their limited or no ability to be removed by the process of self-purification [16]. In oxide form, iron and manganese are minerals that can be found in soil. Although iron (Fe^{3+}) and manganese (Mn^{4+}) oxides are extremely insoluble, they are reduced to lower concentrations when the water contains carbon dioxide or is pH acidic (low). Divalent iron and manganese are therefore dissolved in water [8]. The amounts of these metallic ions are often low in surface water, but they can be significant in other water sources for industries, distribution systems, and eventually consumers [17]. Thus, it is important to indicate that the excessive iron (Fe) toxicity can lead to primary hematochromatosis and even liver cancer [18], diabetes, heart diseases and infertility [8]. While manganese (Mn) can also be the cause of some irreversible neuropathies through its antagonism to calcium [20]. In order to evaluate the level of metallic pollution in the Oued Moulouya, this study discloses its water metallic contamination by Iron (Fe) and Manganese (Mn) through the qualitative characterization of the waters sampled from 8 stations, which in case of an excessive concentration, can present health and environmental threats.

2 Materials and method

2.1 Sampling point design

The water sampling was carried out during two seasonal campaigns spread successively during the months of December-April (***rainy period***) and May-September (***dry period***). Initially, several stations were surveyed for sampling based on the different activities identified in the study area (flow of agro-industrial, domestic and mining potential pollutant. However, other criteria were considered to define only eight stations with high representativeness for the Oued Moulouya, namely, the location of the station in relation to the various tributaries feeding the Oued, the position of the main urban areas on both the left and right banks, and the easy accessibility of the measuring and sampling equipment (Figure 1).

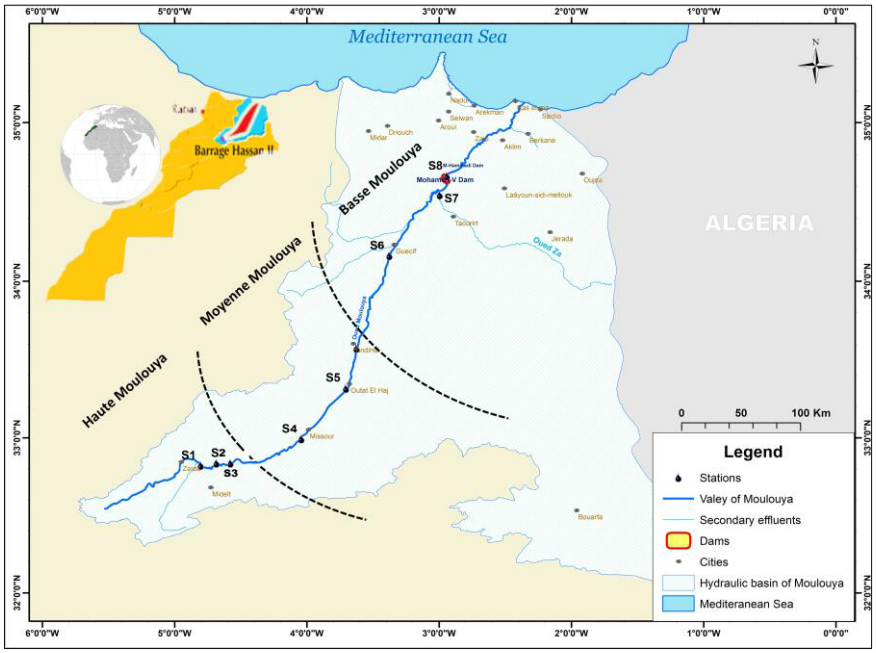

Fig. 1. location map of the sampling stations

These stations are grouped into three geographical clusters from upstream to downstream:

- **Upper Moulouya:**
  - S1: Control station located in the upstream part of the Moulouya.
  - S2: Located upstream of the Aouli mine.
  - S3: Located downstream of the Aouli mine.
- **Middle Moulouya:**
  - S4: Near the city of Missour.
  - S5: Near the Tendite village.
- **Lower Moulouya:**
  - S6: Near city of the Guercif.
  - S7: On the Oued Za tributary.
  - S8: Downstream part of the junction of oued Za and oued Moulouya.

2.2 Analytical Methods

Water was sampled during rainy and dry periods in polyethylene bottles of different volumes. Samples were thereafter filtered using nitrocellulose filters of 0.45 µm porosity, and then stored in a cooler for the duration of the sampling [21]. The hydrogen potential (pH) of the waters was measured in-situ using a potentiometer (*Hanna-99151*). While manganese (Mn) and iron (Fe), were measured in an accredited laboratory following the method of Inductive Coupled Plasma spectrometry (ICP-AES, *Ultima2 JY*) under the standard (*NF EN ISO 11885*) [22].

3 Results and discussions

The evolution of the amount of iron and manganese in the Moulouya waters was studied through the analysis of collected water samples at the eight stations during the sampling period. Figures (2,3,4) report the average values relating respectively to the parameters hydrogen potential (pH), Iron (Fe) and Manganese (Mn) analyzed.

3.1 Hydrogen potential (pH)

The hydrogen potential (pH) of water measures the concentration of H^+ protons contained in water [4]. It summarizes the stability of the balance made between the various forms of carbonic acid. In an aerobic environment, the pH is the main factor that governs the solubility of iron and manganese [8,23].

The pH results (Figure 2) indicate slightly neutral to alkaline values in all stations of Oued Moulouya and during all periods of the year. Indeed, this parameter varies between 7.59 as the minimal value at station S1 during the summer (dry period) and 8.51 as the maximal value at station S2 during the autumn (wet period).

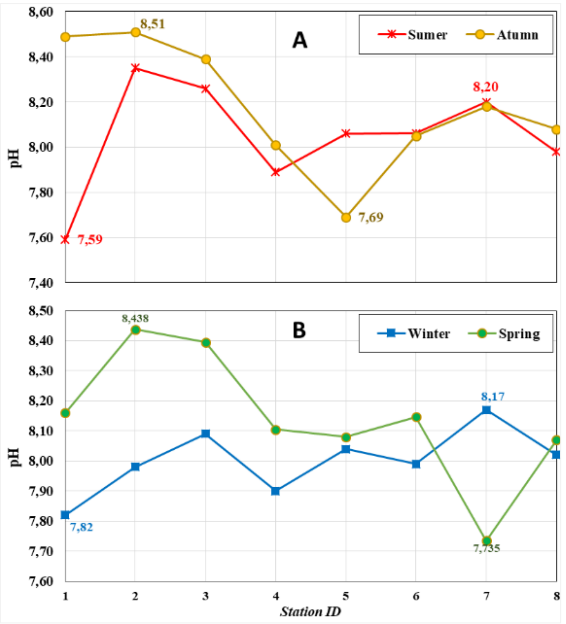

Fig. 2. Spatiotemporal change in pH levels in the Oued Moulouya waters during the dry period (A) and during the rainy period (B).

Thus, the results show a very slight change in pH along the Moulouya. However, such fluctuations, however slight, may be due to the inflow of tributaries on both sides of the Oued, which by crossing geochemically and thermally heterogeneous soils provide water with varying pH over time. It is important to note that for most aquatic species, the favorable pH range is between 6 and 7.2 [21]. Generally, the pH of the Moulouya waters shows, based on this study, values with alkaline trends. This correlates with the results found by Makhoukh et al. [4] during the years 2006 and 2007.

According to these pH values, the Moroccan standards (*Official Bulletin, 2002 - Order No. 1275-01 of 10 Chaabane 1423*) allow to categorize the waters of most monitored stations in Oued Moulouya in the good to excellent classes [24]. As for the use of these waters for irrigation purposes, the values of their pH reveal a compliance with the Moroccan standards for water intended for irrigation, requiring values between 6.5 and 8.4) [25,26].

3.2 Manganese ions (Mn)

During the rainy period, the variation in manganese concentrations is not significant. It takes slightly increasing values from upstream to downstream of the Moulouya; from 0.016 mg/l in station S2 to 0.048 mg/l in station S8 during winter and from 0.016 mg/l in station S3 to 0.071 mg/l in station S5 during spring. As for the dry period, there is an increase in water manganese concentrations from the upstream part (upper Moulouya) to the downstream part (lower

Moulouya). Indeed, values measured in summer range from 0.179 mg/l at station S1 to 4.905 mg/l at station S6 located near the town of Guercif and from 0.169 mg/l at station S2 to 4.465 mg/l at station S6 in autumn. Thus, low manganese concentrations are found in the Oued Za tributary waters during all periods of the year, which affects, certainly the concentrations of Mn in the Moulouya waters (Figure 3).

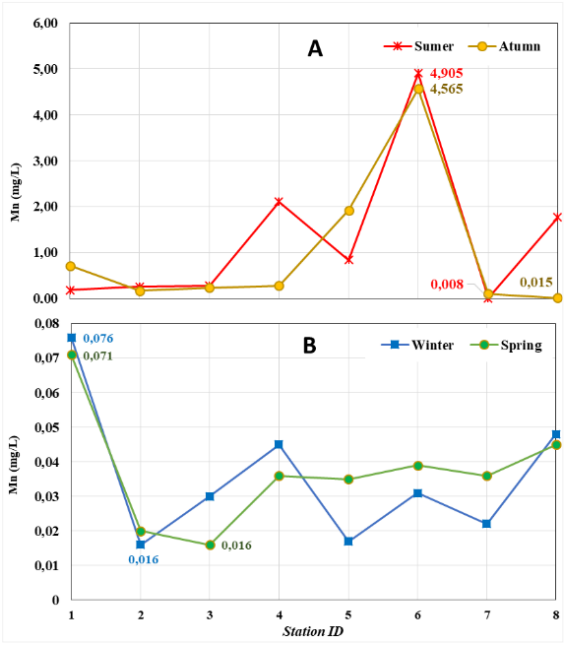

Fig. 3. Spatiotemporal change in Manganese (Mn) concentrations in the Oued Moulouya waters during the dry period (A) and during the rainy period (B).

The Mn concentration values recorded during all periods of the year show, compared to other rivers such as Oued Sebou (Morocco) and Oued la Seine (France), that the manganese content in the Oued Moulouya waters is at tolerable levels [4]. Hence, it is verified, that the manganese concentration is high in waters with high iron content [27]. Therefore, the values found in this study confirm those reported by Brahimi [28].

According to the quality grid of surface waters adopted in Morocco and fixed by the *decree 1275-01 of October 17, 2002* [29,30], the waters of the monitored station (S1) is classified during the dry period, based on the concentrations of iron ions, in a category of average to poor quality with values around 0,5 to 1 mg/l and the stations (S4, S5, S6 and S8) are in a category of very poor quality, being largely exceeded 1 mg/l. Whereas during the wet periods of the year, all the monitored stations still in a good quality class.

It is important to note that downstream of each of the stations studied, a phenomenon of precipitation of manganese ions was observed, which considerably attenuates their high concentrations.

3.3 Iron ions (Fe)

In natural surface waters, iron is present in low concentrations of around a very few mg/l, which is often provided through the leaching of the soils and the industrial activities disposals [22]. As for iron concentrations in the waters of Oued Moulouya range from 0.098 mg/l in station S2 to 0.674 mg/l in station S8 during winter and from 0.055 mg/l in station S2 to 0.285 mg/l in station S8 during spring. While in the dry period the amounts of iron vary between 0.411 mg/l at station S1 to 21.75 mg/l at station S6 in Summer and between 0.191 mg/l at station S4 to 19.63 mg/l at station S6 in Autumn (Figure 4)

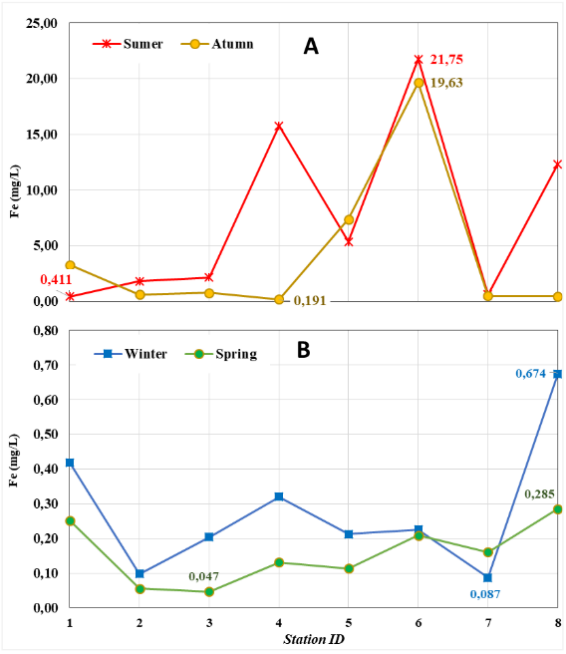

Fig. 4. Spatiotemporal change in Iron (Fe) concentrations in the Oued Moulouya waters during the dry period (A) and during the rainy period (B).

Based on the results of this study, it always appears that the concentrations of iron in the analyzed waters vary simultaneously with those of manganese. The enriching of the Moulouya waters by these components is potentially related to the urban tributaries and the industrial discharges flowing in these tributaries. In the presence of oxygen in water containing iron and manganese, the cations Fe^{2+} or Mn^{2+} trends to precipitate [31], which can explain the decrease of iron and manganese concentration value at station S7. Nevertheless, these iron concentrations appear higher in the waters of the Moulouya compared to those found by Van Coillie et al. (1984)

in the Escoumins River on the North Shore of the St.Lawrence River (0.144 mg/l in the upstream part and 0.23 mg/l in the downstream part) [23].

The concentrations of iron and manganese found in the waters of the Moulouya appear to be much higher than those prevailing in natural waters; where the concentrations of these elements are of the order of 0.2 mg/l (Fe) and 0.03 mg/l (Mn), which characterizes according to Alabaster and Lloyd [32], and Harvey et al. [33], oligotrophic waters.

According to the quality grid of surface waters adopted in Morocco and fixed by the *decree 1275-01 of October 17, 2002* [29,30], the waters of the monitored stations (S2 and S3) are classified during the dry period, based on the concentrations of iron ions, in a category of average to poor quality with values around 1 to 2 mg/l and the stations (S4, S5, S6 and S8) in a category of very poor quality, being largely exceeded 5 mg/l. Whereas during the wet periods of the year, all the monitored stations oscillate between the excellent quality class S1-S7 and the good quality class, for station S8.

Similarly, these Fe ions concentration exceed the limit value (5 mg/l) required by the Moroccan standard of water destined for irrigation [34,35].

The intensity of the iron ions concentration, nevertheless, shows a significant decrease downstream of each of the monitored stations due to the precipitation phenomenon in the depths of the Moulouya watercourse.

4 Conclusion

In the light of the results obtained, it can be seen that the concentration of manganese is high in waters with a high iron content. In addition, a phenomenon of dilution was highlighted through the decrease in concentration of these two elements at the junctions of the Moulouya with its tributaries, especially Oued Za.

In the same way, a phenomenon of precipitation of the metallic load (Fe and Mn) was observed in the reservoir lake (Hassan II dam), leading to a decrease of the concentrations of these elements in the waters of the Moulouya. Moreover, the results obtained affirm a strong seasonality in terms of the quality of the studied waters. Indeed, the variations of the content of these two elements, Fe and Mn, are affected by the geochemical contributions which occur during the dry season and decrease during the rainy season due to physical dilution.

At the end of this study, it appears that the results obtained on the water quality based on the iron and manganese content, highlight a direct influence of the terrains crossed by the watercourse, to which is added the pollution globally generated by the domestic and industrial wastewater produced by the residents on both sides along the Oued Moulouya.

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