

PHYSICO-CHEMICAL, BACTERIOLOGICAL AND HEAVY METALS ASSESSMENT OF SURFACE WATERS IN MARTIL BASIN (NORTH-WESTERN MOROCCO)

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Under the impact of the deterioration of water quality in Martil Basin, an assessment of the water quality was carried out. Our work was based on a characterization of the physicochemical, bacteriological quality of the surface water using two water quality indices (WGQI and CCME-WQI), at 20 sites during spring and summer 2017. After the detection of the most polluted zones, a second study focused on the characterization of the concentrations of twenty-one heavy metals determined from the highest polluted sites (9 stations) during autumn 2018. The results obtained reflect a deficient ecological state, especially downstream.

Keywords: Water quality indices, Heavy metals, Martil Basin, Morocco.

1. Introduction

Over the last few decades, the pace of development has accelerated and various anthropogenic activities have taken place in several areas near major cities and rural areas along rivers [1]. Furthermore, since the concentrations of pollutants condition the aquatic biocenoses, excessive wastewater production affect water quality and serious imbalances in aquatic ecosystems can occur [2].

The assessment of water quality is a complex process involving multiple parameters, as conventional methods were based on comparing the results of the parameters obtained with local standards. However, it does not offer an overall overview of water quality [3, 4, and 5]. Since the birth of the concept of water quality index by Horton (1965) [6], who presented a numerical index to assess the quality of water by selecting and rating the significant physical, chemical and biological parameters, a huge number of indices and many different methods for the calculation have been developed for the assessment of running water [3, 7]. Therefore, the indices of quality were developed as auxiliary tools to provide an overview of water quality and enabling easy interpretation of monitoring data [7].

The Martil Basin, which occupies a strategic position in north-western Morocco, currently represents a human settlement area.

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In a concern to appreciate the health status of this ecosystem, the present work aims at assessing physico-chemical and bacteriological quality of surface waters of the Martil Basin in order to detect the nature of pollutants and pathogenic germs likely to cause nuisances based on CCME-WQI and WGQI indices of water quality. After the detection and location of the pollution black spots that affect this river, a second part of the study aims to determine in particular the level of heavy metal/toxic concentration at the most severely polluted sites in order to identify the contamination levels along this watershed.

2. Material and Methods

2.1 Study area and sampling sites

The watershed of Oued Martil is located in the north-west of Morocco. It is part of Tangier-Tetouan-Al Hoceima Region. The area of Martil watershed is relatively small since it does not exceed 1259 km² [10], it lies geographically between 35.10° and 35.45° north latitudes and 5.17° and 5.38° west longitudes.

The altitudes and slopes of the Martil Basin varies between 0 m on the coast and the plain at 1782 m with an average altitude of about 424 m [11]. The climate is mainly Mediterranean with an annual rainfall of a great variability where it varies between 500 and 750 mm/year and can reach 2000 mm [12].

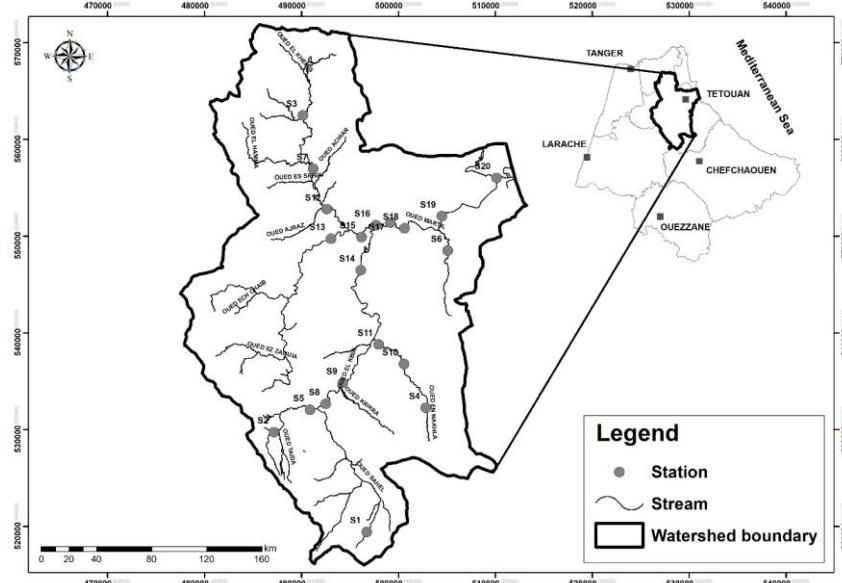


Fig. 1. Location of the Martil Basin at the north of Morocco and the sampling sites.

Oued Martil is a river which is located in the downstream part of the Basin and appropriates the same name as the watershed. It is born in Tamouda from the confluence of its main tributaries, Oueds Mhajrate, Khemis, and Chekkoûr. It is

22 km long and crosses the city of Tetouan, where it is thus surrounded by multiple industrial, agricultural and tourist activities that develop on its borders before flowing into the Mediterranean Sea at the level of the city of Martil [9].

For the completion of this study, 20 stations were retained throughout the watershed of Oued Martil (Fig. 1), taking into account a number of criteria such as equivalent distribution throughout the Basin, upstream/downstream positioning, and sources of pollution. Sampling campaigns for physicochemical and bacteriological parameters were carried out in spring and summer of 2017 at the 20 selected stations, while those for heavy metals were conducted at 9 of the most polluted stations in the Martil Basin in autumn 2018.

2.2 Water analysis

The assessment of the waters of Martil Basin is apprehended on the basis of measurements of a total of twelve physicochemical and bacteriological parameters. Some ones were measured *in situ* like temperature, pH, electrical conductivity, and dissolved oxygen thanks to a specialized portable device (EUTECH CyberScan PCD 650). The other parameters (nitrite, nitrate, suspended matters, sulphate, BOD_5 , COD, faecal coliforms and faecal streptococci) were analyzed in the Laboratory of the Loukkos Hydraulic Basin Agency (ABHL, Tetouan), according to the norms described by Rodier (2009) [13].

Twenty-one heavy metal elements were analysed. They concern: Silver (Ag), Aluminum (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Lithium (Li), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Lead (Pb), Antimony (Sb), Selenium (Se), Tin (Sn), Strontium (Sr), Vanadium (V) and Zinc (Zn) were determined in surface water of Martil Basin by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) at nine sampling stations located near the agricultural, industrial and urban areas of the watershed. The analyses were carried out in the Laboratory of the Public Laboratory for Tests and Studies (LPEE: *Laboratoire Public d'Essais et d'Etudes*) settled in Casablanca (Morocco).

2.3 Water quality indices

In general, water quality indices can be used as mathematical tools to transform a number of values into a single score, which is placed on a scale to assess water quality in categories, thus enabling easy interpretation of monitoring data [16]. In our study, two kinds of indices were applied to assess water quality.

2.4 The weighted global quality index (WGQI)

We used the weighted global quality index, which was recently developed by the Water Research and Planning Department (DRPE) in Morocco [15]. This index is obtained by weighting, which produces a score corresponding to its position in a range of classes according to Moroccan standards for surface water

quality (Table 1). Indeed, the interval values set by the new water quality assessment grids are transformed into unit numbers varying from 0 (very poor quality) to 100 (an excellent quality) to obtain a score according to 5 quality categories (excellent, good, medium, poor, very poor). The global quality index is the lowest index obtained for all the alterations considered.

The mathematical equation used to calculate the weighted index is:

$$WI_{ap} = Li + \left[\frac{(Hi - Li)}{(ub - lb)} \right] x (ub - ap)$$

WI_{ap}: weighted index of the analyzed parameter, Li: Lower index, Hi: Higher index, lb: lower limit, ub: upper limit, ap: analyzed parameter

2.5 The Canadian Water Quality Index (CCME-WQI)

CCME-WQI was developed in 2001 by a committee established within the Canadian Council of Ministers of the Environment (CCME) [7], based on the index developed by the British Columbia Ministry of Environment, Lands, and Parks [16]. The method for the calculation of this index is dependent on the combination of three factors (Scope, Frequency, and Amplitude) from the selected objectives to yield a single numerical score ranging from 0 to 100 (with 1 being the poorest and 100 indicating the highest water quality) [8]. Within this range, the water quality is ranked in five categories to classify water quality as poor, marginal, fair, good or excellent [7]. The classification of water quality was done in accordance with the Moroccan standards of surface water quality (Table 1).

The various mathematical equations of CCME WQI are given below:

1- F1 (scope) corresponds to the percentage of failed variables that do not meet their objectives to the total of variables measured.

$$F1 = \left(\frac{\text{Number of failed variables}}{\text{Total number of variables}} \right) \times 100 \quad (1)$$

2- F2 (frequency) corresponds to the percentage of the individual (failed tests) that do not meet objectives.

$$F2 = \left(\frac{\text{Number of failed tests}}{\text{Total number of variables}} \right) \times 100 \quad (2)$$

3- F3 (amplitude) corresponds to the amount by which failed test values do not meet their objectives and calculated in three operations in the following steps: The number of times by which an individual concentration is further than (or less than, when the objective is a minimum) the objective is nominated an “excursion” and is calculated by.

$$\text{excursion } i = \left(\frac{\text{Objective } j}{\text{Failed Test Value } i} \right) - 1 \quad (4) \quad \text{excursion } i = \left(\frac{\text{Failed Test Value } i}{\text{Objective } j} \right) - 1 \quad (3)$$

The normalized sum of excursions (NSE): It is comprised of summation of excursions calculated, which the individual tests are out of compliance divided by the total number of tests and is given by the following expression:

$$F3 = \left(\frac{nse}{0,01nse + 0,01} \right) \quad (6)$$

$$nse = \left(\frac{\sum_{i=1}^n excursion_i}{Number\ of\ tests} \right) - 1 \quad (5)$$

Once F1, F2, and F3 have been calculated, the WQI is given by the following form:

$$CCME-WQI = 100 \cdot \left(\frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732} \right) \quad (7)$$

Table 1
The grid of the physicochemical and microbiological quality used for the classification of surface waters in Martil watershed [15].

Quality classification	Excellent	Good	Moderate	Poor	Very poor
T (°C)	<20	20-25	25-30	30-35	>35
pH	6.5-8.5	-	8.5-9.2	<6.5 or >9.2	-
EC (µS/cm)	100-750	750-1300	1300-2700	2700-3000	>3000
DO (mg/L)	>7	7-5	5-03	3-1	<1
BOD₅ (mg/L)	<3	3-5	5-10	10-25	>25
COD (mg/L)	1.5-30	30-35	35-40	40-80	>80
SM (mg/L)	<50	50-200	200-1000	1000-2000	>2000
NO₂⁻ (mg/L)	<0.03	0.03-0.3	0.3-0.5	0.5-1	>1
NO₃⁻ (mg/L)	<10	10-25	25-50	>50	-
SO₄²⁻ (mg/L)	1-100	100-200	200-250	250-400	>400
FC (CF/100ml)	<50	50-5000	5000-50.000	>50.000	-
SF (SF/100ml)	<20	20-1000	1000-10.000	>10.000	-

3. Results and Discussion

3.1 Physicochemical and bacteriological quality

The evolution of temperature is characterized by lower values in the spring and higher values in the summer, oscillating between 13.7 °C and 36 °C (Fig. 2a). The pH values show a slightly alkaline tendency stabilizing between 6.54 and 8.71 (Fig. 2b). The recorded levels of electrical conductivity fluctuated between 26.5 µS/cm at M1 located upstream in the spring and 7920 µS/cm at M6 situated quite downstream in summer (Fig. 2c). The seasonal evolution of dissolved oxygen showed higher concentrations and notable variations ranged from 0.2 mg/L in summer at M19 and 15.1 mg/L in the same period at M2 (Fig. 2d).

The BOD₅ contents oscillated in our study area between 4.7 mg/L in M11 and 120 mg/L in M18 (Fig. 3a). The levels of COD ranged from 11.5 mg/L at M11 in spring and 340 mg/L at M18 in summer (Fig. 3b). Seasonal variations of suspended matter ranged from 18.4 mg/L M3 in spring to 420 mg/L in M18 in summer (Fig. 3c).

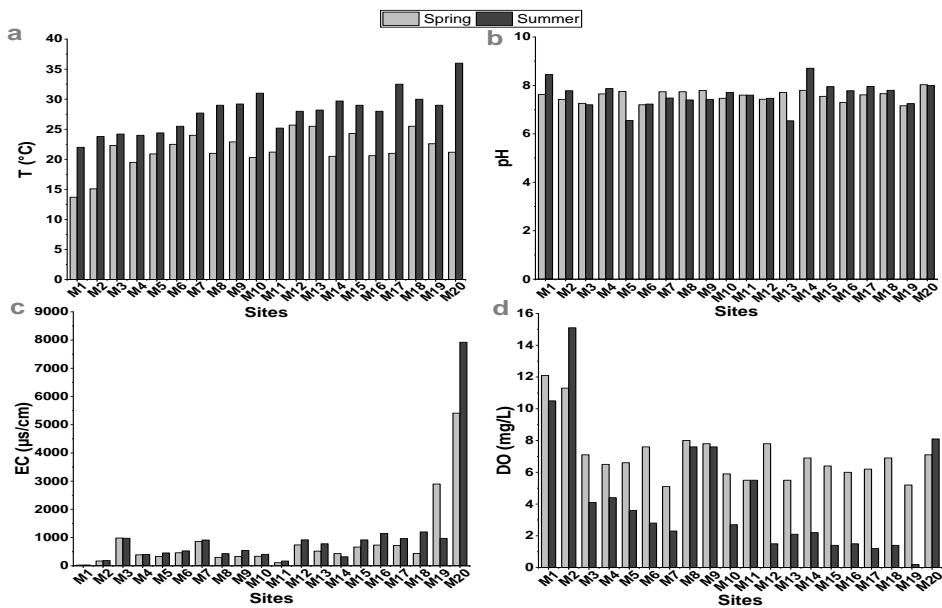


Fig. 2. a. Spatiotemporal variation of temperature ($^{\circ}\text{C}$), b. pH, c. Conductivity ($\mu\text{S}/\text{cm}$), d. Dissolved Oxygen (mg/L) in the Martil Basin.

The SO_4^{2-} levels ranged between 0 mg/L at M1, M2 and M15 in summer and 993.53 mg/L at M20 in the same period (Fig. 3d). The NO_2^- levels of Martil Basin showed low values, oscillating between 0 mg/L in many stations of upper and middle reaches of Martil Basin and 0.19 mg/L at M6 in spring (Fig. 4a).

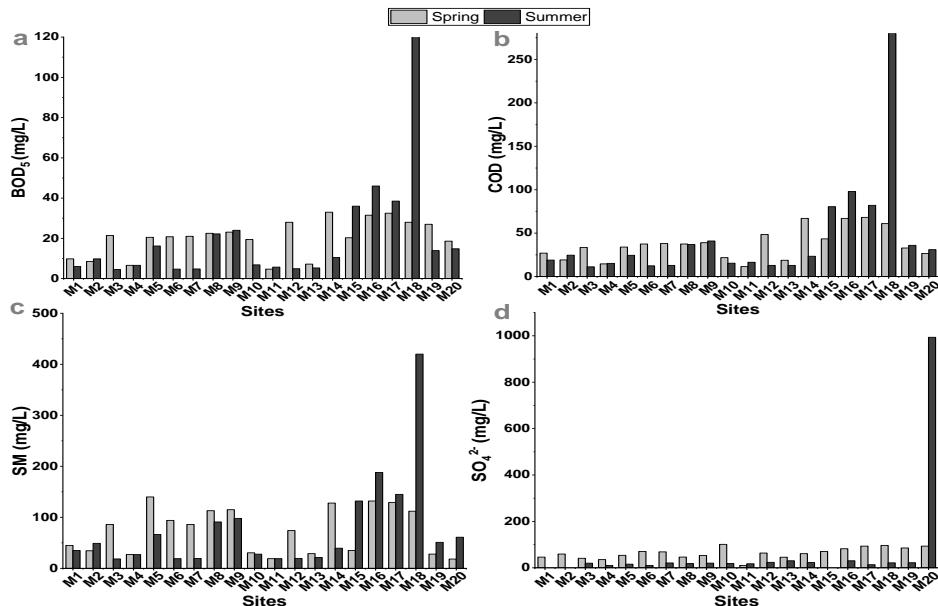


Fig. 3. a. spatiotemporal variation of BOD (mg/L), b. COD (mg/L), c. Suspended Matter (mg/L), d. Sulphate (mg/L) in the Martil Basin.

NO_3^- concentrations show a slight variation between 0 mg/L in various locations of Martil Basin and 34.04 mg/L at M6 in summer (Fig. 4b).

The highest values of faecal coliforms (CF) and faecal streptococci (SF) concentrations 740 SF/100ml at spring and 12000 CF/100ml in summer at M16 showed the existence of hot spots of bacteriological pollution in the lower course along the Oued Martil (Fig. 4c-d).

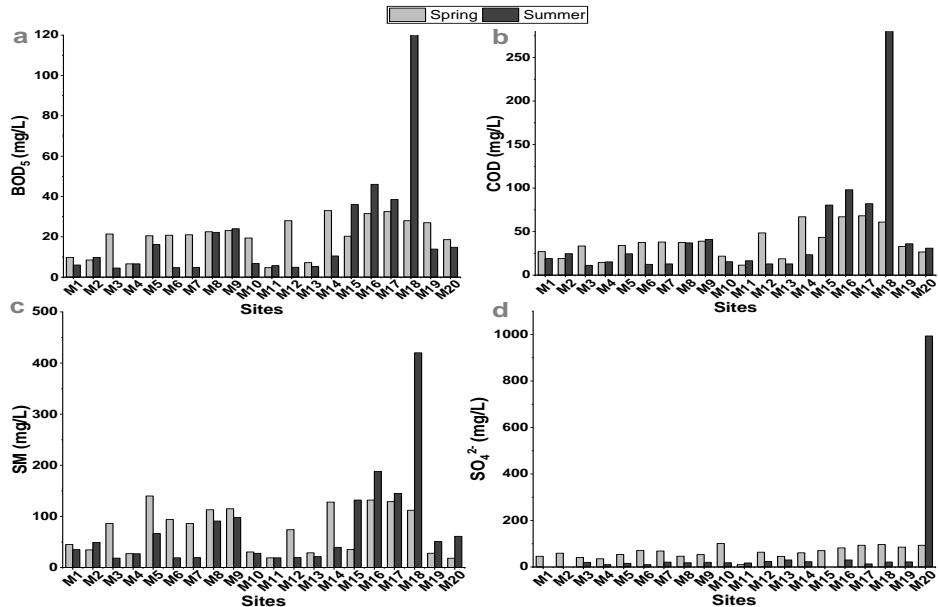


Fig. 4. a. spatiotemporal variation of Nitrite (mg/L), b. Nitrate (mg/L), c. Faecal Coliforms (CF/100ml), d. Faecal Streptococci (SF/100ml) in the Martil Basin.

Moreover, different parameters are responsible for the decline in water quality indices through various stations [17]. For those located midstream, the indices dropped mainly because of the higher contents NO_3^- , SO_4^{2-} and EC due to the agricultural activities that are developed on the banks of the streams [18]. As well as downstream sites, in addition to the direct discharges stemmed from urban sewage, and industrial effluents suggest higher quantities of bacterial and organic pollutants which leads to an increase in the BOD_5 , COD, SM, FC and FS values in Oued Martil [8] and a significant decrease in CCME-WQI and WGQI indices. In addition, it is important to highlight that the same sites at Oued Martil had similar low WGQI's values also observed by Belhaj & Kettani (2013) [9].

3.2 Water Quality Indices

As regards the scores of the weighted index (WGQI), spatial and temporal variations were noted depending on the sites studied. In respect to this index (Fig. 4a), three stations are manifesting good quality (15%), six sites are of medium quality (30%), followed by ten sites of poor quality (50%), and one site is of very

poor quality (5%). WGQI's highest value (79.45) was obtained at Tkaraa (M1) in the upper part of Martil watershed, whereas the lowest value (12.53) was obtained at Diza (M20). The results represented in Figure 4b have shown that the CCME-WQI values were between 80.47 at Tkaraa (M1) and 14.2 at Roumania (M18). Only two sites (10%) display the range of good quality, while the water quality is fair at four stations (20%). The marginal condition was observed for seven sites (35%). Then the conditions fall into poor quality in the seven other sites (35%).

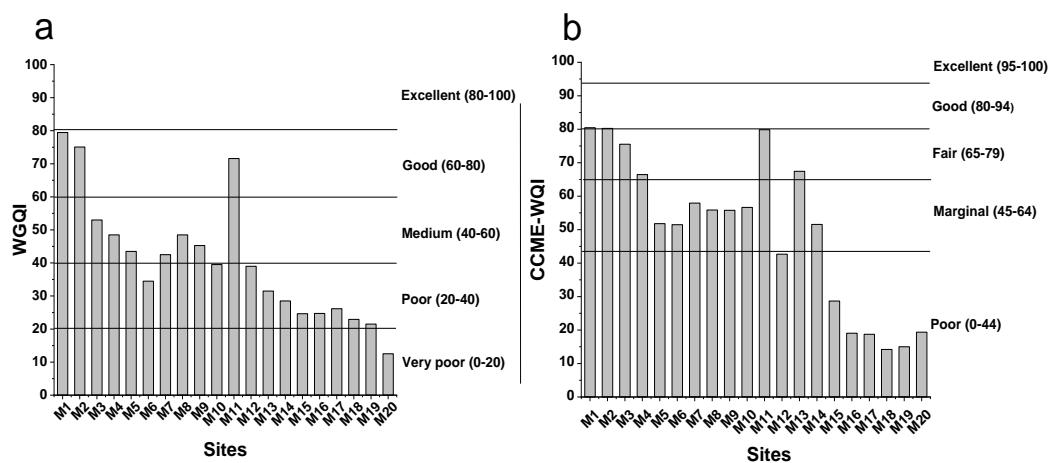


Fig. 5: a. Scores of WGQI, b. CCME- WQI during the study period in the Martil Basin.

In a view of testing the validity of these methods based on index quality in our local conditions, a comparison between the two selected indices revealed that an obvious difference appears between them throughout the majority of the quality classes, especially in the higher ones. The results showed that the average value of the two indices obtained by using CCME-WQI was 41, 39 indicating poor quality, which was lower than the WQGI (49.44) reflecting medium quality. Thus, CCME-WQI is the most rigorous approach to assess water quality in Moroccan streams, puts water quality of Martil Basin in the lowest classes than WQGI method [20].

Along with the benefits of using water quality indices for the purpose of easy interpretation of water quality monitoring data, there are several weaknesses for the application of indices that should be taken into consideration.

The main disadvantage of WQGI is the eclipsing effect. Due to this effect, one parameter which has value above permissible limit represents the index value at the sampling station under study and reflect the overall quality even though if rest of the parameters are within the limits. However, it caters for the problem losing some important information during the processing of the data during the aggregation process. WQGI may not carry enough information about the real quality situation of water [19].

Of the many drawbacks inherent in the development of CCME-WQI index are the following: this index should not be run with a reduced number of parameters [7]. In addition to the impossibility of using this index for a single sampling visit per year, we can also note that the ranges are not fair between quality classes, for example only between 95-100 is considered as excellent quality, on the other hand from 0 to 44 gives us a poor quality.

It appears that the Canadian model tended to be the most efficient for classifying surface water quality as compared to the Moroccan model seen its method of calculating which takes into account all the parameters measured. On the other hand, this index is also the most rigorous one due to the inequality of intervals between its rating scales.

Ultimately, no index is ideal, the choice of the index must be used to evaluate water quality will depend on the objectives to be met. Indices are routinely used despite shortcomings and offer ease of reporting that can be used as an effective tool about the general state of water quality [20]

3.3 Heavy metals

Among the 21 heavy metal elements analyzed, a comparison between the different concentrations recorded in the sites surveyed on Martil basin showed that the contents of Al, As, Ba, Fe, Li, Mn, Sr revealed a significant variations between the different stations, while the Ag, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sn V, and Zn values are below the lowest affected level or not detected.

The maximum concentrations of Aluminium were recorded at M14 with a value of 0.039 mg/L. Arsenic contents were recorded under the limit, with the highest concentration (0.0071 mg/L) found at M18. With the exception of M18 which displays the highest value of Barium (0,106) none of the other sites shows above the recommended limit set by Moroccan standards (0.1 mg/L). Fer levels in the entire sites were below the limit value (0.5 mg/L), with a maximum (0.283 mg/L) registered at M18. As for the Lithium contents, the obtained results show that they range from a minimum value of 0.09 mg/L at M18 to the maximum value of 0.062 mg/L detected at M20. The most important levels of the Manganese were registered in the downstream of Oued Martil (0.491 mg/L and 0.400 mg/L). Results from particular localities such as M6, M18, M19 and M20 exceed the maximum permitted concentration for protection of aquatic life (0.1 mg/L) set by the Moroccan standards. Whereas the Strontium showed a significant variation among different sites, over a very wide range of values from 0.332 mg/L at M14 and 8.113 at M20 (Table 2).

The decreasing order of heavy metals concentrations observed in the studied watershed is as follows: Sr>Mn>Fe>Ba>As>Al and finally Li. Their spatial distribution indicates that the levels in the sites of the upper and middle parts of the Basin were very low, while the maximum were registered at

downstream, which causes a real threat to aquatic life in these contaminated areas. While for the other trace elements such as Ag, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sn V, and Zn, they were not detected in this Basin.

The highest levels of Arsenic (As) were observed at M14, while those of Barium (Ba), Iron (Fe) and Manganese (Mn) were observed at the industrial area of M18, where industrial establishments are concentrated, especially brickworks, cement plants, ceramic units and marble factories that contributes to the enrichment of the concentration of heavy metals in water. Levels of Lithium (Li) and Strontium (Sr) at M20 located quite downstream, were found to be higher than concentrations measured at other stations, probably reflecting the influence of sea level and salinity gradients on Lithium and Strontium [21, 22].

The results obtained revealed that concentrations of heavy metals in surface river water of Martil Basin during autumn showed rather low values, when compared with the previous studies conducted on Al, Fe, Mg, Cd, Cr, Zn, Ni, and Pb in the same study area by Raissouni et al. (2014) [23] at spring of 2010 and 2011, which were higher. The same findings on Al, Ca, Cu, Fe, Pb, and Zn was reported by Raissouni et al. (2016) [24] at winter and summer 2013.

Table 2

Heavy metal concentrations in water samples obtained from the nine sampling stations in Martil Basin

4. Conclusions

The results obtained in the water quality assessment of the Martil watershed show that:

The assessment of physico-chemical parameters showed significant variations between the different sections of the watershed. On comparison of the models used, CCME-WQI provides to be the most stringent one classifying water quality of Martil Basin as marginal or poor especially downstream.

The downstream section of the Martil Basin represented the highest concentrations of mineral, bacterial and organic pollutants especially during the summer, depending on the localities compared to those situated further upstream, which are generally away from anthropogenic disturbances.

Heavy metals values exhibited globally low levels and are below the recommended levels according to Moroccan standards even though they showed significant variations between stations under diverse impacts of human activities. Only the level of strontium which was above normal at M20 situated near the estuary which is mainly influenced by anthropogenic activates and marine waters.

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