Contamination Assessment by Heavy Metals of the Ykem River Sediments (Coastal Meseta, Morocco)

Mohameden Aoufa, Noureddine Chahid, Bouamar Baghdad, Saïd Chakiri, Hassan EL Hadi, and Zahry Fatiha

Abstract—The main objective of this study is to evaluate the degree of pollution of Wadi Ykem through a geochemical study allowing highlighting the physicochemical characteristics as well, the evaluation and the distribution of the heavy metal contents in the sediments. For the environmental assessment of its sediments, a study was carried out to determine the concentrations of major elements and trace elements (Cd, Cr, Al, Pb, Zn, Cu and Ni) during two different hydrological seasons: in summer (June 2017) and in winter (April 2018). In the two campaigns 20 sediment samples were collected in 10 sampling sites. The various sampling sites were distributed upstream and downstream of the Ykem river. These metals were analyzed at CNESTEN using the ICP MS technique. The geo-accumulation index, the Enrichment Factor (EF) and the Pollution Load Index (PLI) were used for the assessment of metallic contamination of the sediments. The results of this study show a homogeneous distribution of the contents of major elements with a dominance of the elements SiO2 and TiO2 in the two campaigns. High Cd contents which exceed the contents of geochemical backgrounds. High levels of Cd, Pb and Al. And low concentrations for (Cr, Ni, Cu, Zn) for the two campaigns. The PLI variations show that all the stations have PLI values greater than 1. The Enrichment Factor does not show contamination at all sampling stations. The values of Igeo show levels which vary from uncontaminated to moderately contaminated.

Index Terms—Heavy metals, major elements, Morocco, sediment, Ykem watershed, pollution.

I. INTRODUCTION

Heavy metals are ubiquitous in all of the earth's reservoirs. They are the result of natural activities such as weathering of rocks, and anthropogenic such as wastewater, industry and agricultural activities [1]-[3]. Coastal environments are the ultimate receptacle for pollutants including heavy metals. The contamination of alluvial and aquatic environments by heavy metals is considered to be one of the most important environmental problems due to their potential accumulation which causes the contamination of rivers, estuaries and consequently oceans [4]. The distribution of these metals in the aquatic environment can lead to adverse effects on human health due to transfer through the food chain [5]. In the aquatic ecosystem, sediments are considered the final sink for heavy metals. They can be considered as good geo-indicators of the quality of the marine environment [6], [7]. Metal contamination of sediments affects water, living species and human health [8]. For this reason, examining heavy metals in these sediments contributes to the identification, understanding and prediction of marine and summer metal pollution.

The Atlantic coastal basins of the Rabat-Salé-Kenitra region have experienced a marked new dynamic in recent years, where agriculture, industry and leisure are the most active sectors, enhancing the attractiveness of the coast. The discharges of wastewater and solid waste, conveyed by the hydrographic networks of Sebou, Bouregreg, Ykem and Cherrat, constitute a real threat to the quality of beach water [9]. Indeed, the surface sediments along these coasts are always exposed to dangerous contaminations by heavy metals, and require more attention and reflection. The pollution of sediments by heavy metals in the coastal basins of the region has been the subject of several studies, in particular the work carried out on the wadis of Sebou and Bourregreg by: [10]-[13].

The Ykem wadi basin, like all the wadis in the Atlantic coastal basins, has experienced significant growth in the main economic (agriculture, industry and tourism) and demographic sectors, especially following the construction of the new town of Tamesna. Downstream from the Ykem wadi, the town of Ain Attig shows a major impact of solid waste and domestic wastewater, the daily volume of which is estimated at 1,304 m3 / day [9]. This is mainly due to the lack of treatment of domestic and industrial wastewater, resulting in the release into the marine environment of large quantities of organic matter, nutrients and contaminants, and the presence of heavy metals in these discharges from industrial activities [9]. Despite all these harmful activities and these environmental studies carried out on the basis of the region, Wadi Ykem has never been the subject of a detailed environmental pollution study which makes it possible to assess the pollution rate of this wadi by heavy metals present in its sediments. The present study aims to assess the metallic pollution of the surface sediments of the Wadi Ykem. The method used for this is based primarily on sampling the sediments and determining their concentrations in EMT (Metal Trace Element) using the spectrometric technique. Then, the estimation of the level of metallic pollution of the
sediments was made by comparing the concentrations of the metals obtained with those of the continental crust of [14], [15] and with those of the unpolluted sediments and using the indices of geo-accumulation (I-geo) and Pollution Load Index (PLI) as well as the Enrichment Factor (EF).

II. MATERIAL AND METHODS

A. Sampling

The sampling area extends over 37 km from the estuary of watershed to the source at the level of the Sidi Battache mountains (Fig. 1). On 10 collection stations 30 samples were taken in two campaigns. For the first campaign (June 23 and 25, 2017) 10 sediment samples were taken. The sediment was collected with a shovel and put in clean plastic bags. The weight of each sample taken is 500g. The sediment samples were transported to the laboratory. The sediments were dried in the air for a few days. For the second campaign on April 21, 2018, 10 sediment samples were taken in small bottles (50 ml). These samples were oven-dried at 40 °C for four days, thus crushed and filtered. The sediment sampling is always between 5 to 10 cm. A GPS was used to record the coordinates of the sampling sites.

B. Preparation and Analyses of Sediments

For the preparation of these samples, we weigh 0.3 g of the soil for each sample in Teflon beakers, well we add 6 ml of nitric acid HNO₃, 3 ml of hydrochloric acid HCL fuming 37% and 3 ml of hydrofluoric acid HF solution 40%. These beakers were left in the open under a high vent overnight. Then these samples are dried using hotplates at a temperature of 90 to 200 °C each time adding 2 ml of nitric acid for the purpose of removing the particles until the sample is soluble, then we put 2 ml of HNO₃ and fill the flask up to 50 ml of distilled water. The resulting solutions will be analyzed by ICP MS at CNESTEN in order to determine their heavy metals contents.

C. Assessment of Contamination

1) The pollution load index (PLI)

The PLI is widely used in heavy metal risk assessment studies in sediment. It allows to compare pollution in different soil sites [16] This is the nth root of the number of contamination factor values for all metals. PLI can be used to determine the level of sediment contamination by reflecting the number of times the heavy metal concentrations in a given sediment sample exceed the background geochemical concentrations [17].

\[ PLI = n \times (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n) \]  \hspace{1cm} (1)

where \( n \) is the number of metals studied and \( CF \) is the contamination factor [18]. The rank of values of \( PLI < 1 \) indicates no pollution: \( PLI = 1 \) present that only baseline levels of pollutant are present and \( PLI > 1 \) indicates polluted sediment [19].

2) Enrichment factor (EF)

The enrichment factor is an indicator for evaluating the intensity of the metallic contamination of the sediments studied by dividing the content of the metal studied on a reference metal. For this pollution indicator (EF), several researchers use the elements, Fe, Sc, Al, Mn and Li as reference elements [20]-[22], for this study Al was chosen as the reference element.

This metal factor is calculated according to the following formula: According to [23].

\[ EF = \frac{(Me/Al)_{sediment}}{(Me/Al)_{naturelle}}. \]  \hspace{1cm} (2)

3) Geo-accumulation index (I-geo)

The geo-accumulation index is an empirical index used to quantify the degree of anthropogenic contamination through a comparison between a given contamination and that of the geochemical background, according to the following formula [24]:

\[ I\text{-geo} = \log_2 \left( \frac{C_n}{1.5 \times B_n} \right) \]  \hspace{1cm} (3)

where: \( C_n \) is the measured concentration of the element in soil; \( B_n \) is the geochemical background value. The constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influence. The samples are classified according to the classification method shown in Table I based on the values of the Geo-accumulation index.

| TABLE I: I-GEO CLASSES [24] |
|-----------------------------|
| Class | Value | Soil quality |
|------|-------|--------------|
| 0    | Igeo<0| Uncontaminated |
| 1    | 0≤Igeo<1| Uncontaminated to moderately contaminated |
| 2    | 1≤Igeo<2| Moderately contaminated |
| 3    | 2≤Igeo<3| Moderately to heavily contaminated |
| 4    | 3≤Igeo<4| Heavily contaminated |
| 5    | 4≤Igeo<5| Heavily to extremely contaminated |
| 6    | Igeo≥5| Extremely contaminated |

III. RESULTS AND DISCUSSION

A. Distribution of Major Elements and Heavy Metals in Sediments

1) Major elements in sediment

The contents of major elements (Table II) vary for
The following order is; $\text{SiO}_2 > \text{CaO} > \text{Al}_2\text{O}_3 > \text{P}_2\text{O}_5 > \text{K}_2\text{O}$. When, for the second campaign (winter), the following order is; $\text{SiO}_2 > \text{CaO} > \text{Al}_2\text{O}_3 > \text{K}_2\text{O} > \text{P}_2\text{O}_5$.

Mean value of $\text{SiO}_2$, $\text{CaO}$, $\text{Al}_2\text{O}_3$, $\text{P}_2\text{O}_5$ and $\text{K}_2\text{O}$ are respectively from the summer to the winter 41.92% to 48.28%, 19.10% to 15.40%, 9.85% to 10.04%, 1.16% to 1.27% and 1.27% to 1.17%.

In the two campaigns, the $\text{TiO}_2$ contents (mg/kg) are higher than the MnO contents (mg/kg). The spatial distribution of the contents of major elements in all the stations is comparatively homogeneous. $\text{SiO}_2$ contents are higher in the stations S5, S6 and S7 near the cities of Tamesna and Sidi Yaya. For $\text{CaO}$, the high contents are downstream at the level of the stations S1 and S2.

2) Distribution of heavy metals

The concentrations of heavy metals in the sediments of Oued Ykem are presented in (Table III), which contains the minimum, average, maximum levels and the coefficient of variation for each metal in the two winter and summer campaigns. Fig. 2 shows the spatial variations of the metal concentrations during winter season.

The comparison of spatial variation of EMT shows that the concentrations in the summer period are higher than in the winter period, except for the element of Cu which shows an increase in 7 different stations. The Results obtained by [32] have shown wide variations in the heavy metal levels varying from high concentration during summer and low concentrations during winter season.

We note that the concentrations of EMT at stations S4 (near a garbage dump), S5 (industrial area) and S9 (area developed for agriculture) are often higher than the other stations.

The calculation of the Coefficients of Variation (CV) is for the purpose of evaluating the variability or homogeneity of the distribution of heavy metal concentrations in the study area. For campaign N° 1, the values of the CV for Zn, Cu, Ni, and Al are less than 0.5 which reflects homogeneity of these metals. For Cd and Pb, the high CV values of 1.84 and 1.173 respectively are due to the high Cd and Pb contents at station S9.

The average levels of EMT in the summer campaign are varied in the following order $\text{Al} > \text{Pb} > \text{Cd} > \text{Ni} > \text{Cr} > \text{Zn} > \text{Cu}$, while in the second campaign they vary by order: $\text{Al} > \text{Pb} > \text{Cd} > \text{Cr} > \text{Zn} > \text{Ni} > \text{Cu}$. The contents of Cd in first campaign vary from 0.017 ppm to 15.007 ppm with an average of 2.849 ppm. These contents show that 7 stations are higher than the value of the background of [14] and that all the stations are higher than [15].

In campaign 2 the Cd contents are (Min: 0.5 ppm, Avg: 0.99 ppm, Max: 1.7 ppm) which represents that all the contents are higher than the reference background [14] and [15]. The Pb contents in 1 campaign are on average 4.8 ppm with a maximum content of 18 ppm at station S9 which exceeds the reference content of [15]. The concentrations of Al are the most dominant among the other trace elements. They have maximum contents in first and second campaigns of 51.12 and 42.182 ppm respectively and a similar average of 34.8 ppm. The other contents such as: Cr, Ni, Cu, Zn show low concentrations in the two campaigns compared to the contents fixed by [14], [15].

| TABLE II: DISTRIBUTION OF MAJOR ELEMENTS IN THE SEDIMENT OF YKEM WATERSHED |
|---------------------------------------------|-----------------------------|
| $\text{Al}_2\text{O}_3$(%) | $\text{SiO}_2$(%) | $\text{P}_2\text{O}_5$(%) | $\text{K}_2\text{O}$(%) | $\text{CaO}$(%) | $\text{TiO}_2$ (mg/kg) | MnO (mg/kg) |
| Min | 4.52 | 15.65 | 0.67 | 0.29 | 1.94 | 958.00 | 286.00 |
| Mean | 9.85 | 41.92 | 1.16 | 1.27 | 19.10 | 5360.33 | 849.78 |
| Max | 16.25 | 65.80 | 1.99 | 2.53 | 52.15 | 10650.00 | 2135.00 |

| TABLE III: CONTENT AND DISTRIBUTION OF HEAVY METALS IN THE SEDIMENTS |
|---------------------------------------------|-----------------------------|
| Heavy metal | Concentrations (ppm) | CV | Winter | Concentrations (ppm) | CV | Background values |
| Min | Mean | Max | | Min | Mean | Max | | [1] | [2] |
| Cd | 0.01 | 2.84 | 15.00 | 1.84 | Cd | 0.58 | 0.99 | 1.72 | 0.37 | 0.3 | 0.102 |
| Pb | 0.06 | 4.83 | 18.15 | 1.17 | Pb | 2.40 | 7.56 | 14.66 | 0.52 | 35 | 17 |
| Al | 19.18 | 34.82 | 51.12 | 0.28 | Al | 22.41 | 34.83 | 42.18 | 0.21 | - | - |
| Cr | 0.05 | 0.32 | 0.84 | 0.75 | Cr | 0.09 | 0.17 | 0.34 | 0.54 | 70 | 35 |
| Ni | 0.12 | 0.44 | 0.67 | 0.42 | Ni | 0.03 | 0.03 | 0.04 | 0.09 | 50 | - |
| Cu | 0.01 | 0.02 | 0.02 | 0.18 | Cu | 0.02 | 0.02 | 0.03 | 0.18 | 30 | 14.3 |
| Zn | 0.05 | 0.07 | 0.10 | 0.24 | Zn | 0.03 | 0.05 | 0.08 | 0.30 | 90 | 52 |

[1] Natural levels in the terrestrial crust [14]
[2] Mean levels in the continental crust [15]
S9. For campaign N° 2, the coefficient of variation is generally homogeneous for all metals (<0.5), except for Pb (0.526) and Cr (0.549).

| Study area                  | Cd    | Pb    | Al    | Cr    | Ni    | Cu    | Zn    | Reference          |
|-----------------------------|-------|-------|-------|-------|-------|-------|-------|-------------------|
| Ykem river (summer)         | 2.84  | 4.83  | 34.82 | 0.32  | 0.44  | 0.02  | 0.07  | This study        |
| Ykem river (winter)         | 0.99  | 7.56  | 34.83 | 0.17  | 0.03  | 0.02  | 0.05  |                   |
| Bou Regreg river            | 2.9   | 128.05| _     | 21.49 | _     | 33.48 | 196.69|                   |
| Sebou river                 | 0.08 –0.57 | 14-167| _     | 30-170| 30-40 | 35-112| 70-220| [13]              |
| Tarfaya                     | 0.16  | 6.13  | 2.72  | 26.6  | 16.5  | 6.60  | 51.7  | [26]              |
| Moulay Bouselham            | 0.02-0.8 | 6.2-32 | _     | 19-113| 11-96 | 22-311| 167-759| [27]             |
| Bouregreg river             | 4     | _     | _     | _     | _     | _     | _     |                   |
| Sebou river                 | 0.14-0.2 | _     | 33.11-47.9 | _     | 88.40-160.9 | 34.19-79.8 | 4.09-29.12 | 64.82-110.7 | [29] |
| Mediterranean coast of Morocco | < DL -1.2 | 2.43-75.8 | _     | _     | _     | _     | _     |                   |
| Oualidia Lagoon             | 0.58  | 6.8   | 3.5   | 68    | 28    | 17    | 104   | [31]              |
| Khnifiss Lagoon             | 0.37  | 6.8   | 5.6   | 65    | 35    | 17    | 69    | [31]              |

The heavy metal contents in the sediments of Ykem river were compared with those of other Moroccan sites in order to assess their degree of contamination (Table IV).

This comparison shows that the metallic elements in Wadi Ykem are low concentrations, except for the elements Cd, Al and Pb. In fact, Cd varies in our study from 0.017 to 15.007 ppm with an average concentration of 2.84 ppm. This shows levels similar to that found in the sediments of Bouregreg watershed [13] which vary from 2.8 to 4 ppm, and higher levels than that of the sediments of the Sebou watershed Cd = 0.08 ppm [25] and at level of Wadi Oum Rbiaa Cd = 0.08 ppm [33]. The Pb contents are comparable with that of the Oualidia lagoon and the Khnifiss lagoon Pb = 6.8 ppm [31], and that of the Khnifiss lagoon of Tarfaya which varies from 2.52 to 12.4 with an average concentration of 6.13 ppm [26] and less than the values found at Moulay Bouselham Pb = 28 ppm [28].
B. The Pollution Load Index (PLI)

The PLI values were determined to control the risk of pollution in the various stations of the Wadi Ykem. The results (Fig. 3) of the PLI showed that all the sediments studied show PLI values > 1, except for station S10 in the summer period and that the generality of the PLI in the summer period is higher than in the winter period. The highest values were recorded at the levels of S4 S9 S6 in the first campaign. In the second campaign, the high contents are S3.

S9 and S7. The values vary in the first campaign of the order: S5> S9> S6> S3> S4> S8> S1> S7> S2> S10. And in the second campaign of the following order: S3> S9> S4> S7> S6> S10> S5> S8> S2> S1. These variations show overall a slight pollution compared to the levels of the ST control station. This variation may be mainly due to human activities at the level of the Ykem watershed. Such as domestic waste evacuated at the levels of Sidi Yahya des Zaer and Tamesna cities and agricultural activities.

C. Enrichment Factor (EF)

The FE contamination factor in sediments was calculated using equation (2) for two different hydrological periods. All the EF variations (Fig. 4) show that the EF contents in the summer period are higher for 4 elements (Cd, Zn, Ni, Cr). EF levels do not show contamination at all stations. These variations show homogeneity for the elements of Pb, Cu and Zn. Enrichments were observed at the level of: - the Station S5 in the summer period for the Cd element mainly due to the sharp increase in this station in Cd content. - The S3 station during the winter period for the Pb. - Station S9 and S1 respectively during the summer period for the Cr and Zn elements; station S2 during the summer period for the Ni and Cu elements. Similar results were found by [30] and [26] which show EF contents generally less than 1 and EF classes which vary from uncontaminated to moderately contaminated.

D. Geo-Accumulation Index (I-geo)

The geo-accumulation index (I-geo) values of the studied metals are very low. During the summer, the Igeo values display the following decreasing order: Al > Cd > Pb > Ni > Cr > Zn > Cu (Fig 5. (a)). The range of Igeo values for different metals are variable; Cd (-3.94 to -0.99), Pb (-2.70 to -0.22), Ni (-3.06 to -1.65), Cr (-2.96 to -1.79), Zn (-3.52 to -3.00), Cu (-3.34 to -3.11). All the Igeo values indicate an uncontaminated status of the studied sediments. Whereas, the Igeo value for Al (0.20 to 0.63), indicates an uncontaminated to moderately contaminated status of the studied sediments.
During winter, the geoaccumulation index (Igeo) values of the studied metals showed the following decreasing order: Al > Pb > Cd > Cr > Ni > Cu > Zn. The range of Igeo values are very low; Pb (-1.16 to -0.31), Cd (-2.63 to -1.93), Cr (-2.92 to -2.18), Ni (-3.06 to -2.84), Cu (-3.32 to -3.04), Zn (-3.52 to -3.11) (Fig 5. (b)). All these Igeo values indicate an uncontaminated status of the studied sediments. Whereas, the Igeo value for Al (0.27 to 0.44) indicates an uncontaminated to moderately contaminated status of the studied sediments.

However, the highest Igeo value obtained for Al (0.63 to 0.54) during winter and summer seasons, respectively may be related to the higher concentration in sediment and lower level in the background sample. The Igeo results of metals in Knifiss sediments show that all the samples studied are classified as “uncontaminated” by heavy metals (Igeo < 0) in the two campaigns in summer and autumn [26].

IV. CONCLUSION

The studied EMT in the present study for 20 sediment samples from the Wadi Ykem were analyzed and evaluated by several techniques and environmental indicators. In fact, the spatial distribution of metallic elements in the two study periods reveals higher rates in the summer period than in the winter period. This distribution also shows that most of the trace elements present a homogeneous variation in the different stations. And that the average order of contamination in the different stations varies during the summer period as follows: Al > Pb > Cd > Ni > Cr > Zn > Cu, while in the winter period varies in the following order: Al > Pb > Cd > Cr > Zn > Ni > Cu. Stations S4, S5 and S9 often have high levels of EMT, which can be explained by their locations near a former municipal landfill, near an industrial area and downstream from an agricultural area.

Following the enrichments observed for certain metals (Cd, Pb, Zn and Cr) in several sampling stations (S5, S3, S9 and S1) which seem to be due to agricultural activities and urban discharges. It is recommended to monitor sources of heavy metals due to agricultural activities and soil leaching upstream at station S9, which was chosen near an area developed for agricultural use. This study also suggests the control of solid waste disposal in the municipal landfill near the S4 station and also the disposal of wastewater without treatment in the sewerage pipes of the city of Sidi Yahya-Zaer. The sharp increase in the content of lead, zinc and copper in the downstream stations: S3, S2 and S1 near the road axis make it necessary to study the distribution of heavy metals on all the lead along the road axis of Rabat-Temara and Skhirat.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Aoufa M.: conducted the research, wrote the paper; Chahid N.: investigation; Bahgdad B., Chakiri, S.: analyzed the data; El Hadi H.: resources.

ACKNOWLEDGMENT

The authors would like to thank National Centre for Energy, Nuclear Sciences and Technique, Rabat, Morocco (CNESTEN) for allowing the analyzes to be carried out in their laboratories.

REFERENCES

[1] S. Štrbac, M. K. Grubin, and N. Vasić, “Importance of background values in assessing the impact of heavy metals in river ecosystems: Case study of Tisza River, Serbia,” Environ Geochem Health, vol. 40, no. 4, pp. 1247-1263, 2018, doi: 10.1007/s10653-017-0053-0.
[2] I. Nassri et al., “Assessment of heavy metal in spring water, of rabat-sale-zemour-zaer area (Morocco),” International Journal of Multidisciplinary Research Review, vol. 5, pp. 3635-3640, 2018.
[3] G. O. Duodu, A. Goonetilleke, and G. A. Ayoko, “Potential bioavailability assessment, source apportionment and ecological risk of heavy metals in the sediment of Brisbane River estuary, Australia,” Marine Pollution Bulletin, vol. 117, no. 1, pp. 523-531, 2017, doi: 10.1016/j.marpolbul.2017.02.017.
[4] H. Sharma, N. Rawal, and B. Mathew, “The characteristics, toxicity and effects of cadmium,” International Journal of Nanotechnology and Nanoscience, vol. 3, pp. 1-9, 2015.
Saïd Chakiri was born in El Jadida (Morocco) in 1964. He obtained his state doctorate in 2002 at the Faculty of Sciences of Kénitra (Morocco) in Geosciences. He is professor of geosciences at Ibn Tofail University in Kénitra since 1993. His areas of research concern the geosciences of natural resources and cartography. He is co-author of more than 30 publications in several disciplinary fields of Geosciences. He is also an active member of the Moroccan Association of Earth Sciences.

Hassan El Hadi obtained his state doctorate in 1998 at Hassan II University of Casablanca, Morocco. His research concerns the geochemistry and petrology of magmatic rocks as well as the environmental assessment by heavy metals. He has over 32 years of teaching and research experience at the Ben M’Sik Sciences Faculty of Casablanca. He is also the general secretary of the Moroccan Association of Earth Sciences.

Zahry Fatiha works in the Elementary Analysis Laboratory, National Center for Energy, Nuclear Sciences and Techniques (CNESTEN), Rabat, Morocco.