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Assessment of the water quality in the main rivers of Morocco

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Abstract

Throughout the world, the use of water resources is increasing with industrial development, agro-food, and economic and demographic growth, which causes the degradation of their quality by polluted discharges. This requires controls and monitoring of these natural resources. In order to develop a diagnostic of the level of pollution of the waters of these rivers and to evaluate the health risks, this work's focus was on the characterization of pollution by metallic trace elements (chromium, lead, and copper) of surface waters in the major Moroccan rivers. In addition, it should be noted that the analysis of metallic elements in sediments is an indicator of contamination of river water by trace metals. The chosen approach focused first on analyzing samples by inductively coupled plasma mass spectrometry. In this sense, six sampling campaigns were carried out at two campaigns per watercourse (dry period and wet period). All the samples analyzed for chromium are of good quality, with average concentrations of 1.75 µg/l for the lower Moulouya and 3.4 µg/l for Oum Er Rbia. On the other hand, 64% of the samples taken at the level of the Sebou are of poor quality with an average concentration of $181.25 \,\mu g/l$, which exceeds three times the standard (50 µg/l). Regarding lead and copper, the analysis results show that the average concentrations are always lower than the quality values (average to excellent for the three rivers). The electrical conductivity values recorded in Oum Er Rbia and lower Moulouya are very high; 71% of the water analyzed in lower Moulouya is of poor quality. To perform this work, the results obtained were analyzed by calculating the existing correlations between the various parameters studied and determining the water pollution index to calculate the overall quality in each sampling station. It can be deduced that the water pollution index in the three rivers studied indicates that the overall quality of the Sebou varies from pure to heavily contaminated. In Oum Er Rbia, the quality is pure to moderately polluted, while in lower Moulouya the quality is pure for all sampling points.

Keywords Contamination · Water pollution index · Sebou · Oum Er Rbia · Lower Moulouya · Morocco

Abbreviations

CE	Electrical conductivity
Cr	Chromium
Cu	Copper

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ICP-MS	Inductively coupled plasma mass spectrometry
ISO	International Organization for Standardization
Pb	Lead
PE	Bouteilles en polyéthylène
pН	Potential hydrogen
T°C	Temperature in degrees Celsius
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WPI	Water Pollution Index

Introduction

Water, like air, is considered essential to the survival of all people and all forms of life on earth. However, population growth and sustainable development (agricultural and industrial) lead to increased water resource exploitation, deteriorating its quality (Derwich et al. 2012). This influenced the

water's physicochemical and biological parameters (Mukate et al. 2019). Surface water is the most affected by pollution, given its exposure to anthropogenic activities (e.g., industrial metallurgical activity, and agriculture) (Imran et al. 2021; Oleiwi and Al-Dabbas 2022), rainfall, and related soil erosion, runoff on the geological substrate (Prasanna et al. 2012; Vasistha and Ganguly 2020). Consuming water tainted with heavy metals that do not degrade naturally in the environment (Nasrabadi 2015) can result in infections either directly or indirectly through the aquaculture food chain due to buildup (Sonone et al. 2020). This could lead to an imbalance in the biodiversity system (Prasanna et al. 2012). For this, metallic trace elements can be used to assess the quality and degree of pollution of surface water or as indicators of environmental quality that can guide decision-making for well-sustainable development (Kumar et al. 2018a, b). These metallic trace elements can increase depending on the discharge of untreated wastewater (Njuguna et al. 2020) or be influenced by climatic variations, which cause an increase in flood flows, generating significant accumulations in the downstream parts of the rivers (Gaagai et al. 2022). The study of variations in the water quality of rivers must be

performed on sufficient spatial and temporal scales (Wu et al. 2018). This evaluation is essential for monitoring and controlling the pollution of water resources and for identifying the main factors that contributed to these variations so that protective measures for water bodies may be put in place (Wu et al. 2018).

Morocco is among the countries on the southern Mediterranean coast characterized by the predominance of a semiarid climate (Sebbar et al. 2011, 2012). It is traversed by a network of rivers that are essential for agriculture, drinking water use, and industrialization (Haddout et al. 2016). Indeed, surface water must be monitored to develop sustainable management plans to minimize pollution. Moreover, the three rivers targeted in this study are the lower Moulouya, the Oum Er Rbia, and the Sebou, classified as significant resources draining almost all of eastern, central, and western Morocco, with high flow rates. These three rivers are essential in water consumption and irrigation (Hayzoun et al. 2015). They are geographically located in the northern part of Morocco (Fig. 1) and occupy three watersheds differentiated by their hydrogeological and hydrodynamic location (Agoumi and Debbarh 2005; Jouilil et al. 2013; Zamrane



Fig. 1 Location of sampling stations on Sebou (from S1 to S14), lower Moulouya (from M1 to M7), and Oum Er Rbia (from P1 to P8)

2016). Because of their geographical proximity, these rivers are susceptible to industrial, agricultural, and urban pollution caused by the discharge of untreated wastewater.

The objective of this study is to monitor the physicochemical quality (pH, temperature, dissolved O₂, and electrical conductivity) and the spatio-temporal quality of metallic trace elements such as copper, lead, and chromium in two successive periods (dry and wet) in the surface waters of the three main rivers in Morocco (lower Moulouya, Oum Er Rbia, and Sebou). Subsequently, comparing these levels with a guide or standard values is done using indices developed to assess and monitor the quality of water polluted by heavy metals (Edet and Offiong 2002; Abdullah 2013; Selvam et al. 2015). In this work, the index (WPI) is used to determine the level of contamination by the metallic trace elements studied, taking into account the other physicochemical parameters such as temperature, dissolved O₂, pH, and electrical conductivity in each sampling point. Therefore, using the index (WPI) in this study makes it possible to identify better and express the close relationship between the overall state of water quality in space and time, to integrate many elements into a single, meaningful index. Then, using this index would make it possible to reveal the main pollution parameters and deduce the location of quality waters (Singh et al. 2005; Kowalkowski et al. 2006; Bu et al. 2010; Fathi et al. 2018).

Materials and methods

Study site

The study areas are the lower Moulouya, Sebou, and Oum Er Rbia rivers (Fig. 1) which constitute the main rivers in Morocco. The Moulouya basin in eastern Morocco has an area of approximately 74,000 km² (Rixhon et al. 2017). It is located between 36 and 39° N and 5.5-7° W (Lamri et al. 2016; Fouzi et al. 2020). It is bounded to the northeast by the Mediterranean, to the northwest by the Beni-Bouyahi chain to the west by the mountains of the Eastern Rif and the folded Middle Atlas, to the south by the High Atlas (Lamri et al. 2016). With a length of more than 600 km, the Moulouya River is the longest Moroccan river that flows into the Mediterranean (Mabrouki et al. 2019; Fouzi et al. 2020). The river originates near the meeting point of the Middle and High Atlas mountain ranges and runs from the southwest to the northeast (Fouzi et al. 2020). This watershed is subdivided into three sub-basins: the Lower, the Middle, and the Upper Moulouva. Regarding the lower Moulouva, this study's subject is a basin with a diverse stratigraphy (Bouabdli et al. 2005). The second river studied is Sebou. The watershed of the said river is located in the northwest of Morocco with an area of 40,000 km² (Derwich et al.

2012; Haddout et al. 2016; Kanga et al. 2020). It is delimited by the Rif Mountains to the north and by the Middle Atlas Mountains to the south, and the Saïs plateau is located between these two mountain ranges, in the lower part of the watershed. The Sebou sub-basin is made up of the great alluvial plain of Gharb (Kanga et al. 2020).

A combined 30% of the nation's potential surface water resources and 20% of its groundwater are mobilized by this basin. While the Gharb plain and the Sais plateau were molded by permeable materials made by limestones, dolostones, conglomerates, and sandstones assigned to Meso-Cenozoic age, the Rif highlands are mostly defined by impermeable clay–marl formations from the Cretaceous (Piqué 1994; Hayzoun et al. 2015; Kanga et al. 2020). This watershed is drained by the Sebou river extending approximately 600 km from its source in the Middle Atlas to the Atlantic Ocean (Haddout et al. 2016). This river is divided into the upper, middle, and lower Sebou (Hayzoun et al. 2015).

The Oum Er Rbia basin is located in the center-west of Morocco. It originates in the Khenifra region at 32°56'22"N5°40'3"W, to the Atlantic Ocean (33°17'16"N8°20 32"W) (El Alami et al. 2020), and covers an area of 48,070 km² (Barakat et al. 2016; Zhim et al. 2019), and a length of 550 km from the Middle Atlas (Barakat et al. 2016; Strohmeier et al. 2020). It empties into the Atlantic Ocean at Azemmour city (Strohmeier et al. 2020). The three rivers studied receive significant pollutant loads generated by industrial and domestic discharges (El Hajjami et al. 2020). Fourteen stations were chosen along the Sebou (20 km upstream from Fez to the mouth at the port of Mehdia), eight at Oum Er Rbia (from Khenifra to the mouth at Azemmour), and seven at lower Moulouya. These stations were chosen based on a variety of factors, including their accessibility to the land, the anthropogenic influences they are exposed to (close proximity to domestic and industrial discharges), agricultural areas, and representativeness (Fig. 2).

In this study, the samples taken for metallic trace elements are 28 from Sebou, 14 from lower Moulouya, and 16 from Oum Er Rbia. The other parameters (pH, electrical conductivity, T°C, and dissolved O_2) are measured in situ (56 measurements for lower Moulouya, 64 sizes for Oum Er Rbia, and 112 for Sebou).

To describe and assess the overall quality of the surface waters of the rivers under study, the distribution of the values of each parameter (Cr, Cu, Pb, pH, T°C, CE, and dissolved O_2) was determined. In addition, the study enriches scientific data on sediment pollution in rivers in developing countries and, subsequently, water contamination by trace metals. The results of this work provide a first comparison of the state of pollution of the three main Moroccan rivers for the first time in such work. Thus, this study makes it possible to develop a preliminary quality grid with a better

Fig. 2 Adopted methodological flowchart





knowledge of the relationships between surface waters and their environments.

Despite being present in very small amounts in river water or sediment, metallic trace elements are poisonous and can result in life-threatening conditions like digestive and respiratory diseases. They thus present a significant risk of ecotoxicity for plants, soil, and aquatic species. Indeed, on a global scale, controlling the levels of these metallic elements is necessary. This work falls within this framework, which relates to evaluating and controlling pollution by metallic trace elements of main Moroccan rivers.

Sampling and methods of analysis

In general, water samples are collected manually using containers tailored to each parameter, in the middle and at representative sites for flow (homogeneity and turbulence). In principle, sampling is done at a depth of about 30 cm below the surface and about 50 cm above the bottom, otherwise at mid-depth to avoid sampling the surface film (Acted 2006). All collected surface water samples were placed in the field in clean polyethylene (PE) bottles. Subsequently, these samples were acidified to pH < 2 with nitric acid (2%) HNO_3 (Ceaeq 2014), and transported at a low temperature (4 °C) to the laboratory (Zhaoyong et al. 2015). In addition, the measurement of the electrical conductivity was carried out according to standard NM ISO 7888 2001: rinsed the probe several times with demineralized water, then two to three times with the water to be examined, then agitated the investigation of the conductivity meter in the water sample until it stabilizes. The hydrogen potential is measured by an electrode immersed in the water to be measured (the reading is taken after stabilization of the pH meter) (NM ISO 10523 2012). Dissolved oxygen is determined by the electrochemical method (NM ISO 5814 2014) using an electrochemical cell isolated from the sample by a selective gas-permeable membrane. Indeed, the water sample must flow continuously in front of the probe's membrane to exclude the possibility of an erroneous measurement due to the local consumption of oxygen at the level of the probe electrode.

The selection of sampling sites is based on a number of factors, including the ease of access to the area, the anthropogenic influences they are exposed to (close proximity to home and industrial wastes), agricultural areas, and representativeness. As a result, when sampling in the three rivers under study, we avoided collecting samples in dead zones, especially at locations with natural or manmade barriers.

Analysis protocol

The determination of extractable metals in surface waters is based on the mineralization of the samples: in a 50 ml tube, introduce 40 ml of a sample and then add 0.8 ml of 20% HCl and 0.8 ml HNO₃ 20% (Ceaeq 2014). After closing and shaking, the samples are heated in a digest block at 95 °C for 2 h. Then, after cooling and settling, the samples were analyzed by ICP-MS (Ceaeq 2014).

In accordance with the process for validating chemical analysis methods, the analytical method is validated. These are the validation results:

For chromium: LDM = $0.005 \mu g/l$; LQM = $0.017 \mu g/l$; the sensitivity results in a slope of 0.9999; the recovery percentage is 94%; replicability (at a 95% confidence interval) is 2%; repeatability (at a 95% confidence interval) is 4%.

For copper: LDM=0.040 $\mu g/l$; LQM=0.133 $\mu g/l$; the sensitivity results in a slope of 0.9999; the recovery percentage is 98%; replicability (at a 95% confidence interval) is 3%; repeatability (at a 95% confidence interval) is 2%. For lead: LDM=0.003 $\mu g/l$; LQM=0.010 $\mu g/l$; the sensitivity results in a slope of 0.9999; the recovery percentage is 97%; replicability (at a 95% confidence interval) is 2%; repeatability (at a 95% confidence interval) is 3%.

Results and discussions

Table 1 presents the reference values for classifying the waters analyzed for each parameter studied.

The physicochemical parameters obtained during this study are presented in Tables 2, 3, and 4.

The samples examined in lower Moulouya had pH readings that ranged from 7.4 to 7.8 in August and from 7.1 to 7.6 in December (Table 2). For Oum Er Rbia (Table 3), the pH values vary from 7.4 to 8.4 in August and from 7.9 to 8.4 in December, while at the level of Sebou (Table 4), the pH varies from 7.7 to 8.4 in August and from 7.5 to 8.4 in December. According to the surface water classification grid BO-5062 (2002), these results show that the surface waters of the three rivers under study are excellent for pH values between 6.5 and 8.5. The hydrogen potential depends on several parameters, namely, the geological nature of the watershed crossed and the origin of the water (Belghiti et al. 2013). This parameter affects a variety of physicochemical equilibrium processes involving the water compartment, carbonates, bicarbonates, and dissolved carbon dioxide. Natural water typically has a pH between 6.0 and 8.5 (Belghiti et al. 2013).

Table 1Surface water qualitygrid according to to order1275–01 of 2002 (BO-50622002)

Parameter	Excellent	Good	Average	Poor	Very poor
pН	6.5-8.5	6.5-8.5	6.5–9.2	<6.5ou>9.2	<6.5ou>9.2
Temperature in °C	< 20	20-25	25-30	30–35	> 35
O ₂ dissolved in mg/l	>7	7–5	5–3	3–1	<1
Conductivity at 20 °C in µs/cm	<750	750-1300	1300-2700	2700-3000	> 3000
Cr in µg/l	≤ 50	≤50	≤50	> 50	-
Pb in µg/l	≤10	≤10	10-50	> 50	-
Cu in mg/l	≤ 0.02	0.02-0.05	0.05-1	>1	-

Table 2	Physicochemical
paramet	ers measured in the
lower M	Ioulouya River in 2019

Parameter	$O_2 (mg/l) CE (\mu$	pH	m)
Period	December Augus	August	December
M1	7.8 4950	7.84	5390
M2	8.1 3740	7.62	3820
M3	7.9 3450	7.41	3690
M4	7.5 3210	7.45	3580
M5	6.9 4010	7.35	3120
M6	8.4 2130	7.42	2070
M7	8.2 2140	7.65	1840
M3 M4 M5 M6 M7	7.934507.532106.940108.421308.22140	7.41 7.45 7.35 7.42 7.65	369 358 312 207 184

Table 3 Physicochemicalparameters measured in theOum Er Rbia River in 2019

Parameter	pН		T°C		Dissolve	d O ₂ (mg/l)	CE µs/cr	n
Period	August	December	August	December	August	December	August	December
P1	8.25	7.94	22.8	13.2	5.2	8.9	2735	2442
P2	8.35	8.24	25.9	14.5	8	9.6	2647	2688
P3	8.31	8.36	27.8	15.7	5.9	7.9	7851	7554
P4	8.4	8.34	26.4	15.4	4.8	6.8	2954	1967
P5	7.77	8.27	27.4	16.1	4.2	7.5	2041	1374
P6	7.89	7.95	29.6	14.2	4.9	8	1897	1046
P7	7.9	8.3	29.4	14.8	5.9	7.4	1745	1263
P8	7.4	7.88	31.2	13	6.5	7.8	13,254	12,999

Table 4 Physicochemicalparameters measured in theSebou River in 2019

Parameter	pН		T°C		Dissolve	$d O_2 (mg/l)$	CE (µs/c	m)
Period	August	December	August	December	August	December	August	December
S1	8.40	8.10	23.7	15.2	8.4	9.7	1107	1011
S2	8.12	7.66	27.2	14.9	1.9	0.5	2710	1453
S 3	8.20	8.10	27.9	16.1	4.2	5.1	1642	1153
S4	8.30	8.14	28.5	16	3.5	2.7	1114	1452
S5	8.30	8.20	28.6	15.4	5.2	1.1	971	1421
S6	7.90	7.89	27.9	15	5.2	5.4	1275	1102
S7	8.10	7.81	29.1	14.7	7.5	5.7	1501	1188
S8	8.40	7.98	27.8	15.7	7.4	6.8	1288	1257
S9	8.20	8.20	28.4	15.9	6	5.3	914	954
S10	8.20	8.40	29.8	14.9	5.2	6.1	1022	1203
S11	8.10	8.20	28.7	15.2	5.8	5.4	702	1145
S12	8.30	8.10	30.2	16.2	6.4	6.2	915	1487
S13	7.80	7.98	29.2	16.2	6.2	5.9	1234	1132
S14	7.70	7.50	30.7	15.3	5.9	4.5	11.966	11.805

The water temperature analyzed in lower Moulouya (Table 2) varies between 22.7 and 27.4 °C in August and between 12.5 and 13.5 °C in December, while for Oum Er Rbia (Table 3). The temperature measurements vary between 22.8 and 31.2 °C regarding Sebou (Table 4). The temperature varies between 23.7 and 30.7 °C in August and 14.7 and 16.2 °C in December.

These values indicate that the temperature in the three rivers studied is suitable in December, of good to average quality for the lower Moulouya in August, and of interest to poor quality for the Oum Er Rbia and the Sebou in August.

Furthermore, dissolved oxygen is an important factor in aquatic life. It enables the evaluation of surface water quality (Escoffier et al. 2016) while ensuring the self-purification of waterways, and the degradation of organic matter, odor, and taste (Bailey and Ahmadi 2014). In addition, O_2 promotes the growth of microorganisms via good oxygenation of aquatic environments (Garvey et al. 2007).

These are impacted by drought issues, particularly during summertime low flow times, which encourage biogeochemical changes that can result in water of poor quality (Gómez-Gener et al. 2020). As a result, dissolved oxygen is an excellent marker of waterway contamination and the growth ofpathogenic organisms (Derwich et al. 2008; Belghiti et al. 2013).

Concentrations of dissolved O_2 in lower Moulouya vary from 7.1 (M7) to 9.1 mg O_2/I (M1) in August and from 7.5 (M4) to 8.4 mg O_2/I (M6) in December. These findings show that the sample zone exhibits good (7–5 mg of O_2/I) to excellent (> 7 mg of O_2/I) quality in all the stations examined (Table 1).

For Oum Er Rbia, dissolved O_2 is 4.2 mg O_2/l (P5) to 8.0 mg O_2/l (P2) in August and 6.8 mg O_2/l (P4) to 9.6 mg O_2/l (P2) in December; then, O_2 dissolved at the level of the river (Oum Er Rbia) is of average quality in 37% samples analyzed while 63% of these waters are of good–excellent. The contents of dissolved O_2 in Sebou

vary from 1.9 (S2) to 8.4 mg O_2/l in August and from 0.5 (S2) to 9.7 mg O_2/l (S1) in December. The low values at station 2 show that Oued Sebou receives high pollutant loads in both periods (wet and dry periods). The quality of O_2 dissolved in 14% of the samples taken in Oued Sebou is excellent, 57% good, 21% average, and 7% bad.

Electrical conductivity is a measure of how well water can transport electric current (Hayzoun 2014a). It provides an idea of the origin of water, dissolved salts, and mineralization (Belghiti et al. 2013).

The electrical conductivity in the lower Moulouya varies from 2130 (M6) to 4950 µs/cm (M1) in August and from 1840 (M7) to 5390 µs/cm (M1) in December. These values indicate that 71% of the samples analyzed from this river (lower Moulouya) are of inferior quality (> 3000 µs/cm), and 29% are of average quality (1300-2700 µs/cm) in the two sampling periods. The values of electrical conductivity in Oued Oum Er Rbia vary from 1745 (P7) to 13,254 µs/cm (P8) in August and from 1046 (P6) to 12,999 µs/cm (P8) in December. In fact, the electrical conductivity quality indicates that 25% of the water studied is of poor quality, while 75% is of average quality. For the Sebou River, the electrical conductivity is from 702 (S11) to 11,966 µs/cm (S14) in August and from 954 (S9) to 11,805 µs/ cm (S14) in December. These values indicate that 71% of the analyzed waters of this Oued (Sebou) are of good quality, 21% are of average quality, and 7% are of poor quality (S14).

Metal trace elements

Chromium

Trivalent chromium (Cr^{3+}) and hexavalent (Cr^{6+}) are the two predominant forms in nature and the most stable (He and Li 2020). Dissolved oxygen has a strong ability to reduce

hexavalent chromium to trivalent chromium (N'guessan 2008). Once Cr (III) is formed in aquatic environments, it precipitates rapidly. It accumulates in the sediments, which may act as a reservoir for river pollutants (N'guessan 2008). In water, the chromate ion (Cr^{3+}) is more stable and less toxic than the chromate ion (Cr^{6+}) (N'guessan 2008). Chromium concentrations in the water may have increased due to natural or industrial causes (tanneries, textile industries, surface treatment industry, and sludge from wastewater treatment plants) (Hayzoun 2014a).

The Cr recorded at Sebou shows Cr values (Fig. 3a) vary between 3 (S7) and 2700 μ g/l (S2) in August and 7 μ g/l (S1) at 410 μ g/l (S4) in December, with average concentrations of 298.6 μ g/l in August and 63.9 μ g/l in December. These values indicate that Sebou had poor quality (> 50 g/l) in more than 64% of samples from August and 28% of samples from December. Generally, the contents found in August are higher than in December. This is explained on the one hand by the fact that the flow in the latter is higher than in August, which causes the dilution effect; on the other hand, by the increase in tanning activity after "Aid al Adha" which is increasing in the city of Fez.

Because of home discharges and effluents from boiler works, tanneries, and textile businesses, this pollution is actually concentrated in the city's downstream area, particularly the station (S2) (Es-Sette et al. 2005). This is probably due to ceramic factories using chromium sulfate as a tanning agent (Hayzoun et al. 2014b). Indeed, the results are comparable to those obtained by other researchers (Foudeil et al. 2013; El Hajjami et al. 2021). In addition, for Oum Er Rbia, the Cr concentrations (Fig. 3b) vary from < 0.005 (P8) to $10.0 \mu g/l$ (P3) in August and from $< 0.005 \mu g/l$ in 75% of samples analyzed (P1, P3, P4, P5, P7, and P8) and 2.1 µg/l (P2) in December. The average concentrations in this river are 6.3 µg/l in August and 0.5 µg/l in December. These concentrations mean that Oued Oum Er Rbia has excellent quality in total chromium (Table 1). The Cr values for the lower Moulouva (Fig. 3c) range from 0.41 (M7) to 3.29 g/l (M5) in August (2019) and from 0.22 (M7) to 2.38 g/l (M5) in December (2019), with an average concentration of 2.13 g/l in August and 1.36 g/l in December. These values remain below 50 µg/l according to decree 1275-01 of 2002 BO-5062 (2002): this translates into the excellent quality of water from lower Moulouva (class 1). The classification of average Cr contents in the three study sites is classified as follows: Cr (Sebou)>Cr (Oum Er Rbia)>Cr (lower Moulouya). This means that the Sebou River has experienced significant pollution due to textile activities and tanneries, especially at the stations near Fez.



Fig. 3 The evolution of concentration in Cr, Cu, and Pb in Sebou (a, d, g), lower Moulouya (c, f, h), and Cr and Pb in Oum Er Rbia (b, e) in August and December 2019

Lead

One of the heavy metals most frequently associated with human toxicity is lead. The aquatic ecosystem can be severely harmed by this trace element, which can occasionally accumulate and even go through biomagnification in species like fish and plants (Abubakar et al. 2015). For example, the presence of Pb in surface waters may result from the natural redistribution of components of the earth's crust or the discharge of industrial wastes (Methneni et al. 2020).

In Sebou (Fig. 3d), Pb varies between < 0.003 (S1) and 68.0 μ g/l (S4), with an average concentration of 17.0 μ g/l in August, while the levels recorded in December vary between < 0.003 (S1 and S6) and 51.0 µg/l (S4) with an average concentration of 12.9 µg/l. These values show that the Pb concentration of the samples taken at the Sebou level varies from excellent to good with a percentage of 50%, average with a percentage of 43%, and poor with a rate of 7%in August (Table 1). Thus, the quality in December varies from excellent to good with 64%, average with a percentage of 21%, and poor with a percentage of 14%. The lead in Oum Er Rbia River (Fig. 3e) in August has values varying between < 0.003 in five stations studied (P1, P2, P5, P7, and P8) and 40.0 (P3) with an average concentration of 11.25 µg/l. In December, the Pb concentrations varied between $< 0.003 \,\mu$ g/l recorded in sampling points (P1, P5, P6, P7, and P8) and 30 µg/l recorded in P3 with an average concentration of 7.5 µg/l. These contents vary from excellent quality ($\leq 10 \,\mu g/l$) with a percentage of 63% to medium quality (10-50 µg/l) with a percentage of 37%. Studies on atmospheric fallout have revealed that rainfall is a source of Pb pollution, particularly in urban areas and close by these sites (Bounahkla et al. 2009; Lamprea 2009). Thus, lead pollution may result from both the geological structure of the earth and the enrichment of soil by this metallic element (Azzaoui et al. 2002; Derwich et al. 2008). Also, phosphorus and nitrogen fertilizer products contain Pb with 3.5 mg/kg (Azzaoui et al. 2002). In addition, landfills can also cause this pollution (Idlahcen et al. 2014). Indeed, the landfill of the city of Fez is located in a section of the Wadi Fez (Azzaoui et al. 2002).

The lead concentrations in the lower Moulouya river vary between 0.47 (M7) and 2.11 μ g/l (M3) with an average concentration of 1.25 μ g/l in August and between 0.39 (M7) and 1.95 μ g/l (M3) with an average concentration of 0.90 μ g/l in December. These values remain below 10 μ g/l, which translates into excellent quality for this river.

Copper

Sebou has very high copper concentrations (Fig. 3g). In August, they range from 0.040 (S1) to 410 g/l (S2), while in December, they range from 0.040 (S1) to 200 g/l (S2). In the

dry period, Cu has a peak downstream from the city of Fez (S2); the concentrations recorded in this period are higher than those during the flood period. These copper inputs come from discharges from the city of Fez, mainly from artisanal activities in the old medina (Derwich et al. 2011). Indeed, the quality of surface water in Sebou varies from excellent (7%) to good (29%) and average (64%). For copper is lower Moulouya (Fig. 3h), the concentrations found vary from 0.674 (M6) to 1.478 µg/l (M2), with an average concentration of 1.097 µg/l in August and 0.464 (M6) to $1.092 \,\mu g/l \,(M5)$ with an average concentration of 0.709 $\mu g/l$ in December. Generally, the dry period's copper concentrations are higher than those during the humid period. However, this river's quality is always excellent (lower Moulouya). At the Oum Er Rbia, the analysis of copper was marked by the total absence of this element in the samples taken during the two sampling periods (Wet and Dry).

In Sebou, the average chromium concentration across the two sampling periods (181.25 g/l) was higher than the values found at Oum Er Rbia (3.4 g/l) and lower Moulouya (1.75 g/l). Similarly, the average chromium concentration in Sebou remains higher than in other studies carried out on different rivers (Table 5): Subarnarekha River in India (Singh and Giri 2014); Liao river and Yellow river in China (Gao et al. 2019) (with values of 0.89 μ g/l, 3.36 μ g/l, and 6.54 μ g/l respectively). However, a comparison of Sebou's average Cr concentration with the WHO (2011) and USEPA (2012) limits reveals likely Cr contamination. Monitoring the water quality at the polluted locations is necessary for this.

Additionally, Sebou's average copper concentration over the course of the two sample periods (68.93 g/l) indicated higher Cu levels than those at lower Moulouya (0.9 g/l) and Oum Er Rbia (0.040 g/l). This remains superior to the results found by other researchers (Warnken and Santschi 2009, Singh and Giri 2014, and Gao et al. 2019) respectively on the Trinity Rivers-USA, Subarnarekha River-India, Liao River Basin-China, and yellow river basin-China. These concentrations show lower levels than those obtained by Munyao and Maritim (2013) in Sabaki River Mouth-Kenya (144 μ g/l). Regarding lead, Sebou and Oum Er Rbia have average concentrations higher than the values quoted by (Warnken and Santschi 2009; Munyao and Maritim 2013, Singh and Giri 2014, and Gao et al. 2019) at the Trinity-USA, Subarnarekha River India, Liao River Basin-China, and Yellow River Basin-China respectively. On the other hand, the study conducted by Munyao and Maritim (2013) in Sabaki River Mouth-Kenya presents (like Copper) a concentration (206.25 μ g/l) higher than those of the studied rivers. So, the comparison of the vulnerability of the rivers studied by ETM with other studies on international rivers (e.g., USA, China, India, Kenya) gives: (i) Cr (Sebou) > Cr (Yellow river in China) > Cr (Oum Er Rbia) > Cr (Liao river in china) > Cr (lower Moulouya) > Cr (Subarnarekha River in India); (ii)

Table 5 Comparison of the concentrations $(\mu g/l)$ of trace elements in water samples from the three rivers studied in Morocco and from other rivers around the world with the drinking water guidelines		Cr	Cu	Pb	References
	Sebou River, Morocco	181.25	68.93	14.9	This study
	Oum Er Rbia River, Morocco	3.4	< 0.040	9.38	
	The lower Moulouya, Morocco	1.75	0.9	1.08	
	Liao River Basin, China	3.36	1.03	0.03	Gao et al. (2019)
(WHO) and drinking water	Yellow River Basin, China	6.54	2.68	0.208	Gao et al. (2019)
standard (USEPA)	Trinity River, USA	-	1.15	0.03	Warnken and Santschi (2009)
	Sabaki River Mouth, Kenya	-	144	206.25	Munyao and Maritim (2013)
	Subarnarekha River, India	0.89	16.6	-	Singh and Giri (2014)
	WHO	50	2000	10	WHO (2011)
	USEPA	100	1300	-	USEPA (2012)

Cu (Sabaki River Mouth-Kenya) > Cu (Sebou) > Cu (Subarnarekha River in India) > Cu (Yellow river in China) > Cu (Trinity-USA) > Cu (Liao river in China) > Cu (lower Moulouya) > Cu (Oum Er Rbia); and (iii) Pb (Sabaki River Mouth-Kenya) > Pb (Sebou) > Pb (Oum Er Rbia) > Pb (lower Moulouya) > Pb (Yellow river in China) > Pb (Liao river in China) > Pb (Trinity-USA).

Correlation coefficients

The correlation measures the correspondence between the different associated values of two variables of a bivariate distribution (Langouet and Porlier 1991). The correlation can be positive, negative, strong, weak, or zero. So the values of this correlation range between 1 and – 1 (Pottier 1994; Saporta 2006). This correlation coefficient is calculated with the following formula (Stancu et al. 2015):

$$Correl(X, Y) = \frac{\sum (x - \overline{x})(y - \overline{y})}{\sqrt{\sum (x - \overline{x})^2 \sum (y - \overline{y})^2}}$$

where \overline{x} and \overline{y} are the averages of the samples of the studied matrices.

Tables 6, 7, and 8 present the matrix of correlation coefficients of metallic trace elements in the surface waters of the three rivers studied.

The results in Table 6 show strong positive correlations, at the Sebou level, between Cr/Pb, Cr/Cu, Pb/Cu, and strong negative correlations between Cr/dissolved O2, Pb/dissolved O2, Cu/ dissolved O₂, and pH/EC with values above 0.6. For the lower Moulouya (Table 7), there are positive correlations between Cr/ Pb, Cr/Cu, Cr/CE, Cu/CE, pH/CE, dissolved pH/O2, and CE/dissolved O2: with values more than 0.5. However, negative correlations (anti-correlated) between pH/T°, T°/EC, and T°/dissolved O₂ were observed, while the correlation between Pb and Cu is weak. The correlations in Oum Er Rbia (Table 8), positive correlations greater than 0.5 between Cr/Pb, Cr/pH, Pb/pH, and a negative correlation between Cr and electrical conductivity with a value of -0.57.

Water pollution index (WPI)

The analyzed parameters were used to calculate WPI and classify each station's water quality in each studied river. From the calculated values of WPI, the water quality is organized into six categories (very pure, pure, moderately polluted, polluted, impure, and heavily impure). The obtained index was considered an index of water pollution recognition (Zueva and Bobrov 2018).

The water pollution index (WPI) represents the sum of the ratios between the parameters analyzed and the normal values according to the following formula (Popovic et al. 2016) (Table 9):

	Cr	Pb	Cu	pН	T°	CE	O_2
Cr	1						
Pb	0.64	1					
Cu	0.94	0.65	1				
pН	-0.16	0.09	-0.02	1			
Τ°	-0.23	-0.01	-0.12	-0.21	1		
CE	-0.05	-0.15	-0.11	-0.72	0.32	1	
O ₂	-0.75	-0.60	-0.82	0.18	-0.22	-0.08	1

Table 6 Correlation coefficient between the metallic trace elements studied in Sebou River

Table 7 Correlation coefficient between the metallic trace elements studied in the lower Moulouya River

Cr

Pb Cu pН Т° CE O_2

Cr

Pb Cu pН

Т°

CE

 O_2

Cr	Pb	Cu	pН	T°	CE	O ₂
1						
0.52	1					
0.63	0.24	1				
-0.19	-0.23	0.10	1			
-0.39	-0.43	-0.17	-0.67	1		
0.51	0.19	0.57	0.72	-0.77	1	
-0.22	-0.14	0.12	0.96	- 0.60	0.69	1
Cr	Pb	Cu	pН	T°	CE	O ₂
1						
0.54	1					
_	_	_				
0.80	0.55	_	1			

-0.30

-0.47

0.08

1

0.28

-0.32

Normative reference

1

0.20

1

Table 8 Correlation coefficient between the metallic trace elements studied in Oum Er Rbia River

ence values of WPI	Parameter	Value	Retained value
	Chromium total (mg/l)	0.05	0.05
	Copper (mg/l)	1	1
	Lead (mg/l)	0.01	0.01
	рН	6.5-8.5	8
	D' 1 10 (/)		-

-0.10

-0.57

0.27

0.21

0.11

-0.16

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Table 9 The refere for the calculation

Chromium total (mg/l)	0.05	0.05	WHO 2017, NM 03.7.001 (2020)
Copper (mg/l)	1	1	NM 03.7.001 (2020)
Lead (mg/l)	0.01	0.01	WHO 2017, NM 03.7.001 (2020)
pH	6.5-8.5	8	NM 03.7.001 (2020)
Dissolved O ₂ (mg/l)	5–7 (good quality)	7	Order 1275–01 (2002)
Electrical conductivity (µS/cm) at 20 °C	2700 750–1300 (good quality)	1300	NM 03.7.001 (2020) Order 1275–01 (2002)
Temperature (°C)	25-30 (medium quality)	30	Order 1275–01 (2002)

$$WPI = \sum_{i=1}^{n} (Ci/Si).1/n$$

where Ci is the measured concentration of each parameter in mg/l except for the pH, the T° in C, and the electrical conductivity in μ s/cm; *n* is the number of parameters; and Si is the maximum value of the Moroccan standard for surface water, water quality for food use, and Guidelines for drinking-water quality. The reference for dissolved O2, temperature, and electrical conductivity is the maximum value of class II (good quality) of Order 1275-01 (2002).

Table 10 gives the classification of water according to the water pollution index.

Based on the WPI values obtained, the three studied rivers are classified into different categories (Tables 11, 12, and 13). If WPI < 1, the watercourse is marked as pure; if WPI > 2, the waterway is polluted; and if WPI > 6, the watercourse belongs to a group of highly polluted waters (Milanovic et al. 2011).

According to the calculation of the Sebou surface water pollution index, this river's water quality in August was pure quality in 50% of the samples, moderately polluted in 36%,

Table 10 Water quality classification according to WPI (Lyulko et al. 2001; Milanovic et al. 2011)

WPI	Class	Characteristics					
Very pure	I	≤0.3					
Pure	II	0.3-1					
Moderately polluted	III	1–2					
Polluted	IV	2–4					
Impure	V	4–6					
Heavily impure	VI	>6					

Table 11 WPI in Sebou River		S 1	S2	S 3	S4	S5	S 6	S 7	S 8	S 9	S10	S11	S12	S13	S14
	WPI-August	0.59	8.96	1.97	2.35	1.23	0.69	0.76	1.27	0.86	0.85	1.14	0.94	0.73	1.82
	WPI-December	0.55	1.22	0.60	2.35	0.71	0.69	0.57	0.77	0.60	0.76	0.91	0.77	0.60	1.67
Table 12 WPI in Oum Er Rbia River Image: State Stat		P1		P2		P3		P4	P5		P6		P7		P8
	WPI-August		0.68		0.75		1.86		0.59		1.04		0.61		1.87
	WPI-December		0.65	0.	86	1.64	4	0.86		0.53	0.	49	0.5	1	1.79
Table 13 WPI in lower Moulouya River			M1		M2		M3		M4		M5		M6		M7
	WPI-August		1.00		0.86		0.81		0.79		0.89		0.66		0.65
	WPI-December		0.96		0.80		0.79		0.75		0.69		0.60		0.57



Fig. 4 Water pollution index (WPI) in each station at the level of the three rivers (Sebou, Oum Er Rbia, and lower Moulouya) in August and December 2019

impure in 7%, and very impure in 7% of the samples. On the other hand, in December, the quality of these waters was pure at 79%, moderately polluted at 14%, and impure at 7%. Regarding Oum Er Rbia (Table 12), the WPI values for August show that 50% of the water is of good quality and 50% is moderately polluted. Moreover, in December, the WPI values indicate that 75% of the water analyzed is pure while 25% is of average quality. For the lower Moulouya (Table 13), 86% is pure quality in August, while 100% of the water withdrawn in December is pure quality.

According to the WPI, surface water quality classification maps at each sampling station are established (Fig. 4).

The limitations of the study

The assessment of metal pollution in river surface waters should always include discussing the study's limitations. Several parameters can influence the diagnosis of river waters, in particular, the period and the sampling technique; the intense industrial discharges discharged without treatment into river waters since industrialists do not treat their effluents before discharge. These parameters may induce sources of error which could have led to an underestimation or an overestimation of the levels of metallic trace elements in the three rivers studied. In addition, the problem of drought experienced by the study areas in recent years in the face of contamination due to the reduction in the flow of river water and concentration of pollution can also influence the results of the analysis of metallic traces.

The study of contamination by metallic trace elements was carried out in specific periods (August and December 2019). This might have a significant impact on how pollutant loads are estimated (over-estimate or under-estimate). For example, the sampling days could coincide with accidental spills at specific control points or water dilution due to the variation in flow rates. In addition, the accumulation of the metals studied in the sediment compartment and the bioaccumulation of trace metals by the plants can play an exciting role in the trace metal results obtained. Furthermore, the interactions between the different parameters, especially nitrogenous and phosphorus elements, pesticides, temperature, oxygen, and bacteriological parameters, can play an interesting role in the presence of metallic traces in the three rivers.

Conclusion

The results of this study allowed for the identification and evaluation of the metallic pollution and physicochemical characteristics of the leading Moroccan rivers' surface waters. The physicochemical measurements in this study showed that the electrical conductivity measurements in the lower Moulouya and Oum Er Rbia are very high, showing that these rivers' waters are highly mineralized. Thus, we found that the rate of dissolved oxygen downstream of the city of Fez is meager (1.2 mg of O_2/l for S2) because this area receives highly polluting organic loads. Indeed, assessing the degree of pollution by Cr, Cu, and Pb in the three rivers studied shows that the Sebou is the river most threatened by these metallic trace elements with average concentrations of 181.25 µg/l, 68.93 µg/l, and 14.90 µg/l, respectively. We have shown that the levels obtained from the metals analyzed in August remain higher than those in December. The overall water quality calculated by the global pollution index (WPI) shows that the quality of the Sebou River varies from pure to very impure; on the other hand, the quality of the lower Moulouya is pure in all the sampling points, and for Oum Er Rbia, the quality is pure to moderately polluted. Overall, this study shows that the surface waters of Oum Er Rbia and lower Moulouya are highly mineralized. This indicates that specific treatment of these waters is necessary if they are to be used for drinking water supply. This work also made it possible to diagnose the pollution of the surface waters of the Sebou river by metallic trace elements due to the industrial and agricultural intensification that this river is experiencing. Faced with this alarming situation, it is essential to

monitor the quality of the surface waters of the three rivers studied and the surrounding groundwater using appropriate tools and to watch all the parameters listed in the surface water quality grid. According to Decree 1275–01 of 2002, monitor, correct, and preserve natural resources that remain important for drinking water, irrigation, and industrialization. Generally, it is advisable to organize several analysis campaigns, which makes it possible to monitor the pollution of river water.

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Data availability The datasets generated during and/or analysed during the current study are available from the corresponding author.

Declarations

Competing interests The authors declare no competing interests.

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