Contribution to the Selouane Wadi's water quality study (Rif-Est, Morocco): physicochemical and biological evaluation and heavy metal contamination

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Abstract. Aquatic ecosystems are exposed to human activities, which has a negative impact on their health. To assess the quality of Selouane Wadi's surface water, physicochemical and biological characterizations were carried out at a total of seven stations, quarterly between September 2021 and June 2022. In addition, an analysis of heavy metals in sediments was carried out during two separate periods (November 2021 and May 2022). The findings from this study have highlighted a significant pollution load as indicated by the measurements of chemical oxygen demand (COD) and the organic pollution index (OPI). These results demonstrate the existence of organic contamination, which increases progressively from the upstream to the downstream areas. The macroinvertebrate distribution assessment has identified 6846 specimens divided into 17 families. The abundance was highest in wet periods while values for the Shannon diversity index and Pielou evenness index showed low biodiversity and high level of contamination. The results from metal analysis in sediment using ICP-OES technique revealed a pollution associated with several heavy metals such as zinc, iron, lead, copper, cadmium, nickel, aluminum, and manganese. The enrichment factor (EF) and contamination factor (CF) highlighted zinc and cadmium as the primary contributors to this pollution. Additionally, the geoaccumulation index (Igeo) emphasized significant pollution attributed to lead. Moreover, the results were compared to the sediment quality guidelines (SQGs). Threshold effect level (TEL) which establishes concentrations below which adverse effects are expected to rarely occur, indicates the potential for adverse effects resulting from zinc, cadmium, copper, and nickel.
Key Words: heavy metals, macro-invertebrates, physico-chemical parameters, Selouane Wadi, water quality.

Introduction. Sustainable management of wetlands requires better preservation of all components, especially aquatic ecosystems, which are exposed to a number of anthropogenic stresses. Indeed, the growing of rural areas' demography, the mechanization of agricultural practices and the surging exploitation of the land present potential threats to natural habitats (Zouaïdia et al 2015). The Nador lagoon (Mediterranean), located in the far east of Morocco's eastern Rif (El-Alami et al 1998), is of major local socio-economic interest (Bloundi et al 2009), yet it is exposed to several anthropogenic pressures that affect its current equilibrium (Hamoumi 2012), including effluent discharges, domestic discharges (Aknaf et al 2015) and discharges from the wastewater treatment plant built near this area (Zerrouqi et al 2013; Mostarih et al 2016). In addition, monitoring based on water management is an essential element in the management of coastal ecosystems (Karim et al 2019). Therefore, it is important to assess its health status by evaluating the running waters of these effluents that are often used by humans in their daily activities. The potential deterioration of water quality can have detrimental effects on local fauna, flora, irrigated soils and subsequently the well-being of the surrounding population (Moussa et al 2012). This evaluation is frequently conducted using conventional measurement techniques, relying on a range of physicochemical parameters (Abouhala et al 1995; Makhoukh et al 2011; Moussa et al 2012; Mounjid et al 2014; Reggam et al 2015) and the analysis of metal contamination (Abboudi et al 2014; Fouad et al 2014). These methods are complemented by biological monitoring based on the general principle that each type of natural environment has a characteristic community of organisms. Any impoverishment of the natural biocenosis therefore reflects a disturbance (Zouggaghe et al 2014). Biological monitoring involves the use of living organisms, including bacteriological analysis (El Addouli et al 2010), the use of benthic macroflora (Najih et al 2016), algae as indicators (Zouaïdia et al 2015), bryophytes (Empain & Lambinon 1974; Roeck et al 1991), protozoa (Sparagano & Grolière 1991) or benthic macroinvertebrates (Alhou et al 2014; Sellam et al 2016; Koumba et al 2017; Ngoay-Kossy et al 2018; Taybi et al 2020; Abdullah et al 2022). Employing macroinvertebrates has proven effective method in identifying environmental degradation in the studied rivers (Eriksen et al 2021). Their presence or absence serves as a biological indicator for the condition of aquatic ecosystems in flowing waters. Any changes in the environment can impact biodiversity and taxonomic diversity, consequently leading to alterations in the taxonomic composition of the populations (Zouggaghe et al 2014). Elevated levels of diversity among these organisms signify favorable developmental conditions within their environments (Foto Menbohan et al 2011). Conversely, any changes in an aquatic ecosystem lead to disruptions in the communities that populate it, as highlighted by Fergani & Arab (2013). Thus, benthic macroinvertebrate assemblages are a very useful means of determining the status of streamwater aquatic ecosystems (Zouggaghe et al 2014), since there are species that are pollution-tolerant (Adandedjan et al 2013) and others that are pollution-sensitive (Koumba et al 2017). In addition, the determination of heavy metals makes it possible to highlight the origins and the nature of metal contamination in order to properly assess the status of aquatic ecosystems. In this context, surface water’s quality was assessed by analyzing metal contamination and both physico-chemical and biological characteristics of Selouane Wadi. The novelty of this study consists in the simultaneous exploration of all these parameters concerning the aquatic ecosystems of the Selouane Wadi.

Material and Method

Description of the study sites. Table 1 and Figure 1 show the location of studied area and sampling stations. This study was carried out on the Selouane Wadi, which extends over around twenty kilometers and is located between Al-Aroui and the Marchica in Nador lagoon.

Table 1

Description of sampling stations

Station	*Locations (longitude and latitude)*	*Site description*
S1	35°01'05"N 2°59'32"W	Upstream side, is considered a water source.
S2	35°01'12"N 2°59'31"W	Located upstream of the Aroui wastewater treatment plant.
S3	35°02'51"N 2°57'52"W	Located downstream of the Aroui wastewater treatment plant.
S4	35°04'37"N 2°55'29"W	Located downstream of the the Selouane industrial zone.
S5	35°05'57"N 2°54'50"W	Located of the Bouarg plain (agricultural activity zone).
S6	35°07'14"N 2°53'26"W	Located downstream of the Bouarg plain.
S7	35°07'50"N 2°53'00"W	Located downstream, at the contact between the Marchica lagoon and the Selouane Wadi.

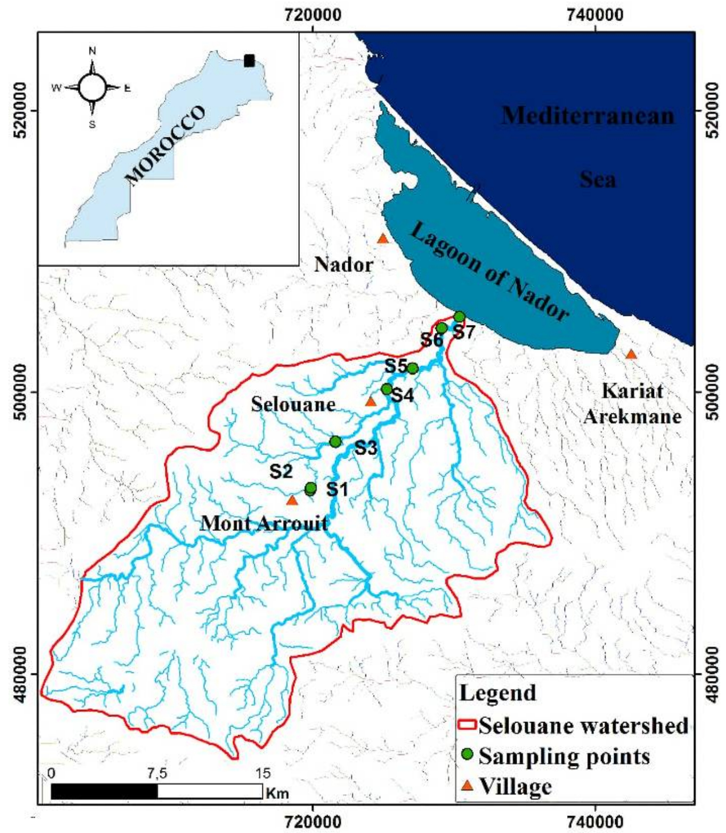

Figure 1. Location of studied area and sampling stations.

Sampling and analysis. Water samples were taken into 500 mL sterile bottles and stored at a temperature of 4°C. Temperature, pH, electrical conductivity (EC) and dissolved oxygen (DO) were determined in situ using a HACH instrument multimeter with specific probe for each parameter. The determination of orthophosphates, nitrates, nitrites, ammonium, total suspended solids (TSS), chemical oxygen demand (COD) and biological oxygen demand (BOD5) was carried out in the laboratory using the methods described by Rodier et al (2009).

Aquatic macroinvertebrates were collected at the seven stations studied, using a Surber-type net with a 25 cm opening and 500 µm meshes, laid on the stream bottom against the current and pulled over a length of 100 cm, on a quarterly basis between September 2021 and June 2022, from upstream to downstream. These periods correspond to a warm-dry period and a cool-wet one. The species collected were sorted and preserved in 90° alcohol. The net contents, made up of plant parts, macroinvertebrates and sediment, were rinsed with water, then the macroinvertebrates removed and preserved in 90° alcohol for sorting in the laboratory (Rodier et al 2009; Sanogo et al 2014). After the triage, determination down to family level was carried out under a binocular magnifying glass, using references and determination keys (Sansoni 1992; Campaioli et al 1994; Tachet et al 2000).

Sampling for metal analysis was carried in June and November. The evaluation of heavy metal pollution involved analyzing the levels of aluminum (Al), iron (Fe), manganese (Mn), zinc (Zn), cadmium (Cd), copper (Cu), nickel (Ni), and lead (Pb) in the sediment from the studied area. The metal content was determined after drying the samples at 105°C for 3 hours and subsequent extraction of the metals in an acid medium in a microwave digestion oven. Approximately 300 mg of dried sediment was weighed into the PTFE containers of the microwave system, and then 7 mL HCl and 2 mL HNO_3 were added. The temperature program consisted of a 25-minute ramp up to 175°C and a 15 minute hold at 175°C. After cooling to room temperature, the solutions were filtered through "white mark" filter paper and the sediments were washed with pure water obtained from the Milli-Q system (Millipore, USA). The filtrates and washing solutions were collected in volumetric flasks and filled up to 50 mL with Milli-Q water. All sediment samples were analyzed in duplicate. Preparation of the blank solution followed the same procedure as for the sample solutions. Metal concentration was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES).

Data analysis. To estimate overall pollution at the studied stations, and to show the spatio-temporal evolution of this pollution, the organic pollution index (OPI) based on the determination of the orthophosphates (PO_4^{3-}), ammonia (NH_4^+), nitrates (NO_3^-) and 5-day biochemical oxygen demand (BOD_5) was used. The estimation was carried out using a method that distinguishes classes of OPI, each indicating a corresponding degree of pollution (Mounjid et al 2014).

Regarding biotic indices, the Shannon diversity index (H') and the Pielou evenness index (E) were calculated (Shannon & Weaver 1948; Kamb Tshijik et al 2015):

$$H' = -\sum_{i=1}^{S} \text{pi} \ln \text{pi}$$

$$pi = Ni/N$$

where: H' = Shannon diversity index;

S = number of species;

i = a species in the study area;

Ni = number of individuals of a particular taxon;

N = number of individuals.

$$E = H'/Hmax$$

$$Hmax = Ln(S)$$

To estimate overall metal pollution, the enrichment factor (EF), contamination factor (CF), pollutant load index (PLI) and geoacumulation index (Igeo) were calculated according to the formulas described below:

EF = (C/Cmetal Al) Sample / (Cmetal) Background) (Maanan et al 2015)

CF = (Cmetal) Sample / (Cmetal) Background) (Hakanson 1980)

PLI = (CF1 x CF2 x CF3 x...xCFn)1/n) (Tomlinson et al 1980)

Igeo = log2 (CTracemetal / 1.5 CBackground) (MacDonald et al 2000)

In addition, the results were compared to the sediment quality guidelines (SQGs) based on the concentration below which adverse effects are expected to occur only rarely (TEL (Zn) = 123 mg kg^{-1}, TEL (Cd) = 0.596 mg kg^{-1}, TEL (Cu) = 35.7 mg kg^{-1}, TEL (Ni) = 18 mg kg^{-1}, TEL (Pb) = 35 mg kg^{-1}) (Smith et al 1996).

Statistical analysis. Pearson's correlation analysis was performed to investigate the relationship between trace and major elements in all investigated samples. An ANOVA test was used to determine whether differences between biomass means were statistically significant. Pearson test and analysis of variance test correlations were performed with SPSS 26.0 software. The study sites map was created using ArcGIS software.

Results and Discussion. Table 2 shows the parameter values measured at each sampling station during the studied period (by quarter).

The results summarized in Table 2 reveal that the water temperature ranged from 15.4°C to 25.8°C which indicates that the water from the upstream stations (S1, S2, S3) is of excellent quality according to Moroccan surface water standards. Additionally, results from station S3, located downstream of the Aroui wastewater treatment plant, showed a marked difference in temperature from one season to another.

The observed average pH values at the studied area are between 7.2 and 8.69 with a maximum value in June at station S6 and a minimum value during March at station S7. The pH of most natural waters is usually between 6 and 8.5 (Mounjid et al 2014). The mean values were close to those obtained in the Merzeg stream (Mounjid et al 2014) and similar to the Oued Ouislane stream (El Addouli et al 2010). The pH values are almost neutral at stations S1, S2 and S7, while they are alkaline at stations S3, S4, S5 and S6, which is close to the results obtained at Oued Moulouya (Makhoukh et al 2011). Thus, an increasing downstream gradient is observed at Oued Khoumane (Moussa et al 2012). Moreover, the consistent pH stability across seasons can be attributed to the geological composition of the rocks, especially those abundant in carbonates, which serve as effective buffers (Makhoukh et al 2011). Based on these findings, we can categorize the water of Selouane Wadi as having excellent quality in terms of pH, in accordance with the Moroccan surface water quality standards.

Table 2

Values of the assessed parameters at the sampling stations during the studied period

Stations	*Season*	*T (°C)*	*pH*	*EC (µs cm $^{-1}$)*	*DO (mg L^{-1})*	*NO_3^- (mg L^{-1})*	*TSS (mg L^{-1})*	*COD (mg L^{-1})*
S1	C1	19.8	7.45	5660	8.2	4.7	8.9	18.7
S2		20	7.72	8210	5.45	33.7	11.8	45.5
S3		20.2	8	9080	6.74	9.1	42.7	58.7
S4		21.6	7.8	9450	4.98	18.1	30	66
S5		21.1	7.9	10200	6.35	13.1	21.6	53.4
S6		22.1	8.41	10160	7.65	18.2	29.8	34
S7		21.3	7.65	11950	7.8	10.8	25.4	35.8
S1	C2	16.1	7.34	5640	7.9	3.5	8.8	14
S2		17.6	7.72	7930	6.62	70.1	3.6	90
S3		16.4	8.2	9890	4.08	9.5	28	80
S4		19.9	8.09	9710	3	31	12.8	88.1
S5		18.2	7.74	10560	5.7	21	11.2	44.2
S6		20.5	8.06	10910	7.5	18.6	7.6	12
S7		19	7.82	11810	8.41	14.5	14.4	8.6
S1	C3	17.3	7.34	5640	7.09	5	11	24.5
S2		18.5	7.64	8990	6.81	12.9	14.5	15
S3		15.4	7.81	9560	8.06	5.1	38	38
S4		19.4	7.83	9590	3.7	3.5	54	125
S5		18.8	7.88	10560	5.7	8.1	21.5	58
S6		21.5	8.58	10050	7.5	13	25.5	33
S7		19.5	7.2	12920	8.1	9.1	21.5	48
S1	C4	21.5	7.56	5560	6.88	3.5	7	27.1
S2		22.4	7.9	7160	4.85	12.3	16	71
S3		24	8	7680	5.54	12.8	60.5	57
S4		24	8.08	8710	5.94	10.7	20	108
S5		24	8.3	9490	7.6	10.2	29.5	35
S6		25.8	8.69	9420	7.95	8.4	54	64
S7		24.4	7.97	11080	7.17	9	40	50
S1	Average	18.68	7.42	5625	7.52	4.18	8.93	21.08
S2		19.63	7.75	8070	5.93	32.25	11.48	55.38
S3		19.00	8.00	9050	6.11	9.13	42.30	58.43
S4		21.23	7.95	9370	4.41	15.83	29.20	96.78
S5		20.53	7.96	10200	6.34	13.10	20.95	47.65
S6		22.48	8.44	10140	7.65	14.55	29.23	35.75
S7		21.05	7.66	11940	7.87	10.85	25.33	35.60

Note: C1 = September; C2 = December; C3 = March; C4 = June.

Electrical conductivity (EC) values ranged from 5560 µs cm^{-1} in S1 to 11940 µs cm^{-1} in S7. It is important to note that the EC at S1 showed certain stability over the 4 seasons, i.e. 5625±40, indicating the absence of any anthropogenic effect at this station. The rise in salinity of the groundwater is primarily attributed to the dissolution of minerals present in the Messinian marls, which constitute the impervious bedrock of the Gareb Bouareg aquifer (El Yaouti et al 2009; Chamrar et al 2019). This rise could also be associated with the low permeability of silts (Carlier 1971). The station S7 has a maximum value of 11940 µs cm^{-1}. These values indicate that the water is highly mineralized (over 8000 µs cm^{-1}). Station S3, located downstream of the Al Aroui wastewater treatment plant, has higher EC value (9050 µs cm^{-1}) than S1 (5625 µs cm^{-1}), indicating the effect of the Al Aroui wastewater treatment plant's discharges. Comparable results were identified in the investigation of pollution in South Africa (Odume 2020). These elevated values seem to be due to the considerable salinity of Garet's groundwater, coupled with the geological characteristics of the region (Carlier 1971), alongside its various inputs, notably domestic effluents, or they might arise from soil leaching. The increase in EC values from upstream to the mouth is due to the low water level in Selouane Wadi and the inflow of water from Marchica lagoon during the dry season.

Values of DO have varied between 3 and 8.41 mg L^{-1}, close to those found in the Tshula River, in the Lake Kivu basin of DR Congo (Mucheso et al 2017). The variation in DO between seasons is minimal in station S1 and maximal in station S5. The lowest DO value (3 mg L^{-1}) occurs at station S4 during December. A positive correlation between reduced DO levels and urban wastewater releases has been established earlier (Getachew et al 2012). The progressive decrease in water's DO content can be elucidated by the microbial consumption of oxygen during the biodegradation process of organic substances comming from household wastewater, as previously demonstrated at Oued Za (Fagrouch et al 2011).

Average TSS values at all stations ranged from 3.6 to 60.5 mg L^{-1}. The lowest values were recorded at S2 (3.6 mg L^{-1}) in December and S1 (7 mg L^{-1}) in June, whereas the highest value (60.5 mg L^{-1}) was documented at S3 in June. It is worth noting that excessive levels of suspended solids characterize stations S3 and S4 which can be explained by discharges from the Al Aroui wastewater treatment plant, located upstream of station S3. The average content at stations S4, S5 and S6 varied between 20 and 30 mg L^{-1}. This downstream decrease is due to decantation along the watercourse, as described in the study carried out on the Oued Seybouse in northeastern Algeria (Reggam et al 2015). With the exception of station S1, the values obtained in the wet period were higher than those measured in the dry period. This result is in concordance with the study carried out at Oued Moulouya (Makhoukh et al 2011). The average TSS values in the wet-period for most of the stations ranged between 25 and 50 mg L^{-1}, which are in accordance with the results found in the Yangtze River (Wang et al 2021). In comparison to the Moroccan surface water standard for TSS levels, the water quality was considered excellent, except for station S3, where a value of 60.5 mg L^{-1} was recorded in June.

COD values varied from 8.6 to 125 mg L^{-1}. Downstream stations (S4, S5, S6, 57) showed higher values (close to 60 mg L^{-1}) compared to upstream stations (S1, S2 and S3). The high COD values can be explained by a source of pollution that contains inorganic elements (discharges from the Selouane industrial zone), in addition to urban wastewater discharges (Getachew et al 2012). These results exceed the figures reported in Oued Awash in Ethiopia (Kebede et al 2020), but are still below the maximum values identified in Oued Hassar in Morocco (Fouad et al 2014).

The mean concentrations of nitrates varied between 4.18 and 32.25 mg L^{-1}, with the lowest value at station S1 (4.18 mg L^{-1}), while the station S2, which is located downstream the Al Aaroui raw sewage discharge, reached a maximum value of 32.25 mg L^{-1}. Moving downstream, nitrates concentration decreased which is explained by self-purification. Average nitrate levels were similar to those found in Oued Moulouya (Talhaoui et al 2020), Oued Guigou (Abboudi et al 2014), while they were higher than those found in Oued Hassar in Casablanca (Fouad et al 2014), and Oued Tighza (Hachi et al 2023).

Figure 2 shows the spatio-temporal variation in OPI for the studied stations. According to Leclercq & Maquet (1987), the OPI value indicates the degree of organic pollution (between 4.6 and 5.0: unpolluted; between 4.0 and 4.5: low pollution; between 3.0 and 3.9: moderate pollution; between 2.0 and 2.9: high pollution; between 1.0 and 1.9: very high pollution). In this study, OPI values ranged from 1.25 to 3.5.

Station S3 is considered the most polluted, with a minimum OPI value (equal to 1.25) during September, accompanied by a significant coefficient of variation (30.86%). This variation is explained by the variation in the pollutant load of raw wastewater from Al Aroui and discharges from the Al Aroui city treatment plant (high organic pollution), which is in accordance with the findings of the work of Mounjid et al (2014) carried out at Wadi Merzeg. Station S1 located upstream of the watercourse has a maximum OPI value (3.5) during June with a low coefficient of variation (12.77%), indicating the stability of the quality of these waters with moderate pollution. The same result in terms of quality was found at the Ourika watershed level (Zuedzang Abessolo et al 2021). Station S4, located downstream of the city of Selouane, recorded an average POI value (2.06), showing the high level of organic pollution in this station. This is explained by the discharge of raw sewage from Selouane and the Al Omran urban area. Moving downstream, OPI values increased as a result of the self-purification phenomenon of the watercourse. This result is in line with the study carried out on Wadi Tighza (Fès-Meknès region) (Hachi et al 2023).

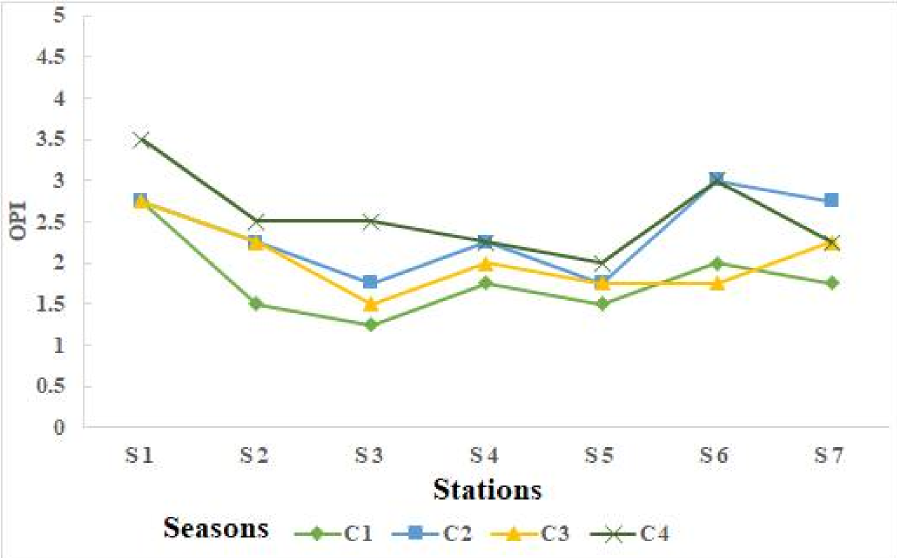

Figure 2. Spatio-temporal fluctuations of the organic pollution index (OPI) across the research sites.

Table 3 shows the classification of the sampled macroinvertebrates and values of the biodiversity indices across the investigated sites. To assess the biological characteristics, a total of 6846 specimens of aquatic macroinvertebrates were collected. Abundances were higher in the wet period (4065 individuals across all 7 stations with an average of 290 individuals/station) compared to the dry period (2781 individuals across all 7 stations, but with an average of 198 individuals/station). This difference may be due to the unfavorable conditions of the low-water period, which is in agreement with the evidences found for the hydrographic network of the Soummam watershed in Algeria (Zouggaghe et al 2014).

Table 3

Classification of the sampled macroinvertebrates and values of the biodiversity indices across the investigated sites

Class	*Order*	*Family*	*S1*	*S2*	*S3*	*S4*	*S5*	*S6*	*S7*
Insecta	Trichoptera	Hydropsychidae	3	207	-	-	2	15	-
	Amphipoda	Gammaridae	1186	31	-	-	-	-	383
	Ephemeroptera	Caenidae	8	564	-	20	144	250	17
		Baetidae	-	434	-	37	94	64	27
	Diptera	Anthomyiidae	-	7	-	-	-	-	-
		Chironomidae	5	272	791	533	304	129	35
		Dixidae	-	-	-	3	-	-	-
		Psychodidae	-	-	-	-	-	-	8
		Simuliidae	-	114	35	24	-	-	2
		Tabanidae	-	3	2	-	-	-	-
	Gastropoda	Melanopsidae	806	75	-	-	-	10	-
		Hydrobiidae	-	40	7	-	35	36	3
	Hemiptera	Corixidae	-	3	30	-	-	-	-
		Nepidae	-	-	-	20	-	-	-

Odonata	Libellulidae	-	7	-	-	-	-	-
Coleoptera	Dytiscidae	-	-	-	-	-	7	-
	Hydrophilidae	-	9	-	-	-	5	-
Abundance	C1	672	321	132	89	124	95	73
	C2	586	355	49	61	97	102	25
	C3	529	662	325	244	181	170	343
	C4	221	428	359	243	177	149	34
Richness	C1	2	6	4	4	5	5	3
	C2	2	10	2	3	3	4	4
	C3	2	7	1	5	4	5	3
	C4	4	10	2	1	4	7	4
Shannon index	C1	0.63	1.30	0.99	0.95	1.21	1.17	0.70
	C2	0.69	1.55	0.62	0.71	0.88	1.05	1.22
	C3	0.52	1.12	0.00	0.86	1.18	1.31	0.24
	C4	0.33	1.58	0.10	0.00	0.99	1.46	1.18
Pielou evenness index	C1	0.92	0.73	0.71	0.69	0.75	0.73	0.64
	C2	0.99	0.67	0.89	0.65	0.80	0.76	0.88
	C3	0.75	0.58	0.00	0.54	0.85	0.81	0.22
	C4	0.24	0.69	0.14	0.00	0.71	0.75	0.85

A total of 17 families were distinguished within the Wadi Selouane samples. This level of richness appeared relatively low in comparison to the findings from Gabon as reported by Ngoay-Kossy et al (2018), but notably exceeded the diversity documented in the case of Wadi Tighza in Morocco as studied by Hachi et al (2023).

Figure 3 presents the variation in distribution of macroinvertebrate families over the studied period. Regarding the spatial distribution, the majority of stations showed low macroinvertebrate abundance and diversity, which is in line with a result found by Mboye et al (2018). The predominant species observed was from the Chironomidae family, accounting for 30.22% of the total, and it is known to exhibit resistance to pollutants as noted by Odume (2020). Moreover, Simuliidae, recognized as sensitive to pollution, displayed higher concentrations at station S2, an area characterized by abundant plant cover, implying comparatively lower pollution levels in those waters as suggested by Kebede et al (2020).

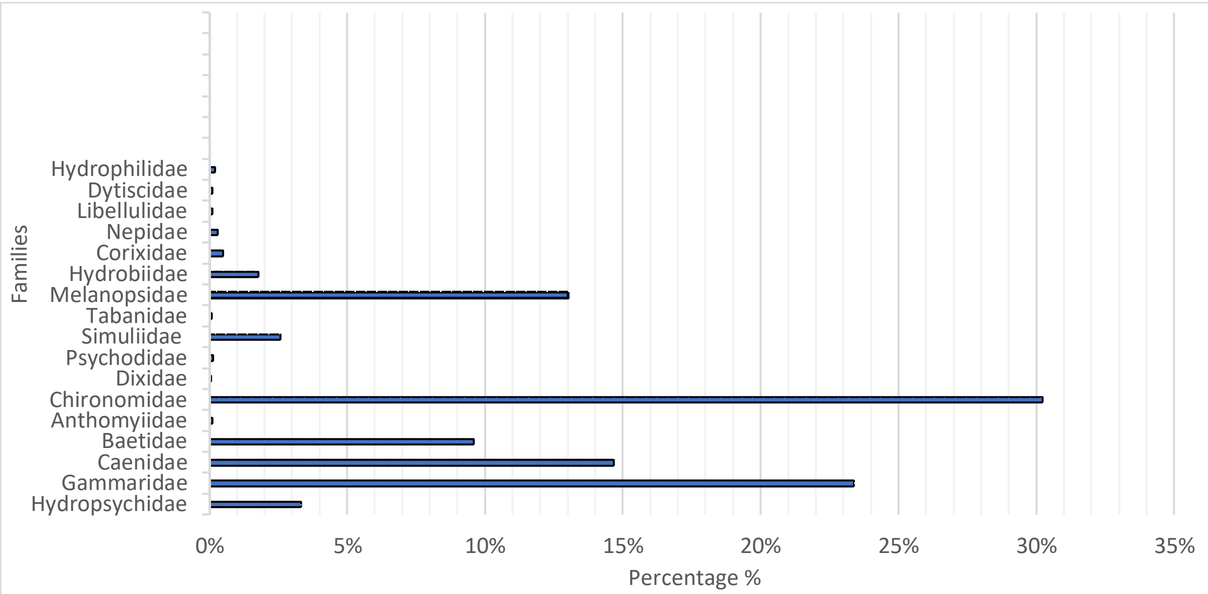

Figure 3. Percentage distribution of the main observed families in Selouane Wadi.

Figure 4 shows the variations in Shannon diversity index values, with significant variations according to station and season, ranging from 0 to 1.58. Station S2 recorded the highest value (1.58) during December, while stations S3 and S4 showed low Shannon diversity index average values (0.43 and 0.63 respectively). However, stations S5, S6 and S7 record intermediate values (≈1).

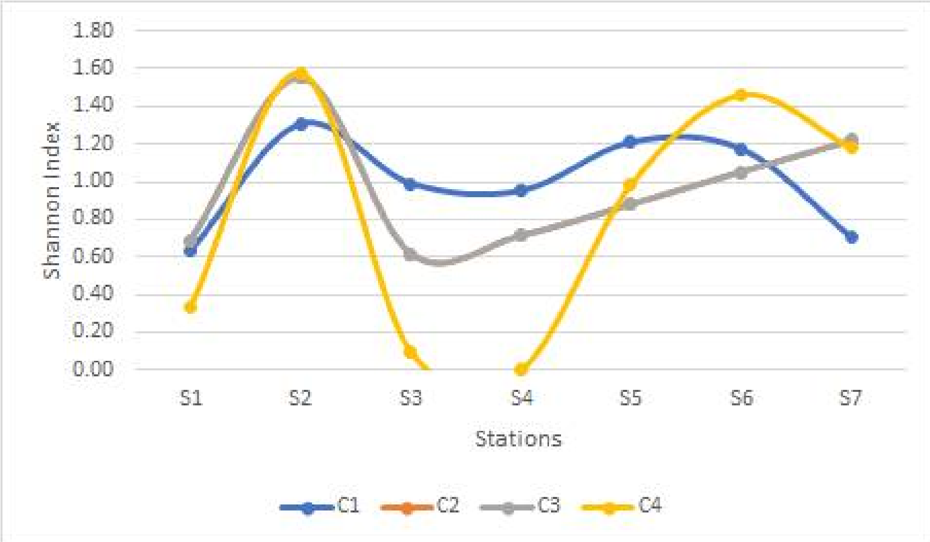

Figure 4. Spatio-temporal variation of Shannon index within the studied areas at Wadi Selouane.

Figure 5 shows the variation in Pielou evenness index values, with results ranging from 0 to 0.92. Station S1 recorded the highest value (0.92) in September while stations S3 and S4 recorded zero-values in March and June. The mean values of stations S3 and S4 showed low values (0.44 and 0.47, respectively) while stations S5 and S6 recorded high values (0.78 and 0.76, respectively)

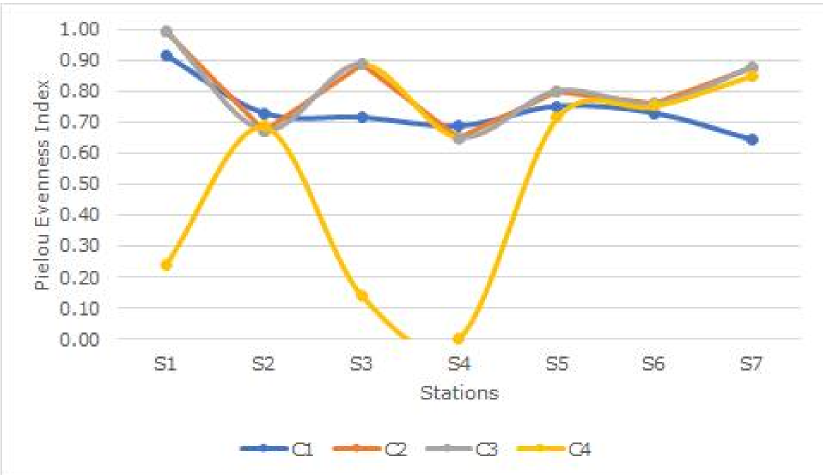

Figure 5. Spatiotemporal variation of the Piélou evenness index at Wadi Selouane stations.

These results show that the distribution of benthic macroinvertebrate taxa is more balanced at stations S5, S6 and S7 than at S3 and S4. Low values of the Shannon-Weaver index (H' < 1.58) indicate significant degradation and correspondingly reduced biological diversity within this environment. A similar result was mentioned at a stream (Dougogou) in the Moukalaba Doudou National Park in Gabon (Koumba et al 2017) and in Turkey (Türkmen & Kazanci 2010) while higher values of H' were found at Nguitto in the Central African Republic (Ngoay-Kossy et al 2018).

A Pielou's evenness index of zero signifies an imbalance where a single family dominates the entire ecosystem, particularly evident in the prevalence of Chironomids, which are recognized as indicators of substantial pollution. The mean values found in this work (between 0.44 and 0.76) were comparable to those found in DR Congo (Kamb Tshijik et al 2015), Turkey (Türkmen & Kazanci 2010), and Gabon (Mboye et al 2018). These findings indicate that the population within this river ranges from relatively unbalanced to highly unbalanced, as observed in the study conducted by Nahli & Chlaida (2018). Both indices (Shanon and Pielou) showed that sites S3 and S4 were characterized by high degradation.

In terms of metal contamination, the fluctuation of the pollution load index (PLI) present in Figure 6 indicates that values were greater in June compared to November across all monitoring stations. Among these, station S1 displayed the smallest value (0.22), whereas Station S3 exhibited the highest value (0.81) in June. In a broader context, the PLI values remain below 1 for all stations, implying the lack of metallic pollution, as indicated by Tomlinson et al (1980). Moreover, the utilization of the PLI by Saddik et al (2021) confirmed the absence of metallic contamination.

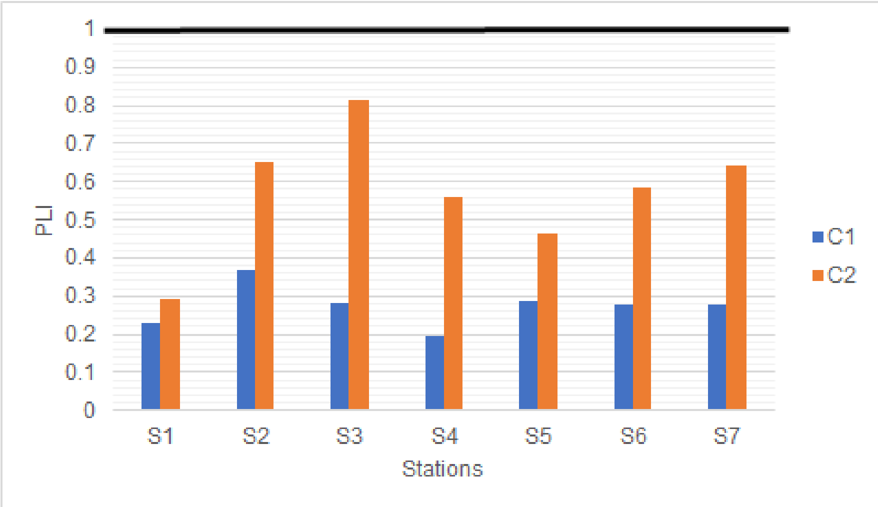

Figure 6. Variation of PLI index at studied stations C1: November, C2: June.

Figure 7 shows the variation of the enrichment factor (EF). The EF was calculated using the method described by Maanan et al (2015), and the degree of contamination (EF < 2: minimal pollution; 2 < EF < 5: moderate pollution; 5 < EF < 20: heavy pollution; 20 < EF < 40: very heavy pollution) was determined based on the interpretation suggested by Maanan et al (2021). Values of Fe, Mn and Ni were below 5 for all stations in both periods (November and June), with little variation between seasons, indicating a moderate level of pollution for these elements. Values of Cu were higher in June than in November, station S2 recorded a significant increase between the two periods (EF raised from 2.1 to 8.44), indicating a high level of pollution. The EF values for Cd exceeded 10 across all monitoring stations, signifying elevated pollution levels at stations S1, S2, S4, S5, S6, and S7. Notably, station S3 exhibited extremely high pollution levels during June, reaching a peak value of 30.81. During the month of June, concentrations of Zn were notably higher compared to those observed in November. In June, Zn values exceeded 5 for all monitoring stations, suggesting a significant degree of pollution in that period. Station S3 showed a maximum value (24.92) during June, indicating a very high level of pollution. Concerning Pb, values were above 5 at S1, S3, S4 and S6 across both periods showing a high level of pollution at these stations. To summarize, the findings indicate a pronounced degree of Pb contamination, while Cd and Zn contamination levels were exceptionally elevated at station S3.

Similar contamination patterns involving Pb, Cd, and Zn were documented in the vicinity of Oued Tafna in Algeria by Benabdelkader et al (2018). Likewise, in the regions near the estuaries of Oued Nador and Oued Mazafran in Algeria, Guendouzi et al (2021) observed substantial enrichment with EF values ranging from 10 to 25 for Cd and Zn in sediment samples. Moreover, heavy metal contamination caused mainly by Cd and Zn was detected at Gabes in Tunisia (El Zrelli et al 2015). In addition, Othmani et al (2015) found significantly high values for Cd, Zn and Pb in the Touiref watershed in Tunisia.

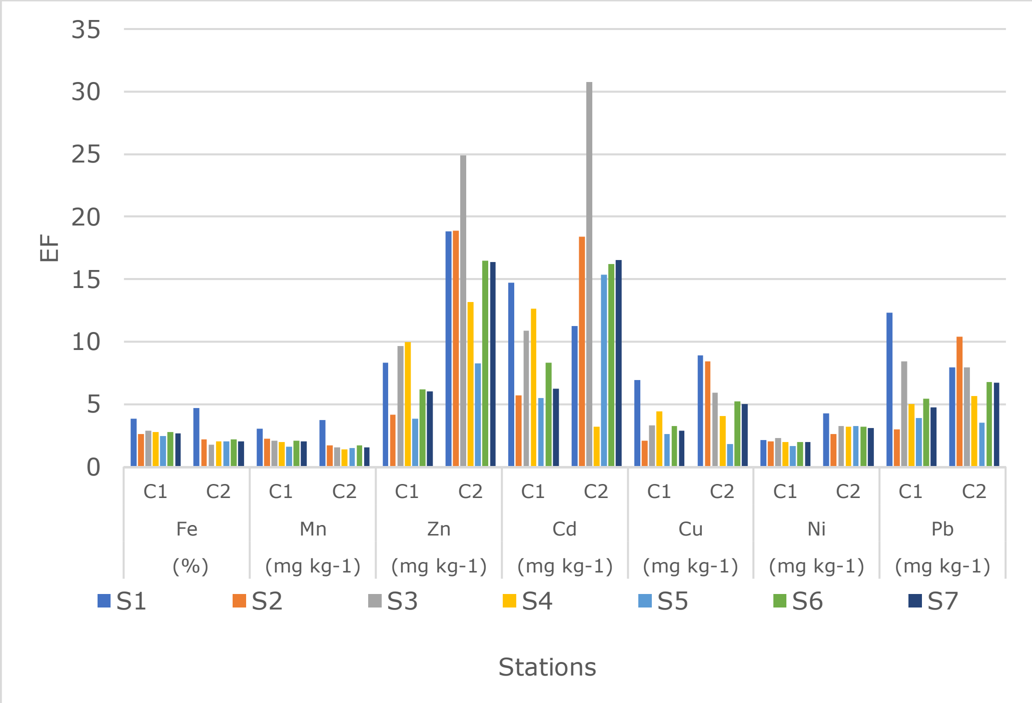

Figure 7. Variation in enrichment factor (EF) within the studied stations (C1: November, C2: June).

Figure 8 shows the variation of the contamination factor (CF). The CF was established using the ratio of the measured concentration of each metal in the sediment to the background metal concentration, as described by El Zrelli et al (2015) and Kouali et al (2022). The classes of pollution (unpolluted: CF < 1; slightly polluted: 1 < CF < 2; moderately polluted: 2 < CF < 3; heavily polluted: CF > 3) were determined by the classification proposed by Hakanson (1980). In November, CF values for Al, Fe, Mn, Ni, Zn, Cu, and Pb remained below 1 across all stations, signifying the lack of pollution from these elements. However, during June, Cd values exceeded 1 especially at stations S2 and S3, indicating the occurrence of minor pollution from this element. Saddik et al (2021) outlined in his work that the CF values indicated minimal contamination from Pb, Cd, Cu, Ni, and Zn. In our study during June CF values for Al, Fe, Mn, and Ni remained below 1, showing lack of contamination from these elements. However, Cu values exceeded 1 at stations S2, S3, and S7, pointing to slight pollution at these sites. Cd values surpassed 3 at points S3, S5, and S7, suggesting a notable presence of severe pollution from this element. For Pb, stations S2, S3, S4, S6, and S7 displayed values greater than 1, denoting the occurrence of mild pollution resulting from Pb. Maanan et al (2014) noted that areas with agricultural activity near Selouane Wadi exhibited the highest potential for heavy metal contamination, primarily involving Pb and Cu. Concerning Zn, CF values suggested the presence of contamination across all stations except S1. Notably, stations S5 and S6 experienced slight pollution (with CF values between 1 and 2), whereas S2, S4, and S7 exhibited moderate pollution levels (CF values between 2 and 3). In contrast, station S3 displayed a significant level of pollution (CF greater than 3) with respect to Zn. This pattern of Cd contamination finds similarity in an industrial zone located in El-Jadida along the Atlantic coast, as reported by Kouali et al (2022).

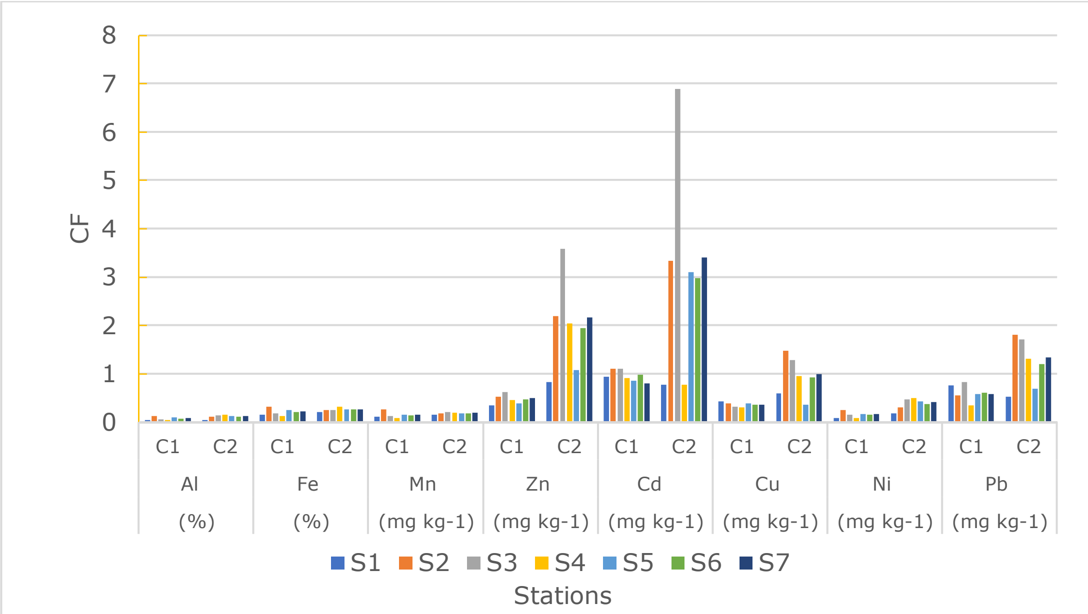

Figure 8. Variation in contamination factor (CF) values across the stations studied (C1: November, C2: June).

The geoaccumulation index was calculed using the method proposed by Muller (1979), the interpretation and classification (Igeo < 0: not polluted; 0 < Igeo < 1: not polluted to moderately polluted; 1 < Igeo < 2: moderately polluted; 2 < Igeo < 3: moderately to heavily polluted; 3 < Igeo < 4: heavily polluted; 4 < Igeo < 5: heavily to extremely polluted; Igeo > 5: extremely polluted) was based on the suggestions given by Gonzales et al (2007), Harikumar et al (2010), Maanan et al (2021) and Chahouri et al (2023).

Table 4 presents the spatio-temporal variation in the geoacumulation index (Igeo).

Table 4

Geoaccumulation index (Igeo) values across the monitored stations

			S1	*S2*	*S3*	*S4*	*S5*	*S6*	*S7*
Geoaccumulation index (Igeo)	Al	C1	-0.19	-0.28	-0.22	-0.2	-0.26	-0.23	-0.24
		C2	-0.2	-0.27	-0.3	-0.31	-0.28	-0.27	-0.29
	Fe	C1	-0.3	-0.43	-0.32	-0.27	-0.36	-0.33	-0.34
		C2	-0.33	-0.37	-0.37	-0.42	-0.38	-0.37	-0.38
	Mn	C1	-0.27	-0.39	-0.28	-0.24	-0.3	-0.3	-0.3
		C2	-0.3	-0.33	-0.35	-0.35	-0.33	-0.33	-0.34
	Zn	C1	-0.47	-0.66	-0.8	-0.59	-0.51	-0.6	-0.63
		C2	-1.2	1.8	0.79	2.2	-2.12	2.61	1.86
	Cd	C1	-1.39	-2.06	-2	-1.3	-1.16	-1.49	-1.04
		C2	-1	0.91	0.47	-1	1	1.07	0.88
	Cu	C1	-0.55	-0.52	-0.45	-0.44	-0.52	-0.49	-0.48
		C2	-0.75	-36.04	-4.42	-1.52	-0.48	-1.46	-1.69
	Ni	C1	-0.25	-0.39	-0.3	-0.25	-0.32	-0.3	-0.31
		C2	-0.33	-0.44	-0.59	-0.63	-0.55	-0.5	-0.54
	Pb	C1	-1.03	-0.7	-1.16	-0.47	-0.73	-0.78	-0.74
		C2	-0.67	3.67	5.25	-5.17	-0.89	-3.18	-6.19

Igeo < 0: not polluted; 0 < Igeo < 1: not polluted to moderately polluted; 1 < Igeo < 2: moderately polluted; 2 < Igeo < 3: moderately to heavily polluted; 3 < Igeo < 4: heavily polluted; 4 < Igeo < 5: heavily to extremely polluted; Igeo > 5: extremely polluted. C1: November; C2: June.

In November, Igeo values for all elements at all stations were below 0, suggesting the absence of contamination during this period. The absence of Cu, Pb and Cd contamination was noted at the mouth of Oued Souss assessed by Igeo (Chahouri et al 2023). Likewise, in June, Igeo values for Fe, Mn, Al, Ni and Cu were below 0 at all stations, indicating the absence of pollution by these elements. Elsewhere (Guendouzi et al 2021) found an identical result (absence of contamination) for Cu, Mn and Al. The findings revealed that Pb values were below 0 at all stations during June, except for stations S2 and S3. These two stations exhibited notably elevated values (3.67 and 5.25, respectively), pointing towards heavy pollution at station S2 and an even more severe state of pollution at station S3 with respect to Pb contamination. In terms of Cd, the Igeo ranged from 0.47 to 1.07 during June at stations S2, S3, S5, S6, and S7. This range indicates that the sediment at these stations range from unpolluted to slightly polluted regarding Cd contamination. With regard to Zn, station S6 recorded a maximum value (2.61), showing that the sediments are moderately to heavily contaminated with this element. The observed result can be explained by the fact that station S6 is located in the agricultural zone of Bouarg which subsequently leads to the application of fertilizers containing a notable amount of zinc (El Hajjami et al 2021).

Table 5 presents a comparison between the obtained results and the sediment quality guidelines (SQGs) using the threshold effect level (TEL).

Table 5

Comparison with sediment quality guidelines (SQGs)

		TEL (mg kg^{-1})				
	Station	*Zn*	*Cd*	*Cu*	*Ni*	*Pb*
C1	S1	+	+	+	+	+
	S2	+	+	+	+	+
	S3	+	+	+	+	+
	S4	+	+	+	+	+
	S5	+	+	+	+	+
	S6	+	+	+	+	+
	S7	+	+	+	+	+
C2	S1	+	+	+	+	+
	S2	-	+	-	+	+
	S3	-	-	-	-	+
	S4	-	+	+	-	+
	S5	+	+	+	-	+
	S6	-	+	+	+	+
	S7	-	+	+	-	+

TEL = the concentration below which adverse effects are expected to occur only rarely. C1: November; C2: June.

During November, the results recorded the absence of effect from all the elements studied on the majority of living organisms across the stations investigated. Furthermore, our research findings indicate the absence of significant impacts from Pb during June across all stations. Moreover, no notable effects were observed from Cu and Cd at stations S1, S4, S5, S6, and S7. Similarly, there were no discernible effects of Ni at stations S1, S2, and S6, and the absence of impacts from Zn was noted at stations S1 and S5. To summarize, station S3, identified as the most exposed, experienced adverse effects attributed to Zn, Cu, Cd, and Ni. A high ecological risk for benthic organisms due to metals, mainly Cd and Ni, has been observed in the Bizerte Lagoon in Tunisia (Ben Mna et al 2022).

The indices used, namely EF, CF and Igeo, and the comparison of the results with the SQGs based on TEL, revealed a degree of pollution caused mainly by Zn, Cd and Pb, at station S3. These findings can be explained by the fact that S3 is located downstream of the industrial zone that contains the majority of industrial units (the mining industry) and by the discharge of poorly treated wastewater (Bloundi et al 2009). In 2017, an ecotoxicological risk assessment of trace elements using PI and SQG showed contamination of the Marchica watershed by Pb, Zn and Cu (Oujidi et al 2020). In addition, results from the Marchica lagoon showed the impact of the watershed, particularly in the contribution of sediments rich in trace elements, notably Mn, Ni, Cr, Pb, Zn, Cu and Cd (Gonzalez et al 2007; Maanan et al 2021). Earlier, Afgane et al (2021) presented results revealing Pb pollution in the Larbaa basin.

Pearson correlation factors (Table 6) showed strongly negative correlations between DO/COD, which is in agreement with the results of Makhoukh et al (2011). However, the correlations were positively significant ($p < 0.05$) between pH/SS as already found by Reggam et al (2015), and between COD/NO_3^- in accordance with the results of Moussa et al (2012).

Table 6

Pearson correlation coefficients between physicochemical parameters

		pH	*DO*	*EC*	*SS*	*COD*	*NO_3^-*
pH	Pearson correlation	1					
DO		-0.118	1				
EC		0.282	0.062	1			
SS		0.471*	-0.11	0.241	1		
COD		0.25	-0.723**	0.075	0.369	1	
NO_3^-		0.053	-0.322	0.15	-0.117	0.390*	1

** correlation is significant at the 0.01 level; * correlation is significant at the 0.05 level.

Pearson correlation results (Table 7) between metals showed strongly positive correlations with values above 0.7 between Al/Ni, Al/Fe, Al/Mn, Al/Zn, Fe/Mn, Fe/Ni, Mn/Ni, Zn/Cu, Zn/Pb, Zn/Ni,Cu/Pb,Cd/Zn, Pb/Cd, Cd/Cu, Cu/Ni, and Ni/Pb which indicates that they may be derived from anthropogenic activities (industrial or urban). Earlier, highly significant positive correlations were observed between Cd/Cu, Cd/Zn, Pb/Cu, Pb/Zn and Pb/Cd in Oued Sebou (El Hajjami et al 2021). The correlation between Cd, Zn and Pb may suggest that they have the same origin (anthropogenic origins) (Ech-Charef et al 2023).

Table 7

Pearson correlation coefficients for heavy metals

		Al	*Fe*	*Mn*	*Zn*	*Cd*	*Cu*	*Ni*	*Pb*
Al	Pearson correlation	1							
Fe		0.887**	1						
Mn		0.824**	0.945**	1					
Zn		0.704**	0.46	0.51	1				
Cd		0.571*	0.281	0.419	0.866**	1			
Cu		0.586*	0.434	0.463	0.906**	0.706**	1		
Ni		0.911**	0.757**	0.717**	0.829**	0.661*	0.673**	1	
Pb		0.642*	0.439	0.455	0.909**	0.741**	0.954**	0.704**	1

** correlation is significant at the 0.01 level (2-tailed); * correlation is significant at the 0.05 level (2-tailed).

Bloundi et al (2009) obtained results indicating high correlation coefficients between Pb, Zn, Cu and Fe in Marchica lagoon sediments, while there was no correlation with Al level. The results presented by Gonzales et al (2007) indicated elevated levels of Al, Fe, Co, Mn, Cu, Zn, Cd, and Pb in the agricultural lands surrounding Oued Selouane. As a consequence, it is likely that these elements are discharged through erosion processes and subsequently become deposited within the wadi sediments (Johansson et al 1995). Thus a significant correlation between the heavy metals concentration including Ni, Pb and Cd, suggests that these elements could have the same source (Maanan et al 2015).

The ANOVA test for metal concentration showed that the level of Al, Zn, Cd, Cu, Ni, and Pb varied significantly between seasons ($p < 0.05$), while Fe and Mn were unaffected by seasonality ($p > 0.05$). Kouali et al (2022) indicate that trace metal pollution was highly seasonal.

Conclusions. This study has illustrated the presence of an anthropogenic impact (primarily organic in nature). This is evident from the observed elevation in pollution indicator parameters, combined with the decreased levels of factors favoring the development of aquatic ecosystems, such as temperature and dissolved oxygen. Notably, the presence or absence of benthic macroinvertebrates serves as a crucial biological indicator for assessing the health of running-water aquatic ecosystems. Cases of reduced macroinvertebrate diversity and the prevalence of pollution-tolerant species like Chironomidae are indicative of pollution presence and habitat degradation. Across the majority of monitoring sites, low abundance and diversity were observed. The findings revealed a moderate ecological status for the upstream locations, in contrast to a poor status for the downstream sites. Additionally, the evaluation of metal contamination unveiled anthropogenic-driven pollution, primarily from Cd, Zn, and Pb. This contamination was particularly pronounced at station S3, situated downstream from the industrial zone. These results clearly show the necessity for immediate actions aimed at enhancing, preventing, and conserving this vulnerable aquatic ecosystem, which significantly and directly impacts the Marchica lagoon.

Confict of interest. The authors declare that they have no conflict of interest.

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