



Efficiency of Fez WWTP: multi-parameter evaluation of water and sediment quality

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Received: 14 December 2020 / Accepted: 12 July 2021 / Published online: 6 August 2021
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Abstract In order to assess the impact of the proper functioning of wastewater treatment plants (WWTPs) and sanitation networks on the quality of water and surface sediments of the Oued Fez River and its tributaries, and ultimately their outlet in the Sebou River, physico-chemical, geochemical and mineralogical analyses were performed. The components were studied in high- and low-water regimes at eight sites. Seven heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn) were investigated in the sediments, with a decreasing trend being identified as $Zn > Cu > Pb > Cr > As > Ni > Cd$, and a mobility sequence as $Cu > Pb > Zn > Ni > Cr$. A comparison of the total heavy metal concentrations in the Oued Fez and Sebou River sediments with those of previous studies indicated a reduction in the harmful and polluting contribution of the Oued Fez to the Sebou River. The heavy metal assessment was achieved using environmental indices and sediment quality guidelines. The obtained results indicate that the presence of heavy metals in the sediment mainly comes from anthropogenic activities. Based on these results and their comparison with those from previous studies, the contribution of WWTPs and sanitation networks to improving the water quality of the middle Sebou River is clearly noteworthy.

Keywords Heavy metal contamination · Pollution indices · Surface sediment · WWTP · Oued Fez · Sebou River · Morocco

Introduction

Heavy metals are a primary environmental concern because of their toxicity and accumulation behaviour (Islam et al., 2015; Martin et al., 2015). Especially in the riverine system, heavy metal concentrations can effortlessly be increased by anthropogenic activities (Sánchez-Chardi et al., 2007). Sediment constitutes one of the main sinks for heavy metals released into the environment (Bettinetti et al., 2003; Hollert et al., 2003). In the riverine system, sediments have a high potential for storing contaminants. In the hydrological cycle, less than 0.1% of metals are dissolved in the water, while more than 99.9% accumulate in the sediments (Karbassi et al., 2007; Pradit et al., 2009). Moreover, the metals act as carriers and potential sources of pollution by not being permanently fixed by the sediments, and can be discharged back into the water through environmental changes and conditions. As a result, such waters can become sufficiently polluted to affect biological communities (Toluna et al., 2001; Venugopal et al., 2009).

In Morocco, as in many developing countries and over many decades, untreated wastewater has been discharged into neighbouring riverine ecosystems, giving rise to environmental challenges.

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Furthermore, in recent years, human, industrial and agricultural water demands have been increasing, and repeated periods of drought in Morocco have sensitised decision-makers into considering wastewater as an important water resource, which has directed a need to envisage a national programme for wastewater treatment. Numerous water-treatment plants have been built, including the wastewater treatment plant (WWTP) at Fez.

Since 2014, this WWTP, located 5 km downstream of Fez city, has treated all of the city's sewage, which had previously been flushed directly into the natural watercourses. Nevertheless, for several decades previously, the untreated domestic and industrial wastewater produced by the city of Fez had led to seriously high pollution in the Oued Fez and Sebou Rivers. Various studies have been carried out on the physico-chemical and biological properties of the water and sediments in these rivers (Azzaoui et al., 2002; Koukal et al., 2004; Dominik et al., 2007; Derwich et al., 2008; Hayzoun et al., 2014; Perrin et al., 2014; Hayzoun et al., 2015; Hassimi et al., 2016), with most of them having detected surface water contamination. The situation arose due to the demographic growth and acceleration of progress in the vital social and economic sectors of agriculture and industry in Fez (Hayzoun et al., 2015).

For a long time, the Oued Fez and its tributaries had been receiving untreated wastewater from the city of Fez, making it a source of pollution for the Sebou River, located at the exit from the city. In 2014, the first WWTP was built in Fez, with the aim of treating domestic and industrial wastewater before discharging it into the Sebou River. To achieve this, a great deal of effort was made to improve the conditions of the sewage network, and connect this to the new WWTP. The aim of this study was, thus, to assess the impact of the proper functioning of the WWTP and linked sanitation networks on the water and surface sediment quality of the Oued Fez and its tributaries, and ultimately on their outflow via the Sebou River. To achieve this, precise objectives have been set: (1) to evaluate the physico-chemical, geochemical and mineralogical parameters of the water and sediments of the Oued Fez and its tributaries and the Sebou River; (2) to estimate the total concentration of heavy metals and evaluate their mobility using ethylenediaminetetraacetic acid (EDTA); and (3) to assess the pollution levels and the ecological risk of these

river sediments, using pollution indexes and sediment quality guidelines (SQGs).

Materials and methods

Study area

Located in northern central Morocco, the city of Fez is the third largest city by demographic weight, exceeding 1,115,581 inhabitants (Wunderlin et al., 2001). It produces an annual volume of wastewater of up to 38 million m³. Before the implementation of the Fez WWTP in 2014, the wastewater of the city was discharged directly in the Oued Fez and Sebou Rivers without any treatment. Currently, the station has a treatment capacity of 130,000 m³/day and 72 tons of biochemical oxygen demand (BOD₅) per day, resulting in a considerable reduction (> 85%) of the pollution generated by the city (Yahyi, 2010).

The *Sebou River* is one of Morocco's largest rivers, draining approximately 40,000 km². It is situated in northwestern Morocco, between 33–35° N and 4° 15'–6° 35' W. It traverses 600 km from its source in the mountains of the Middle Atlas to the Atlantic Ocean (United Nations Environment Programme, 2005). This river plays an integral role in supplying its watershed area with water for drinking, irrigation and industrial use (Idriss, 2018). The *Oued Fez*, a tributary of the Sebou River, is the main water body of the city. The river streams eastwards from its source at Ras el Ma, crossing the medina of Fez. It flows into the Sebou River 4 km downstream of Fez, and has a catchment area of 615 km² (Lombard-Latune, 2010). The Oued Fez receives several tributaries all along the way to the Sebou River, with the major ones being the Mahraz and Boufekrane, which are characterised by their seasonal to intermittent flows.

A semi-arid continental climate prevails in the Fez region, characterised by hot, dry summers and cold, wet winters. The pedological cover is dominated by calcimagnesian, vertisol and alluvial soils, which overly various sedimentary deposits, including limestones, marls and alluvial materials (Bellarbi, 2015).

Water and sediment sampling

From the upstream to downstream in Fez city (Fig. 1), eight sampling sites were selected along the Oued

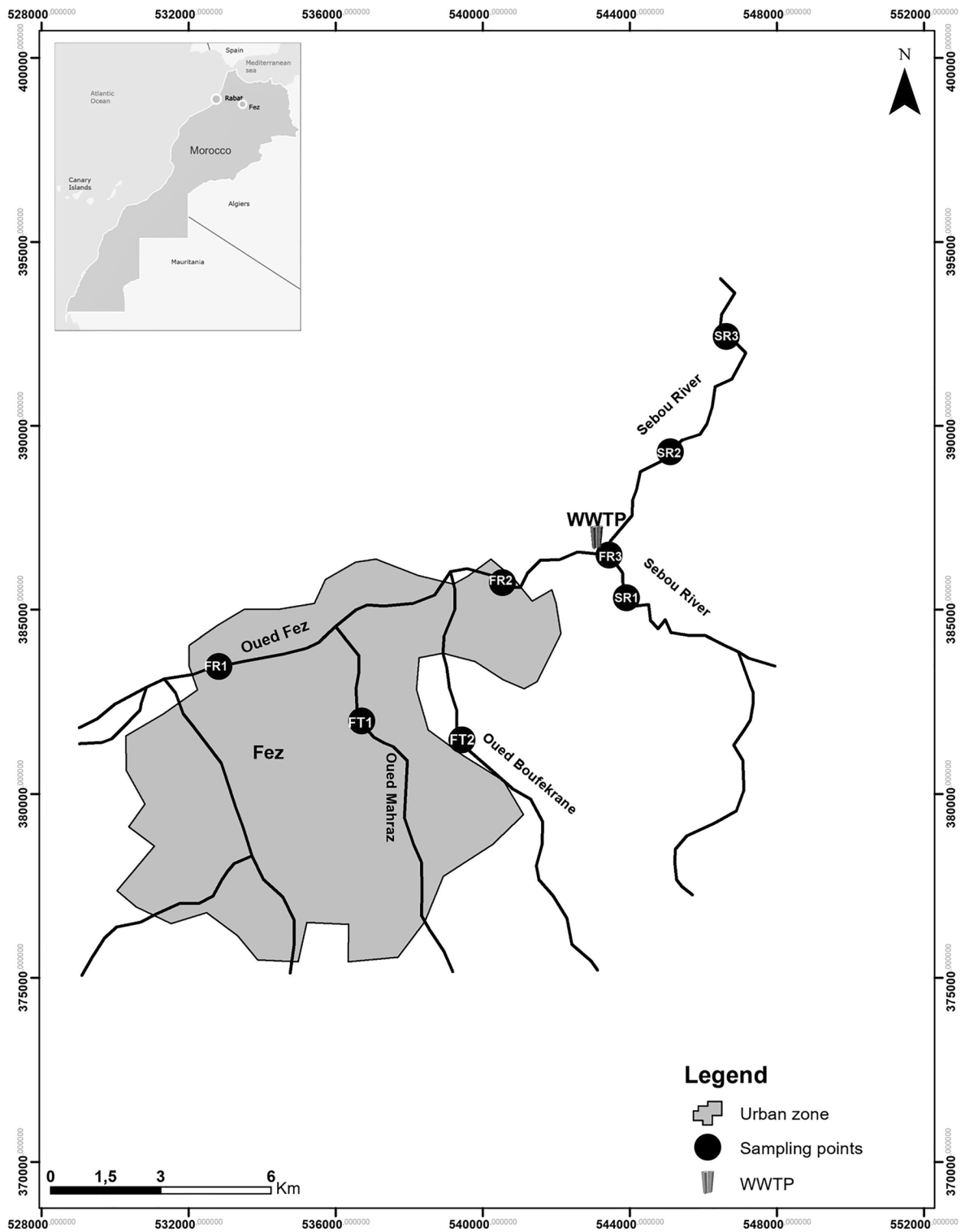


Fig. 1 Sample location sites in Fez and Sebou Rivers

Fez FR1 (upstream), FR2 (urban catchment output), FR3 (Oued Fez–Sebou river confluence) and its tributaries (FT1, FT2) and the Sebou SR1 (upstream), SR2 (downstream, 4 km from the confluence) and SR3 (downstream, 10 km from the confluence).

Two sampling campaigns were carried out, in March 2016 and September 2017 (respectively, during high- and low-water regimes). The sediment and water samples were collected according to a river sampling guide (The Loire Brittany Water Agency (2016). Technical guide of river samplin).

Sampling was performed on the river banks, using a plastic scoop to collect the surface sediments (0–10 cm). The samples were then stored in clean polyethylene bags before being transported to the laboratory, where they were disaggregated, hand-mixed and air-dried at room temperature (20–22 °C).

Treatment and analysis procedures

Water analysis

Measurements of the physico-chemical parameters of the water were undertaken at each of the eight stations in order to determine the water quality, using probes attached to a multi-parameter Hach Lange HQ40d metre. Temperature (T°C), pH (EC) and dissolved oxygen (DO) were recorded. Other parameters—suspended matter (SM) and nutrients (nitrates, total phosphorus and ammonium—were analysed in the laboratories of the Regie Autonome Intercommunale de Distribution d'Eau et d'Electricité de Fes (the Fez water and electricity management authority).

Sediment analysis

The physico-chemical measurements were taken in accordance with sediment quality standards, and on triplicate subsamples.

Samples for the analyses followed preparation standard NF ISO 11–164 in order to obtain representative results. This process included drying the samples in an oven at 105 °C, quartering them for homogenisation, and selecting representative samples. The samples were also sieved to remove large fragments, while the <2-mm fraction was retained, this being the most reactive sediment fraction. Finally, the samples were ground to obtain a fine powder in order to promote the dissolution of the elements being analysed.

A series of standard physico-chemical analyses were undertaken, including obtaining the humidity content (ISO 11,465), pH (NF ISO 10,390), EC (NF ISO 11,265), organic matter (OM) content (NF EN 12,879) and volumetric calcimetry (NF ISO 10,693).

The mineralogical contents of the bulk and clay fractions were analysed by X-ray diffraction (XRD, PANalytical Xpert Pro). Disoriented slides were prepared, and dried in an oven at 55 °C overnight. The clay fraction was suspended by ultrasonic disaggregation in distilled water. This suspended component was separated into three steps, using a centrifuge at 300, 500 and then 3500 rpm for 3, 5 and 30 min, respectively. Oriented slides were prepared in three ways for XRD analysis—by air-drying, heating for 4 h at 490 °C, and being saturated with ethylene glycol. The XRD scans covered the 2 θ range of 4.00–59.98° over a scan step time of 59.69 s. The clay minerals were semi-quantified based on the intensity of the XRD peaks.

The heavy metal content and their mobility were determined by standard triacid attack digestion (NF ISO 14,869–3) and the addition of a complexing agent (EDTA) (Nowack et al., 2001) to the samples. Both components were analysed by inductively coupled plasma-atomic emission spectrometry (Thermo Scientific iCAP 6500). The heavy metal measurements were performed in triplicate, and blank control samples were also run.

Pollution indices

The use of pollution indices is an approach that allows the assessment of the level of sediment pollution and the risk associated with any metallic pollutants present in it. These indices are generally based on the results of studies that combined metal contamination with organismal responses (Duoduo et al., 2016). In the present study, the enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF), contamination degree (CD), modified contamination degree (mCD) and pollution load index (PLI) were used to evaluate the intensity of heavy metal pollution in the sediments.

Enrichment factor

Due to the lack of any geochemical background data concerning trace elements in the region, and knowing

that geochemical background is defined as the level of heavy metals that are not under the direct influence of human activities (Salminen & Gregorauskiene, 2000). Site FR1, located in the upstream part of Oued Fez (Fig. 1), was used as a local background geochemical reference due to its remoteness from any anthropogenic activity comparatively to the others studied sites. Aluminium (Al) was used as the reference element for geochemical normalisation, with C_n being the metallic concentration of element n , as expressed in the EF equation:

$$EF = \frac{\left(\frac{C_n}{Al}\right)_{\text{sediment}}}{\left(\frac{C_n}{Al}\right)_{\text{reference}}}$$

where the EF index of the sediment is indicated by a range of seven classes, as suggested by Sakan et al. (2009), from $EF < 1$ (no enrichment) to $EF > 50$ (extremely severe enrichment).

Geo-accumulation index

The I_{geo} was defined by Müller (1971). This empirical index compares the metal n concentration (C_n) in the sediments with the geological background and a coefficient factor of 1.5 (F_g), which takes into consideration variations in geochemical background levels that can be caused by lithological effects. This index is defined as:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 * F_g}\right)$$

Seven I_{geo} classes, ranging from 0 ($I_{geo} \leq 0$, unpolluted) to 7 ($I_{geo} > 5$, very severely polluted), have been defined.

Contamination factor

The CF is the ratio obtained by dividing the concentration of each metal (C_n) in the sediment by the background value (Håkanson, 1980):

$$CF = \frac{C_n}{C_n\text{Background}}$$

To evaluate the degree of sediment contamination, Håkanson (1980) proposed four levels of

classification, with $CF < 1$ indicating low contamination and $CF > 6$ indicating very high contamination.

Contamination degree (CD) and modified contamination degree (mCD)

The CD is the sum of the CF for each sample:

$$CD = \sum_{n=1}^{i=n} CF$$

Regarding the CD, Håkanson (1980) suggested four classes, with $CD < 6$ indicating low contamination and $CD > 24$ indicating high contamination and serious anthropogenic pollution.

The mCD is the ratio obtained by dividing the CD by the number of elements analysed for (Abraham et al., 2005):

$$mCD = \frac{\sum_{n=1}^{i=n} CF}{n}$$

To classify and describe the mCD in sediments, Abraham et al. (2005) proposed seven classes, from $mCD < 1.5$ (very low) to $mCD > 32$ (ultra-high).

Pollution load index (PLI)

The PLI corresponds to multiplying the CF_n^{th} root by n metals (Tomlinson et al., 1980):

$$PLI = \sqrt[n]{CF_1 * CF_2 * \dots * CF_n}$$

$PLI < 1$ indicates perfection, $PLI = 1$ indicates that only background levels of pollutants are present and $PLI > 1$ indicates a deterioration in the quality of the site.

Sediment pollution assessment using sediment quality guidelines

SQGs provide a basis for the interpretation of sediment chemistry, by identifying potential concentrations of substances that may contribute significantly to harmful effects on sediment-dwelling organisms (MacDonald et al., 2000). Although such SQGs can provide valuable tools for determining the concentrations of individual heavy metals exceeding acute or chronic toxicity thresholds, they can also determine the extent of sediment pollution associated with a particular heavy metal by comparing the concentration

of the metal detected in the sediment with that of correlative references (MacDonald et al., 2000; Long et al., 2006).

To assess the ecotoxicology of the heavy metals in the sediments, and the sediment quality conditions, the following SQGs were used: the probable effect level (PEL); the threshold effect level (TEL); the threshold effect concentration (TEC); and the probable effect concentration (PEC) (MacDonald et al., 2000).

Data analysis

Principal component analysis (PCA) is a statistical multivariate analysis technique that can be used to investigate the variability of data (Benson et al., 2018). It is commonly used for environmental data, where the database is difficult to interpret, and complex interrelationships among variables are not obviously identifiable or visualisable (Syms et al., 2008; Reid et al., 2009).

Here, statistical analysis of the physico-chemical data was carried out on a data matrix consisting of seven variables and 48 samples. These were distributed along eight transects through Oued Fez and Sebou.

The statistical software XLSTAT was used for data processing and creating the correlation matrix for examining their different sources and associations.

Results and discussion

Physico-chemical properties of the water

The physico-chemical parameters of the water (pH, DO, EC, SM, ISM, OSM) and the total phosphorus, nitrates and ammonium of the present study and a previous one performed in the region (Perrin et al., 2014) are shown in Table 1. A comparative analysis between these current and prior data allowed the impact of the WWTP implementation and sanitation networks on the water quality of the Oued Fez and Sebou Rivers to be determined. The water quality status was classified using Moroccan grids for surface and irrigation water quality (Society of Environmental and Ecological Engineers [SEEE] 2007).

As described in previous studies (Hayzoun et al., 2014; Koukal et al., 2004; Perrin et al., 2014),

the Oued Fez and Sebou Rivers are characterised by an alkaline pH that was found in our study to vary slightly between 7.66 and 8.40. According to the Moroccan surface and irrigation water quality standards, this indicates good to excellent quality (SEEE, 2007). The mean DO values ranged between 12 and 63.60%. The EC was relatively high, with the values ranging between 904.50 and 1730.50 $\mu\text{S}/\text{cm}$. Compared to previous studies, the EC values were similar, except for the confluence site (FR3), where a decrease in EC was noted, compared to the highest level recorded during previous work (Bellarbi et al., 2015). As with the DO saturation, the current EC has changed for the better between the WWTP input site (FR2) and the confluence site (FR3). Because the previous study showed an opposite trend (Perrin et al., 2014), this may indicate that the WWTP is working properly. Concerning the SM, the mean values ranged between 44.30 and 324.67 mg/L, with an obvious predominance of the organic phase in the urban watercourses (>80%). Along Oued Fez, the predominantly organic SM load increased from the upstream (FR1) to the downstream (FR2) site. This urban watershed collects all the discharge flow from the city, including stormwater, runoff and wastewater, all carrying SM.

Regarding the nutrient components, their concentrations were mostly low. The nitrate, ammonium and total phosphorus concentrations ranged between 1 and 4.2 mg/L, 0.13 and 0.40 mg/L and 0.05 and 0.25 mg/L, respectively (Table 1).

The results of nutrient analyses allowed us to classify the quality of the waters of Oued Fez and Sebou as excellent to good. Prior to the installation of the WWTP, the total nitrogen and total phosphorus measurements were highest in the reaches under the influence of wastewater discharge (FT2, FR2 and FR3) compared to the others sites (Perrin et al., 2014). Currently, except for the site located at the Oued Fez–Sebou River confluence (FR3), the urban area sites (FR1, FT1, FT2 and FR2) along the Oued Fez and its tributaries have nitrate, ammonium and total phosphorus concentrations that are very low. This obvious decrease in nutrient content along the Oued Fez is most likely due to the efficiency of the wastewater and stormwater networks and the Fez WWTP.

Table 1 Water quality of Oued Fez and Sebou river

Water quality										
Samples	pH	DO (%)	EC (us/cm)	SM (mg/L)	ISM (%)	OSM (%)	Nitrate (mg/L)	Total phosphorus (mg/L)	Ammonium (mg/L)	
Present study										
FR1	7.66	12.00	904.50	44.33	18.05	81.95	1.10	0.07	0.15	
FT1	7.95	38.10	1320.50	98.67	10.81	89.19	1.50	0.08	0.18	
FT2	7.97	40.30	1215.00	173.33	19.81	80.19	1.30	0.09	0.16	
FR2	7.68	13.60	1480.50	324.67	19.92	80.08	1.00	0.05	0.13	
SR1	8.05	63.60	1225.50	232.00	12.50	87.50	1.10	0.06	0.14	
FR3	8.40	59.40	1279.00	219.33	17.93	82.07	4.20	0.25	0.40	
SR2	7.95	26.00	1512.50	150.08	58.64	41.36	3.00	0.14	0.32	
SR3	7.89	20.40	1730.50	138.33	61.45	38.55	1.40	0.06	0.22	
Perrin et al., 2014										
FR1	7.97	68.00	803.00	-	-	-	2.40	0.20	0.10	
FT1	8.18	97.00	965.00	-	-	-	2.70	0.60	0.10	
FT2	7.99	57.00	1502.00	-	-	-	3.50	4.60	23.10	
FR2	7.97	80.00	1727.00	-	-	-	2.50	5.20	18.30	
SR1	8.2	98.00	1062.00	-	-	-	2.30	0.20	0.00	
FR3	7.7	14.00	1851.00	-	-	-	1.50	4.30	17.20	
SR2	7.86	39.00	1436.00	-	-	-	1.20	2.70	10.10	
SR3	7.74	19.00	1232.00	-	-	-	1.10	1.80	8.40	
Moroccan surface water guidelines (S.E.E, 2007)	6.5–8.5	> 84.72	100–750				< 10.0	< 0.1	< 0.1	
Good	6.5–8.5	84.72–60.52	750–1300				10.0–25.0	0.1–0.3	0.1–0.5	
Moderately polluted	6.5–9.2	60.52–36.31	1300–2700				25.0–50.0	0.3–0.5	0.5–2.0	
Polluted	< 6.5–> 9.2	36.31–12.1	2700–3000				> 50.0	0.5–3.0	2.0–8.0	
Highly polluted		< 12.1	> 3000					> 3.0	> 8.0	
Irrigation water quality standards (S.E.E, 2007)	6.5–8.4		12,000.00	100–200			30.00			

EC electrical conductivity, DO dissolved oxygen, SM suspended matter, ISM inorganic suspended matter, OSM organic suspended matter

Mineralogical characteristics of the sediment

The river mineral content comprises an assemblage of different types of particles, reflecting the rock types and weathering conditions of the source areas. Two watersheds were distinguished in the study area, characterised by the lithological formations present, as described below:

- In the catchment area of the Oued Fez, as determined by Dridri et al. (2001) and Lasri (2015):
 - Yellowish sandy marls of the Miocene, located in the slopes overhanging the valley of the upstream Oued Fez;
 - Lacustrine limestones of the Pliocene, occurring in the western part of the Saï's of Fez;
 - Red tuffs and silts, largely covering the northern bank of the Oued Fez;
 - Travertines, located at the Medina of Fez and its borders; and
 - Massive limestones and white marls, situated at the summits of the Jbels Tghat and Zalagh.
- The Sebou River obtains its lithological signature from drainage from the Middle Atlas. Thus, the materials that feed its waters have a geological origin dominated by Liassic carbonate formations.

The XRD analysis showed that the crystalline phases of the samples were dominated by calcite and quartz, with percentages varying from 55–70% and 10–30%, respectively, and with dolomite at 10–15% and clay at 5–15% (Fig. 2).

Secondary minerals, especially clays derived from the primary minerals in the bedrock, are considered to be the main mineralogical constituents that contribute to metal pollutant adsorption. Clays possess several physico-chemical properties that commonly give them a high capacity for adsorption due to their large specific surfaces, high cation exchange capacity and ability to adsorb heavy metals in their interfoliar spaces (Bentahar, 2016). Considering their different structures, smectite has the highest absorption power, then illite, chlorite and, finally, kaolinite.

The mineralogical compositions of the fine fractions of the sediments from both rivers are comparable, since the clayey fraction is dominated by

four clay minerals (Fig. 3): illite (20–50%), smectite (10–45%), kaolinite (10–30%) and chlorite (10–30%). The distribution of clays in the two watersheds is almost identical, suggesting that heavy metal retention is not related to the clay fraction of the sediments, but rather to the other components.

Physico-chemical characteristics of the sediment

As shown in Table 2, the pH values, ranging between 7.47 and 8.22, are mostly alkaline, probably due to the carbonate lithology that prevails in the Oued Fez and Sebou River watersheds. In fact, the sediments studied are rich in carbonates, ranging from 26.7 to 90%, with a maximum concentration in Oued Fez effluent of 90%, mainly associated with landfill leachates and industrial activity, such as bone processing and paper recycling (Hammes et al., 2003). The measured OM values varied from 0.52 to 20.48%. Several studies have examined the great variation in OM values that occurs in different freshwater sediments, such as lakes, rivers and reservoirs (Poté et al., 2008; Haller et al., 2009; Mubedi et al., 2013; Deverajan et al., 2015; Mwanammoki et al., 2015; Kayembe, 2018). They estimated that an OM range of 0.1 to 6.0% occurs in uncontaminated freshwater sediment. More than 6% is considered to be OM contamination, with OM rising to over 30% in contaminated sediments (Poté et al., 2008; Haller et al., 2011). In this study, all the river sites were found to be uncontaminated by OM, except for FT2, FR2 and FR3.

The highest EC was found in Oued Fez, with a maximum value of 257 $\mu\text{S}/\text{cm}$ at FR2, and a minimum value of 109 $\mu\text{S}/\text{cm}$ at SR1 in the upstream Sebou River.

Spatial distribution of total heavy metal content

In order to define the heavy metal contents, and determine their spatial distributions and sources in the surface sediments, the geochemical results are presented in Table 3 and Fig. 4 in the form of block diagrams, alongside the average concentrations of heavy metals in the upper continental crust (UCC) (Hans-Wedepoh, 1995), shales (Turekian et al., 1961) and French standards for quality thresholds (Order of 9 August 2006).

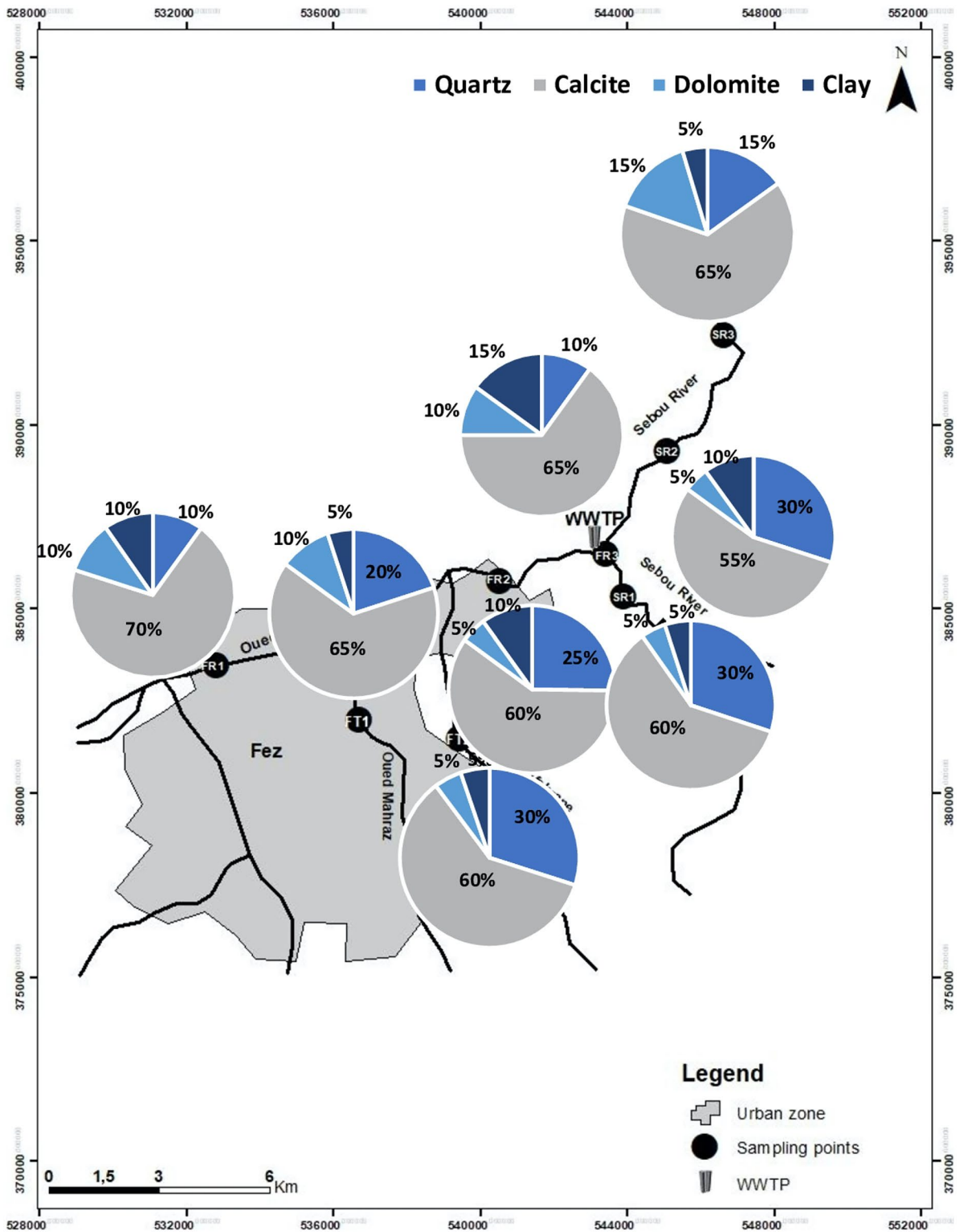


Fig. 2 Mineralogical composition (%) of studied sediments

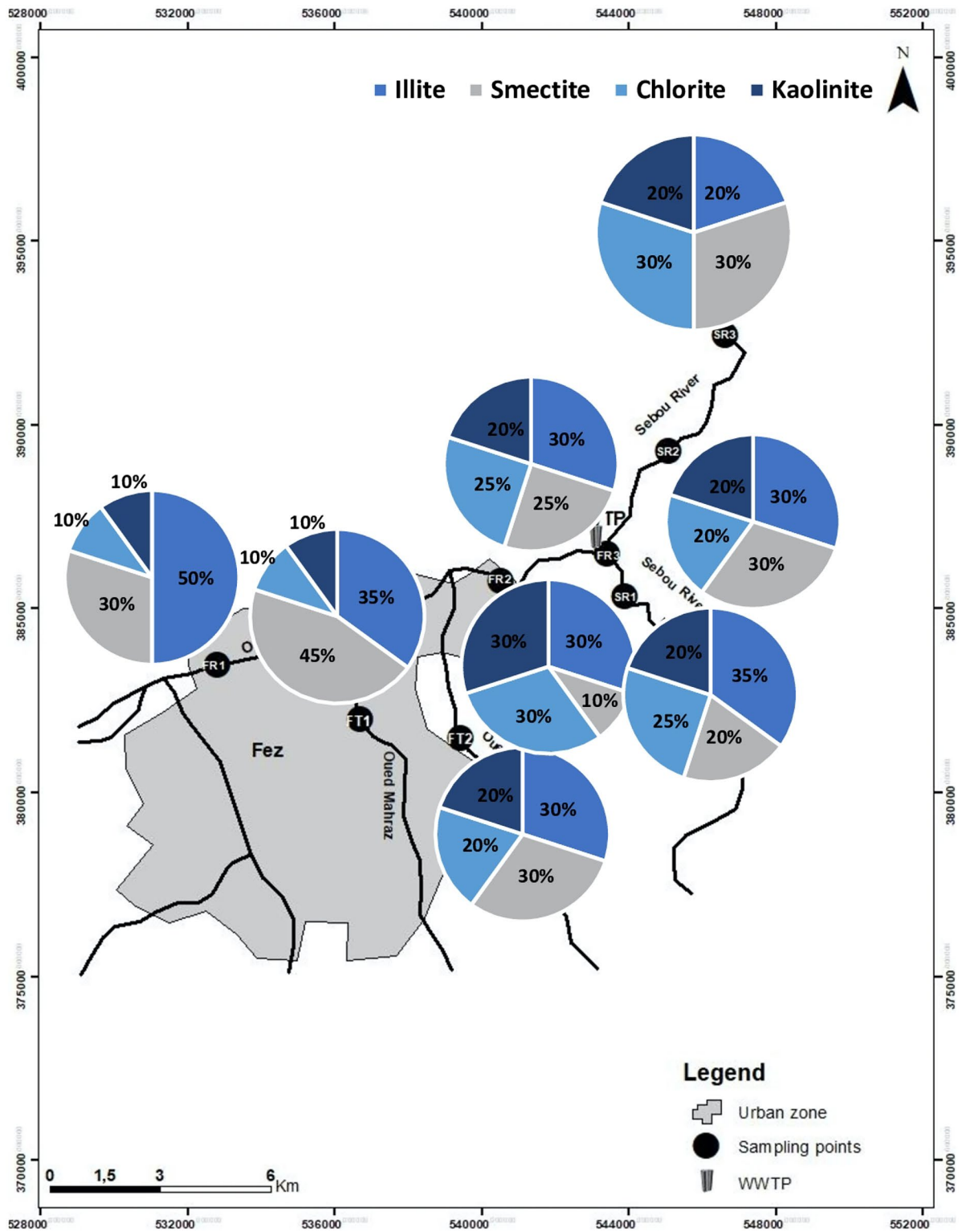


Fig. 3 Clayey composition of studied sediments

Table 2 Sediment quality of Oued Fez and Sebou river

Sediment quality						
Present study	Samples	OM (%)	EC (µs/cm)	pH	CaCO ₃ (%)	
	FR1 (N=6)	Min-max	0.71–4.98	138.00–166.20	7.47–8.17	56.70–60.00
		Avg	2.85	149.62	7.84	58.90
	FT1 (N=6)	Min-max	0.55–3.97	110.50–198.00	7.78–8.20	56.70–73.30
		Avg	2.95	141.37	7.99	66.67
	FT2 (N=6)	Min-max	5.55–8.05	118.30–136.70	7.67–8.17	26.70–46.70
		Avg	6.04	125.13	7.92	40.03
	FR2 (N=6)	Min-max	16.85–20.48	168.10–257.00	7.54–7.76	80.00–90.00
		Avg	14.84	217.10	7.66	84.43
	SR1 (N=6)	Min-max	3.44–5.75	109.30–125.70	7.80–8.22	60.00–8330
		Avg	3.48	116.12	8.03	60.00
	FR3 (N=6)	Min-max	6.33–9.82	217.00–250.00	7.68–7.78	83.30–90.00
		Avg	8.01	223.10	7.73	86.67
	SR2 (N=6)	Min-max	1.27–5.06	176.30–222.00	7.76–7.86	56.70–61.70
		Avg	3.81	196.98	7.80	58.90
	SR3 (N=6)	Min-max	0.52–2.46	147.70–247.00	7.73–7.97	53.02–57.66
		Avg	1.67	209.92	7.85	55.54

OM organic matter, EC electrical conductivity

As shown in Table 3 and Fig. 4, the metal concentrations of the sampled sediments of the Oued Fez and Sebou Rivers are as follows: As 21.68–80.72 µg/g; Cd 0.62–2.72 µg/g; Cr 2.66–469 µg/g; Cu 7.14–957.1 µg/g; Ni 4.50–65.3 µg/g; Pb 10.88–929.67 µg/g; and Zn 10.52–1251.16 µg/g.

- The total concentrations of As in the sediments of the Oued Fez and Sebou Rivers indicate enrichment in all samples. However, the As content increased from the upstream part of the Oued Fez (FR1) to the downstream (FR2), probably due to anthropogenic activities related to the city of Fez (Aktar et al., 2017; Baeyens et al., 2019). The highest concentrations were recorded at SR2 (89.36 µg/g) and SR3 (80.72 µg/g), which exceed the UCC (2 µg/g) and shale (13 µg/g) standards. These concentrations can be explained by the proximity of these locations to agricultural soils (Mateo-Sagasta et al., 2017), which, as a result of leaching, are enriching the sediments with As;
- The spatial distribution of Cd shows a similar trend to that of As, and can be explained by a common anthropogenic origin;
- High levels of Cr in sediments are frequently associated with tanneries, smelters and plating facilities (Berry et al., 2004). The Cr at Oued Fez

peaks at a maximum concentration of 469 µg/g (at FR3), with a minimum of 42.73 µg/g at FR1. The content increase from FR1 to FR3 supports the findings of previous studies, in which pollution was reported to increase from the upstream to downstream of Oued Fez (Perrin et al., 2014; Hayzoun et al., 2015; Hassimi et al., 2016);

- The Cu content in the sediments was characterised by concentrations of 7.13 µg/g at FR1 as a minimum, and 957.09 µg/g at FT1 as a maximum, the latter exceeding the standard UCC (14.30 µg/g) and shale (45 µg/g) values. This very high Cu content at FT1 supports the hypothesis of a non-agricultural, urban origin for this metal;
- The Pb concentrations are characterised by a minimum of 10.88 µg/g (at FT1) and a maximum of 929.67 µg/g (at FT2), the latter exceeding the standard UCC (17 µg/g) and shale (20 µg/g) values. As with Cu, the high Pb concentrations at FT2 appear to be partly related to the heavy road traffic. Pb used as an antiknock agent in vehicle engine fuels is released directly into the atmosphere through the exhaust pipes. This contamination is likely directly related to atmospheric deposition, or indirectly from road leaching by rainwater (Luoma & Rainbow, 2008);

Table 3 Total concentration of heavy metals in sediment of Oued Fez and Sebou river

Present Study	Samples	ETM						
		As (ug/g)	Cd (ug/g)	Cr (ug/g)	Cu (ug/g)	Ni (ug/g)	Pb (ug/g)	Zn (ug/g)
FR1 (N=6)	Min-max	21.68–40.10	0.72–1.36	23.29–57.05	7.14–78.56	10.32–28.23	10.88–34.08	25.77–75.97
	Avg	28.61	0.95	42.73	48.45	21.73	20.66	54.45
FT1 (N=6)	Min-max	46.84–46.84	1.42–1.42	27.35–207.50	160.14–957.10	15.76–35.75	76.48–929.67	90.60–632.22
	Avg	46.84	1.42	106.29	488.07	25.73	447.73	349.76
FT2 (N=6)	Min-max	22.34–27.62	0.62–0.86	2.66–197.62	14.72–136.03	4.50–40.81	14.90–56.63	16.26–271.79
	Avg	24.41	0.75	75.44	58.60	18.66	28.10	122.16
FR2 (N=6)	Min-max	66.92–79.30	2.24–2.72	14.88–268.31	38.88–210.34	8.54–39.41	28.48–91.59	132.08–428.41
	Avg	74.59	2.49	139.22	117.97	23.05	57.05	265.14
SR1 (N=6)	Min-max	41.02–67.44	1.38–2.20	31.70–76.96	9.80–482.18	8.10–30.75	112.59–222.77	10.52–819.44
	Avg	50.75	1.66	51.96	242.38	20.19	165.69	378.53
FR3 (N=6)	Min-max	23.62–46.46	0.82–1.00	153.81–469.00	21.16–350.62	26.38–65.30	199.92–269.70	80.33–1251.16
	Avg	32.59	0.91	230.01	173.52	37.17	227.85	537.64
SR2 (N=6)	Min-max	68.86–80.72	2.13–2.35	38.91–338.28	32.98–206.52	20.16–49.56	19.49–196.42	126.27–539.70
	Avg	76.60	2.24	134.47	121.68	35.47	107.24	328.85
SR3 (N=6)	Min-Max	40.48–89.36	1.52–1.89	41.37–156.52	37.23–79.40	21.50–41.78	48.07–69.69	101.63–257.86
	Avg	64.92	1.70	90.61	61.07	32.52	55.69	165.98
Local background		28.61	0.95	42.73	48.45	21.73	20.66	54.45
UCC (Wedepohl, 1995)		2.00	0.10	35.00	14.30	18.60	17.00	52.00
Shale (Turkian & Wedepohl, 1961)		13.00	0.30	90.00	45.00	68.00	20.00	95.00
Quality thresholds S1 (French standards)		30.00	2.00	150.00	100.00	50.00	100.00	300.00

- The Zn contents were very high, up to 1251.16 $\mu\text{g/g}$ at FR3, exceeding the UCC (52 $\mu\text{g/g}$) and shale (95 $\mu\text{g/g}$) values, but not at the upstream Oued Fez site (FR1). At the urban (Oued Fez and its tributaries) and rural (Sebou River) sites, the Zn contents were of the same order of magnitude (Fig. 4), which suggests different origins for the Zn. Indeed, anthropogenic activity, including municipal wastewater discharge and manufacturing processes involving metals, and atmospheric fallout are the major sources of the Zn pollution (Luoma & Rainbow, 2008), and these largely exist in the city of Fez. Soils contribute to the Zn concentrations by the

leaching of fertilisers used in agriculture (Derwich et al., 2010).

- Variations in Ni content were marked by maximum and minimum average concentrations of around 4.5 and 65.3 $\mu\text{g/g}$, these values being close to those of the UCC (18.60 $\mu\text{g/g}$) and shale (68 $\mu\text{g/g}$) standards, and thus representing expected natural concentrations for these sediments.

Except for Ni, generally, the heavy metals had concentrations that exceeded those of the shale standard, suggesting contamination by heavy metals in the surface sediments.

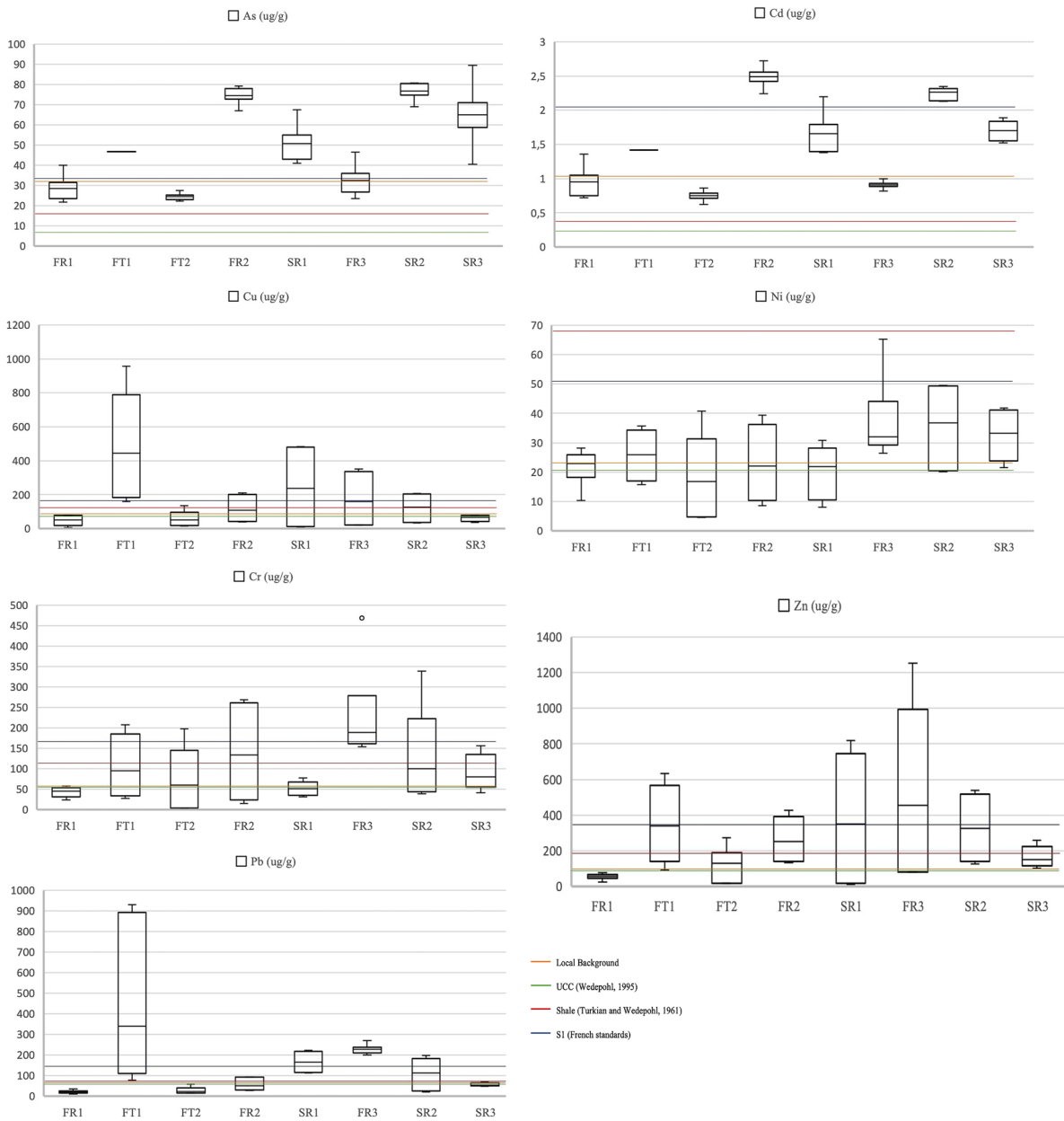


Fig. 4 The total concentration of heavy metals (As, Cd, Cr, Cu, Ni, Zn and Pb) in sediment of Oued Fez and Sebou river

In the urban areas, from the upstream to downstream of Oued Fez, the sediment pollutant load increased due to the increasing input of metals, mainly by the Oued Fez tributary (FT2). In the rural areas, from the upstream to downstream of the Sebou River, the sediment pollutant load decreased as a result of self-purification. Finally, it

is interesting to note that the FR1 site considered as local geochemical background reference exhibit the lowest values of heavy metals (Table 3).

In summary, the heavy metal contents and spatial distributions primarily reflect anthropogenic activity, such as industrial and artisanal processes, irrigation, fertilisation and the use of pesticides.

Inter-element relationships

In order to determine possible associations among the heavy metals, a Pearson correlation matrix and a PCA were carried out. Possible sources of the heavy metals were elaborated using Pearson correlation coefficients between the heavy metals measured at all the sampling sites.

Table 4 shows a significant correlation between As and Cd ($R=0.971$, $p<0.0001$), indicating that they might have similar anthropogenic sources. Cr has a significant correlation with Ni ($R=0.738$, $p<0.037$) and Zn ($R=0.735$, $p<0.038$). Pb has a significant positive correlation with Cu ($R=0.966$, $p<0.0001$). These results suggest that the sediments of the Oued Fez and Sebou Rivers received various pollutants from similar sources, or from spatially similar emission sources.

PCA was used to identify the potential sources of contamination. The results were refined by applying a varimax rotation (Fig. 5) in order to reduce the number of heavy metals that had high loadings on each factor (Zhang et al., 2018). The first major component (F1) accounted for 43.41% of the total variance, and was strongly associated with Cr, Pb and Zn, but not Cu and Ni, which had low to medium correlations. F1 had a tendency to originate from anthropogenic (industrial and artisanal) activities. F2 represented 29.50% of the total variance, and was highly loaded with As and Cd, which corroborated the Pearson correlation analysis. The coexistence of As and Cd indicates an origin from an agricultural pollution source.

Available fraction of heavy metals extracted by EDTA.

Figure 6 presents the results of the extraction of the available fraction of Cr, Cu, Ni, Pb and Zn by EDTA. This shows a moderate tendency of the metals to be mobilised, with an average

extraction of <25%. Indeed, the extraction rates of Cr (0.06–0.28%) and Ni (1.84–12.58%) were quite low, while those of Pb (0.13–27.61%), Zn (5.44–27.91%) and Cu (4.58–44.31%) were more noticeable. These results reflect that Cr and Ni were the least mobile metal, while Zn, Pb and Cu were the most mobile, the mobility sequence for all the sediments being $Cr < Ni < Zn < Pb < Cu$.

In addition, two groups of heavy metals were identified as being related by their availability behaviour: Cr and Ni, representing a group that mobilised very weakly, consequently probably being of geogenic origin, especially Ni, and Zn, Pb and Cu, representing a more easily mobilised group, and being more likely anthropogenic in origin.

Pollution indices

Table 5 illustrates the pollution index values (EF, I_{geo} , CF, CD, mCD and PLI) calculated for the heavy metals studied (As, Cd, Cr, Cu, Ni, Pb and Zn).

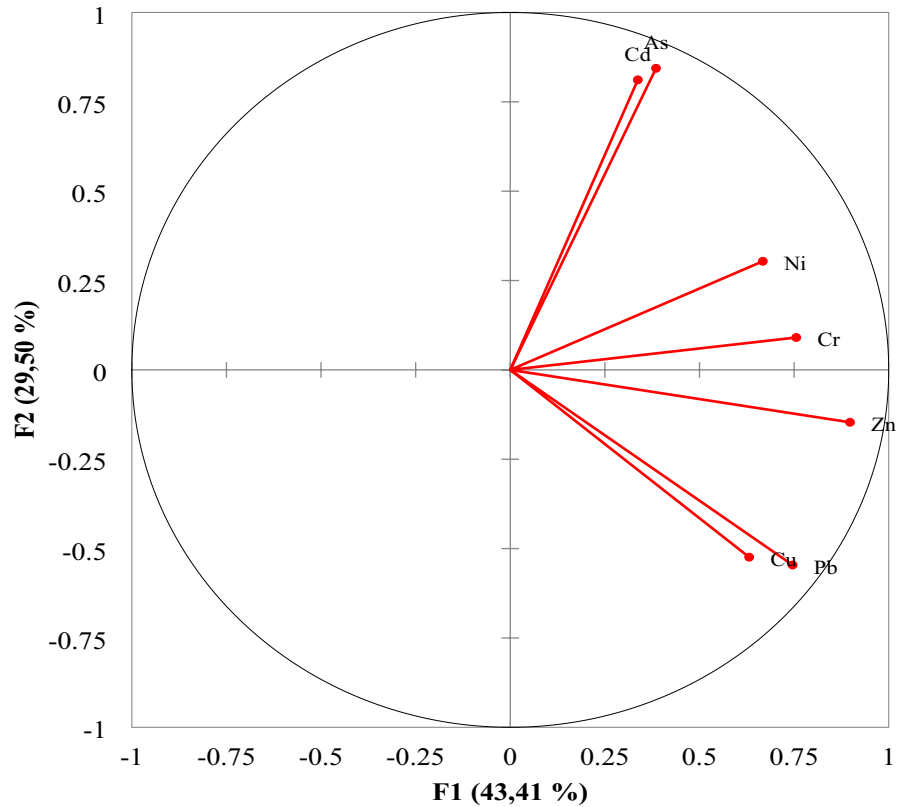
Concerning the EF index, the average values ranged between 1.0 and 3.94 (Ni), 1.0 and 4.99 (Cd), 1.0 and 5.45 (As), 1.0 and 8.60 (Cr), 1.0 and 21.36 (Zn), 1 and 33.48 (Cu) and 1.0 and 72.09 (Pb), indicating that Ni, Cd and As were moderately enriched ($1 < EF < 5$), unlike the other heavy metals, Cr, Cu, Zn and Pb, which were significantly enriched ($5 < EF < 20$).

For each site, and according to the EF categories, the FR1 upstream part of the Oued Fez did not record any significant enrichment in any of the heavy metals studied ($EF=1$), while the Oued Fez tributary (FT1) showed the highest enrichment in heavy metals, especially Zn ($EF=21.36$), Cu ($EF=33.48$) and Pb ($EF=72.09$).

Table 4 Correlation matrix

	As	Cd	Cr	Cu	Ni	Pb	Zn
As	1						
Cd	0.971*	1					
Cr	0.148	0.099	1				
Cu	0.012	0.040	0.104	1			
Ni	0.344	0.176	0.738*	-0.014	1		
Pb	-0.039	-0.045	0.312	0.966*	0.195	1	
Zn	0.153	0.143	0.735*	0.534	0.529	0.640	1

Fig. 5 PCA of heavy metals



For the other sites, the sediments were characterised by moderate to significant enrichment, especially in Cu, Zn and Pb.

The I_{geo} was used to estimate the range of heavy metal pollution (Table 5). The average I_{geo} values were -1.33 to 0.12 (Ni), -0.94 to 0.80 (Cd), -0.82 to 0.83 (As), -1.40 to 1.73 (Cr), -0.66 to 1.81 (Zn), -1.01 to 2.42 (Cu) and -0.67 to 3.23 (Pb). As with the EF index, the I_{geo} values were lower for Ni, As and Cd and higher for Cr, Cu, Zn and Pb, assuming that the sediments were unpolluted to polluted at a low level by Ni, Cd and As, and low to moderately polluted by Cr, Cu, Zn and Pb.

For each site, and according to the I_{geo} categories, FR1 and FT2 were the unpolluted sites, while FT1 and FR3 exhibited moderate pollution by, respectively, Zn, Cu and Pb, and Cr, Zn and Pb.

The CFs for the seven heavy metals studied from each site are listed in Table 5. The average CF values

were 0.86 – 1.71 (Ni), 0.85 – 2.68 (As), 0.79 – 2.63 (Cd), 1.00 – 5.38 (Cr), 1.00 – 9.87 (Zn), 1.00 – 10.07 (Cu) and 1.00 – 21.67 (Pb), indicating once again that, overall, the surface sediments in the Oued Fez and Sebou Rivers were contaminated at low and moderate levels by Ni, Cd and As. In contrast, these sediments were more highly contaminated by Cr, Cu, Zn and Pb, especially at FT1 and FR3.

The results of the multi-metal pollution indices (CD, mCD and PLI) are presented in Table 5, which emphasises the following main findings:

- All the sites, except for FR1 where the sediments were unpolluted (average PLI=0.93, mCD=0.98, CD=6.00), were moderately to very highly contaminated, especially FT1, which was the most polluted (average PLI=4.19, mCD=8.09, CD=43.41);
- In the Oued Fez, from the upstream (FR1) to downstream (FR3) (average PLI=3.1,

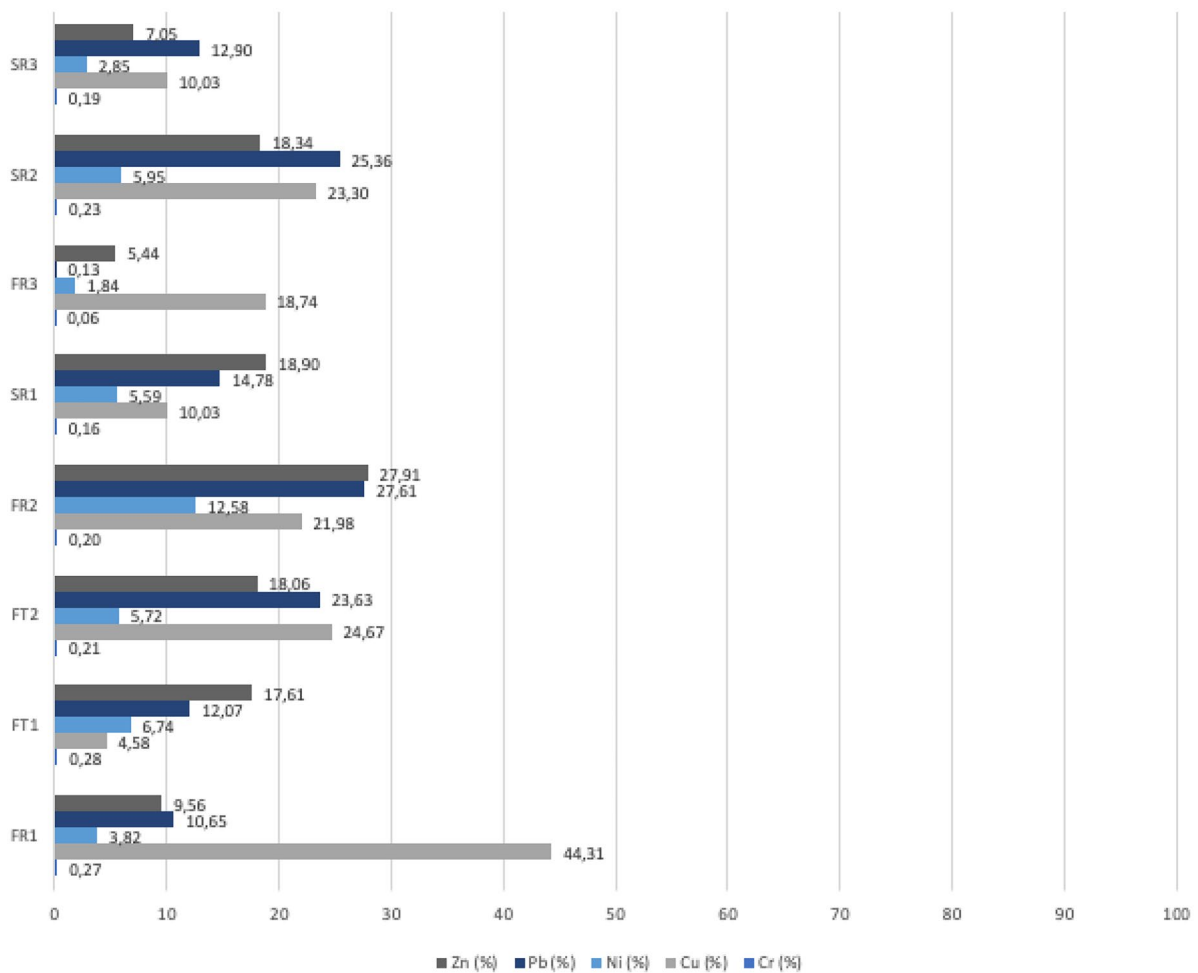


Fig. 6 Percentage of heavy metals leached by EDTA in sediment of Oued Fez and Sebou river

mCD=5.18, CD=32.63), the sediments became steadily more contaminated, likely due to the input of urban pollutant metals;

- In the Sebou, an unexpected finding was that even the sediments of the upstream site (SR1) were obviously contaminated by heavy metals (average PLI=2.91, mCD=4.46, CD=23.88). Moreover, from the upstream to downstream of the Sebou River, contamination progressively decreased by self-purification (SR2 average PLI=2.76, mCD=3.06, CD=21.15; SR3 average PLI=1.90, mCD=2.13, CD=12.40).

Sediment quality guidelines

To assess the ecotoxicological impact of heavy metals on the sediment-dwelling faunas of the Oued Fez and Sebou Rivers, the heavy metal contents were compared with the SQG values (TEL, PEL, TEC and PEC) (Table 6). Generally, two scenarios can be emphasised; when the heavy metal concentrations fall below the TEL and TEC values, there are no adverse effects on sediment-dwelling faunas, but when the concentrations fall above the PEL and PEC values, adverse effects can be expected to occur often.

Table 5 Pollution indexes of Oued Fez and Sebou river. ^aIgeo<0 unpolluted; 0<Igeo<1 unpolluted to moderately polluted; 1<Igeo<2 moderately polluted; 2<Igeo<3 moderately to strongly polluted; 3<Igeo<4 strongly polluted; 4<Igeo<5 strongly to extremely polluted; 5<Igeo extremely polluted. ^bEF<1 indicates no enrichment; 1<EF<3 is minor enrichment; 3<EF<5 is moderate enrichment; 5<EF<10 is moderately severe enrichment; 10<EF<25 is severe enrichment; 25<EF<50 is very severe enrichment; and EF>50 is extremely severe enrichment. ^cCf<1 indicates low contamination; 1<Cf<3 is moderate contamination; 3<Cf<6 is considerable contamination; and Cf>6 is very high contamination.

^dCd<6 indicates a low degree of contamination; 6<Cd<12 is a moderate degree of contamination; 12<Cd<24 is a considerable degree of contamination; and Cd>24 is a high degree of contamination indicating serious anthropogenic pollution. ^emCd<1.5 is nil to a very low degree of contamination; 1.5 mCd<2 is a low degree of contamination; 2<mCd<4 is a moderate degree of contamination; 4<mCd<8 is a high degree of contamination; 8<mCd<16 is a very high degree of contamination; 16<mCd<32 is an extremely high degree of contamination; mCd>32 is an ultra-high degree of contamination. ^fPLI>1 means that pollution exists; otherwise, if it is <1, there is no metal pollution

Samples			FR1 (n=6)		FT1 (n=6)		FT2 (n=6)		FR2 (n=6)		SR1 (n=6)		FR3 (n=6)		SR2 (n=6)		SR3 (n=6)	
			avg	min-max	avg	min-max	avg	min-max	avg	min-max	avg	min-max	avg	min-max	avg	min-max	avg	min-max
Individual metals	As	Igeo	-0.64	(-0.99) - (-0.1)	0.13	0.13 - 0.13	-0.82	(-0.94) - (-0.64)	0.79	0.64 - 0.89	0.21	(-0.07) - 0.65	-0.46	(-0.86) - 0.11	0.83	0.68 - 0.91	0.52	(-0.08) - 1.06
		FE	1.0	0.78 - 1.40	5.45	5.37 - 5.52	2.93	2.69 - 3.25	3.66	3.26 - 3.95	1.74	1.23 - 2.48	1.82	1.26 - 2.82	3.57	3.15 - 3.82	3.22	2.01 - 4.44
		Cf	1.00	0.76 - 1.40	1.64	1.64 - 1.64	0.85	0.78 - 0.97	2.61	2.34 - 2.77	1.77	1.43 - 2.36	1.14	0.83 - 1.62	2.68	2.41 - 2.82	2.27	1.41 - 3.12
	Cd	Igeo	-0.65	(-0.98) - (-0.06)	0.10	0 - 0.09	-0.94	(-1.20) - (-0.72)	0.80	0.66 - 0.94	0.19	(-0.04) - 0.63	-0.65	(-0.79) - (-0.51)	0.65	0.59 - 0.70	0.28	0.14 - 0.41
		FE	1.00	0.74 - 1.43	4.99	4.92 - 5.06	2.71	2.26 - 3.05	3.69	3.30 - 3.92	1.71	1.25 - 2.45	1.50	1.32 - 1.67	3.14	3.07 - 3.19	2.56	2.34 - 2.84
		Cf	1.00	0.76 - 1.44	1.50	1.50 - 1.50	0.79	0.65 - 0.91	2.63	2.37 - 2.87	1.75	1.46 - 2.32	0.96	0.87 - 1.06	2.36	2.25 - 2.44	1.83	1.65 - 1.99
	Cr	Igeo	-0.65	(-1.46) - (-0.17)	0.31	(-1.23) - 1.70	-1.40	(-4.59) - 1.62	0.37	(-2.11) - 2.07	-0.37	(-1.02) - 0.26	1.73	1.26 - 2.87	0.58	(-0.72) - 2.40	0.35	(-0.63) - 1.29
		FE	1.00	0.56 - 1.33	8.27	2.13 - 16.15	6.11	0.21 - 16.29	4.56	0.51 - 8.56	1.17	0.78 - 1.76	8.60	5.48 - 19.03	4.17	1.21 - 10.35	3.01	1.36 - 5.20
		Cf	1.00	0.54 - 1.34	2.49	0.64 - 4.86	1.7700	0.06 - 4.62	3.2600	0.35 - 6.28	1.2200	0.74 - 1.80	5.3800	3.60 - 10.97	3.15	0.91 - 7.92	2.12	0.97 - 3.66
	Cu	Igeo	-1.01	(-3.35) - 0.11	2.42	1.14 - 3.72	-0.81	(-2.30) - 0.90	0.13	(-0.90) - 1.53	0.08	(-2.89) - 2.73	0.23	(-1.78) - 2.27	0.29	(-1.14) - 1.51	-0.31	(-0.97) - 0.13
		FE	1.00	0.15 - 1.62	33.48	10.99 - 64.85	4.18	1.05 - 9.89	3.41	1.17 - 5.92	4.81	0.21 - 9.90	5.58	0.69 - 10.47	3.34	0.90 - 5.62	1.79	1.08 - 2.33
		Cf	1.00	0.15 - 1.62	10.07	3.31 - 19.75	1.21	0.30 - 2.81	2.44	0.80 - 4.34	5.00	0.20 - 9.95	3.58	0.44 - 7.24	2.51	0.68 - 4.26	1.26	0.77 - 1.64

Samples			FR1 (n=6)		FT1 (n=6)		FT2 (n=6)		FR2 (n=6)		SR1 (n=6)		FR3 (n=6)		SR2 (n=6)		SR3 (n=6)	
			avg	min-max	avg	min-max	avg	min-max	avg	min-max	avg	min-max	avg	min-max	avg	min-max	avg	min-max
Individual Metals	Ni	Igeo	-0.65	(-1.66) - (-0.21)	-0.41	(-1.05) - 0.13	-1.33	(-2.86) - 0.32	-0.77	(-1.93) - 0.27	-0.85	(-2.01) - (-0.08)	0.12	(-0.31) - 1.00	0.01	(-0.69) - 0.60	-0.05	(-0.60) - 0.36
		FE	1.00	0.49 - 1.30	3.94	2.38 - 5.40	2.96	0.73 - 6.62	1.49	0.57 - 2.47	0.89	0.39 - 1.31	2.72	1.85 - 5.21	2.17	1.23 - 3.09	2.12	1.39 - 2.73
		Cf	1.00	0.48 - 1.30	1.18	0.73 - 1.65	0.86	0.21 - 1.88	1.06	0.39 - 1.81	0.93	0.37 - 1.42	1.71	1.21 - 3.01	1.63	0.93 - 2.28	1.47	1.00 - 1.92
	Pb	Igeo	-0.67	(-1.51) - 0.14	3.23	1.30 - 4.91	-0.31	(-1.06) - 0.87	0.71	(-0.12) - 1.56	2.35	1.86 - 2.85	2.87	2.69 - 3.12	1.25	(-0.67) - 2.66	0.83	0.63 - 1.17
		FE	1.00	0.51 - 1.65	72.09	12.32 - 147.73	4.70	2.54 - 9.66	3.87	1.88 - 6.19	7.72	4.81 - 10.97	17.37	14.75 - 22.64	6.91	1.25 - 12.59	3.82	3.30 - 4.75
		Cf	1.00	0.53 - 1.65	21.67	3.70 - 44.99	1.36	0.72 - 2.74	2.76	1.38 - 4.43	8.02	5.45 - 10.78	11.03	9.68 - 13.05	5.19	0.94 - 9.51	2.7	2.33 - 3.37
	Zn	Igeo	-0.66	(-1.66) - (-0.10)	1.77	0.15 - 2.95	-0.04	(-2.33) - 1.73	1.53	0.69 - 2.39	0.55	(-2.96) - 3.33	1.81	(-0.02) - 3.94	1.74	0.63 - 2.72	0.95	0.32 - 1.66
		FE	1.00	0.49 - 1.39	21.36	5.54 - 38.12	7.73	1.03 - 17.58	6.83	3.39 - 10.72	6.65	0.17 - 12.93	15.67	2.30 - 39.86	8.04	3.16 - 13.52	4.33	2.65 - 6.73
		Cf	1.00	0.47 - 1.40	6.424	1.66 - 11.61	2.24	0.30 - 4.99	4.87	2.43 - 7.87	6.95	0.19 - 15.05	9.87	1.48 - 22.98	6.04	2.32 - 9.91	3.05	1.87 - 4.74
	Multi-metals	Dc	6.00	2.64 - 8.92	43.41	17.46 - 79.20	8.26	3.24 - 17.04	17.00	11.38 - 24.72	23.88	10.67 - 37.86	32.63	17.80 - 58.64	21.15	6.10 - 36.95	12.4	8.23 - 17.80
		mCd	0.98	0.53 - 1.27	8.09	2.49 - 15.84	1.53	0.46 - 3.41	3.07	1.63 - 4.94	4.46	1.52 - 7.57	5.18	3.56 - 8.38	3.06	1.22 - 6.16	2.13	1.65 - 2.66
		PLI	0.93	0.45 - 1.23	4.19	2.12 - 7.27	1.39	0.35 - 3.20	2.68	1.22 - 4.44	2.91	0.91 - 5.02	3.1	2.01 - 5.13	2.76	1.07 - 4.46	1.9	1.43 - 2.38

Table 5 displays the results from all sites, indicating that the concentrations of heavy metals, except for As, were frequently lower than the TEL and TEC levels, with about 40% of the measured Cd values, 63% of Cu, 70% of Cr, Zn and Pb and 75% of Ni being lower than their threshold effect. Consequently, 40–75% of the metals pose no ecological risk. On the

other hand, 100% of the As exceeded the PEL and PEC levels, and 25% of the Cr, 23% of Pb, 19% of Cu, 17% of Ni and 13% of Zn, except for Cd, with no value exceeding its probable effect level.

Consequently, the greatest toxicological concern was found to be from As, and the least from Cd. As for the other metals, about 13 to

Table 6 Comparison between sediment quality guidelines (SQGs), PEL, TEL, LEL, MET, ERL, PEC and TEC with mean values of heavy metals in sediments (unit in $\mu\text{g/g}$)

Samples. N= 48			Sediment quality guidelines (SQGs)			
Metal	Min - Max	Avg	Threshold effect concentrations		Sediment quality assessment guideline	
			PEL	TEL	TEC	PEC
As	21,68 - 89,36	49,92	17,00	5,90	9,79	33,00
Cd	0,62 - 2,72	1,36	3,53	0,60	0,99	4,98
Cr	14,88 - 469,00	108,84	90,00	37,30	43,40	111,00
Cu	7,14 - 957,10	110,17	197,00	35,70	31,60	149,00
Ni	4,50 - 65,30	26,81	36,00	18,00	22,70	48,60
Pb	10,88 - 929,67	138,75	91,30	35,00	35,80	128,00
Zn	10,52 - 1251,16	275,31	315,00	123,00	121,00	459,00

		As	Cd	Cr	Cu	Ni	Pb	Zn
Measured values	Min	21,68	0,62	14,88	7,14	4,50	10,88	10,52
	Max	89,36	2,72	469,00	957,10	65,30	929,67	1251,16
	Avg	49,92	1,36	108,84	110,17	26,81	138,75	275,31
SQG (%)	Samples < TEC	0	39	69	63	77	69	69
	Samples > PEC	71	0	23	19	6	15	13
	Samples < TEL	0	0	67	63	73	69	71
	Samples > PEL	100	0	25	15	17	23	13

25% of the analysed sediments contained significant ecological risk, with the sequence being $\text{Cr} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Zn}$.

The SQG analysis, however, also highlighted that no ecotoxicity risk was present in the Oued Fez sediments at FR1 and FT2, while at FT1 and FR3, there were obvious ecological risks, especially those relating to Pb and Cu at FT1, and Cr and Zn at FR3. In the Sebou River, the upstream surface sediments at SR1 were, unusually, the most prone to ecological risk, especially from Zn, Cu and Pb.

Temporal distribution of the total heavy metal content

From 2014 to the present, the installation of the Fez WWTP and improvement of the sewer and storm-water networks have probably improved the quality of the surface water and sediments of the Oued Fez and Sebou Rivers. To estimate this, a comparative

study was performed between the heavy metal values from the present study and those of previous studies carried out prior to the installation of the WWTP (Hayzoun et al., 2014). The results of this analysis are summarised in (Table 7).

In the present-day downstream part of the Oued Fez (FR2), a decrease in the concentrations of all heavy metals was noted, especially with respect to Cu, with a decrease of 47%, highlighting a reduction in the harmful and polluting contribution of Oued Fez to the Sebou River. However, in the Sebou River (SR1 upstream, SR2 downstream), the results indicate high heavy metal contents in the present-day surface sediments, especially from Zn, Cu and Pb, which makes the Sebou River a potentially polluting watercourse, contradicting the findings of previous studies that have represented the Oued Fez as the primary polluted stream in the region.

Table 7 Comparison of heavy metal contents in sediment before and after WWTP installation

Samples			Cr	Cu	Ni	Pb	Zn	
Present study	FR2	Content	Min-max	14.88–268.31	38.88–210.34	8.54–39.41	28.48–91.59	132.08–428.41
			Avg	139.22	117.97	23.05	57.05	265.14
		Pollution indexes	Igeo	Min-max	(-2.11)–2.07	(-0.90)–1.53	(-1.93)–0.27	(-0.12)–1.56
	Avg			0.37	0.13	-0.77	0.71	1.53
	FE		Min-max	0.51–8.56	1.17–5.92	0.57–2.47	1.88–6.19	3.39–10.72
			Avg	4.56	3.41	1.49	3.87	6.83
Hayzoun et al., 2014	FR2	Content	Min-max	98.4–1.11	117–294	24.6–237	127–402	150–389
			Avg	404.00	174.00	85.00	196.00	243.00
		Pollution indexes	Igeo	Min-Max	1.3–4.8	3.1–4.4	0.3–3.6	2.5–4.7
	Avg			404.00	174.00	85.00	196.00	243.00
	FE		Min-max	7.3–80.8	28.7–68.6	3.5–30.4	28.7–117.0	5.10–13.0
			Avg	30.5	42.90	11.80	56.80	8.30
Present study	SR1	Content	Min-Max	31.70–76.96	9.80–482.18	8.10–30.75	112.59–222.77	10.52–819.44
			Avg	51.96	242.38	20.19	165.69	378.53
		Pollution indexes	Igeo	Min-Max	(-1.02)–0.26	(-2.89)–2.73	(-2.01)–(-0.08)	1.86–2.85
	Avg			-0.37	0.08	-0.85	2.35	0.55
	FE		Min-Max	0.78–1.76	0.21–9.90	0.39–1.31	4.81–10.97	0.17–12.93
			Avg	1.17	4.81	0.89	7.72	6.65
Hayzoun et al., 2014	SR1	Content	Min-Max	19.6–57.4	9.2–15.6	10.9–28.3	9.8–21.5	31.2–115
			Avg	44.00	12.50	20.70	12.50	67.60
		Pollution indexes	Igeo	Min-Max	(-1)–0.5	(-0.6)–0.2	(-0.90)–0.80	(-0.70)–0.50
	Avg			0.10	-0.20	0.03	-0.30	0.30
	FE		Min-Max	0.90–3.30	0.9–2.6	1.0–2.7	0.9–4.0	0.6–2.9
			Avg	1.7	1.6	1.5	2.1	1.2
Present study	SR2	Content	Min-Max	38.91–338.28	32.98–206.52	20.16–49.56	19.49–196.42	126.27–539.70
			Avg	134.47	121.68	35.47	107.24	328.85
		Pollution indexes	Igeo	Min-Max	(-0.72)–2.40	(-1.14)–(-1.51)	(-0.70)–0.61	(-0.67)–2.66
	Avg			0.58	0.29	0.01	1.25	1.74
	FE		Min-Max	1.21–10.35	0.90–5.62	1.23–3.09	1.25–12.59	3.16–13.52
			Avg	4.17	3.34	2.17	6.91	8.04
Hayzoun et al., 2014	SR2	Contents	Min-Max	51–579	85–217	20.1–73.1	57.7–133	139–361
			Avg	136.00	126.00	43.00	96.00	206.00
		Pollution indexes	Igeo	Min-Max	0.40–3.90	2.60–3.90	0.3–1.90	1.80–3.10
	Avg			1.47	3.10	0.90	2.50	1.10
	FE		Min-Max	1.4–35.6	7.2–28.3	1.0–7.5	6.7–27.9	2.0–6.2
			Avg	5.60	14.70	3.00	13.50	3.20
SQG		TEL	37.30	35.70	18.00	35.00	123.00	
		PEL	90.00	197.00	36.00	91.30	315.00	

Conclusions

The physico-chemical parameters (pH, DO, EC, SM, ISM, OSM) and total phosphorus, nitrates and ammonium of the studied samples indicated an improvement in water quality compared to previous studies, likely due to the efficiency of the new wastewater and stormwater networks and the proper functioning of the Fez WWTP.

Despite the lithological differences between the two catchment areas of Oued Fez and Sebou, the mineralogy was found to be very similar, with the mineralogical analysis indicating that heavy metal retention was not related to the clay fraction of the sediment, but rather to the other components.

The spatial distribution of the total heavy metal contents in the urban areas, from the upstream to downstream of the Oued Fez, suggested that the pollutant load of the sediments increased due to an increasing input of metals mainly from the Oued Fez tributary. In the rural areas, from the upstream to downstream of the Sebou River, the sediment pollutant load decreased by self-purification. The Pearson correlation, coupled with PCA, validated all the hypotheses concerning the pollution sources and correlations between the heavy metals in the Oued Fez and Sebou River sediments. Cr, Pb and Zn tended to originate from anthropogenic (industrial and artisanal) activities, while As and Cd aligned with an agricultural source of pollution.

The available fraction of metals extracted by EDTA indicated that Cr and Ni represented heavy metals that could be only very weakly mobilised, while Zn, Pb and Cu were easily mobilised.

Pollution index values for all the sites, except FR1, at which the surface sediments were unpolluted (average PLI=0.93, mCD=0.98, CD=6.00), indicated moderate to very high contamination, especially at FT1, which was the most polluted site (average PLI=4.19, mCD=8.09, CD=43.41).

In the Sebou River, the upstream at SR1 was contaminated by heavy metals, although the contamination progressively decreased from the upstream to downstream by self-purification.

The SQGs' analysis highlighted that no ecotoxicity risk was present in the Oued Fez sediments at FR1 and FT2, but that there were obvious ecological risks at FT1 and FR3, especially from Pb and Cu at FT1 and Cr and Zn at FR3. In the Sebou River, the surface

sediments at the upstream SR1 were the most affected by potential ecological risk, especially induced by Zn Cu and Pb.

After comparing the new results with previous research, we noted a reduction in the harmful and polluting contribution of the Oued Fez to the Sebou River, observing a decrease in the concentrations of the majority of the heavy metals.

Acknowledgements The authors would like to thank the reviewers and editors for their thoughtful and helpful comments on our manuscript.

Data availability All data generated or analysed during this study are included in this published article.

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