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Impact of rapid urbanisation and industrialisation on river sediment metal contamination

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Abstract This study aimed at evidencing contaminant inputs from a rapidly growing population and the accompanying anthropogenic activities to river sediments. The Fez metropolitan area and its impacts on the Sebou's sediments (the main Moroccan river) were chosen as a case study. The Fez agglomeration is surrounded by the river Fez, receiving the wastewaters of this developing city and then flowing into the Sebou. The sediment cores from the Fez and Sebou Rivers were extracted and analysed for major elements, butyltins and toxic metals. Normalised enrichment factors and geoaccumulation index were calculated. Toxicity risk was assessed by two sets of sediment quality guideline (SQG) indices. A moderate level of contamination by butyltins was observed, with monobutyltin being the dominant species across all sites and depths. The lowest level of metal pollution was identified in the Sebou's sediments in upstream of Fez city, whilst the Fez' sediments were heavily polluted and exhibited bottom-up accumulation trends, which is a clear signature of recent inputs from the untreated wastewaters of Fez city. Consequently, the sediments of Fez and Sebou at the downstream of the confluence were found to be potentially toxic, according to the SQG levels. This finding is concerned with aquatic organisms, as well as to the riverside population, which is certainly exposed to these pollutants through the daily use of water. This study suggests that although Morocco has adopted environmental regulations aiming at restricting pollutant discharges into the natural ecosystems, such regulations are neither well respected by the main polluters nor efficiently enforced by the authorities.

Keywords Fast-developing country · Sediment quality · Toxic metals · Anthropogenic pollution · Sebou and Fez Rivers

Introduction

Rapid worldwide urban and economic growth has a massive impact on the environment, especially in aquatic environments, which are the ultimate receiving sink for wastewater discharges. Inputs of pollutants, particularly of toxic metals, to the aquatic environment are increasingly worrying (Sin et al. 2001; Peng et al. 2009). Among the possible sources, the discharge of

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untreated industrial effluents and domestic sewage into rivers and estuaries is to be considered because these sources can significantly increase metal contamination. Trace metals are harmful to the natural environment due to their toxicity, persistence and bioaccumulation (Pekey 2006; Varol and Şen 2012). Recently, environmental concerns about organotin compounds have also remarkably increased, especially tributyltin (TBT) and triphenyltin (TPhT), which are used as biocides in antifouling paints and pesticides (Hoch 2001; Strand et al. 2003). The TBT degradation products, dibutyltin (DBT) and monobutyltin (MBT), are mainly used as heat and light stabilisers for PVC material, and DBT is also increasingly used as a binder in water-based varnishes (Antizar-Ladislao 2008).

In aquatic systems, some of these pollutants can enter the food chain through accumulation in microorganisms and aquatic flora and fauna, which, in turn, may result in human health problems (Cooke and Andrews 1990). Furthermore, a rapid transfer of some toxic metals from the water to the sediment may occur through settling particles (Vystavna et al. 2012).

Sediments therefore have a large capacity to retain contaminants from tidal waters, rivers and storm water runoff and often act as sinks for pollutants from these sources (Harbison 1986; Hoch 2001; Nasehi et al. 2013; Rigaud et al. 2013). The fate of the pollutants in sediments is related to a large number of biogeochemical processes (Charriau et al. 2011) as well as to their relative mobility or degradation under varying redox conditions. Trace elements can adsorb to organic substances and minerals, such as clays, and Fe and Mn oxides. However, these processes can be reversed when the equilibrium between sediments and the overlying water body is disrupted, causing the sediments to become sources of pollutants after direct discharges cease (Dowson et al. 1993; Teuchies et al. 2010).

The study of geochemical characteristics of sediment cores has provided valuable information concerning sediment source, transport and human impact. Moreover, understanding the concentration profile and the distribution of trace metals in sediments can play a key role in detecting sources of pollution in aquatic systems (Bubb and Lester 1994; Förstner and Wittmann 1979). In addition, anthropogenic disturbance to the environment often has significant impacts on sediments.

The Sebou, Morocco's largest river, is an ideal setting for studying the impact of anthropogenic pressures on a river. Indeed, during its journey, the Sebou crosses several cities and urban areas, among which Fez is the most important. The rapid development of industrial and artisanal activities, the rapid urbanisation and population growth, and the inadequacy of controlled waste management strategies and waste treatment plants in Fez have increased the pollution problems of the Sebou. Several studies have examined the critical situation of the Sebou and Fez Rivers (Amri et al. 2007; Azzaoui et al. 2002; Dominik et al. 2007; Koukal et al. 2004).

The industrial effluents and domestic wastewaters from Fez city have been and continue to be directly released, untreated, into the Fez, the main water body that crosses the city, which, in turn, discharges into the Sebou River. The total water discharged from the city is 110,000 m^3 day^{-1} and will reach 130,000 m^3 day^{-1} by 2015 (RADEEF 2007). The Sebou has become the sole receiving water for waste waters from Fez city, making it one of the most polluted rivers in Morocco. This is of particular concern because the water from this river is still used to irrigate several types of crops in the region, a practice that could cause significant health risks. In the Fez region, tanneries are one of the most prominent sources of toxic pollution to the Fez and Sebou Rivers. Chromium tanning agents, primarily basic chromium sulphates, are used during the tanning process. Chromium compounds introduced into the river temporarily accumulate in bottom sediments (Pawlikowski et al. 2006). The affinity of Cr(III) for the particulate phase decreases its bioavailability to phytoplankton, but high concentrations in the sediments could have detrimental effects on the benthic organisms and, ultimately, on the highest levels of the aquatic food chain.

Previous studies have shown that the Sebou's sediments are severely contaminated with metallic elements. However, to the best of the authors' knowledge, these studies have only focused on spatial variations in surface sediments (Amri et al. 2007; Azzaoui et al. 2002; Dominik et al. 2007; Fekhaoui et al. 1996), and there have been no published works on the depth profiles of toxic metals and butyltin compounds in Fez and Sebou Rivers sediments.

This study presents the environmental quality assessment of three sediment cores from the Fez (downstream Fez city) and the Sebou (upstream and downstream of its mixing point with the Fez River) through their geochemical characteristics. Furthermore, the potential toxicity of these sediments was evaluated using various indices, including the index of geoaccumulation, the enrichment factor (EF) and different sediment quality guidelines (SQGs).

Materials and methods

Study area

The Sebou is the largest Moroccan river, draining approximately 40,000 km^2, which represents 6 % of Morocco's total land area. It flows approximately 500 km from its source to the Atlantic Ocean. The Sebou originates in the Middle Atlas chain, which is characterised by a mild Mediterranean climate and predominantly calcareous–dolomitic bedrock. The karst properties of the upstream watershed can influence the stream flow. The watershed morphology reflects the geographical differences between the north and south. The mid-Sebou basin lies within the Rif and Prerif Mountains, characterised by an average altitude of 2,000 m, very steep slopes, a strong rainfall gradient across the basin averaging 2,000 mm and a bedrock composed of shale, marl and sandstone (Arthurton et al. 2008). The climate of the Fez region is semi-arid to temperate in winter, but semi-continental. Precipitation is characterised by high inter- and intra-annual variation, with an average year rainfall ranging from 200 to 530 mm over the last 10 years. On its way to the Atlantic, the Sebou runs north through the overgrazed scrub and grasses of the Atlas foothills where one tributary, the Fez, merges. The Fez River flows in an easterly direction from the springs of "Ras el Ma" to the Sebou, 4 km downstream of Fez city. Sebou River plays a vital role in supplying water for drinking, irrigation and industry to the Sebou watershed.

Fez is a city characterised by a growing population from 100,000 to more than 1,000,000 inhabitants during the last century. There is also extensive industrial development. The major industrial activities include tanneries, textiles, canneries and oil production. Leather tanning is of great importance to Fez's economy, as it represents up to 53 % of the city's employment, 24 % of industrial production and 23 % of added value (PREM 2004). The economic growth and urban development in this region have led to excessive waste release into the Sebou. The wastewater treatment capacity of the city of Fez is very limited; only a small percentage of the industrial wastewater is treated before discharge. This is expected to change in the future when a wastewater treatment plant (activated sludge) will treat all wastewaters from Fez city. This treatment plant will ensure that the discharge of sewage and stormwater into the Sebou after treatment meets the environmental requirements (RADEEF 2012).

Sediment sampling, treatment and chemical analysis

Sediment core samples were collected in July 2011 at three different locations. One sampling station was downstream of Fez city (F, 34°4′38.18″N–4°56′1.32″O; Fig. 1), representing the converging area of all the effluents from Fez city (domestic, industrial, craft and also medical) before joining the Sebou. The two other stations are located on the Sebou, upstream and downstream of the confluence with the Fez River (S1, 34°4′9.20″N–4°55′7.81″O and S3, 34°5′19.12″N–4°54′52.89″O, respectively; Fig. 1).

Sampling was performed from the river banks, with researchers collecting submerged sediments (approximately 50 cm underneath the surface) using a gravity-type sediment corer that was 0.5 m in length (Plexiglastube with 10 cm diameter).The corer was inserted into the water–sediment interface. Pressure was applied to ensure that the corer penetrated to the maximum depth. After reaching the bottom, the corer was then closed, moved vertically and transported to the laboratory within a few hours for further processing. The supernatant water was removed, and each sediment core was sliced to every 2 cm size using a polyethylene spatula. The core lengths differed between the stations due to the substratum nature, 26, 20 and 30 cm for S1, F and S3, respectively. Each sediment slice was then homogenised and placed into pre-cleaned high-density polyethylene (HDPE) bottles and was deep frozen (−18 °C). All samples were later freeze-dried and sieved at 2 mm.

The analysis of total and inorganic carbon contents was performed using a TOC-VCSH analyser (Shimadzu), coupled with a SSM-5000A module. The total carbon content was determined using the high-temperature (900 °C) catalytic oxidation method followed by CO_2 detection. The inorganic carbon content was determined after addition of H_3PO_4 (Fisher Scientific, Analytical Reagent grade, 85 %) at 200 °C followed by CO_2 detection. Organic carbon was then calculated from the difference between total carbon and inorganic carbon, with an accuracy of 0.1 mg$_C$.

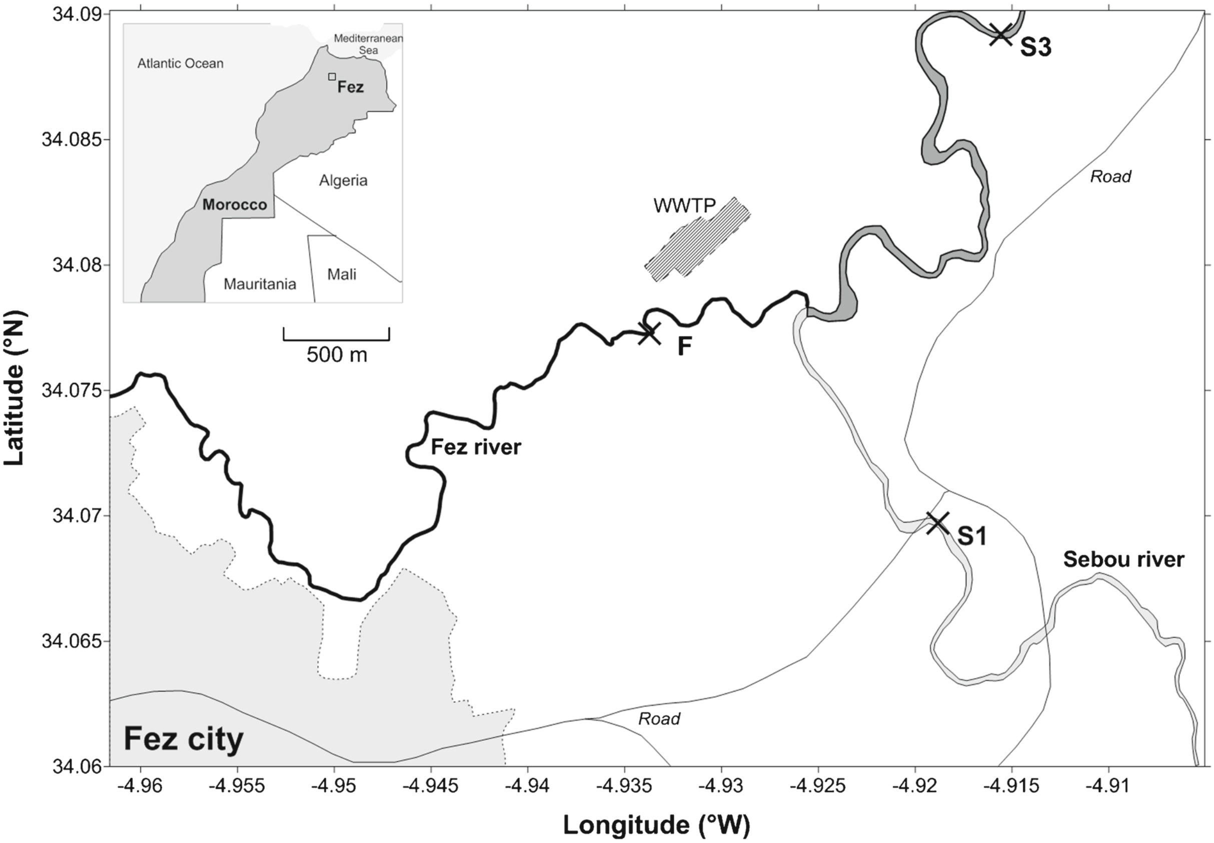

Fig. 1 Location of sampling sites in Sebou and Fez Rivers. (WWTP: waste water treatment plant, under construction)

Major elements (Al, Ca, K, Fe and Mn) and trace elements (Cr, Cu, Ni, Pb and Zn) were determined according to a semi-total digestion protocol previously described (Tessier et al. 2011). Briefly, 100 mg of dried and homogenised sediment was placed in an acid-washed Teflon vessel. The digestion was performed with 8 mL of aqua regia (HNO_3/HCl 1 V:3 V, Fisher Scientific Trace Analysis grade, HNO_3 70 %, HCl 37 %) in 50 mL Teflon (PTFE) bombs using a microwave oven (AntonPaar MW 3000). The final solution was then filtered through a pre-cleaned on-line filter (0.22 μm, Sartorius), diluted to 100 mL and analysed using ICP-AES (Horiba Jobin Yvon's Activa). The reagent blanks were monitored throughout the analysis and were used to accredit the analytical results. Standard reference material (River sediment LGC 6187; Table SI) was analysed at the same time to ensure quality control and accuracy of the analysis.

Hg sediment content analysis was conducted directly in 50 to 100 mg of sediment using Advanced Mercury Analyser AMA 254 (LECO Corporation). The analytical accuracy was estimated by replicate measurements of international reference material (MESS-3; Table 1), blanks and duplicate sediment samples.

For analysis of butyltin compounds, sediments were gently extracted to prevent any modification of Sn speciation (Bancon-Montigny et al. 2001) using glacial acetic acid under agitation for one night. Alkylation of acidic extracts of organotin compounds was then performed as described by Carlier-Pinasseau et al. (1996). MBT, DBT and TBT were determined using a gas chromatography (Focus GC–Thermo Fisher Scientific) with an inductively coupled plasma mass spectrometer (ICP-MS) (X Series II-Thermo Fisher Scientific). The X Series ICP-MS performance was tested, tuned and optimised as required for GC-ICP-MS analysis. Quantification was performed by standard additions. The accuracy of this methodology was evaluated by analysis of the sediment standard reference material, PACS-2 (National Research Council, Canada), certified for MBT, DBT and TBT (700 ng Sn g^{-1}, 1,100±135 $ng_{Sn} g^{-1}$ and 832±95 ng Sn g^{-1}, respectively). The recovery of MBT,

Table 1 Characteristics of the three studied cores (S1, F and S3)

Sample/description		Parameter	OC (%)	IC (%)	Al (mg g^{-1})	Ca (mg g^{-1})	Cr (μg g^{-1})	Cu (μg g^{-1})	Fe (mg g^{-1})	Hg (ng g^{-1})	K (mg g^{-1})	Mn (mg g^{-1})	Ni (μg g^{-1})	Pb (μg g^{-1})	Zn (μg g^{-1})	∑BTs (ng$_{Sn}$g^{-1})
S1 (*N*=13)	Content	Range	0.2–2.1	3.3–6.7	9.4–36.5	131–300	19.6–57.4	9.2–15.6	14.2–29.2	4.1–25.3	2.2–8.3	0.28–0.47	10.9–28.3	9.8–21.5	31.2–115	1.7–6.5
		Average	0.98	4.90	24.5	202	44.0	12.5	22.1	13.4	5.5	0.38	20.7	12.5	67.6	4.1
	Normalised EF	Range	–	–	–	–	0.9–3.3	0.9–2.6	–	0.9–1.7	–	1.1–2.9	1–2.7	0.9–4	0.6–2.9	–
		Average	–	–	–	–	1.7	1.6	–	1.2	–	1.7	1.5	2.1	1.2	–
	Igeo	Range	–	–	–	–	−1.0 to 0.5	−0.6 to 0.2	–	−0.8–1.9	–	−0.6 to 0.1	−0.9 to 0.8	−0.7 to 0.5	−0.7 to 1.2	–
		Average	–	–	–	–	0.1	−0.2	–	0.7	–	−0.2	0.03	−0.3	0.3	–
F (*N*=10)	Content	Range	0.9–1.6	4.6–5.6	11.0–13.2	173–275	98.4–1,110	117–294	11.5–12.8	96.6–578	1.7–2.8	0.20–0.25	24.6–237	127–402	150–389	4.8–11.4
		Average	1.12	4.82	11.0	218	404	174	11.6	205	2.3	0.22	85	196	243	8.1
	Normalised EF	Range	–	–	–	–	7.3–80.8	28.7–68.6	–	16.2–116	–	1.5–2.1	3.5–30.4	28.7–117	5.1–13	–
		Average	–	–	–	–	30.5	42.9	–	43.6	–	1.8	11.8	56.8	8.3	–
	Igeo	Range	–	–	–	–	1.3–4.8	3.1–4.4	–	3.5–6.4	–	−1.2–0.81	0.3–3.6	2.5–4.7	1.5–2.9	–
		Average	–	–	–	–	2.8	3.6	–	4.5	–	−1.0	1.8	3.5	2.1	–
S3 (*N*=15)	Content	Range	0.7–13.3	2.8–5.1	13.2–39.3	145–232	51–579	85–217	14.5–28.8	43.3–168	2.5–7.8	0.27−0.41	20.1–73.1	57.7–133	139–361	3.7–17.5
		Average	3.35	4.10	25.5	186	136	126	22.2	88	4.9	0.34	43	96	206	6.7
	Normalised EF	Range	–	–	–	–	1.4–35.6	7.2–28.3	–	4.1–13.1	–	1−1.9	1–7.5	6.7–27.9	2–6.2	–
		Average	–	–	–	–	5.6	14.7	–	8.2	–	1.3	3.0	13.5	3.2	–
	Igeo	Range	–	–	–	–	0.4–3.9	2.6–3.9	–	2.6–4.6	–	−1.1 to 0.5	0–1.9	1.8–3.1	0.6–1.9	–
		Average	–	–	–	–	1.47	3.1	–	3.5	–	−0.8	0.9	2.5	1.1	–
AL-S1 French level[a] JORF no. 184, 10-08-2000			–	–	–	–	150	100	–	1	–		50	100	300	–
Sediment quality guidelines values[a] (Macdonald et al. 2000)																
TEL			–	–	–	–	37.3	35.7	–	0.17	–		18	35	123	–
PEL			–	–	–	–	90	197	–	0.47	–		36	91.3	315	–
ERL			–	–	–	–	80	70	–	0.15	–		30	35	120	–
ERM			–	–	–	–	145	390	–	1.3	–		50	110	270	–
UCC			–	–	77.4	–	35	14.3	30.9	0.06	–	0.53	18.6	17	52	–
Local background[a]			–	–	10.2	–	26.6	9.2	14.7	0.01	–	0.29	13.3	10.3	34.4	–

N number of analysed sediments, *OC/IC* organic/inorganic carbon, trace metals and ΣBT contents, *EF* enrichment factor, *Igeo* geoaccumulation index, *AL-S1 French action level limit* French limit for dredging sediments, *TEL* threshold effect level, *PEL* probable effect level, *ERL* effect range-low, *ERM* effect range-median *UCC* upper continental crust composition (Wedepohl 1995)

[a] Values are presented as micrograms per gram (μg g^{-1})

DBT and TBT were within the 95 % confidence interval of the certified value.

Results and discussion

Major elements and organic carbon depth profiles

The distribution profiles of major elements and organic carbon contents in the three sampling stations are shown in Fig. 2. The average organic carbon (OC) contents reached 0.9, 1.1 and 3.3 % in S1, F and S3 cores, respectively, with an unexpected enrichment in the S3 surface layers (0–10 cm) (Fig. 2). As the OC content in core F sediments is not high, these elevated levels in S3 (13.3 % in 0–2 cm) are most likely not related to the inputs from Fez city, but most likely to the vegetable fibres observed in the corresponding slices of this core. The results obtained for inorganic carbon (IC) indicated average values of 4.9, 4.8 and 4.1 % in S1, F and S3, respectively. The correlation (R^2 0.68; slope of 0.77 in eq/eq; Fig. SI-1) between Ca and IC contents demonstrates that Ca is mainly deriving from the carbonate rocks present in the catchment study area. However, the obtained IC/Ca ratio (eq/eq) value of 0.77 for all the studied sediments suggests the presence of additional mineralogical forms of Ca.

The S1 co-represented the highest contents of Al, K, Fe and Mn, and the corresponding depth profiles appeared to be fairly constant for the first 10 cm, indicating a stable regime for settling particles during recent years. At greater sediment depths, Al, Fe and Mn contents presented lower values, which were offset by higher Ca content values (Fig. 2). Similar trends were observed for the S3 core, which even exhibited two distinct regions of low Al, K, Fe and Mn, as well as high Ca contents, at ~15 and ~25 cm (Fig. 2). These opposite trends resulted in clear negative correlations between Ca and Al (R −0.95 and −0.76 for S1 and S3, respectively; Fig. SI-1). Such results most likely attest to the predominance of two main lithogenic particle types (aluminosilicates/oxyhydroxides and carbonates), suggesting different material origins or geochemical transformation behaviour during weathering and transport. Al, K, Fe and Mn contents were significantly lower in the F core than in the S1 and S3 cores, which suggests a lower aluminosilicate/oxyhydroxide ratio. This is partly offset by higher Ca (and IC) contents, even if the observed Ca vs. Al negative correlation is no longer significant. The lack of a correlation in core F most likely arises from the fact that Ca may be derived, in that case, from industrial/urban inputs. In addition, the S3 depth profiles reflect periodic enrichment every 10 cm for Al, K, Fe and Mn (Fig. 2). These episodic depositional events could result from erosion, resuspension and redeposition of sediments during periods of high river discharge (i.e. floods). The comparison of the Al (and co-occurring elements) contents in S3 sediments, which were slightly lower than those of S1 samples and significantly higher than those of F samples, indicated a greater contribution of inputs from the Sebou, relative to the Fez in the final mixing zone (S3 site), indicative of the two rivers' respective particulate discharges.

As a typical lithogenic element, Al is considered to be one of the main indicators of terrestrial inputs caused by catchment area erosion. The significant correlations

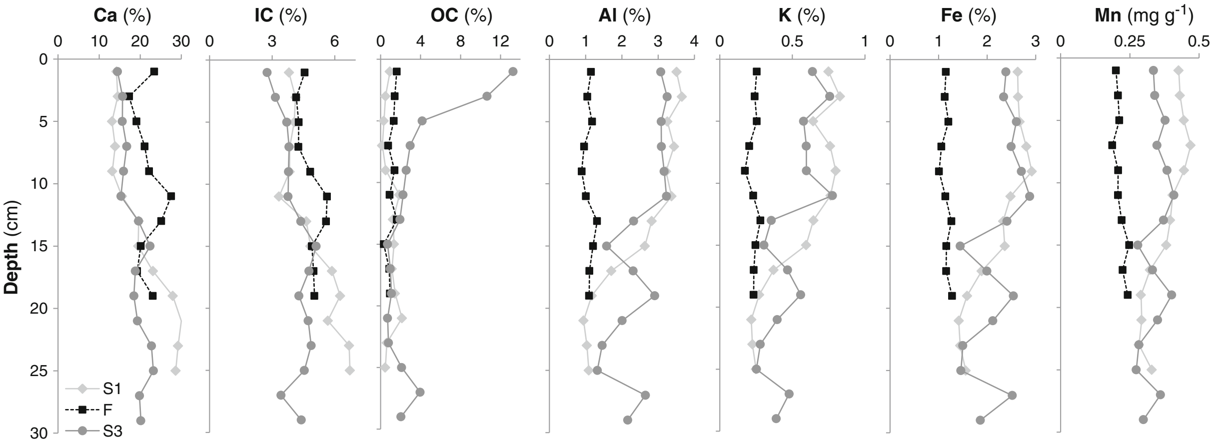

Fig. 2 Depth profiles of major elements, inorganic and organic carbon in the sampled sites (S1, F and S3 cores)

(R>0.80, data not shown) between Al, K, Fe and Mn may indicate that these elements originated from similar sources. The significant correlation between K and Al (R^2 0.95; Fig. SI-1) which is observed for all the studied sediments and associated with a low K/Al ratio (eq/eq= 0.14) most likely indicates the presence of a dominant clay mineral (e.g. smectites) in the particles transported by the Sebou and Fez Rivers. The strong correlations between Fe, Mn and Al (R^2 0.92 and 0.80 for Fe-Al and for Mn-Al, respectively; Fig. SI-1) could suggest the co-occurrence of Fe and Mn oxyhydroxides and aluminosilicates (Varnavas et al. 2001).

Trace elements and butyltin compounds

The trace element and butyltin contents measured in the three cores are depicted in Fig. 3 and summarised in Table 1, including average values and content ranges for all the studied elements, in comparison to the metal values from the upper continental crust composition (UCC) (Wedepohl 1995), and the local background is further defined. In the absence of any Moroccan regulations concerning sediment contamination, the obtained trace element concentrations were compared to the action levels of the French AL-S1 limit, concerning continental sediment dredging (Table 1; JORF no. 184, 10-08-2000).

The three studied stations can easily be differentiated by their sedimentary butyltin and trace metal contents. The non-negligible ΣBT levels encountered at S1 (Fig. 3) indicated a source of pollution in upstream of Fez city even though the recorded contents remained low (1.7 and 6.5 $\text{ng}_{\text{Sn}}\,\text{g}^{-1}$). Higher ΣBT levels were measured in F, leading to an increased content in S3 compared to S1. The surface sediments were the most contaminated, demonstrating significant recent pollution (Fig. 3, Table 1). For all of the studied sites, the dominant species was MBT (Fig. SI-2), which implies either contamination by this species through a direct input (e.g. caused by leaching from PVC materials; Diez et al. 2002) or important photo- or biodegradation from TBT to DBT, then MBT. As a matter of fact, it has been demonstrated that the TBT degradation rates were faster than those of its degradation products (DBT and MBT), as determined based on sedimentation rates, bacterial activity and inputs of TBT (Wang et al. 2008).

The S1 core exhibited the lowest levels for all the measured trace elements. In comparison to the UCC values (Table 1), S1 sediments appeared to be slightly enriched in Zn, Cr and Ni but depleted in Pb, Cu and Hg. This site, located upstream from any major pollution sources, can therefore be considered an unpolluted location (below French action level AL-S1 limits). For each studied element, the three lowest values in core S1 were averaged to define the local background (Table 1).

By contrast, the F core had the highest level of the studied contaminants and showed increasing concentration trends with decreasing sediment depth. Measured Pb, Cu, Zn, Ni, Hg and Cr levels in surface sediments (0–2 cm) were 2 to 11 times higher (for Pb and Cr, respectively) than the deeper strata, and 8 to 116 times higher (for Ni and Hg, respectively) than the local background values (Table 1). The Cr concentrations (Fig. 3) were extremely high in Fez River sediments, with values as high as 1,110 µg g^{-1} in the 0–2 cm slice

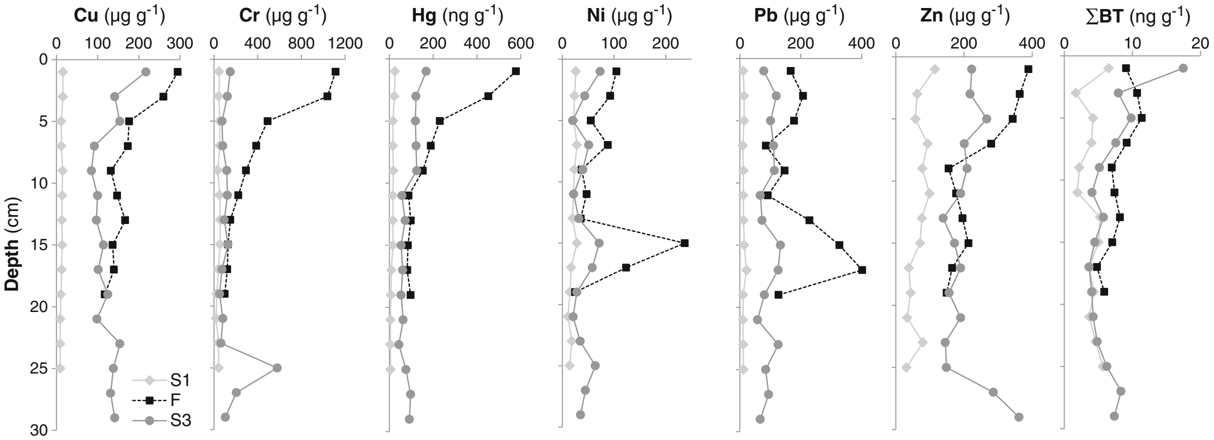

Fig. 3 Depth profiles of trace metals and ΣBTs measured in the sediments of S1, F and S3 cores

(seven times higher than the AL-S1 French limit) (Table 1). Such dramatic contamination is most likely associated with effluent from tanneries (Dominik et al. 2007). Indeed, tanning industries produce up to 23 tons of waste per day, which are significantly polluted with elements such as Cr, sulphide and NH_4^+ (PREM 2004; SEE 1999). The chemical composition of these wastewaters varies widely, depending on the nature of the tanning processes. The modern technique uses Cr as a finishing product to stabilise the leather (Congeevaram et al. 2007; SEE 1999). The F core surface sediments were also polluted in Ni, Pb, Cu and Zn, with concentrations of 105, 167, 294 and 390 µg g^{-1} respectively. These values were significantly higher than the AL-S1 French limit and at least one order of magnitude higher than the local background. The Hg depth profile showed a similar pattern compared to Cr, with a maximal value in surface sediments of 578 ng g^{-1}, 2 orders of magnitude higher than the local background. In contrast to Cr, Cu, Zn and Hg, which continuously decreased with depth, Ni and Pb presented additional peaks in the 14–18 cm layer, a signature that likely indicates a common historical pollution event. Such high levels of ETM, especially in the surface layers, are the signature of recent inputs, demonstrating the negative impact of non-compliance with regulation on industrial/urban discharges, amplified by the increasing population and rate of industrial activities of the last decades. In addition to tanneries, metal finishing facilities are among the most polluting activities in the studied area. Their wastewaters contain high concentrations of contaminants, primarily toxic metals. These contaminants are discharged as salts during rinsing operations. Daily toxic pollution entering into the Sebou from the Fez was estimated at approximately 600 and 100 kg per day for Cr and Ni, respectively (PRIDE 1996).

Compared to the levels recorded in the S1 core, trace metal contents in the S3 core were higher for all contaminants, which demonstrated the impact of the Fez metropolitan region on the Sebou, despite the fact that the Fez's particulate load into the Sebou is most likely small, according to the results obtained for major elements (cf. Section "Major elements and organic carbon depth profiles"). The absence of any sedimentation rate data for the studied cores prevented a direct comparison of the depth profiles for the various elements studied. However, considering the similar pattern (mostly a vertical decrease; Fig. 3) observed for most of the elements not only along the uppermost centimetres in the F and S3 sediment cores but also deeper (e.g. Pb and Ni peaks in the 14–18 cm layer) and assuming that the top layer (0–6 cm) of each core corresponds to recent inputs from a comparable time period, it is possible to evaluate the extent to which the observed increase in contaminant concentrations from the S1 to the S3 sediment core is explained primarily by the accumulation of polluted particles originating from the Fez or from other sources. Values of X_F/X_{S1} and X_{S3}/X_{S1} ratios for the measured major and trace element contents of the first three slices of each core (where X_i corresponds to the element content in the core i) were calculated and plotted in Fig. 4. A clear relationship (R^2 0.95) was observed between concentrations of most of the elements (Al, Ca, Fe, K, IC, Mn, Ni, Pb, Zn, ΣBT), which indicated the impact of polluted particles from the Fez on Sebou sediments. The fact that other major contaminants (OC) and trace elements (Cr, Cu, Hg) were significant outliers could be explained by additional sources (e.g. organic fibres clearly visible in S3 surface sediments) and/or non-conservative behaviour (e.g. reactions) during the mixing of sediments from the F with waters from the Sebou due to their strongly different physical–chemical compositions (pH, Eh, %O_2,…). To validate this hypothesis, further studies are needed to evaluate the behaviour of major and trace elements (e.g. dissolved/particulate fractionation) in the mixing zone under various conditions (season, river flow levels, etc.).

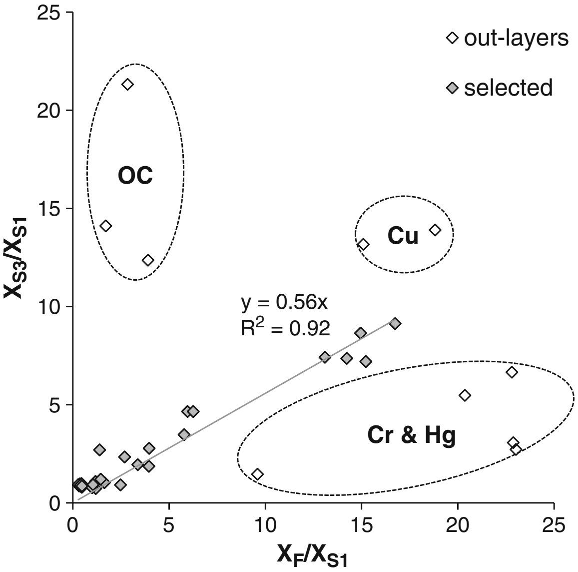

Fig. 4 Relationship between major and trace elements contents in the surface sediments of the three studied cores (S1, F and S3) (see text for explanation)

The measured concentrations of metals in F and S3 surface sediments (0–6 cm slice) were compared with those recorded in other rivers from various countries, including Morocco (Table 2).

The metal concentrations measured in the Fez were lower than those recorded in heavily polluted rivers such as the Deûle (Lesven et al. 2010), which received direct discharges from metallurgical industry in the area. However, the Fez concentrations appeared to be significantly higher than environments receiving comparable urban inputs, particularly with respect to Cr concentrations.

Inter-element relationships

Inter-element relationships, i.e. trace vs. major and trace vs. trace, can provide interesting information on elements' sources and their possible associations. Some typical results are depicted in Fig. 5. In the S1 core, the concentrations of all trace metals showed strong correlations with each other (e.g. r 0.92 for Hg-Cu, r 0.80 for Hg-Ni and r 0.73 for Cr-Ni) and showed significant correlations with Al (r 0.94, 0.85, 0.84 and 0.70 for Hg, Cu, Ni and Zn, respectively) and its co-occurring elements (Fe, Mn, K), as shown in Fig. 5a for Hg. Interpreted in combination with the relatively low levels of metals encountered in S1 sediments, these results suggested that these elements are likely naturally occurring in this context and primarily associated with fine particles such as aluminosilicates or oxyhydroxides. By contrast, the negative correlations (data not shown) with Ca (and IC) suggested that carbonates were not a significant carrier phase for trace metals in the studied systems. In Fez sediments, trace metals were also significantly correlated (e.g. Cr vs. Hg on Fig. 5b) but were not found to be correlated with Al (e.g. Hg on Fig. 5a). Taking into account the high metal contents measured in these sediments, as well as the trace vs. trace element relationships observed, these results indicate the anthropogenic nature of these contaminants, with common main sources and similar behaviour during transport (Suresh et al. 2011). In the S3 core, the trace vs. trace element relationships were less significant, most likely due to less variation in the measured contents (compared to the F core), suggesting different behaviours during Fez/Sebou mixing, as previously discussed (Section “Trace elements and butyltin compounds” and Fig. 4). The present study revealed no significant association between metals and organic matter.

Assessment of sediment pollution and ecotoxicological risks

Enrichment factor and geoaccumulation Index (Igeo)

To assess the impact of environmental contamination on the Sebou's sediments, it is necessary to establish pre-anthropogenic background concentrations of toxic metals. Geochemical natural backgrounds refer to element concentrations present in sediments without any anthropogenic enrichment. These values are normally indicated by the average geochemical concentration of pre-industrial sediments and can be used to assess the geochemical enrichment in modern sediments (Mil-Homens et al. 2006). As already mentioned, the

Table 2 Comparison of maximal trace metal contents in Sebou and Fez Rivers surface sediments in the present study and other studies of other Moroccan and international rivers

Authors	River, location	Layer (cm)	Pb (μg g^{-1})	Zn (μg g^{-1})	Cr (μg g^{-1})	Ni (μg g^{-1})	Cu (μg g^{-1})
Saadallah (1991)	Boufekran, Morocco	Surface	22	88	45	22	26
Barakat et al. (2012)	Day, Morocco	0–10	135.3	145.5	311.7	–	740.8
Singh et al. (2005)	Gomti, India	Surface	40.3	41. 7	8.15	15.7	5.0
Lasheen and Ammar (2009)	Nile, Egypt	Surface	3–685	60–262	37–46	54–65	27–90
Gonzalez et al. (2000)	Guadaia, Spain	0–10	20	51	38	37	25
Mohiuddin et al. (2010)	Tsurumi, Japan	0–10	41	381	103	37	133
Lesven et al. (2010)	Deûle, French	0–6	2,490	5	–	28,333	179
Suresh et al. (2011)	Ponnaiyar, India	Surface	85.2	182.9	87.3	29.5	81.8
Present study	Sebou (downstream of Fez), Morocco	0–6	100	236	115	46	171
Present study	Fez, Morocco	0–6	184	365	881	84	244

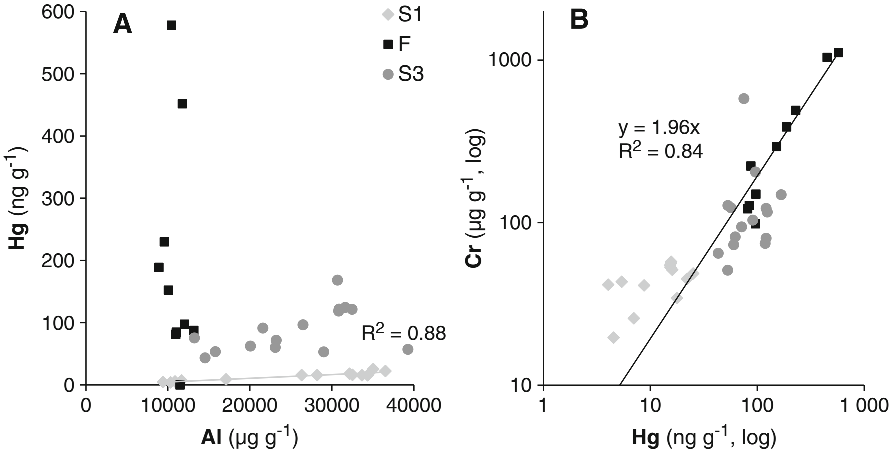

Fig. 5 Hg vs. Al (**a**) and Cr vs. Hg (**b**) relationships for the all the studied sediments

less polluted part of the S1 core was used as a natural background sediment to define the geochemical local background. The EF and geoaccumulation index (Igeo) are the most commonly used indicators to estimate anthropogenic inputs. The EF is a useful tool in determining the degree of anthropogenic heavy metal pollution (e.g. Trefry and Presley 1976; Sakan et al. 2009; Tessier et al. 2011; Balkis et al. 2010). To identify the trace element enrichment in Sebou and Fez sediments, a normalised EF was calculated according to the following equation:

$$\mathrm{EF} = {}^{[\mathrm{Me}/X]_{\mathrm{sample}}}/{}_{[\mathrm{Me}/X]_{\mathrm{background}}}$$

where X (Fe, Al, Th, Ti, Zr,…) corresponds to a conservative element.

Five degrees of contamination are commonly defined (Sutherland 2000): EF <2, deficiency to low enrichment; EF 2–5, moderate enrichment; EF 5–20, significant enrichment; EF 20–40, very high enrichment; EF >40, extremely high enrichment.

Normalisation to a conservative element is usually performed to counterbalance lithogenic influences of granulometric and mineralogical variations of the sediment. In the present study, Al was chosen as the conservative element for normalisation and as a representative constituent of clay minerals, which are the predominant carrier phase for trace metals in sediments. This choice was justified by the significant correlations observed between K and Al for all the studied sediments (Section "Major elements and organic carbon depth profiles") and between trace elements and Al for the S1 core, which was selected as our reference site (Section "Inter-element relationships"; Fig. 5a). The calculated EFs for Pb, Zn, Cr, Ni, Cu and Hg in the studied sediments are summarised in Table 1. The results show that the calculated EFs in S1 were lower than or closed to 1, which was expected according to the observed relationships between trace metals and Al, confirming the pristine status of the Sebou's sediments in the upstream of its confluence with the Fez. On the basis of the calculated enrichment factors, sediments from the F and S3 cores appeared particularly enriched in their surface layers. Indeed, the EF reached the values of 87, 65, 58, 53, 12 and 12 for Hg, Cr, Cu, Pb, Zn and Ni, respectively, in the upper layer of the F core. These sediments can therefore be considered to be extremely highly enriched, in reference to the classification defined by Sutherland (2000). EF values recorded for most of the studied elements in the S3 surface sediments (up to 15 for Cu) demonstrated once more the significant impact of contaminated particulate loads from the Fez (and likely originating from the Fez metropolitan area) to the Sebou. In contrast to the EF values observed for the F core, the highest EF values measured for the S3 core were encountered in the deeper layers (up to 36 for Cr in the 22–26 cm layer) due to the lower Al content, which potentially attributed to the Sebou's lower sediment contributions during the corresponding period of time, which may have enhanced the impact of inputs from the Fez.

The geoaccumulation index (Igeo) defined by Müller (1979) was also used to assess metal pollution in sediments. The geoaccumulation index was calculated according to the following equation:

$$\mathrm{Igeo} = \log_2(C_\mathrm{n}/1.5 \times B_\mathrm{n})$$

where C_n is the measured content of a metal (n) in the sediment and B_n is the geochemical background content of the metal (n). The constant 1.5 was introduced to minimise the effect of possible variations in the background values that may be attributed to the natural lithologic variations in the sediments. The index of geoaccumulation consists of seven grades, according to Müller's classification system (1979): ≤0 unpolluted, 0–1 unpolluted to moderately polluted, 1–2 moderately polluted, 2–3 moderately to strongly polluted, 3–4 strongly polluted, 4–5 strongly to extremely polluted, >5 extremely polluted. Igeo was calculated using the local background values (Table 1).

As already indicated by the EF values, the Igeo results revealed that the Sebou's sediments in upstream of the Fez metropolitan area were unpolluted. Based on the Igeo values, the surface layer of the F core appeared to be heavily contaminated with Hg (Igeo 6.36) and Cr (Igeo 4.80) and moderately to strongly contaminated with Cu, Pb, Zn and Ni. Similarly, in downstream of the Fez metropolitan area, the sediments appeared strongly polluted by Cu (Igeo 3.9), Pb (Igeo 3.1) and Hg (Igeo 4.6). The Igeo values for Cr also indicated that deeper sediments in the S3 core are were heavily polluted (Igeo 3.9), whereas surface sediments were generally moderately polluted.

Assessment of sediment pollution using sediment quality guidelines

To estimate the possible ecotoxicological consequences of the presence of trace metals in sediments, the concentrations of these metals were compared to SQGs. Such guidelines were developed to protect animals living in or near sediments from the deleterious effects associated with sediment-bound contaminants (Macdonald et al. 2000). SQGs have advantages and limitations which can influence their application (Long et al. 2000). Specifically, there can be variability in the toxicological responses of organisms to different contaminants due to regional differences or inherent pollutant bioavailability (Long et al. 2000). However, the authors concluded that such guidelines can reliably be used to estimate the probability of acute toxicity, despite slight geographical variations. Two sets of SQGs developed for freshwater ecosystems were used to evaluate heavy metal ecotoxicology in sediments: (a) "effect range low (ERL)/effect range median" (ERM) guidelines and (b) "threshold effect level" (TEL)/"probable effect level" (PEL) values (Long and MacDonald 1998; Long et al. 1995; MacDonald et al. 2000). Low-range values (i.e. ERLs or TELs) refer to concentrations below those that would frequently impart adverse effects upon sediment dwelling fauna. Conversely, ERMs and PELs represent concentrations above which adverse effects are likely to occur (Long and MacDonald 1998). The TEL/PEL and ERL/ERM comparison frameworks showed that the S1 sediments did not contain the studied contaminants at concentrations representing significant toxicological concern because most of the studied metals were below TEL, except for Cr and Ni, which exceeded their TEL values and ranged between the TEL and PEL levels, thus indicating possible biological effects. Downstream of the confluence with the Fez (S3), the measured values fell within the range between TEL and PEL levels, except for some toxic metals that exceeded PEL (Cr, Cu and Ni) or ERM (Cr and Ni) levels in surface sediments. Hg concentrations were associated with the lowest toxicological concern because the measured content all along the S3 core did not exceed the corresponding TEL value. Fez sediments (F) were found to be heavily toxic, as PEL values exceeded for all metals. Furthermore, ERM values also exceeded for Pb, Zn, Cr and Ni.

To estimate the toxicity risk resulting from metal mixtures, the ratio of the measured metal contents to their corresponding PEL values was summed to calculate the ΣTU value (Pedersen et al. 1998). The depth distributions of the calculated ΣTU values are presented in Fig. 6a, and the respective contribution of each studied metal to the ΣTU values is presented in Fig. 6b for the 0–6 cm slices of each core. The obtained results confirmed that the greatest toxicity risks occurred for Fez sediments, particularly in the surface layer (ΣTUs of 17.4, Fig. 6a), with a predominant impact of Cr (~60 %) on the ΣTU value. Ni and Pb also contributed significantly to the overall toxicity of these sediments (Fig. 6b). Accordingly, the ΣTU value strongly increased in the 14–18 cm layer due to historical contamination by Ni and Pb. Though lower levels of contamination were observed in the S3 core, the ΣTUs depth profile for this core followed a similar trend. While the findings of this work should be confirmed by a biological survey of sensitive aquatic species, it is readily apparent that the high loadings of industrial/urban wastewaters originating from the Fez metropolitan area have a dramatic effect on the sediment quality in the Fez and, consequently, significantly alter the sediments of the Sebou downstream of the confluence.

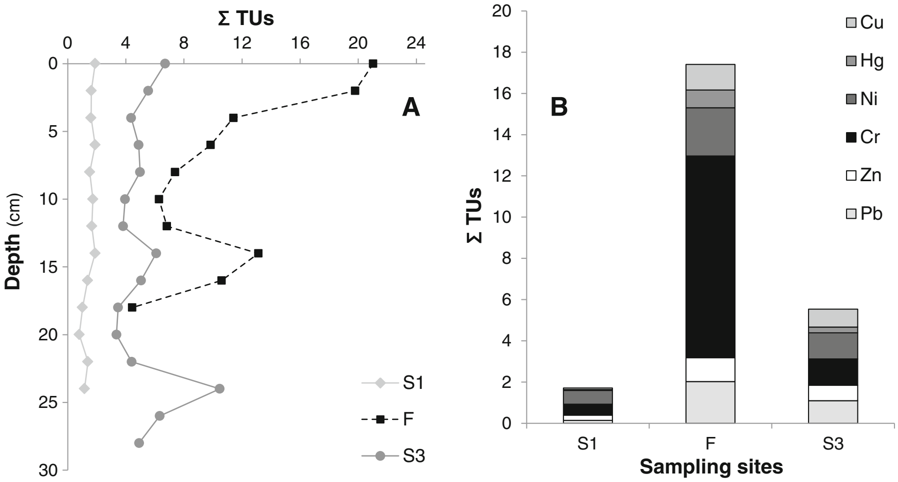

Figure 6 Depth profiles of ΣTU values calculated for the 3 studied cores (**a**), and contribution of each studied metals on the ΣTU value for the 0–6 cm slice (**b**) (see the text for more explanation)

Conclusions

This study aimed at characterizing sediment cores sampled in the largest Moroccan river, the Sebou upstream and downstream from the confluence with the Fez which collects the waters from the Fez metropolitan area (~1 million inhabitants). Major element concentration analyses revealed the predominance of carbonates and aluminosilicates (and co-occurring minerals such as oxyhydroxides), which appeared to have different origins. Significant contamination of sediments with butyltin compounds (BTs) upstream of Fez city was demonstrated, as the recorded ΣBT values were non-negligible. The higher ΣBT levels encountered in the F core indicated loadings from the Fez that led to an increase of BTs in the Sebou's sediment in the downstream of the confluence. Such inputs were recent, with the highest levels being measured in surface sediments. At all sites and depths studied, the main butyltin species observed was MBT. This finding could be due to direct inputs of this compound and/or from significant degradation of TBT. It should be noted that no inorganic tin content measurements were performed, and such measurements could provide additional information about the initial levels of contamination with this metal.

Trace metal contents in Sebou sediments in the upstream of Fez metropolitan area exhibited low values, suggesting that these species were mainly of natural origin, particularly considering the significant relationship between these metals and conservative elements such as Al. Conversely, Fez sediments were heavily polluted with numerous metals, particularly Cr, which reflected the strong impact of the untreated urban and industrial wastewaters from the Fez metropolitan area. Moreover, the continuous bottom-up increase of metal concentrations were representative of the significant population growth and accompanying intensification of industrial activities in Fez over the recent decades. The negative impacts of non-compliance with monitoring and regulatory requirements for wastewater discharge quality are also clearly observed in this study and could be representative of many cities in developing countries. The noticeably different major element compositions of the Fez and Sebou's sediments allowed the authors to conclude that particulate inputs from the Fez into the Sebou were most likely low, which was a reasonable assumption considering their respective sizes. However, the heavy contamination of Fez particles induced a significant increase in the contamination of Sebou sediments after the waters of the two rivers were mixed. Consequently, in reference to various sediment quality guideline values, the sediments of both rivers appeared to be potentially toxic to organisms, especially in Fez, and these findings raised questions about the possible risks for the local population using these waters, notably for irrigation. Hg data indicated a recent anthropogenic enrichment in the surface layers, but this toxic element does not represent a major ecotoxicological concern in the Sebou relative to the sediment quality guidelines used, as the measured values remained below the threshold effect level (TEL). The results of the present study recommend initiating the following: (1) a detailed environmental monitoring of both rivers and their respective catchment areas to evaluate the pollutant origins, fluxes, dynamics and fates and (2) development of a practical remediation strategy for regulating pollutant discharges to reduce the contamination of this ecosystem. The future waste water treatment plant, which will treat wastewater from Fez city before discharging it into the Fez, will likely improve the water quality in the region, as several studies have demonstrated that such treatment considerably reduces total metal loads (e.g. Buzier et al. 2011), even if treated wastewater continues to be a non-negligible source for the contamination of the environment (e.g. Oursel et al. 2013).

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