Radionuclide activities and metal concentrations in sediments of the Sebou Estuary, NW Morocco, following a flooding event

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Abstract This study presents metal concentrations (Fe, Mg, Mn, Co, Cu, Zn, Pb, As, Sr and V) and radionuclide activities (^{40}K, ^{137}Cs, ^{210}Pb, ^{226}Ra, ^{228}Ac, ^{234}Th and ^{212}Pb) in surface deposits and a sediment core from the Sebou Estuary, Northwest Morocco. Samples were collected in April 2009, about 2 months after a flooding event, and analysed using a well-type coaxial gamma-ray detector and inductively coupled plasma–quadrupole mass spectrometry. Activities of radionuclides and concentrations of almost all elements in surface samples displayed only moderate spatial variation, suggesting homogenous deposition of eroded local soil in response to intense precipitation. Excess ^{210}Pb displayed relatively constant activity throughout the sediment core, preventing dating and precluding determination of the historical accumulation rates of pollutants at the core site. Some elements showed non-systematic trends with depth and displayed local maxima and minima. Other elements presented relatively systematic concentration trends or relatively constant levels with discrete maxima and/or minima. Except for Mn, Sr and Cr, all metal concentrations in sediment were below levels typical of polluted systems, suggesting little human impact or losses of metals from sediment particles.

Keywords Sebou Estuary · Sediment contamination · Metals · Radionuclides · Gamma spectrometry · ICP-QMS

Introduction

Sediments comprise an important compartment in estuarine environments, and their analysis can be informative about radionuclide and metal pollution. Fine sediment particles act as a sink for trace pollutants within such systems, but can also be a source of these pollutants through adsorption/desorption and re-dissolution processes (Laissaoui and El Mrabet 2008). Pollutant concentrations in estuarine water change constantly as a consequence of mixing of seawater and river inputs under tidal

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dynamics. Consequently, detection of pollution in the aqueous compartment is less reliable than in sediments, where concentrations can also vary over time, but at a much slower rate than in water. For this reason, surface sediments in estuaries have been the samples of choice for assessing pollution. Furthermore, sediment cores are frequently used to determine historical rates of pollutant accumulation in these important coastal ecosystems.

The Sebou catchment is the second largest basin in Morocco, draining 40,000 km^2 and traversing some 600 km from its source at over 2,800-m altitude in the middle Atlas Mountains to the Atlantic Ocean in the northwest. Along its course, it suffers from urban pollution from residences and industries and from agricultural activities in the Gharb coastal plain, for which it provides irrigation water. Six large reservoirs were built in the last century to regulate flow in the upper, middle and lower catchments. Social and economic development is threatened by increasing deterioration of water quality. Domestic and industrial sewage from the city of Fez, located ~160 km from the Sebou Estuary, is discharged directly into the Sebou River. Water quality studies conducted in this area demonstrated the presence of many toxic chemicals, generated mainly by textile producers and tanneries (Koukal et al. 2004; Giorgetti et al. 2011).

In February 2009, heavy rainfall caused Sebou Estuary water levels to exceed flood stage. Precipitation increased from an average annual value of ~300 mm to about 1,064 mm, with a stream flow of 720 m^3/s in the lower Sebou River. This was the situation about 2 months before sediment samples were collected for this study.

The main objective of this work was to determine metal concentrations and radionuclide activities in surface sediments and a core from the Sebou Estuary. Radionuclides ^{40}K, ^{137}Cs, ^{210}Pb, ^{226}Ra, ^{228}Ac, ^{234}Th and ^{212}Pb were measured with a well-type gamma-ray detector, and metal concentrations (Fe, Mg, Mn, Co, Cu, Zn, Pb, As, Sr and V) were determined by inductively coupled plasma–quadrupole mass spectrometry (ICP-QMS). Results were compared to previous data from the area and from other natural aquatic systems to assess the impact of flooding on sediment contamination in the Sebou Estuary.

Materials and methods

Sampling and sample treatment

Six surface sediment samples were collected along the Sebou Estuary during low tide on April 2009 (Fig. 1). A sediment core was also taken, using a stainless steel tube (10-cm ID), from the upper part of the estuary, about 15 km from the mouth (Fig. 1). The 60-cm core was sectioned immediately after retrieval into 2-cm increments, which were transferred to labelled plastic bags for subsequent analyses of metals and radionuclides. The outer layer of each core slice was discarded to avoid cross-contamination among sections. This approach also prevented contamination of sediment from the metal coring tube.

Bulk samples were dried at 70–80 °C for 24 h, then gently disaggregated with mortar and pestle and passed through 2.0- and 0.5-mm sieves to remove large particles. Dried samples of approximately 6 g were placed in plastic vials and sealed with a rubber stopper to prevent escape of ^{222}Rn gas ($T_{1/2}$=3.8 days) and were stored for at least 20 days to achieve secular equilibrium between ^{226}Ra and ^{214}Pb; the latter was used to estimate ^{226}Ra, i.e. supported ^{210}Pb activity.

Radionuclide analyses

Total ^{210}Pb activity was determined by its gamma emission at 46.5 keV, and ^{226}Ra activity was estimated from the 295 and 352 keV γ-rays emitted by its daughter isotope ^{214}Pb. ^{137}Cs was measured by its emission at 662 keV. The absolute efficiencies of the detectors were determined using calibrated sources, and corrections were made for the effect of self-absorption of low energy γ-rays within the sample. Each sample was counted for 1 to 3 days, and activity values were standardised using IAEA reference materials (IAEA-444 and IAEA-447). The specific activity (in becquerels per kilogram) of each sediment sample was calculated from the detector efficiency, gamma intensity and sample weight. All values are reported as the activity on the date of sampling. Errors reflect one sigma counting statistics.

The main gamma-ray detector was a low-background Canberra high-purity germanium (HPGe) GCW-3023-S well-type coaxial detector. The nominal volume is 160 cm^3 (50-mm well depth and 16-mm well diameter). The detector has a relative efficiency of 30 % and a

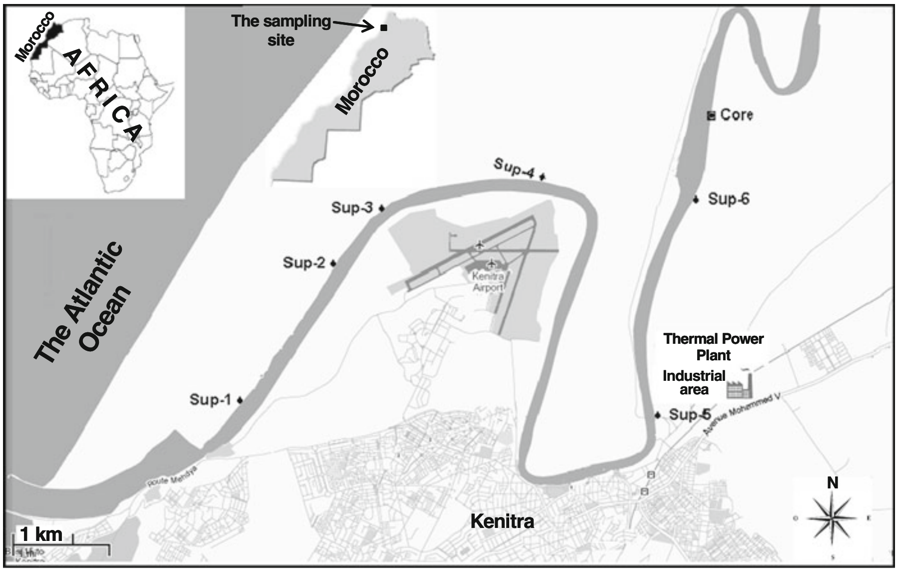

Fig. 1 Sketch map of the study area showing the sampling locations

resolution of 2.3 keV for the 1,332.5 keV ^{60}Co γ-rays. The HPGe is surrounded by a Saint-Gobain thalium-doped sodium iodide [NaI(Tl)] annular single crystal of 6.0-cm internal diameter, 12-cm thickness and 30-cm height and by a NaI(Tl) cylindrical plug coupled to six photomultipliers. The whole assembly is housed in a 10-cm-thick, high-purity lead shield. Pulses from the NaI anti-Compton detectors and germanium detector are treated by an electronic chain to suppress cosmic ray events registered by the NaI(Tl) detectors as well as Compton-scattered gamma-quanta registered by both the HPGe and NaI(Tl) detectors. The electronic setup consists of a Timing Filter Amplifier module (Canberra 2111) with selectable differentiation and integration time constants and a Constant Fraction Discriminator (CFD) module (Canberra 2126) connected to the NaI(Tl) and HPGe detectors. A Time to Amplitude Converter (TAC) module (Canberra 2145) is started with the pulse from the CFD of the NaI(Tl) and stopped with the pulse from the CFD of the germanium detector, generating an output pulse whose amplitude is linearly proportional to the time interval between these input pulses. The TAC output signal is shaped and delayed by a Delay&Gate module and used to block the ADC. The integral background was reduced in this manner to 0.08 cps between 46 and 2,000 keV.

Metal analyses

Metal concentrations were measured by ICP-QMS following microwave-assisted digestion. The digestion method was based on the US EPA 3050 method (EPA 1996), as modified by Hassan et al. (2007). Nitric acid digestion alone cannot achieve total digestion of sediment samples, even when a microwave oven is used. The EPA 3050 method offers a reasonable estimate of leachable/total concentrations of elements in soils, sediments and sludges (Link et al. 1998). It allows the analyst to calculate the leached mass instead of the total mass of the starting material and thus eliminate bias introduced by the variable amount of non-reactive, residual material (Gelinas et al. 1998). The use of HF is recommended to assure decomposition of the refractory matrix, but HF cannot be aspirated by our ICP-QMS. Possible ways to overcome this drawback are the following:

1. Evaporation of the sample to complete dryness and recovery using 1 % HNO_3. This method, however, can cause loss of volatile elements, even when evaporation is performed at low temperatures.
2. Dilution of samples until the HF concentration declines to an acceptable level, usually <100 ppm. According to common digestion schemes (e.g. Negre et al. 2009), the final dilution of the sample should be in the range of 27,000 ml/g, a value that would compromise the detection limit of the technique.
3. Use of H_3BO_4 in a post-digestion step, along with a microwave-assisted reaction. Several authors have proposed this technique to remove excess HF by borate tetrafluoride formation. During this process, however, mono-fluoroboric acid is generated, and it also damages the quartz/glass ICP-MS components.

As a consequence, the method proposed by Hassan et al. (2007) was used. An aliquot of the sample was diluted in 1 % HNO_3 until a final dilution factor of 3,500 ml/g was achieved. Figure 2 shows recoveries of the analysed elements using this method for two certified reference samples, NIST SRM-1646 and IAEA SL-1, a lake and an estuary sediment sample, respectively. Quantitative recoveries were achieved for almost all the certified elements except Al, Ca and Ti, for which recoveries were only qualitative and should be interpreted considering the limitations explained above. Qualitative recovery of Al precludes normalising other element concentrations to Al to assess enrichment factors.

An Agilent 7500c ICP-quadrupole MS was used for metal analyses. The instrument has an octopole reaction system, which operated in He-mode at 3.5 ml/min. A conventional Babington nebuliser was used for multi-element analysis, and analytical runs (three replicates per analysis) were performed according to the US EPA 200.8 protocol (Creed et al. 1994). Therefore, different data quality tests were used during instrument runs, such as replicate, matrix matching and memory effects, as well as digestion, analysis and laboratory blank checks.

Results and discussion

Radionuclides

Specific activities of naturally occurring radionuclides ^{40}K, ^{210}Pb, ^{226}Ra, ^{212}Pb, ^{234}Th and ^{228}Ac, along with the fission product nuclide ^{137}Cs, in the six samples of surface sediment are shown in Table 1. To our knowledge, these are the first such data regarding radioactive elements in the Sebou Estuary. Only slight to moderate spatial variation in activity was measured for each of the studied radionuclides along the estuary, the only exception being the relatively low activity of ^{40}K in sample SUP-5. This sample had relatively high water and organic matter content during pre-treatment, but evidently, this did not affect values for other nuclides. There were no previous data on radionuclide activities in Sebou Estuary sediments, so we compared our data set with activities and inventories measured in other regions. ^{234}Th and ^{226}Ra activities are nearly equal to one another in each sediment sample. This unexpected radioactive equilibrium indicated that no fractionation had occurred in the sediment, and that the deposits were probably derived from sedimentation of eroded soil particles rather than suspended matter carried by river water currents. Heavy rains about 2 months before the sampling campaign (April 2009) were responsible for the erosion, transport and deposition of large amounts of soil. ^{210}Pb activities were smaller than those reported by Laissaoui et al. (2008) in the Mediterranean Sea (650 Bq/kg) and by Zourarah et al. (2007) in the Lagoon of Oualidia (1,300 Bq/kg). ^{210}Pb activities in the Sebou Estuary sediments are similar to those measured in Moroccan soils (Mabit et al. 2008), which corroborates the hypothesis of soil translocation. ^{137}Cs activities were within the range of values reported for marine sediment from the Alboran Sea (Laissaoui et al. 2008).

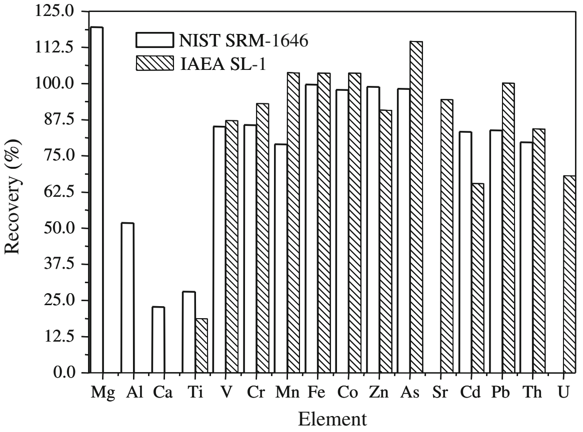

Fig. 2 Recovery rates for analysed elements in two certified reference sediment samples, using the methods described in the text. Results are the average of one to two sample aliquots

Distributions of ^{40}K and ^{137}Cs activities in the sediment core show a similar behaviour with sediment depth (Fig. 3). This is a consequence of the similar geochemical behaviours of the two elements, with adsorption and ion exchange being the dominant mechanisms for their binding to sediment particles (Cahill and Steele 1986).

Although ^{137}Cs activity did not decline to zero in the deepest layers, the partial inventory for ^{137}Cs was determined by summing the product of each layer's activity, bulk density and thickness. The calculated value, 3,720 Bq/m^2, is much higher than literature values. For instance, Laissaoui et al. (2008) reported a total inventory of 284 Bq/m^2 in the Alboran Sea. Such a high inventory in the Sebou Estuary could only be explained by massive deposition of local soil, accompanying the flooding event in winter 2009. In

Table 1 Radionuclides activity obtained in the surface samples (in becquerels per kilogram dry weight) by gamma spectrometry

Sample	^{40}K	^{137}Cs	^{210}Pb	^{226}Ra	^{234}Th	^{212}Pb	^{228}Ac
SUP-1	348±16	3.1±0.3	43±12	19±2	19±4	29±1	21±4
SUP-2	348±14	3.2±0.6	42±2	17±1	20±5	30±1	20±1
SUP-3	339±14	2.2±0.2	43±3	19±2	16±6	29±1	18±1
SUP-4	385±17	3.4±0.3	55±4	16±2	20±4	27±1	17±2
SUP-5	209±18	3.5±0.4	50±4	17±1	19±5	26±1	16±2
SUP-6	283±13	1.7±0.3	39±11	18±2	17±7	26±2	20±1

addition, the profiles display a well-defined subsurface maximum at 32–34 cm (Fig. 3). ^{137}Cs is present in the deepest layers, with activities between 6 and 8 Bq/kg, greater than surface activity, suggesting that the radionuclide cannot be used in this core to identify the period of maximum atmospheric fallout in 1963. The high ^{137}Cs activities throughout our 60-cm-long sediment core indicate that we retrieved only the very recent history of sediment deposition in the estuary.

Figure 4 depicts the vertical distributions of total ^{210}Pb, ^{226}Ra and excess ^{210}Pb$_{xs}$, calculated by subtracting supported ^{210}Pb (i.e. ^{226}Ra) activity from total ^{210}Pb on a layer-by-layer basis. We originally intended to calculate historical rates of pollutant delivery to the sediment by dating the core. Unfortunately, high sediment mixing induced by water turbulence resulted in homogenous distribution of ^{210}Pb$_{xs}$ along the length of the core, preventing dating by conventional means and rendering the core useless for study of sediment accumulation processes. ^{226}Ra activity was fairly constant along the core, the only exception being a slight decline at 12–14-cm depth. The measured values are quite similar to those of typical soils worldwide (UNSCEAR 2003). Vertical distribution of activities of short-lived radionuclides ^{212}Pb (half-life=10.64 h), ^{228}Ac (half-life=6.13 h) and ^{234}Th (half-life=24.1 days) was also determined in the sediment core (Fig. 5). ^{234}Th, which is produced in situ from ^{238}U, was nearly constant throughout the core, with a mean activity of 22 Bq/kg, whereas both ^{212}Pb and ^{228}Ac, which are decay products of ^{232}Th, had mean activities along the core of about 32 and 22 Bq/kg, respectively.

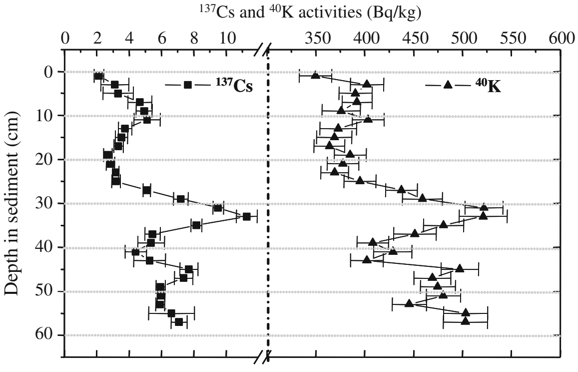

Fig. 3 Vertical distributions of ^{137}Cs and ^{40}K activity in the sediment core from the Sebou Estuary

Trace elements

Trace elements were extracted from sediment samples using diluted nitric acid as explained in "Materials and methods," and the parallel analysis of two international reference materials allowed controlling the percentages of recovery for each element. Some elements, such as Pb, As, Co, Fe and Mn, were completely extracted using

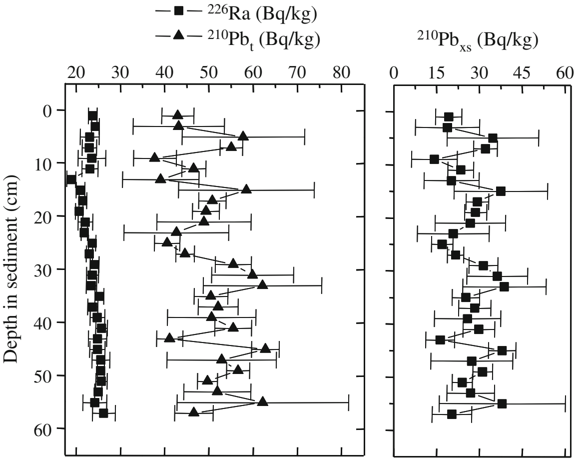

Fig. 4 Total ^{210}Pb, ^{226}Ra and excess lead-210 (^{210}Pb$_{xs}$) activities in the core from the Sebou Estuary. ^{210}Pb$_{xs}$ activity was calculated by subtracting supported ^{210}Pb (=^{226}Ra) activity from total ^{210}Pb on a layer-by-layer basis. Errors are 1σ, and activities are in becquerels per kilogram dry weight

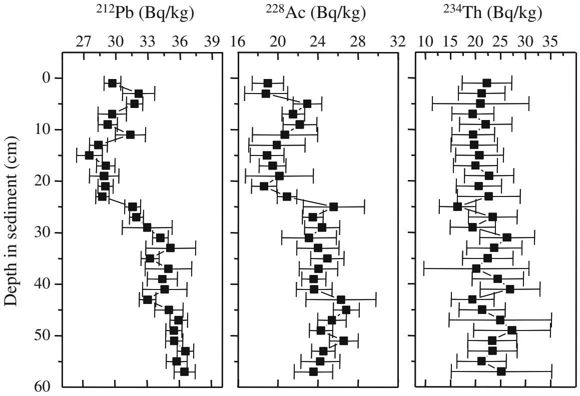

Fig. 5 Vertical distributions of ^{212}Pb, ^{228}Ac and ^{234}Th activity in the sediment core from the Sebou Estuary. Errors are 1σ, and activities are in becquerels per kilogram dry weight

this method, while recoveries for the other elements were almost all above 80 %. Thus, comparison of the values found with literature data in which total digestion was used should take into account this fact.

Element concentrations in surface samples are shown in Table 2. Sample SUP-5 was not analysed because of its high organic content (>25 %). Similar to radionuclides, element concentrations in surface deposits are similar throughout the sampling area, with coefficients of variation of <25 %. Sediment from SUP-6, located in the upper part of the study area, had the lowest element concentrations, except for Mn and Sr. Concentrations of Cu, Zn, Mn and Cd are lower than those reported by Cheggour et al. (2005) for the period 1992–1995 and by Fekhaoui et al. (1996) in the same area. This was probably a consequence of a “cleaning effect” of sediment particles and/or incorporation of less contaminated soil particles during the 2009 flooding event. On the other hand, concentrations of V, Cr, Fe and Cu are similar to those measured in the Bouregreg Estuary, also located in the Sebou Basin, an estuary that has been described as slightly polluted (Bounouira et al. 2008). Mean concentrations of Mn and Sr of 740 and 105 μg/g, respectively, were reported in the Bouregreg Estuary, values much lower than those found in this study (4,370 μg/g for Mn and 307 μg/g for Sr). As and Cd levels registered in the Bouregreg Estuary (30 and 0.5 μg/g, respectively), however, are much higher than those found in surface sediment from the Sebou Estuary (5.5 μg/g for As and 0.16 μg/g for Cd, which was detectable in only two sites).

Significant correlations ($p<0.05$) were found in surface sediment samples for the element pairs Cr–Mg (0.8830), Cr–V (0.7156), Mn–Zn (−0.8190) and Pb–Zn (0.9431). These associations indicate similar sources for Cr, V, Pb and Zn. The negative correlation between Mn and Zn, however, seems to suggest that soil runoff is not related to the high concentration of Mn found in these samples. Some metals, such as V, Cr, Zn, As, Pb and Th, showed pronounced fluctuations with depth and multiple maxima and minima (Fig. 6). On the other hand, Mg, Mn, Cu, Co, Sr and, to a lesser extent, Fe displayed relatively constant

Table 2 Elements concentration found in the collected surface samples

Sample	SUP-1	SUP-2	SUP-3	SUP-4	SUP-6
Mg (mg/g)	13.71±0.22	15.8±0.4	15.56±0.23	14.83±0.20	13.31±0.22
Fe (mg/g)	38.4±0.7	35.9±0.6	37.8±0.9	37.3±1.2	33.0±0.9
Mn (mg/g)	4.19±0.07	4.85±0.11	4.59±0.05	3.75±0.05	4.49±0.07
Zn (μg/g)	98±2	93±2	93.0±1.4	160±2	75.6±1.3
V (μg/g)	73.1±1.0	73.6±1.1	82.5±1.2	70.9±0.8	56.5±0.8
Cr (μg/g)	78±2	87.8±1.4	92±2	80±2	60.9±1.0
Co (μg/g)	15.0±0.2	13.7±0.4	14.4±0.3	13.6±0.2	13.7±0.2
Cu (μg/g)	22.3±1.1	18.6±0.5	19.5±0.7	21.7±0.3	9.1±0.4
As (μg/g)	4.86±0.07	4.56±0.11	6.59±0.11	7.0±0.2	4.4±0.2
Sr (μg/g)	243±4	375±7	323±4	279±4	318±5
Cd (μg/g)	ND	ND	0.16±0.04	0.153±0.010	ND
Pb (μg/g)	19.6±0.2	17.0±0.2	19.1±0.3	24.9±0.3	14.8±0.3

The sample SUP-5 was not analysed due to its high organic content

ND not detected

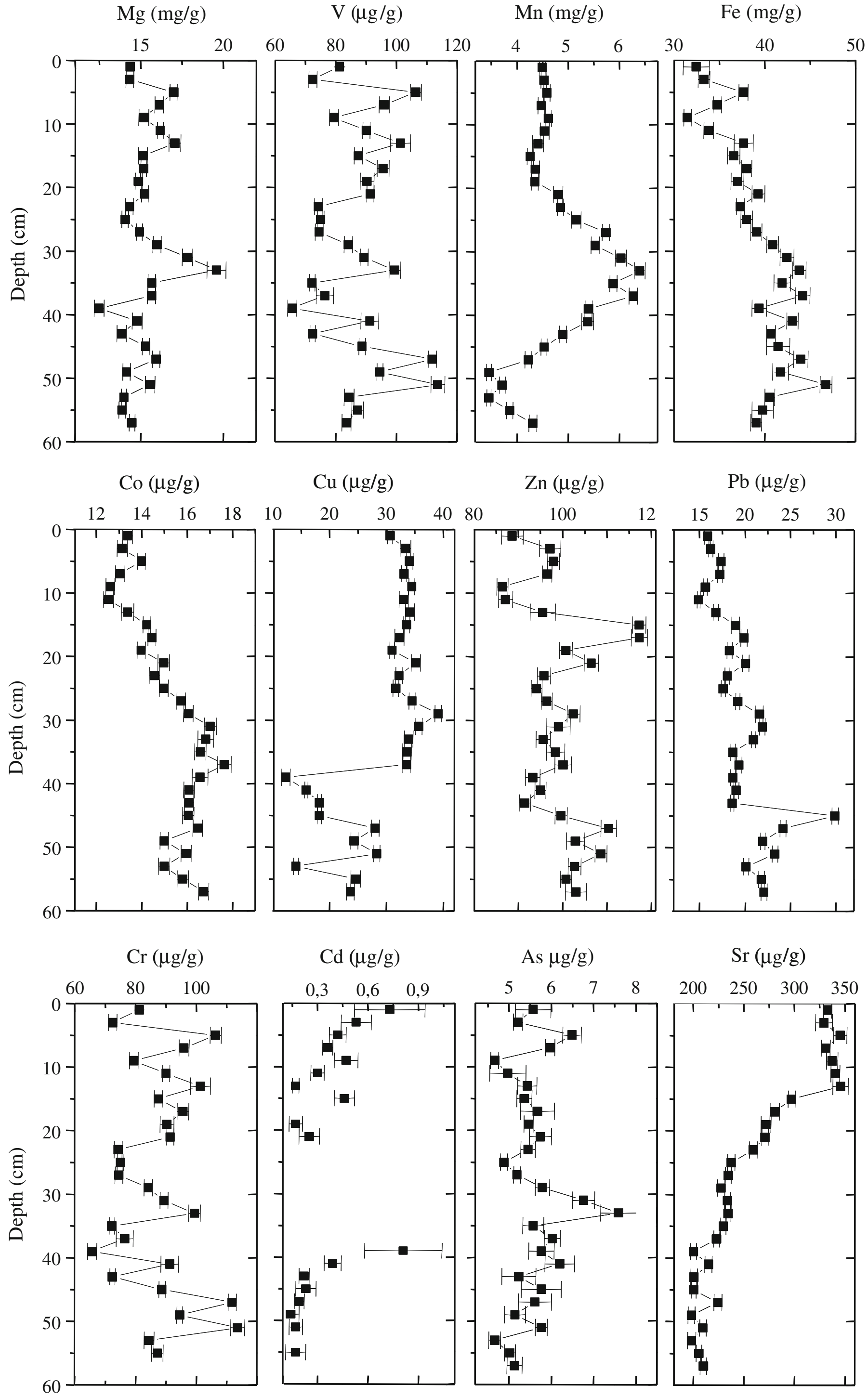

Fig. 6 Vertical distributions of elements in the sediment core collected from the Sebou Estuary

levels with a relatively well-defined maximum or minimum.

Metal concentrations can be summarised as follows:

1. A peak concentration of Mg was registered at 32–34-cm depth. The range of concentrations (12–20 mg/g) is consistent with those expected

for carbonate rocks (Pfeifer et al. 2000). The values are about 25–50 % of those registered at Bouregreg River (Bounouira et al. 2008), also located in the Sebou Basin.

2. Concentrations of V are of the same order magnitude as those reported for Bouregreg River by Bounouira et al. (2008), but pronounced fluctuations were recorded for this element throughout the core. Such vertical distribution, which is exceptional with respect to the other metals, could be explained by two processes: (1) minerals with different composition were mixed within the depositing sediment layers, and (2) the Eh of the water mass changed dramatically, causing different oxidation states of V and, consequently, different precipitation regimes. Concentrations of V were in the range of values reported for sediments not affected by significant anthropogenic sources (Gomes et al. 2009).
3. Concentrations of Cr were higher than those published by Bounouira et al. (2008) and more than an order of magnitude higher than those detected in Oum Er Bia Estuary (Zourarah et al. 2009). The levels found were also >50 % higher than those found for the Souss River, which can be considered a good background value (Moukrim et al. 2008). These comparisons indicated that Cr pollution was observed in the Sebou Estuary, which, according to the sediment quality guidelines proposed by Long and MacDonald (1998), could produce occasional toxicity to biota in a large proportion of the sediment layers. In addition, Cr, in its oxidation state 3+, remains strongly bound to soil and clay particles (Desjardin et al. 2002). The origin of such high concentrations could be essentially the Cr in the particulate form travelling from more than 100 km upstream to the study area. Extensive tannery industry located at the city of Fez uses chromium compounds in the pre-treatment of raw leather, and the resulting wastes are directly discharged into the Sebou River (Giorgetti et al. 2011).
4. Concentrations of Mn are more than an order of magnitude higher than those detected for Souss Estuary, even after the commissioning of a wastewater treatment plant (Moukrim et al. 2008), and also higher than those reported by Bounouira et al. (2008) for Bouregreg River. They are 40 times higher than those detected for Sebou River (Cheggour et al. 2005) and even more than an order of magnitude higher than Mn concentrations detected at Nador Lagoon, which is impacted by effluents from a nearby wastewater treatment plant that serves a population only about 25 % the size of Kenitra. Natural concentrations, corresponding to carbonate-type soils, are in the range of 540 μg/g. For shale-type deposits, expected Mn concentrations are about 850 μg/g (Pfeifer et al. 2000). Such high concentrations could be attributed, in addition to natural sources and urban sewage, to a combination of car exhaust emissions and the close proximity of the thermal power plant (Lytle et al. 1995).
5. The Cu concentrations were near the lowest range registered at Sebou Estuary during the period 1992–1995 (Cheggour et al. 2005) and close to those of the coastal zone of Nador Lagoon (Ruiz et al. 2006). They were also similar to those registered at Bouregreg River (Bounouira et al. 2008) and Oum Er Bia Estuary (Zourarah et al. 2009), sites slightly affected by Cu pollution as a consequence of intensive agricultural practices.
6. The Fe values were similar to those of Souss Estuary (Moukrim et al. 2008) and overlap both the range of concentrations in the Marrakech region, which are affected by acid mine drainage (El Gharmali et al. 2004), and values previously published for the Sebou Basin (Cheggour et al. 2005). The Fe values here also show overlap with those found by Bounouira et al. (2008) in Bouregreg River sediments and with those collected at Oum Er Bia Estuary, which is not clearly polluted by anthropogenic activities (Zourarah et al. 2009). The Fe values were typical of carbonate rocks (Pfeifer et al. 2000).
7. Most of the Co data are similar to values from unpolluted areas of Morocco, although several values fall outside this general range (Ruiz et al. 2006). There is an upward decline in Co concentration in the topmost 30 cm of the core, similar to that of Mn, which is also associated with sewage. However, no enrichment over previous sampling could be established, as was done for Mn, because of a lack of Co data in this region. It is possible that the up-core decline in Co concentration could be a result of its desorption from the sediment.
8. Concentrations of Zn were generally below levels found in polluted estuaries (400–900 μg/g) (Barreiro et al. 1994). The values measured were

slightly above the levels registered at Souss Estuary (Moukrim et al. 2008) and smaller, but of the same order of magnitude, as previous data for the Sebou River Basin (Cheggour et al. 2005). Levels of Zn were, in general, below the limits proposed by Long et al. (1995) regarding expected toxicity to biota.

9. Concentrations of As were comparable to the lowest values found at the Nador Lagoon (Ruiz et al. 2006) and well below values for Bouregreg River (Bounouira et al. 2008). They were also well below the toxicity limits proposed by Long et al. (1995). Therefore, we conclude that there is no enhancement of As by anthropogenic activities in the Sebou Estuary. A distinct maximum concentration was registered at 30–32-cm depth.
10. Concentrations of Sr displayed relatively constant values in the upper sediment, down to 15 cm. Below 15 cm, values decline exponentially but remain relatively constant in the basal 20 cm of the core. This distribution could be due to diagenetic re-dissolution with Fe/Mn oxides, under suboxic conditions (Zourarah et al. 2009). On the other hand, our results were higher by a factor of 2–6 than those found along the Bouregreg River (Bounouira et al. 2008), indicating enrichment of Sr over background values. Nevertheless, concentrations were similar to those expected for shale rocks, in accordance with the hypothesis of local soil deposition and mixing with bed sediment under stormy weather conditions.
11. No previous data for Pb concentration are available for this study site. The values are of the same order of magnitude as those found in Oum Er Bia Estuary (Zourarah et al. 2009) and below those registered for the Nador Lagoon (Ruiz et al. 2006). They are also below the ERL toxicity level proposed by Long et al. (1998). Thus, unless the low concentrations are due to incomplete extraction during digestion, no clear anthropogenic impact can be associated with Pb concentration in the sediment.
12. Cd could not be detected in all stratigraphic levels of the sediment core. Similar values were found at unpolluted locations near the study site (Zourarah et al. 2009; Bounouira et al. 2008; Ruiz et al. 2006). Furthermore, concentrations were below those found in a previous study in the same area (Cheggour et al. 2005). From Fig. 2, it can be seen that Cd presented almost the lowest recovery during sediment digestion process, which could be behind the low values found in this study. It was expected that concentrations of Cd would have been higher than those measured because the study area is characterised by high agricultural activity involving increasing use of phosphate fertilisers, which are an important source of Cd in the environment. More than 90 % of available Cd is usually concentrated in soil or plant roots after plant use (Enamorado et al. 2009). Nevertheless, high losses of Cd from the sediment during inundations could alternatively be behind the low concentrations found, as has been reported in other studies (Zwolsman et al. 1993).

Conclusion

We studied distributions of radionuclides and trace metals in surface sediments and a sediment core from the Sebou Estuary. There was only moderate spatial variation in activities of radionuclides and concentrations of elements throughout the sampling area, reflecting local soil deposition and mixing with sediment. Excess ^{210}Pb displayed nearly constant activity throughout the sediment core, precluding reliable dating and calculation of pollutant accumulation rates. Some of the metals showed more or less well-defined maxima or minima within the sediment core.

Our results suggest that pollutants in the studied sediment have two primary sources: (1) those in soil particles that were incorporated into the sediment bed during heavy rainfall events and subsequent inundations, and (2) those originally bound to sediment particles. Both components have undergone mixing induced by water turbulence and were “cleaned” by large volumes of uncontaminated rain water. Except for Mn, Sr and Cr, all the metals displayed concentrations in sediment below levels typical of polluted systems, suggesting little human impact or losses of metals, to varying extents, from the sediment particles.

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