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Changes in the Sediment Trace Metal Contamination after the Commissioning of a Municipal Wastewater Treatment Plant in the Souss Estuary (South Morocco)

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Abstract Monthly samples of sediment were collected from the Souss estuary, to determine the changeswhich have occurred in the concentrations of ten metals between 2001 when the low estuary was receivingthe wastewaters from Agadir city and 2003 after stopping the sewage dumping. The annual contents of Cu,Fe, Zn (in 2001) and those of Cr, Cu, Fe, Mn, Ni, Pb, and Zn (in 2003) showed significant correlations withthose of Al, indicating that fluctuations of their concentrations were only due to those of the aluminosilicatefraction of the clayey sediment. After normalization of these metallic concentrations in relation to those of Al,the contents of the different metals showed insignificant correlations between both years, except for Znwhich significantly dropped in 2003 and Cu which increased in 2003. The observed metallic fluctuations aremore influenced by the natural conditions of the estuary than the anthropogenic ones.

Keywords Metal contamination · Sediment · Wastewater · Souss estuary

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Numerous studies concerning the trace metal contamination of estuarine sediments have been carried out in countries under a temperate climate (for example, in Ireland: Byrne and O'Halloran 1999, or in USA: Ross and Lowe 2002) as well as in semiarid zones (Morocco: Cheggour et al. 2001, 2005). However, only little has been published on arid countries, where rivers are dry the most part of the year. Among those, the Souss estuary (south-western Morocco) gives an interesting case, where the flux of water arising from the catchment is episodic (rainfall only during winter months) but where large amounts of wastewater originating from the surrounding towns (16,000 m^3 day^{-1} generated by Agadir City, 500,000 inhabitants) were discharged for a long time (Ait Alla et al. 2006), so that they were often the single source of fresh water in the estuary (Mouneyrac et al. 2006). In November 2002, a sewage treatment plant (STP) was implanted in the vicinity of the estuary, discharging its depurated waters out of the estuary. This new situation has reinforced the importance of marine waters in the lower estuary (increased salinity and hydrodynamics mainly governed by the tides), changing this former estuarine area into a quite marine ecosystem. In addition, a large input of chemical contaminants has stopped. Knowing these new developments, we took the opportunity to establish the initial status of contamination (levels of contaminants before the setting up of the STP) and to study the impact of this latter commissioning. The contamination was studied in surface sediments as recommended by Davies et al. (1991) or Hanson et al. (1993) and turned on trace metals selected for their potential occurrence, as generally originating from sewage effluents (Förstner and Wittman 1983; Ruiz and Saiz-Salinas 2000). Additionally, some key parameters (Al, Fe, Mn, Organic matter, carbonates) were measured all along the study in order to characterise the sediment.

Materials and Methods

During 2 years (year 2001 for the initial status and year 2003 for the impact of the STP), three samples of surface sediment (1 cm thickness) were collected monthly from a site located at about 1 km from the point of wastewater discharges (Fig. 1), using a small plastic spatula to avoid a supplementary metallic contamination. Samples were put into polyethylene bags before their transport to the laboratory and their storage at −20°C. Sediment was dried at 60°C up to obtain a constant weight (12–24 h) and was subsequently sieved at 63 µm using a nylon sieve and distilled water. For a better comparability between samples of different granulometry, the fine fraction (<63 µm) of sediment was used for metal analyses. Total digestion was achieved by a mixture of HNO_3, HCl, and HF according to Loring and Rantala (1992). The metal concentrations (mean of the three replicates) were determined using atomic absorption spectrophotometry, Al by N_2O–acetylene flame, Fe, Mn, and Zn by air-acetylene flame (Varian, model AA600), Cd, Cr, Cu, Ni and Pb by graphite furnace (Varian, model AA-800 with Zeeman correction) and Hg using an automatic mercury analyser (ALTEC, model AMA 254). Quality assurance relies on the control of blanks and the accuracy and reproducibility of data relative to certified reference material (Table 1). Participation in international intercomparison exercises (e.g., the EU QUASIMEME project) is done on a regular basis. The organic matter content was estimated from the weight loss of the fine sediment after calcination at 520°C for 6 h (Kristensen and Andersen 1993). Bernard's calcimetry (AFNOR standard X31-105) was used to measure the content of calcium carbonates. For a statistical point of view, the LSD test (Statistica V6.1) was used to establish levels of significance.

Table 1 Performances of the quality control with the CRM MESS-2 from the NRCC

	Detection limit	Obtained value	Certified value
Al (%)	0.2	8.7 ± 0.3	8.6 ± 0.3
Fe (%)	0.01	4.3 ± 0.2	4.2 ± 0.2
Mn (µg g^{-1})	7	360 ± 10	365 ± 21
Cd (µg g^{-1})	0.01	0.27 ± 0.02	0.24 ± 0.01
Cr (µg g^{-1})	0.15	102 ± 5	106 ± 8
Cu (µg g^{-1})	0.4	38 ± 3	39 ± 2
Hg (µg g^{-1})	0.007	0.089 ± 0.001	0.092 ± 0.009
Ni (µg g^{-1})	0.2	50 ± 3	49 ± 2
Pb (µg g^{-1})	0.4	23 ± 1	22 ± 1
Zn (µg g^{-1})	6	158 ± 6	172 ± 16

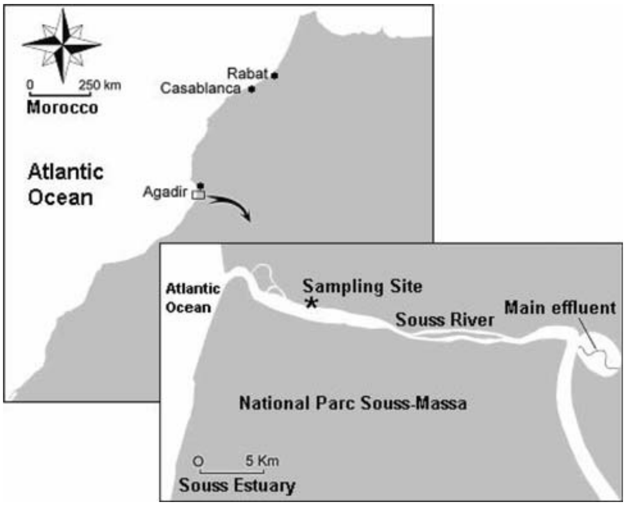


Fig. 1 Souss estuary with the sampling site and the main effluent (removed in 2002)

Results and Discussion

On a general point of view, the quality of sediment has only little changed between the 2 periods (Table 2). If it seems to appear a light fall of the organic matter content and a light increase in $CaCO_3$ (what was expected after the STP commissioning), this evolution is not significant due to the much larger variability of these parameters during the year 2003. It is the same for Al, representative of the clay fraction, and Fe and Mn witness of the redox conditions. Actually, this variability is well illustrated in Fig. 2, which shows during the year 2003 a clear increase for example in aluminium load versus time whereas a remarkable stability was observed in 2001. It is then necessary to take in account this change only due to the mineralogy and granulometry variations and which could be a bias in the interpretation of eventual fluctuations of trace metal contents. Thus, the concentrations of the studied metals have been "normalised" using the ratio: [metal]/[Al] in order to highlight the anthropogenic impact in the dataset (Schropp and Windom 1988; Loring and Rantala 1992). In that context, the time evolution of Fe/Al and to a lesser extent of Mn/Al (Fig. 2) shows that the observed fluctuations in Fe and Mn loads are mainly due to changes in the quality of the sediment. The first observable impact of the STP is thus an evolution of the surface sediment towards a fine fraction enriched in clay, which can be due to an ascent of downstream sediments or an in situ transformation caused by a marine fauna settling this place.

The mean concentrations of metals found in the sediment of the Souss river (Table 3) are ranged in the same order than those reported in other estuaries as several Moroccan estuaries other than the Souss Estuary (Cheggour et al. 2005). With

Table 2 The main physicochemical characteristics of estuarine water and sediment

Year	<63 μm (%)	Organic matter (%)	$CaCO_3$ (%)	Al (%)	Fe (%)	Mn (μg/g)
2001	71 ± 7	5.2 ± 0.9	9.2 ± 1.7	6.6 ± 0.3	3.4 ± 0.1	420 ± 22
2003	70 ± 5	4.7 ± 2.0	11.0 ± 3.2	7.5 ± 2.1	3.5 ± 1.0	482 ± 137

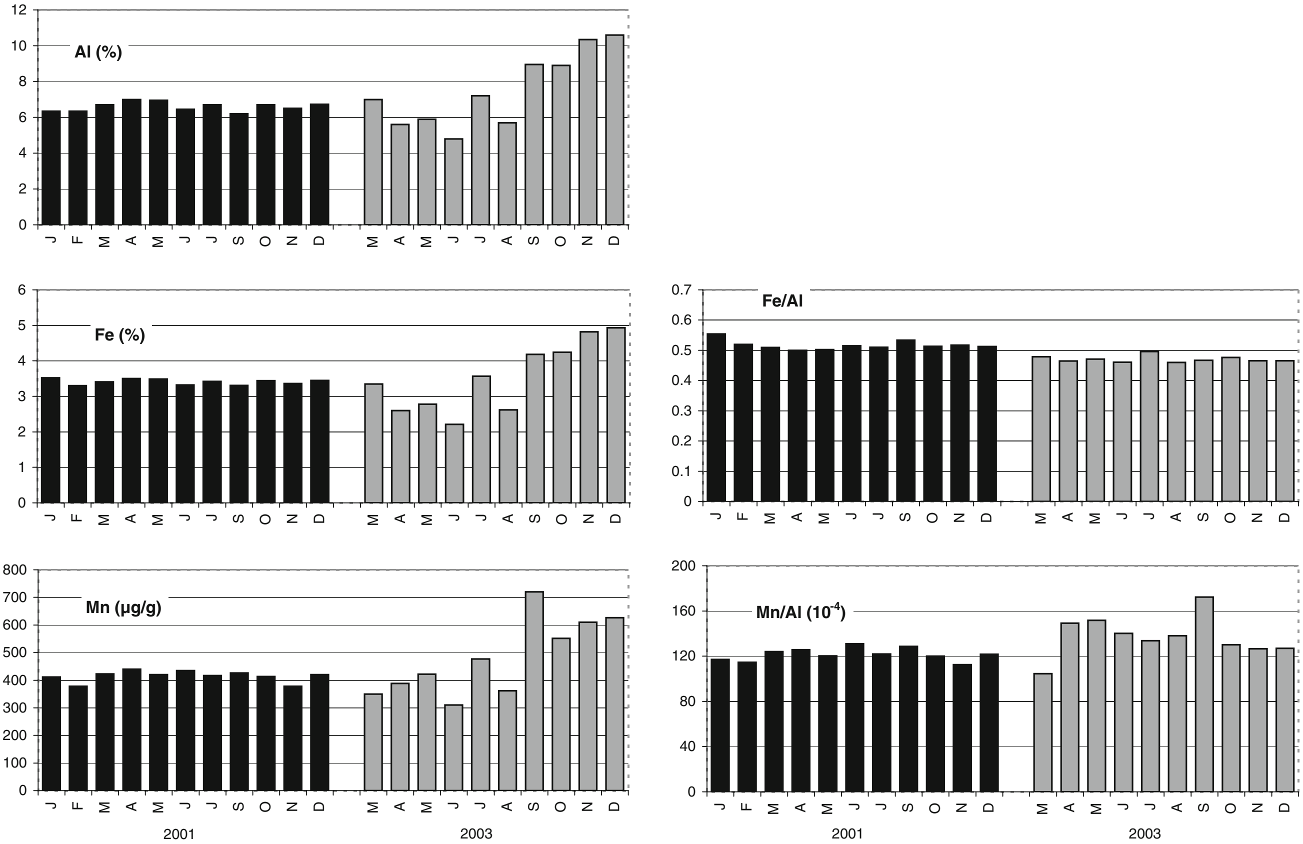


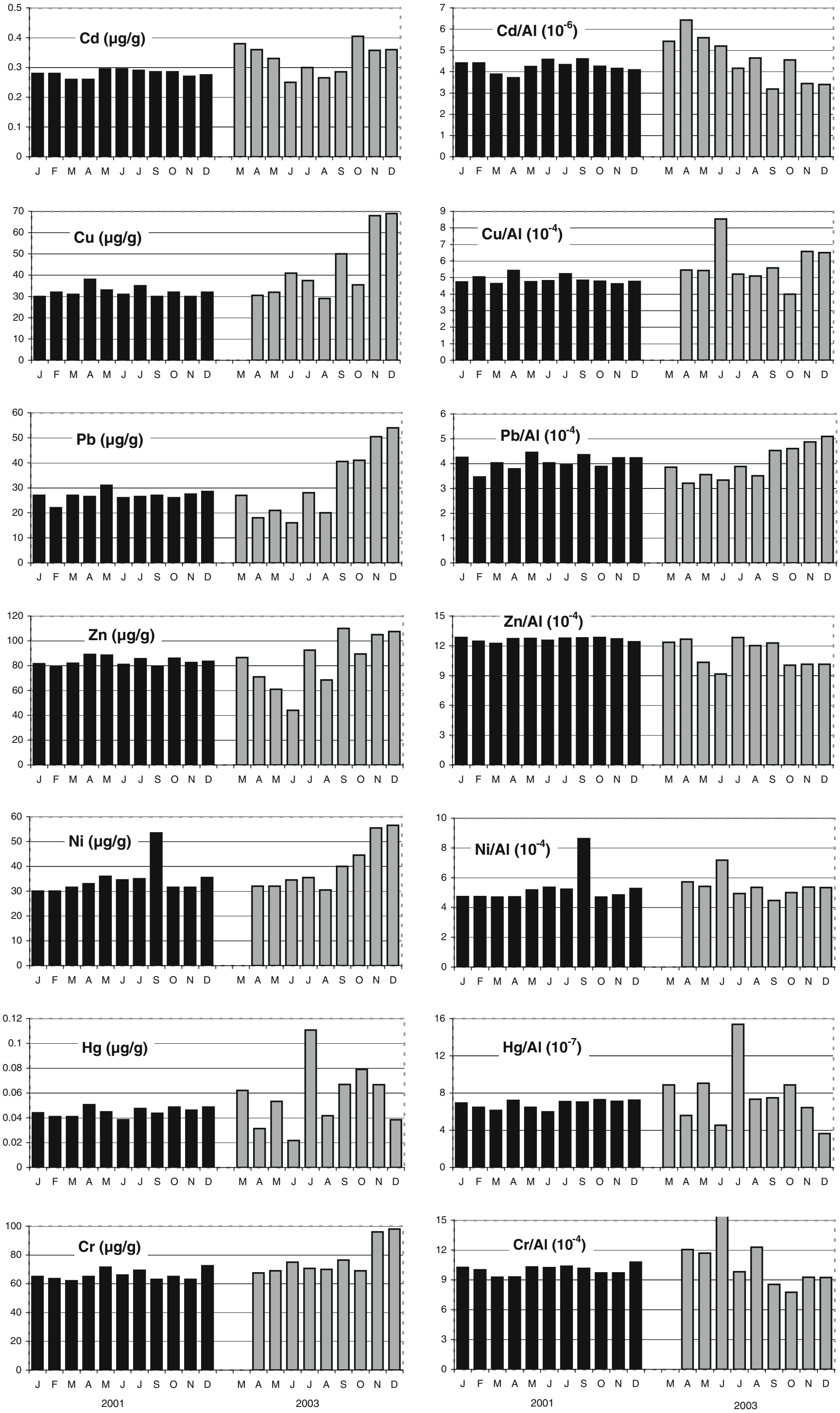
Fig. 2 Temporal variations of major elements in surface sediments (<63 μm) from the Souss estuary

Table 3 Means ± SD for the annual concentrations of metals in the estuarine sediment of the Souss river in 2001 and 2003

	Year 2001		Year 2003	
	Concentration (μg g^{-1})	Me/Al (10^{-4})	Concentration (μg g^{-1})	Me/Al (10^{-4})
Cd	0.28 ± 0.01	0.042 ± 0.003	0.33 ± 0.05	0.046 ± 0.011
Cr	67 ± 4	10.1 ± 0.5	77 ± 12	10.7 ± 2.4
Cu	32 ± 2	4.9 ± 0.2	44 ± 15	5.8 ± 1.3
Hg	0.045 ± 0.004	0.0068 ± 0.0005	0.057 ± 0.026	0.0077 ± 0.0034
Ni	35 ± 7	5.3 ± 1.1	40 ± 10	5.4 ± 0.7
Pb	26 ± 2	3.9 ± 0.3	32 ± 14	4.0 ± 0.7
Zn	83 ± 3	12.6 ± 0.2	84 ± 22	11.2 ± 1.4

respect to these contaminants, the Souss Estuary can be considered as a non contaminated estuary, compared for example with that of Bilbao, Spain (Ruiz and Saiz-Salinas 2000) or the Seine Estuary, France (Chiffoleau et al. 1994). These findings are in accordance with those of Moukrim et al. (2000) and Banaoui et al. (2004) who showed that the Agadir coastal region was not impacted by trace metal compared with industrial and urban areas located northern on the Atlantic coast. The seasonal variability can be observed in steady state situation, when no dramatic event may disturb the normal

Fig. 3 Temporal variations of trace contaminants in surface sediments (<63 µm) from the Souss estuary



functioning of the system. Before the setting up of the STP, we can thus observe a remarkable stability of the trace metal levels (Fig. 3) except a questionable Ni concentration in September 2001. This stability suggested several hypotheses: (1) there were no disturbance of the surface layer due either to tides or to floods. In that case, as the rate of sedimentation

Table 4 Quality guidelines proposed by Long et al. (1998) to characterise the toxicity of a metal (μg.g^{-1}) in an estuarine sediment towards benthic organisms

Toxicity	Scarce	Occasional	Frequent
Cd	<1.2[a]	1.2–9.6	>9.6
Cr	<81[a]	81–370	>370
Cu	<34	34–270[a]	>270
Hg	<0.15[a]	0.15–0.71	>0.71
Ni	<21	21–52[a]	>52
Pb	<47[a]	47–218	>218
Zn	<150[a]	150–410	>410

[a] Values of metallic concentrations found in Souss sediment

might be rather low it would not have been expected to observe seasonal variations, the sampling technique taking in account 1 cm of surface sediment and thus integrating numerous months of inputs. This situation is reinforced by the biological activity with mixes vertically the first centimetres of the sedimentary column; (2) the surface layer is periodically eroded by the hydrodynamic activity. In that case, the constancy of the sediment contamination on the scale of the month suggests a constancy of the contamination of the wastewater inputs on the scale of years.

In 2003, it seems very clear that the situation has changed (Fig. 3). For example, the constancy observed in 2001 is not observed anymore, as attested by the higher standard deviations in the mean concentration of 2003 (Table 3). Moreover, the concentrations of Cd (LSD test: 0.0049, $p < 0.01$), of Cr (0.0088, $p < 0.01$) and of Cu (0.0266, $p < 0.05$) were significantly higher from those of 2001. However, we must keep in mind the change in granulometry discussed in a former section and effectively we don't observe the same pattern with the normalised concentrations than with the raw ones (Fig. 3). For example, when Cu, Pb and Ni increased with time in 2003, the Al-normalised concentrations of these same elements show less clear variations. Except for the normalised concentration of Zn which significantly decreased in 2003 and that of Cu which significantly increased, the other metals didn't show any significative difference between 2001 and 2003 (Table 3). Finally, a more precise observation of the normalised values suggests even though a possible evolution with time which should be interesting to verify in a further study: a decrease of Cd/Al, Hg/Al and Cr/Al and an increase in Pb/Al. These evolutions could be due to the biogeochemical behaviour of these contaminants, e.g., solubilisation of Cd and Hg in a more saline aquatic environment, on the contrary more important precipitation of iron in this new medium, hypothesis that it should be necessary to validate before concluding about an hypothetical evolution of this coastal region. At least, the decrease in the Zn concentration in 2003 (observed also in the Zn/Al evolution; see Fig. 3) indicated that an important part of this metal originated from wastewater in 2001, and then was highly linked to anthropogenic activity. Indeed Zn is known, at least in Moroccan context, as a best urban sewage indicator (Cheggour et al. 2001). In view of this finding, it can be suggested that Zn was the metal which was the most directly linked to wastewater discharges in the Souss river.

To estimate the toxicity of trace metals in the estuarine sediment of the Souss River, we have used the ranges of concentrations that Long et al. (1995, 1998) and MacDonald et al. (2000) have reported for each metal, determining its toxicity towards benthic organisms. Under these conditions, the annual values recorded for Cd, Cr, Hg, Pb, and Zn, were under the guidelines proposed by these authors (Table 4), so that their toxicological effects were low or non-existent. The concentrations of Cu and Ni found in the present study were combined with a medium toxicological risk. So the impact of pollution caused by domestic wastewater in the Souss estuary was low in 2001 as well as in 2003.

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