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Geochemical characteristics of water and sediment in summer period of the Loukkos and Sebou estuaries (NW Morocco): preliminary study

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Abstract. The high touristic potential of the north-west region in Morocco plays an important socio-economical role, raising the question of the monitoring of its environmental quality. This study provides a preliminary dataset for dissolved heavy metal concentrations in water and grain-size, mineralogy, carbon (organic and inorganic) and heavy metal contents in surface sediments from the Loukkos and Sebou estuaries). The results refer to samples taken at six sites in June 2009. In this article, the concentrations of twelve heavy metals (Al, As, Cd, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb and Zn) in sediments with grain size and mineralogy, and concentration for 7 heavy metals (As, Cd, Cu, Fe, Ni, Pb and Zn) in water are reported. The results show, in general, a low concentration of almost all of the studied metals in water and sediments, but with random higher levels. In water, the highest levels were found for Cu, Ni and Zn denoting some toxicity for living organisms. For estuarine sediments, As and Cr show strong levels of contamination, ranging from 7.96 to 18.5 mg kg^{-1} for As and from 33 to 137 mg kg^{-1} for Cr in Loukkos and from 7.77 to 8.34 mg kg^{-1} for As and from 85 to 109 mg kg^{-1} for Cr in Sebou. Stations L1 and S1, with predominantly sandy sediments, present the lower metals concentrations (except L1 for As), which is in agreement with the knowledge that metal concentrations are generally higher in areas richer in clay sediments than in sandy sediments. The As and Cr values are above the upper-EAC (The Ecotoxicological Assessment Criteria) and can have long-term and acute biological effects. The strong Cr concentration can be explained by the presence of tanneries located along both rivers, upstream from collection sites, denoting a direct anthropogenic source. The As is linked to sand that has a beach and shelf sediments predominant source. The hypothesis that can be considered is these sediments richer in As are injected to the Loukkos lower estuary by the tidal influence.

Key words: geochemistry, metal concentrations, Sebou, Loukkos, Morocco.

Caractéristiques géochimiques de l'eau et du sédiment en été des estuaires du Loukkos et du Sebou (NW du Maroc) ; étude préliminaire.

Résumé. Le potentiel touristique de la région nord-ouest du Maroc joue un rôle socio-économique important, de ce fait, la surveillance de la qualité de son environnement devient primordiale. Cette étude fournit un ensemble de données préliminaires sur la concentration des métaux lourds dans l'eau et dans les sédiments de surface des estuaires du Loukkos et du Sebou. Ces résultats s'appuient sur des échantillons prélevés sur six sites en Juin 2009. Dans cet article, les concentrations de douze métaux lourds (Al, As, Cd, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb et Zn) dans les sédiments avec leurs granulométries et leurs minéralogies et la concentration de 7 métaux lourds (As, Cd, Cu, Fe, Ni, Pb et Zn) dans l'eau sont rapportées. Les résultats montrent, en général, une faible concentration de presque tous les métaux étudiés dans l'eau et les sédiments, les niveaux les plus élevés ont été trouvés pour Cu, Ni et Zn dénotant une certaine toxicité pour les organismes vivants. Pour les sédiments estuariens, As et Cr montrent des niveaux élevés de contamination, allant de 7,96 à 18,5 $mg.kg^{-1}$ pour As et de 33 à 137 $mg.kg^{-1}$ pour le Cr dans le Loukkos et de 7,77 à 8,34 $mg.kg^{-1}$ pour As et de 85 à 109 $mg.kg^{-1}$ pour Cr dans Sebou. Les stations L1 et S1, avec des sédiments principalement sableux, présentent des concentrations plus faibles de métaux (sauf L1 pour As), ce qui est en accord avec l'idée que les concentrations de métaux sont généralement plus élevés dans les régions les plus riches en sédiments argileux que dans les sédiments sableux. Les valeurs As et Cr sont au-dessus de la partie supérieure de la CAE (les critères d'évaluation éco-toxicologiques) et peut avoir à long terme des effets biologiques aigus. La forte concentration de Cr peut être expliquée par la présence de tanneries situées le long des deux rivières en amont de sites de collecte, ce qui dénote une source directe d'origine anthropique. As est lié au sable d'origine marine (plage et plateau continental). L'hypothèse qui peut être considéré ici est que ces sédiments riches en As sont injectés dans l'estuaire du bas Loukkos par l'influence des marées.

Mots clés: géochimie, concentrations, métal, Sebou, Loukkos, Maroc.

INTRODUCTION

Sediments are recognized to be an appropriate medium to assess the environmental quality of rivers, as they reflect the integrate contaminant inputs in the marine and river environment, allowing sources and sinks to be identified (Rowlatt & Lovell 1994). The rivers discharging into the sea are often used as transport agents for the disposal of industrial, agricultural and urban wastes. The presence of increased level of pollution in aquatic environment has been of much concern due to its adverse effect on living organisms and in food chains leading to man (Förstner & Müller 1973, Farmer 1991, Yang & Rose 2003). Another important problem is that it may affect the development of tourism by degrading the sanitary quality of beaches and generating unpleasant odors and aesthetics.

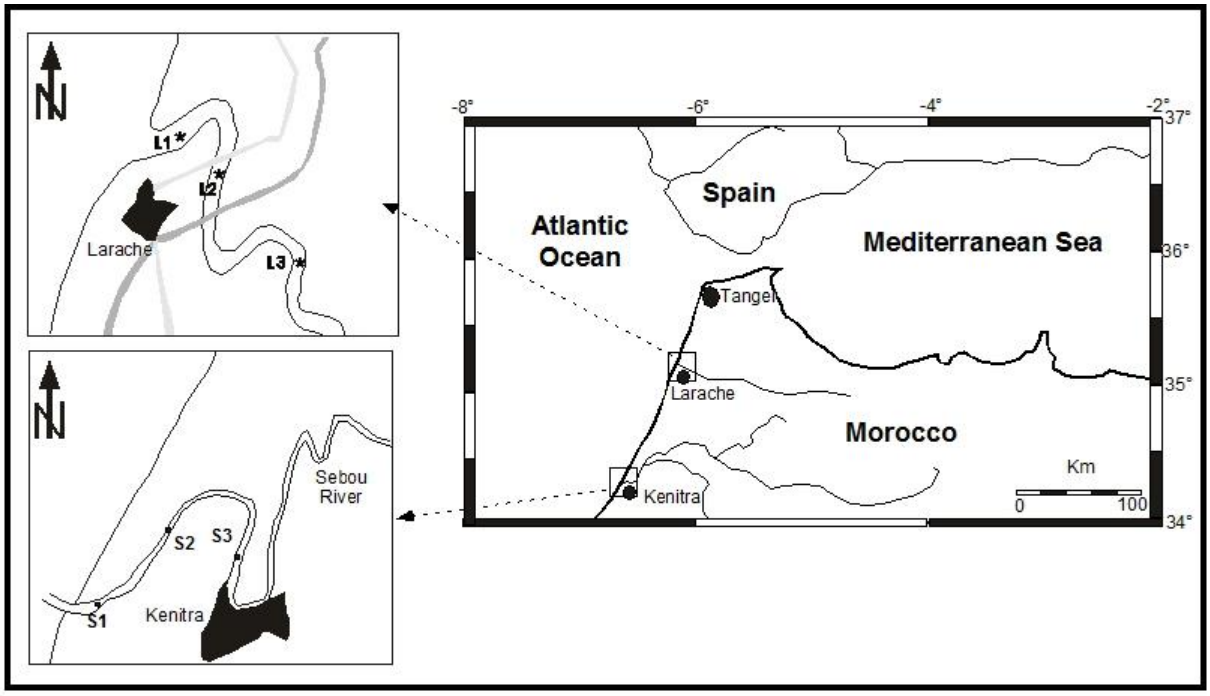

Figure 1. Study area (right) and stations where samples were collected (left).

Marine sediments in coastal regions near estuaries are frequently polluted by heavy metals and other pollutants, which are usually present in amounts several times higher than their natural background level (Förstner & Müller 1973, Shropp *et al.* 1990, Bryan & Langoston 1992, Singh *et al*. 1997, Liu *et al.* 2003, Alagarsamy 2006).

Today, the Moroccan littoral is a complex space, exposed to profound alteration and perpetual transformations. It is subjected to all kinds of anthropogenic aggressions to the environment, namely: anarchic construction, human and industrial pollution, degradation of beaches and dunes, etc. The Northwest region of Morocco is among the most interesting regions, with a high touristic potential and fisheries activity. Between Kenitra and Tangier, the most important rivers are the Loukkos and Sebou, that discharge into the Atlantic Ocean near Larache and Kenitra, respectively (Fig. 1).

There are some general pollution studies related with these rivers: Fekhaoui *et al.* (1996), Bennasser *et al*. (2000), Banaoui (2004), Cheggour *et al*. (2005), Maanan (2008), Piazza *et al*. (2009), but they are mainly focused on the description of a few geochemical parameters, namely contamination levels of some heavy metals, without the concern of the correlations between them.

This work is part of a wider program where the general oceanography, sedimentology and shelf geochemical characteristics are under study. This is a first attempt to estimate the geochemical signature of the Loukkos and Sebou rivers in the adjacent shelf. In the two estuarine areas, grain size, mineralogy, TOC (total organic carbon) and heavy metal concentrations were determined in order to identify a characteristic impact on the shelf.

The Ecotoxicological Assessment Criteria (EAC) from OSPAR (Bignert *et al*. 2004, OSPAR 2008) are also used to evaluate the potential risks for the organisms living in the study area and also for human health. This preliminary data can be useful for subsequent studies and also for assessing the health hazard in this coastal area.

MATERIALS AND METHODS

Study area

The study area is situated in the Northwest of Morocco (Fig. 1) and includes the estuaries of two large rivers: Sebou and Loukkos. The climate of the two basins perimeter is Mediterranean with an oceanic influence The Loukkos is one of the most important rivers due to its flow values, agricultural and economic activity. The watershed extends over an area of 3,740 km^2; topographically, it is characterized by a very flat (10-15 masl- meters above sea level) lower valley, with a negligible inclination (actually, 44 km upstream the river mouth, the bottom is even below sea level). The main channel depth varies from 2 to 4 m but it may reach 15 m (Snoussi 1980).

In the Loukkos basin, the estimated average annual rainfall is 700 mm. (El Gharbaoui 1981). The hydraulic network of the Loukkos perimeter is formed by surface waters of the Loukkos river and its tributaries (Drader, Soueir, Skhar and M'da), and its drainage is characterized by an irregular interannual regime: the lower flow values are generally zero, except for streams that drain the water from R'Mel (Sakhsokh, Smid El Ma and El Kihel) with an average flow of 500 l s^{-1} and those draining the water from Drader-Souiere. The mesotidal Loukkos estuary (tide: 3.5 m,

Table I. Sampling sites coordinates.

	Long.	Lat.
L1	35º 12' N	-6º 09' W
L2	35º 11' N	-6º 51' W
L2	35º 11' N	-6º 07' W
S1	34º 16' N	-6º 38' W
S2	34º 18' N	-6º 37' W
S3	34º 18' N	-6º 35' W

semi diurnal) is a tide-dominated system, according to the classification of Dalrymple (1992). The Loukkos estuary is currently in a filling phase which occurred during the Flandrian (Mellahian) transgression and more recently by the progression of the sandy spit (Aloussi 2008, Carmona 2009). This presence supports the fast sedimentation of fine particles (silt and clays) and also of sand.

The Sebou River is also one of the largest Moroccan rivers, draining approximately 40,000 km^2, stretching about 600 km from its source in the Middle Atlas to the Atlantic Ocean. The physiography of the watershed is strongly influenced by the altitude distribution between the north and the south. The watershed has been described by Benaabidate (2000). The Sebou River is the primary source of water for a variety of purposes, i.e. drinking, agriculture, industry, recreation (El Herradi 1989). The Sebou is navigable for about 20 km up to the city of Kenitra, with a channel bathymetry varying between 2 and 5 m (Snoussi 1982). The funnel shaped estuary with tide amplitude of 3 m (semi diurnal) is a tide-dominated system, according to the classification of Dalrymple (1992). The mean annual rainfall is about 600 mm in the west and 450 mm in the southeast, and its average flow is about 200 $m^3.s^{-1}$ at the mouth. Although it is highly regulated by a network of dams for irrigation purposes, which may sometimes lead to a rate near zero, its maximum flow can still reach 5,000 $m^3.s^{-1}$ during high floods (El Herradi 1989). The Al Wahda dam, constructed on the Ouerrha River (tributary of Sebou) between 1991 and 1996, is the second most important dam in Africa after the High Aswan dam. It has a storage capacity of 3.8×10^3 km^3 and a height of 88 m.

Sampling and analysis

Sampling of water and sediment was done at low tide (10:00 am) on 9 June 2009 for the Loukkos river and on 23 June 2009 for the Sebou river. Six sampling sites were selected taking into account the accessibility and proximity to the margin, with three stations (L1, L2, L3, S1, S2 and S3) in each lower estuary (Fig. 1, Tab. I). In relation to water and in order to validate results, duplicated samplings and analyses were done from each site. The mean of both analyses were used to obtain the final heavy metals content.

The river water was sampled at 2 m depth, using plastic bottles (high- or low-density polyethylene) rinsed with nitric acid (*v*/*v* 10%, *p.a.)* and Milli-Q water. River water samples were filtered through a cellulose nitrate filter (0.45 ìm pore diameter, Sartorius), acidified with nitric acid (*v*/*v* 1%, *Suprapur*), and then stored at +4◦C. For the determination of Cu, Fe, Zn, Cd, Ni and Pb contents, the analysis was done by pre-concentration with dithio-carbamate complexation and subsequent extraction into freon followed by back extraction into nitric acid (Danielson *et al.* 1978, Statham 1985). Arsenic was firstly reduced to As(III) using a reducing agent composed of a mixture of potassium iodide and ascorbic acid in HCl. Sodium borohydride was added to convert As(III) to the volatile hydride that was purged from the solution by a stream of argon gas.

The quantitative analysis was done by atomic absorption spectroscopy with flame for Cu, Fe and Zn; graphite furnace was used for Cd, Pb and Ni, and hydride generation for As.

Surficial sediments were collected with a grab sampler for geochemical characterization. After collection, the sediments were immediately frozen (–18ºC). Grain size analysis, organic carbon content and heavy metals (As, Al, Cd, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Zn) were performed on the total sediment sample. The mineralogy was determined from the fine fraction (<63 µm).

All samples were kept frozen until processing. Surface sediment samples were freeze-dried, homogenized and reduced to a fine powder with a mortar and pestle. The determinations of the total metal concentrations in sediments were made under a quality control regime routinely used in laboratories (recovery of standards, replicates in 10% of the samples and use of CRM). The sediment content of metals was obtained after digestion using a microwave oven (ETHOS PLUS) through a three step procedure (5 min. at 100ºC and 250 Watt; 10 min. at 180ºC and 800 Watt and 20 min. at 180ºC and 800 Watt), using a mixture of 2 mL of hydrofluoric acid and 6 mL of aqua regia. After digestion, each solution was neutralized with boric acid, and concentrations of heavy metals were analysed by atomic absorption spectrometry (Solaar-Thermo Elemental), by flame for Al, Cd, Cr, Cu, Fe, Li, Mn, Ni, Pb, Zn, and hydrate generator for As. Hg concentrations were directly measured in homogenized freeze-dried sediment samples by atomic absorption spectrometry with thermal decomposition, using an Direct Mercury Analyser (DMA). The procedure follows the guidelines within the ICES- International Council for the Exploration of the Sea (Loring & Rantala 1990). Certified reference materials (marine sediment SRM 2702 and estuarine sediment SRM 1646) were also analyzed following the same process, showing that the total digestion method used in the study provided complete extraction for the sediments. The agreement between the analytical results for certified and measured values was satisfactory, with recoveries between 80 and 100% for all metals.

The participation in interlaboratory studies, namely Quasimeme, Aquacheck and PACQS (Tab. II) demonstrate the data quality with more than 90 % of satisfactory results ($z < 2$).

Table II. Results of participation in interlaboratory studies [Z= (participant result - assigned value)/standard deviation for proficiency].

	Sediments (%)			Seawater(%)
	Quasimeme		Aquacheck	Quasimeme
	TOC	Metals	Metals	Metals
n=	21	96	41	48
$\|Z\|<2$ Satisfactory	100	95	93	90
$2<\|Z\|<3$ Questionable	—	4	7	6
$\|Z\|>3$ Unsatisfactory	—	1	—	4

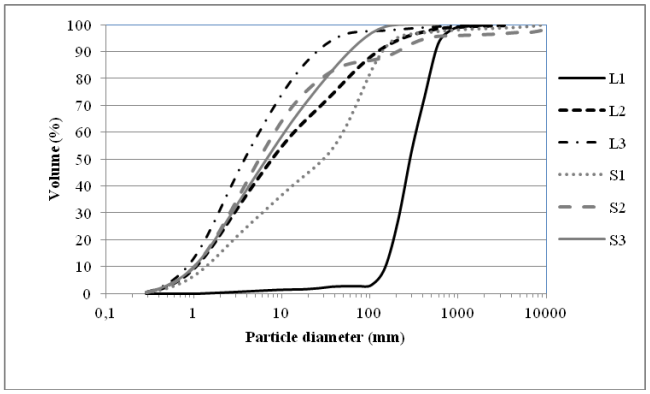

Figure 2. Cumulative particle size distribution for Loukkos and Sebou rivers.

Grain size in surface sediments was determined by laser forward scattering (MALVERN 2000 instrument) for the fraction under 500 µm, and by sieving for particles > 500 µm. The Malvern instrument was certified using three types of NIST (National Institute of Standards and Technology) standard reference materials, of 9 µm, 1 µm and 0.3 µm (Duke Standards uniform polymer microspheres) particle size and also participating in PACQS (Particle Analysis and Characterization Quality Scheme) inter lab calibrations (LGC standards). The determined expanded uncertain (2009-2011) is for D10=0.23: D50=0.07; D90=0.12. Total carbon (TC) was measured with a Strohlein C-mat 5500, by combustion of 0.1 g of sample at 1350ºC and detecting the produced CO_2 by an infrared detector. Inorganic calcareous carbon ($CaCO_3$) was also measured by infrared detector after acidification of the sediment samples with H_3PO_4. Total organic carbon (TOC) was calculated by subtracting inorganic carbon from total carbon. Calibration with certified material and inter lab calibrations were also performed. The mineralogical analysis was done by X ray diffraction (XRD). This analysis was conducted on a Panalytical X-PERT diffractometer, with ceramic X ray tube and Cu anode (Cu Kα radiation). Samples were scanned with steps of 0.02º, between º2θ = 4 and 60º, with a counting time of 1 s per step. Peak areas of the basal reflections of the main minerals were determined using the X'Pert HighScore program (Version 1.0f) and weighted by empirically estimated factors. For semi-quantitative determination, criteria recommended by Schultz (1964), Thorez (1976) and retaken by Rocha (1993) have been followed.

The Ecotoxicological Assessement Criteria (EAC) from OSPAR (Bignert *et al*. 2004, OSPAR 2008) evaluates the potential risks for the organisms and also human health. OSPAR (2004) establishes two limits - upper and lower. These values are derived taking in account that "The lower EAC value is a concentration derived for the protection of all marine species from chronic effects, including the most sensitive species, and the upper EAC is defined as the highest (transient) concentration that is expected not to cause acute toxic effects". Pearson statistical analysis was performed with EXCEL (ANOVA) software.

RESULTS AND DISCUSSION

Heavy metals in water

The concentrations of dissolved metals in water of the Loukkos and Sebou estuaries are presented in table III and compared with the Ecotoxicological Assessement Criteria (EAC) from OSPAR (2004). These EAC values are normally used to identify potential areas of concern.

For As, Cd, Pb, the values are within the accepted limits. On the other hand, the Cu, Zn and Ni values exceed the upper EAC limit in both estuaries.

Consequently, the most problematic metals for living organisms are Zn, Ni and Cu. Zn and Ni present values three times higher and Cu one hundred times higher than the upper values of EAC, possibly related with anthropogenic local sources. These values could be potentially harmful for the main estuary ecology and even toxic for living organisms.

Grain-size, carbon, mineralogy and heavy metals in sediments

The cumulative particle size curve of the river samples is presented in figure 2. The results show a predominantly sandy sediment for the Loukkos lower estuary (L1) with a D10 of 178 µm (10 vol% of particle below 178 µm), a D50 of 340 µm and a D95 of 781 µm, and an increase of the muddy content in the other samples (>80%). In the Sebou samples the sandy component is much smaller (less than 11%) and the silt-clay (mud) components predominate with a D10 of 1.6 µm, a D50 of 34.8 µm and a D95 of 240 µm, for S1 sample.

The results of carbon analysis (TOC, TIC, TC) and mineralogical investigations by XRD are given in table IV. The TIC's higher value was found in the Loukkos lower estuary (L1), decreasing upstream. This higher value is possibly related to estuarine sediment contamination with beach carbonated sandy sediments normally richer in carbonated biogenic remains and very poor in organic carbon (<0.1). This result can be an indicator of the silting

Table III. Concentration of dissolved metals (µg L^{-1}) of waters from Loukkos (L) and Sebou (S) estuaries.

	Loukkos			Sebou			OSPAR
	L1	**L2**	**L3**	**S1**	**S2**	**S3**	**2004**
As (µg L^{-1})	0.835	0.512	0.447	0.495	0.458	0.436	1-10
Cd (µg L^{-1})	0.094	0.105	0.079	0.033	0.082	0.127	0.01-0.1
Cu (µg L^{-1})	3.57	2.737	2.687	2.67	2.35	5.04	0.005-0.05
Fe (µg L^{-1})	150	124	325	216	323	241	0.005-0.05
Ni (µg L^{-1})	5.69	3.40	9.60	4.36	2.94	2.31	0.1-1
Pb (µg L^{-1})	<0.03	0.035	<0.03	0.039	<0.03	0.187	0.5-5
Zn (µg L^{-1})	16.1	29	24	10.4	15.6	10.2	0.5-5

Table IV. XRD results and carbon content (TC- Total carbon; TIC- Total inorganic carbon; TOC- Total organic carbon) for the Loukkos and Sebou rivers.

Mineral (%)	Loukkos			Sebou		
	L1	**L2**	**L3**	**S1**	**S2**	**S3**
Calcite	51.2	58.7	52.6	62.6	70.4	67.2
Quartz	18.9	23.1	20.9	14.8	9.2	10.3
Plagioclase	8.3	5.4	6.0	5.7	3.9	4.3
Opal	—	—	4.8	2.2	—	2.5
Kaolinite	12.9	6.4	15.7	—	—	—
Anatase	8.7	6.3	—	—	—	—
Chlorite	—	—	—	2.2	3.2	6.3
Illite	—	—	—	4.8	10.4	6.5
Dolomite	—	—	—	7.7	2.9	2.8
TIC	4.2	1.2	1.0	2.8	2.7	2.2
TOC	0.1	1.2	0.9	1.3	1.3	0.8
TC	4.3	2.3	1.9	4.1	4.0	3.0

and confinement of the estuary, as previously found in other coastal zones (Lopes *et al.* 2010). In the Sebou, the TIC values are very homogeneous throughout the estuary but slightly higher than in the Loukkos estuary. As far as the TOC is concerned, all samples present low values (<1.3%), with no major differences between estuaries, excepting for L1, with an even lower value.

Calcite is the main mineral in both rivers (mean 60%), with slightly higher values in the Sebou river. The other major minerals are quartz (16%) and plagioclase (6%). Opal is vestigial (<4%). Kaolinite (12%) and anatase (5%) were detected in Loukkos. By opposition, illite/muscovite (7%), chlorite (4%) and dolomite (4%) were only found in the Sebou river.

All minerals present in these estuarine systems are common and can be transported to the estuaries by fluvial sources. Calcite/dolomite can be derived from geological formations with limestones - chalks and dolostone - and sandstones; quartz and plagioclase can also come from sandstones and vulcano-sedimentary formations, present in both basins. However, the clay mineralogy differentiation (kaolinite to Loukkos and , Chlorite+illite to Sebou) reflect some singular rock formations sources well visible in the main geological formations of the two rivers basins: Sebou with schists, flyschs I-III, dolomies and schalks with karstic dissolution; and Loukkos with sandstones and marls, flyschs. The presence of schists in the Sebou basin can be the main source of chlorite and illite to the sediments. Kaolinite, (Neoformations) occurs in pore spaces of sandstones and dolomitic formations outcropping in the Northern flank of the High Atlas (El Herradi 1989, Benaabidate 2000).

The studies of metals in sediments are normally divided in two groups: metals that are characteristics of sediment and related with the mineralogical structure and metals that are related with anthropogenic activities and if present in strong concentration can be dangerous for the living organisms. In the first group we can include Al, Fe, Mn and Li, and in the second group As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. The concentration of metals in Loukkos and Sebou stations are present in Table V, and the lower and upper Ecotoxicological Assessment Criteria (EAC) from OSPAR, 2008.

The cadmium concentrations in all sediment samples are always below the quantification limit. The concentrations of Al, Fe, Mn and Li are in the same order and without significant variations possibly related with the rocky geological formations.

Station L1, with predominantly sandy sediments (97% of sand) presents the lowest concentrations, with the exception for Arsenic. For all metals (except for As), these values are in agreement with the knowledge that metal concentrations are generally higher in areas richer in clay sediments than in sandy regions.

For the Cu, Hg, Ni and Zn metals the values presented here are not elevated and no significant differences between the collection sites and the two rivers were detected.

Concerning Pb, the concentrations are higher in Sebou compared with Loukkos river, but they can be considered among accepted levels. In a previous study on some heavy

Table V. Concentration of metals Al, Fe (m g^{-1}) and As, Cd, Cr, Cu, Hg, Li, Ni, Pb, Zn and Mn (mg kg^{-1}) in sediments from Loukkos (L) and Sebou (S) estuaries and Lower and Upper EAC from OSPAR, 2008.

	Loukkos			Sebou			OSPAR 2008	
	L1	**L2**	**L3**	**S1**	**S2**	**S3**	**LOWER EAC**	**UPPER EAC**
As (mg kg^{-1})	18.5	7.96	14.0	7.79	7.77	8.34	1	10
Cd (mg kg^{-1})	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.1	1
Cr (mg kg^{-1})	33	126	137	85	103	109	10	100
Cu (mg kg^{-1})	6.99	25	24	25	33	34	5	50
Ni (mg kg^{-1})	3.17	20	24	17.6	21	23	5	50
Pb (mg kg^{-1})	<2	3.15	2.88	5.92	9.37	9.43	5	50
Zn (mg kg^{-1})	42	117	116	110	154	109	50	500
Hg (mg kg^{-1})	0.004	0.055	0.033	0.050	0.078	0.052	0.05	0.5
Li (mg kg^{-1})	23	53	60	40	47	51	0.05	0.5
Mn (mg kg^{-1})	350	308	217	289	363	362	—	—
Al (mg g^{-1})	19.2	71	82	52	66	69	—	—
Fe (mg g^{-1})	18.9	35	32	27	34	36	—	—

metals in the Loukkos river sediments, El Morhit (2008) found an important level of Pb (a mean of 102,9 mg/kg). He compared this value with other studies, on the most important rivers in Morocco, and noted that it was very high. He didn't provide any explication, but it could be due to exceptional discharges, upstream the river, of waste (industrial or domestic) in the period of this study.

As for As and Cr the results show strong levels of contamination in both rivers sediments. The strong Cr concentration can be explained by the presence of tanneries located upstream the rivers (Dominik *et al.* 2007), being directly derived from anthropogenic sources. The deposition of Cr in the sediments and the subsequent transport by the tides and major floods explain the values found in the lower estuary. For As, the explanation is not as straightforward. Arsenic is a trace element present in all waters, although concentrations may differ considerably in different areas. It is a common element occurring in several types of geological deposits, as volcanogenic massive sulphide, porphyry copper or epithermal gold deposits (Arehart *et al.* 1993, Çifçi *et al* 2005, Leybourne & Cameron 2008). It is generally associated with precious metals (such as gold) in sulphides. Arsenic is commonly found in minerals such as arsenopyrite, or present in substitution within the crystalline lattice of pyrite (Abraitis 2004, Blanchard 2007). Most of the time, this metalloid is economically not exploitable, and the minerals that contain As are concentrated in the mine wastes as much as possible during mine ore processing. Oxidation of sulphide minerals in mine wastes stored at the surface and exposed to atmospheric conditions can release As in solution. In this study the low concentration of As in the water samples and higher in sediments seems to indicate the same process as in Cr, deposition and absorption of As in the sediment, as suspended particulate matter. However, with the scarce data information about this heavy metal, in water and sediments, one can speculate that possible origins of this metal are mine wastes rich and also the geological deposits richer in arsenopyrite and gold, where As can be released to the environment. For instance the Draa Sfar mines located further south, (Marcoux *et al.* 2008). Nevertheless, there is a lack of in situ geological studies to confirm this hypothesis.

By opposition to the other heavy metals, the stronger As value was found in station L1. The As is linked to sandy sediments that came predominantly from the beach and shelf sediments. The hypothesis can be considered that these sediments richer in As are contaminated elsewhere and are injected to the Loukkos lower estuary by the tides. An interesting correlation between plagioclase and As (R^2=0.7674) was also found (not shown).

On the other hand, the main source for the other heavy metals is the upper estuary with a subsequent dilution of the sediment concentrations to the lower estuary, due to the incorporation of non contaminated shelf sediments.

In the Loukkos estuary, the comparison of these data with the EAC upper values, for As, stations L1 and L3 and for Cr, stations L2 and L3, present values higher than the upper limit of EAC. In the Sebou estuary stations S2 and S3 present values of Cr near the upper limit. Other metals are within the limit values of EAC. The As and Cr values above the upper-EAC can have long-term biological effects (e.g. impaired growth, reproduction and survival) and acute biological effects (survival) (Bignert *et al.* 2004). Therefore, it is necessary to find the reasons of this contamination and establish a monitoring program.

In order to correct metal concentrations for the influence of the natural variability in sediment composition, like grain size, organic matter and mineralogy it is important to normalize the concentrations (OSPAR Guidelines 1998). The grain size is one of the most important factors control-

Table VI. Pearson correlation coefficients between metals element, fine fraction (<63 µm) and TOC.

	<63µm (%)	TOC(%)	Al (mg g^{-1})	Fe (mg g^{-1})
<63 µm (%)	1,000			
COT (%)	0,819	1,000		
Al (mg g^{-1})	0,957	n.s.	1,000	
Fe (mg g^{-1})	0,898	n.s.	0,918	1,000
As (mg kg^{-1})	n.s.	-0,891	n.s.	n.s.
Cr (mg kg^{-1})	0,921	n.s.	0,990	0,897
Cu (mg kg^{-1})	0,874	n.s.	0,767	0,886
Ni (mg kg^{-1})	0,993	n.s.	0,974	0,931
Pb (mg kg^{-1})	n.s.	n.s.	n.s.	n.s.
Zn (mg kg^{-1})	0,873	0,898	0,801	0,835
Hg (mg kg^{-1})	n.s.	0,882	n.s.	n.s.

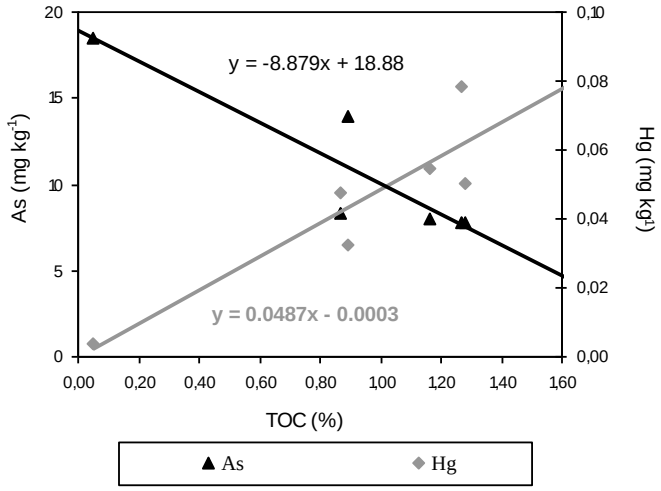

Figure 3. TOC vs As and TOC vs Hg in sediments of river Loukkos and Sebou.

ling the distribution of natural and anthropogenic components in the sediments, therefore it is important to normalize for the effects of grain size in order to provide a basis for meaningful comparisons of the occurrence of substances in sediments of various grain-sizes and texture within individual areas. In some cases it is also important to normalize the metal concentrations to some element of detrital origin, such as iron or aluminum.

Regression analysis of data from the 6 sampling sites produced significant relationships ($p<0.001$) between Cr, Cu, Ni and Al, Fe, fine sediments (%< 63 µm) (Table VI). Figure 3 shows that Hg and As only have a strong correlation with TOC, but with opposite signal (As is negative and Hg is positive). For Pb, no relation was found but by contrary Zn correlates with all the normalizers.

CONCLUSIONS

The Loukkos and Sebou estuaries are characterized by the same level of contamination of heavy metal concentrations in water and surficial sediments. However in both estuaries, elevated levels of EAC for Cu, Ni and Zn in waters are found, possibly related with anthropogenic local sources . In sediments, As and Cr are above the upper EAC values.

The strong Cr concentration can be explained by the presence of tanneries located upstream the rivers, as the concentration values decrease downstream, being directly derived from anthropogenic sources.

The As is a common element occurring in several types of geological deposits, as volcanogenic massive sulphide, porphyry copper or epithermal gold deposits and the hypothesis can be considered that these sediments richer in As come from the shelf and are injected in the Loukkos lower estuary by tidal input.

Additional analysis to verify these findings are necessary and appropriate management actions could involve identification of the reason(s) for this elevated level(s), implementation of a monitoring strategy for specific elevated contaminants and consideration of resource or emission management issues.

An attempt to confirm the hypotheses raised with these results will be made confronting them with shelf sediment results. The high touristic potential of this entire region should lead us to increase awareness to preserve its environmental quality.

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