

Accumulation trends of metal contamination in sediments of the former Pb–Zn mining district of Touiref (NW Tunisia)



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ABSTRACT

Wastes of the former Pb–Zn mining district of Touiref (Pb/Zn) can be eroded during strong rainfall. The presence of a downstream lake offers the opportunity to perform geochemical characterisation of lacustrine sediments and analyze the temporal evolution of metal contamination. For this reason, a sedimentary core (C1) has been collected at the outlet of the Oued Sidi Bou Said which runs along the North side of the dike flotation tailings and a second core (C2) was sampled in front of the river flowing outside the mine site and reaching the plain on the East side of the endoreic study area. The scope of the present paper is characterize the temporal variability of major and minor elements in both sedimentary cores. The study of the historical contamination in both Touiref cores shows a clear impact of mining on the total endoreic basin, especially for the period going from 1914 until 1955 as well as the influence of urban development.

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1. Introduction

On a global scale, anthropogenic activities such as mining and agriculture, the production of residential and industrial wastes and urban wastewater can result in the discharge of dissolved and particulate metals into rivers, which can have a significant impact on the sustainability of water resources (Bruggemann et al., 2004; Deycard et al., 2014). In North African countries, geochemical characterisation of water and sediments are of increasing interest to scientists and managers facing a growing population, accelerating urban and industrial development, and the extension of irrigated agriculture, all of which have led to an increase in water demand and a rapid decline in the quality of scarce water resources (El Yaouti et al., 2009; Re et al., 2014, in Morocco; Dib, 2009 in Algeria; Hamzaoui-Azaza et al., 2011; Helali et al., 2013 in Tunisia). Mining activities are often regarded as a major source of contaminant metals in aquatic systems (e.g. Simpson et al., 2000; Van Den Berg et al., 2000; Audry et al., 2006, 2007; Monteiro et al., 2012; Omanović et al., 2015). The most serious problem comes from mine tailings, which are frequently abandoned with little or no remediation work. In the past, the improper management of mine tailings has resulted in the

migration of metals into the surrounding environment, contributing to the contamination of soil substrates, the destruction of the ecological landscape, and surface water and groundwater pollution (Quevauviller, 1989; Frommichen et al., 2004; Denimal et al., 2005; Sarmiento et al., 2009; Tessier et al., 2011; Lanceleur et al., 2011; Duffa et al., 2011; Duarte and Caçador, 2012; Vrhovnik et al., 2013; Fernández-López et al., 2014; Giuseppe et al., 2014; Pougnet et al., 2014). During the last century, the mining industry in northern Tunisia was very active and it still remains a fundamental component of the Tunisian economy. Mines were developed near farmlands and within the watersheds of the main watercourses, thus the erosion and weathering of the mine wastes act as sources of water contamination.

Previous geological, mineralogical and geochemical studies have been carried out in order to assess the geochemical behavior (speciation and mobility) of the mine tailings from the former mining Touiref district (Othmani et al., 2007, 2013, 2014). However, studies in areas affected by Touiref tailings do not fully evaluate the impact of the mining activities on the environment. The former mining district of Touiref offers the opportunity to investigate the geochemical and environmental development of the region and especially the impact of mining activity over time. This historical analysis is possible thanks to the presence of lacustrine sediments

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that have the ability to record the geochemical evolution of a natural system. This approach has been widely used in both pristine and metal contaminated sites as observed in other sedimentary environments (Coynel et al., 2007; Larrose et al., 2010; Serrano et al., 2011; Heim and Schwarzbauer, 2013; Jeziorski et al., 2013; Clark et al., 2014; Arora et al., 2014; Zhang et al., 2014). Previous studies have identified contaminated sites caused by industrial activities across the globe, and particularly during the last century, even in environments very far from industrial areas such as the Arctic Circle and very high mountain ecosystems (ten Hulscher et al., 1992; Valette-Silver, 1993; Hong et al., 1994; Renberg et al., 1994; Shotyk, 1996; Shotyk et al., 1996, 2000; Shotyk, 2002; Callender, 2003; Hernandez et al., 2003; Maanan et al., 2013; Fathollahzadeh et al., 2014; Andrades-Moreno et al., 2014; Ayrault et al., 2014; Mwanamoki et al., 2015; Dhivert et al., 2015). A greater coherence was generally observed between the geochemical record and historical human activities in these regions (Valette-Silver, 1993; Salomons, 1995; Nieminen et al., 2002; Sonke et al., 2003; Audry et al., 2004; Larrose et al., 2010; Grosbois et al., 2012; Giuseppe et al., 2014; Pougnet et al., 2014). In addition, the work carried out in or near mining sites has revealed that, in most cases, mining has been a long-standing threat to the environment (Zhao et al., 2012; Maftai et al., 2014; O'Neill et al., 2015).

Based on the mineralogical and geochemical characterization of two sedimentary cores, the objective of this study is to evaluate the extent of contamination recorded in the endoreic plain of El Goreaa, known for the abundance of trace metals in the environment. This study also aims to reconstruct the impact of anthropogenic activity on the Touiref watershed by correlating the depth profile distributions of metals (Cd, Zn and Pb) with historical changes of industrial activities within the watershed.

2. The Touiref mining area

The Touiref study area is located in the mountainous region of Ouargha (NW Tunisia), near the Algeria–Tunisia border and 56 km to the West of El Kef. It is in the northern part of the Tunisian Atlas Mountains, at the southern limit of the flysch zone (Fig. 1), and corresponds to an anticline structure intruded by Triassic evaporates and surrounded by Cretaceous outcrops (Sainfeld, 1952). The geology of this area belongs to the Coniacian–Burdigalian period, which consists of alternating marls and limestone.

Mineralization occurs as veins related to E–W to WNW–ESE secondary oblique faults, NW–SE transverse faults and local stratification joints. The mineralization consists of lead (galena, cerussite), zinc (zincite in surface, sphalerite in depth), and iron (oxides and pyrite) hosted in hard carbonate formations (SERMI, 1965). Mine tailings are 12 m in height with an estimated volume of 300 Mm³.

The climate of the region is semi-arid, with average monthly temperatures ranging from 8 °C in January to 29 °C in July with a mean annual rainfall of 455 mm. High intensity precipitation commonly occurs for short periods. The annual potential evaporation typically exceeds 1340 mm, and the (INM, 2004).

3. Material and methods

Two cores were sampled in the mouth of two rivers that join an endoreic plain, located 1.6 km downstream of the mine tailings. The first core (C1) was taken in the mouth of the Oued Sidi Bou Said that drains mine tailings, and the second core (C2) was sampled far from source of contamination (Fig. 1b). Both cores were collected using a coring tube method which involved the manual penetration of a PVC tube with a diameter of 40 mm. The recovery is carried out by aspiration of the sedimentary column by closing the top of the tube

with a PVC cap. Once recovered, the base of the core was sealed with an identical cap. In the laboratory, the length of each core was measured and divided into ~5 cm sections using a piston and plastic spatulas to avoid sample contamination. After measuring the pH, samples were air dried at 50 °C to a constant weight. The physico-chemical parameters, mineralogical characterization, chemical composition and selective extraction procedures were all carried out at the Unity of Research (ONM) and Geosciences Department of the Aveiro University (Portugal).

3.1. Physico-chemical parameters (pH, organic carbon, particle size)

Sediment pH values were determined in a 1:2.5 sediment/water suspension. Organic carbon (OC) was determined using the Walkley–Black titration method (Walkley and Black, 1934). Particle-size distribution was determined by a combination of the Robinson pipette and sieving methods.

3.2. Mineralogical characterization

Mineralogical characterization was performed on bulk samples and on the <2 µm fraction using a PANalytical X'Pert PRO X-ray Diffractometer equipped with automatic slit, X'celerator and Co-K α radiation at a scan speed of 0.04° 2 θ /s and acceleration powers of 40 kV and 40 mA. Polished thin sections embedded in epoxy resin were prepared for petrographic observation and microchemical analyses.

3.3. Chemical composition

The dissolution of samples for Si, Al, Fe, Mg, Ca, Na, K, P and Ti analyses was performed by fusion (0.06–0.08 g of soil sample was added to 0.7 g of di-boron trioxide anhydrous (B₂O₃) and 0.74 g of pure lithium carbonate (Li₂CO₃) in a graphite crucible). Melting of the mixture is carried out in an induction furnace at a temperature >1200 °C. The obtained pearl was subsequently mixed with 100 ml of 2% nitric acid in a teflon bomb and then homogenized using a magnetic stir bar on a magnetic stirrer until completely dissolved. Then, the solution was decanted in a volumetric flask and adjusted to 200 ml with double distilled water. Solutions were analysed with an atomic absorption spectrometer (PYEUNICAM SOLAAR S4). The dissolution of samples for Cd, Pb and Zn analyses was carried out by tri-acid digestion (HCl, HF, HNO₃). Mineralization was performed on a hot plate at moderate temperatures (95 °C) until total evaporation of the acids. The residue is dissolved with 5 ml of concentrated hydrochloric acid until complete dissolution. Heavy metal concentrations were measured by ICP (Inductively Coupled Plasma). The analytical error was less than 5%. Analytical precision and accuracy were determined by inserting a blind duplicate and Canadian-Certified Reference Sample LSKD-1.

3.4. Methods to estimate the intensity of metal pollution

In order to evaluate the extent of the historical heavy metal pollution, an enrichment factor (EF) was calculated as follows (e.g. Sinex and Helz, 1981):

$$EF = (Me/Al)_{\text{sample}} / (Me/Al)_{\text{background}}; \quad (1)$$

where (Me/Al)_{sample} is the concentration ratio of a given metal to Al in both sediment cores and (Me/Al)_{background} is the average ratio of the same metal to Al in the reference sample (non-polluted site). Due to the complex lithology and weathering features within the drainage areas, it is sometimes difficult to determine the typical

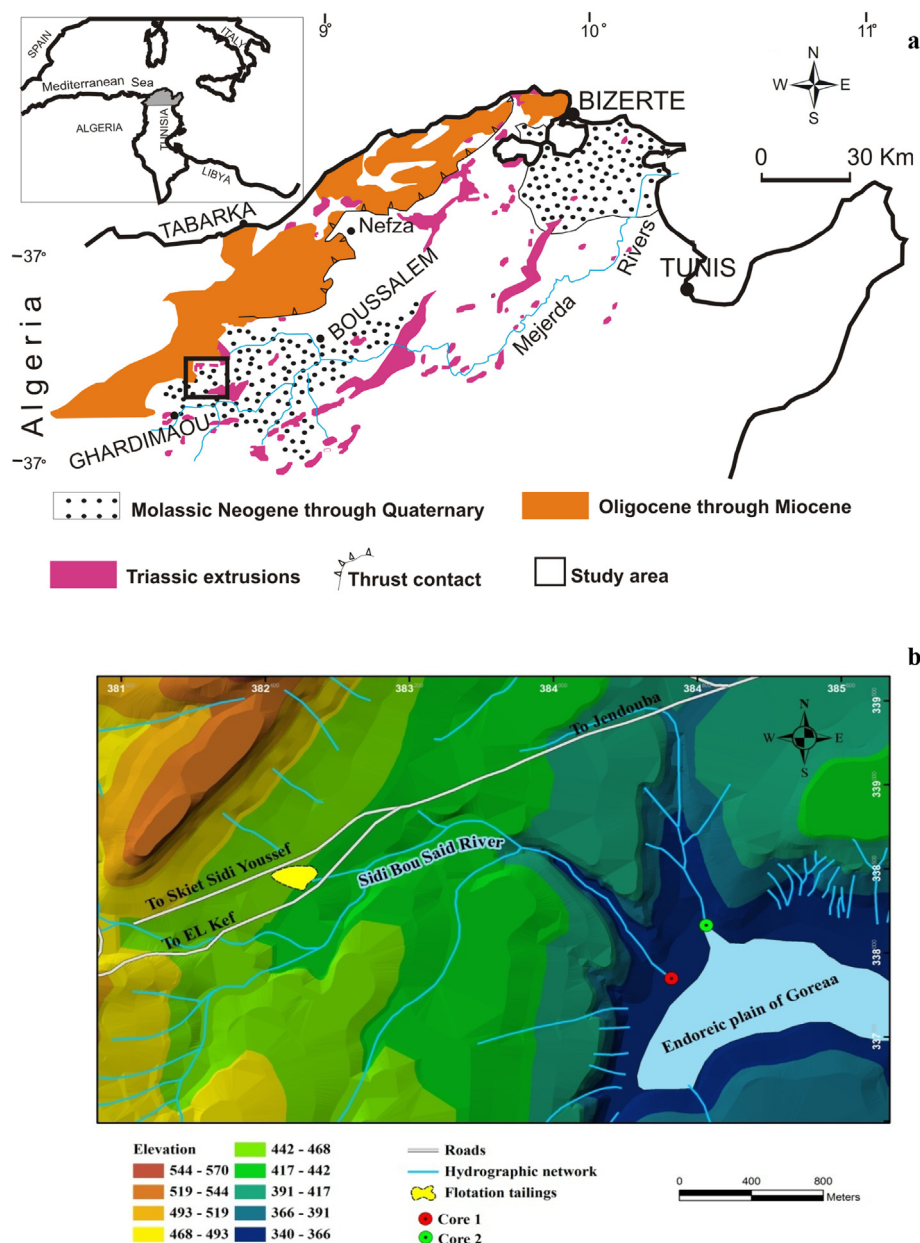


Fig. 1. a) Geological framework of the extreme North of Tunisia (modified after Rouvier, 1977); b) Map of the study area showing the location of the flotation tailings and also the sampling sites.

geochemical background value (Zhang, 1995). In this study, the $(Me/Al)_{background}$ was estimated by calculating the mean of the concentrations observed in the deep layers of the sediment samples in both studied cores.

The EF values were interpreted as suggested by Sakan et al. (2009): EF < 1 indicates no enrichment, EF 1–3 minor enrichment, EF 3–5 moderate enrichment, EF 5–10 moderately severe enrichment, EF 10–25 severe enrichment, EF 25–50 very severe enrichment, and EF > 50 extremely severe enrichment.

The Geoaccumulation Index (I_{geo}) was also calculated as a second criterion to evaluate the intensity of heavy metal contamination (Muller, 1979):

$$I_{geo} = \log_2 \left(\frac{[Me]_{sed}}{1.5 [Me]_{background}} \right); \quad (2)$$

where $[Me]_{sed}$ is the concentration of a given element and

$[Me]_{background}$ the mean concentration observed in the deep layer samples of both studied cores.

The I_{geo} values were interpreted as: $I_{geo} \leq 0$ – practically uncontaminated, $0 < I_{geo} < 1$ – uncontaminated to moderately contaminated, $1 < I_{geo} < 2$ – moderately contaminated, $2 < I_{geo} < 3$ – moderately to heavily contaminated, $3 < I_{geo} < 4$ – heavily contaminated, $4 < I_{geo} < 5$ – heavily to extremely contaminated and $5 < I_{geo}$ – extremely contaminated (Müller, 1969).

3.5. Selective extraction procedures

Samples from C1 and C2 were sequentially treated with different reagents so that metals with different affinities for the mineral matrix could be released. The method used follows a 6-step sequential extraction procedure, proposed by Cardoso Fonseca and

Ferreira da Silva (1998). According to these authors, the following extractants and operationally-defined chemical fractions were taken: (a) F1: ammonium acetate (1 M NH_4Ac , pH 4.5) – water soluble and dissolved exchangeable ions, specifically adsorbed and carbonate-bound; (b) F2: hydroxylamine hydrochloride (0.1 M $\text{NH}_4\text{OH.HCl}$, pH 2) – elements bound in Mn oxyhydroxides; (c) F3: ammonium oxalate (dark) (0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ – 0.1 M $\text{H}_2\text{C}_2\text{O}_4$, pH 3.3 – Tamm reagent in dark) – elements linked to amorphous Fe oxides; (d) F4: H_2O_2 35% – elements associated to organic matter and authigenic sulfides; (e) F5: ammonium oxalate (UV) (0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ – 0.1 M $\text{H}_2\text{C}_2\text{O}_4$, pH 3.3 – Tamm reagent under UV radiation) – elements associated to crystalline Fe oxides; (f) F6: mixed-acid ($\text{HCl} + \text{HNO}_3 + \text{HF}$) decomposition – elements associated to matrix elements in lattice positions, resistant oxides and some sulphides. After each reaction, the solutions were centrifuged and filtered. For metal speciation (Cd, Pb, and Zn) the sampled solutions were analyzed by Atomic Absorption Spectrometry (AAS) using a GBC906 spectrophotometer.

4. Results

4.1. Physicochemical parameters

The physico-chemical conditions, shown by pH analysis, reflect neutral settings and no significant temporal variation along both cores, with values ranging from 7.7 to 8.1. The fraction lower than 63 μm represents 75% of particles for C1 and 79% for C2, excepted for two sand levels (respectively 55 cm and 75 cm; and 5 cm and 50 cm) in which this fraction is about 25–30% of particles. For both cores, deeper levels are marked by an increase of <63 μm fraction (87%). The average OC concentration is about 0.8% on surface samples. At depth, for both cores, variations of OC contents were observed (values ranging between 1 and 1.5%). This tendency could be attributed to either agricultural runoff and the drill or discharges of untreated urban sewage.

4.2. Mineralogy of both cores

The mineralogy of the two sediment cores was analysed using an X-ray diffraction (XRD) technique. Fig. 2 shows the XRD spectra for two different depth levels of the two cores; C1 (55 cm) and C2 (5 cm). All spectra are strongly affected by the signal lines of calcite and quartz. The abundance of these minerals is determined by the nature of the parent material of the soil and the geological context of the carbonated region. Another mineral, dolomite, is also common at different depths, but in a much smaller proportion than calcite. The only sulphide mineral identified is galena in C1 at 55 cm depth; other sulphides (pyrite, marcasite etc) were not identified since they were below the XRD detection limits.

4.3. Concentration profiles

4.3.1. Major elements

Table 1 summarizes the geochemical results obtained for C1 and C2. Major element concentrations (SiO_2 , Na_2O , K_2O , MgO and Fe_2O_3) show similar profiles in both cores. These elements have a common mineralogical source. Samples from C1 and C2 show high SiO_2 (4.4–16.0%) and CaO (14.1–29.0%) concentrations and are less rich in Al (2.9–4.5%). A linear relationship is observed between Al_2O_3 and Fe_2O_3 concentrations in both core samples ($R^2 = 0.76$ and 0.91), reflects probably a constant Fe/Al ratio of 0.64 for C1 and 0.58 for C2 (Fig. 3). This suggests that Oued Sidi Bou Said sediments are dominated by clay minerals (kaolinite – Al) and chlorites (Fe). The association of these elements reflects lithological contributions through the weathering and erosion of the basin by an upstream

process. However, a duality is observed between silica and CaO , showing that the carbonate inputs that may have originated from the mining site, can momentarily override the silicate particle transport (high concentration of CaO observed at 55 cm depth of C1). The similar values of alumina and silica show that these two elements appear to be related to the same kind of mineral component and aluminosilicates, i.e. clays.

4.3.2. Trace elements

The evolution of trace elements (Pb, Zn and Cd) in both cores is summarized in Table 1. These elements have similar concentration profiles for each core: C1 has an increase in element concentration as a function of increasing depth with high concentrations in the middle section (50–90 cm), while C2 contains higher concentrations in the first 50 cm, especially at the very surface of the core.

Trace element concentrations measured in the core bottom layers (i.e. 140, 77 and 2.7 mg kg^{-1} for Zn, Pb and Cd, respectively) are much lower than those found in the top and middle sections.

The results of C1 show four enriched levels (peaks at 40, 58, 65 cm and the bottom – Table 1) for Pb, Zn and Cd; the second peak concentration is more marked for Zn and Pb thus representing a very high enrichment (550 and 520, respectively) compared to the geochemical background concentrations. Finally, beyond 90 cm, metallic concentrations decrease to become lower than those of the surface layers (138, 95 and 2.8 mg kg^{-1} for Zn, Pb and Cd). In C2, the top 10 cm show significantly higher concentrations of Zn, Pb and Cd (Table 1), reaching 12050, 7230, and 110 mg kg^{-1} , respectively. The second and third peaks were recorded at 40 and 50 cm depth, the same as those observed in C1 but with a lower intensity. The similar temporal trend of Zn, Pb and Cd suggests a common origin which is possibly related to the sedimentation of minerals such as sphalerite and galena.

4.3.3. Aluminum normalized particulate metal profiles

Trace metal concentration measurements show high temporal evolution in both cores. However, surface sediments could acquire different and variable proportions of mineral phases, such as biogenic fractions, which could increase the trace elemental concentration in one sample. This is the reason why, in order to compare and correlate these variable concentrations it is recommended to normalize these elemental concentration by aluminum (Al) overcome the matrix effect (Calvert et Pedersen, 1993; Shoty et al., 1996; Tribouvillard et al., 2006; Smuc et al., 2009; Ayrault et al., 2010; Souza et al., 2011).

Different chemical elements (Pb, Zn and Cd) are strongly related to the mineralization of the Touiref mine. Aluminum normalized metal profiles do not show strong variations from those of total concentrations (Fig. 4). Mining activity has affected the standardized profiles of both cores; normalization shows that concentrations of these elements are always higher for 40, 58, 65 and 78.5 cm depth levels in C1 while for C2, Al-normalized profiles show a decrease for all elements beyond the first few centimeters of the surface where there is an enrichment of various metals.

4.3.4. Selective chemical extraction

Reactive Fe oxyhydroxides and Mn oxides, known to be reactive hosts for metal and metal partitioning, can dominate metal-bearing phases in sediments, especially for Pb (Bird et al., 2003). Indeed, in smelting-waste drainage environments with acid surface waters, metals are preferentially linked to Fe oxides that typically form at $\text{pH} < 7$. However, a previous study in the Lot-Garonne River (France) reported that reactive Mn oxides can play an important role for the fraction F2 with circum neutral pH conditions. The distribution of Cd, Pb, Zn, Fe and Mn in the different metal-bearing phases has been studied in samples representative of the surface,

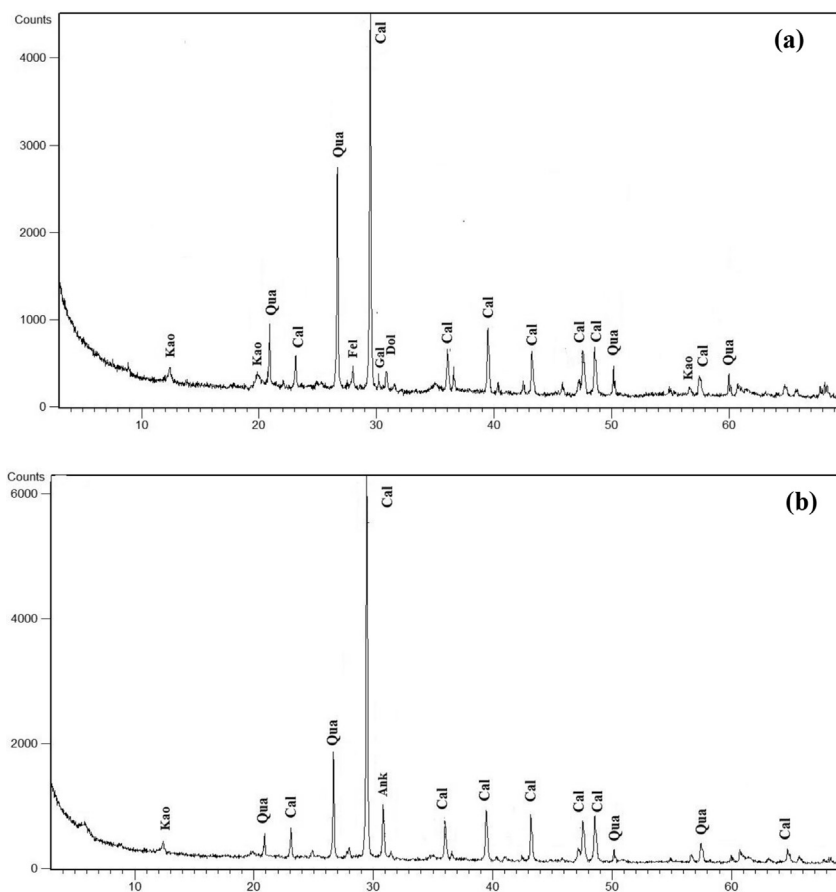


Fig. 2. XRD analysis of the two cores C1 and C2 (kao: Kaolinite; Qua: quartz; Cal: calcite; Dol: dolomite; Ank: Ankerite; Fel: Feldspar; Gal: galena).

intermediate and bottom layers: five different depths for C1 (5, 25, 55, 75, and 105 cm) and four depths for C2 (5, 25, 55, and 75 cm – see Fig. 5). The bottom samples represent the local geochemical background of the region.

Fe has a very similar distribution for all samples (Fig. 5b). It is mainly associated with the crystallized fraction (~72%) for the polluted sediments in C1 (55 cm and 75 cm) and C2 (5 cm and 55 cm) and ~66% in non-polluted sediments in C1 (5 cm, 25 cm and 105 cm) and C2 (25 cm and 75 cm). Amorphous oxides represent ~26% and 20% for polluted and non-polluted sediments, respectively. Only small percentages (<~20%) were extracted by the ammonium acetate, ammonium oxalate and hydroxylamine hydrochloride solutions.

Unlike Fe, Mn is mainly extracted with the solution of ammonium acetate (~65%) (Fig. 5c), i.e. water-soluble and dissolved exchangeable ions, specifically adsorbed and carbonate-bound. By order of importance, the other bearing phases for Mn are ~12% Fe oxyhydroxide, ~8% residual fraction and ~5% Mn oxides.

In non-polluted and polluted sediments, Zn is mainly bound to the carbonate phase and Fe oxyhydroxides (Fig. 5e), and subsequently in smaller proportions between Mn oxyhydroxides fractions, Fe amorphous oxides and organic matter. Lead is essentially linked to acid-soluble phases in all samples (Fig. 5d), especially in the most contaminated levels (more than 80% at 55 and 75 cm in C1 and more than 70% at 5 and 55 cm in C2). In bottom samples, Pb is mainly linked to amorphous and crystalline Fe oxyhydroxides, organic and residual phases (more than 40%).

The Cd speciation is homogenous in both C1 and C2 but very different from that of Zn. Cadmium is mainly associated with acid-soluble phases (carbonates). Its pattern is relatively similar to Pb

(Fig. 5a). Only small percentages (<9.3%) were extracted by the hydroxylamine hydrochloride solution.

5. Discussion

5.1. Intensity of metal pollution

The EF profiles for Cd, Pb and Zn, taking into consideration the proposed values for the local geochemical background, are quite similar (Fig. 6). The EF values calculated for C1 samples are less than 1 between 0 and 30 cm depth, suggesting no enrichment. The enrichment of all elements in C1 is recorded between 55 and 75 cm depth. At 55 cm depth, the EF values are at a maximum for all elements (14.5 for Cd, 47.7 for Pb and 51.9 for Zn). Towards the bottom of the core (beyond 80 cm depth) the EF values are well below 1. For C2, a significant EF is observed in the most superficial sediments with highest values at 5 cm depth (56.3 for Cd, 141 for Pb and 126 for Zn). Other significant EF values are recorded in the middle section of C2 (35–45 cm) but with the lowest order of magnitude (Fig. 6).

The calculated I_{geo} values for Cd, Pb, and Zn in C1 (Fig. 7) indicates that the surface sediments (0–25 cm) are considered “unpolluted to moderately polluted”. The highest I_{geo} values are recorded between 55 and 85 cm. Indeed, the I_{geo} values of Pb and Zn range between 6 and 7, which results in “very highly polluted” sediments while I_{geo} values for Cd (4.3–4.9) classify these sediments as “highly polluted”. The minimum I_{geo} (I_{geo} class < 1) determined in the deeper samples confirms that samples are classified as “unpolluted”.

In the C2 surface sediments (to 5 cm deep), very high Pb and Zn

Table 1
Concentrations of the major (%) and trace (mg kg^{-1}) acquired in this study.

	Depth	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	As	Cd	Pb	Zn
		%								mg kg^{-1}		
C1	5	34.3	19.8	11	4.8	1.1	1.3	0.8	36	6	381	680
	10	33.1	21.0	10.3	4.5	1.0	1.1	0.6	40	7	447	942
	15	31.9	21.0	11.2	4.6	1.1	1.3	0.7	33	5	294	586
	20	34.2	21.6	10	4.5	1.0	1.1	0.6	33	5	375	476
	25	34.8	20.7	10	4.3	1.0	1.1	0.7	34	5	267	440
	30	32.6	22.6	8.2	3.6	1.2	1.0	0.2	24	3	80	123
	35	32.5	20.5	9.4	4.9	1.2	1.2	0.6	67	26	3635	4053
	40	32.7	20.9	9	4.5	1.4	1.0	0.6	72	28	3532	4114
	45	33.7	20.4	9.3	4.7	1.4	1.1	0.8	72	28	3551	4089
	50	33.6	21.2	8.6	3.8	1.1	1.0	0.2	24	3	91	142
	55	9.4	40.6	2.7	2.5	1.0	0.2	0.2	275	125	12414	22957
	60	21.9	29.8	6.2	3.1	1.6	0.9	0.6	118	100	7714	11824
	65	20.8	31.3	5.6	3.1	1.9	0.8	0.4	115	108	9005	13831
	70	20.8	30.6	6	3.2	1.9	0.8	0.5	102	104	8143	12920
	75	18.6	31.8	5.3	2.9	2.1	0.7	0.4	108	124	9527	15251
	80	24.0	28.3	6.7	3.6	1.8	0.9	0.6	78	85	7027	9701
	85	35.0	19.2	10.5	5.0	1.4	1.4	0.9	39	23	1497	3196
	90	31.2	22.1	9	3.8	1.1	1.2	0.3	24	3	74	142
95	31.3	21.5	9.3	4.0	1.1	1.2	0.5	23	3	76	148	
100	31.0	21.5	9.3	4.0	1.1	1.2	0.4	23	3	82	152	
105	33.0	21.6	8.6	3.7	1.1	1.2	0.3	23	3	90	146	
110	33.3	22.5	8	2.6	1.0	1.0	0.2	23	3	95	139	
115	32.4	20.9	8.8	4.0	1.2	1.2	0.3	24	3	94	146	
C2	5	22.9	30.4	6.5	3.1	2.0	1.0	0.5	97	110	7227	12045
	10	36.8	18.0	10.8	4.6	1.1	1.5	0.9	37	17	1098	2101
	15	36.8	17.8	11.2	4.6	1.1	1.5	0.9	34	15	913	1765
	20	36.5	17.9	11.8	4.7	1.1	1.5	0.9	34	14	909	1694
	25	36.5	18.2	11.9	4.6	1.1	1.3	0.8	36	16	1054	1860
	30	34.4	19.1	10.5	4.5	1.1	1.4	0.8	42	24	1183	2080
	35	35.6	19.2	10	4.5	1.1	1.3	0.8	44	27	1861	3299
	40	35.7	19.2	10.5	4.5	1.1	1.3	0.8	46	29	1995	3420
	45	32.3	21.9	8.6	3.9	1.1	1.1	0.3	24	3	65	130
	50	34.8	21.0	8.7	4.2	1.2	1.1	0.6	68	29	3886	4534
	55	32.9	21.5	8.8	3.8	1.1	1.1	0.3	24	3	94	149
	60	30.6	23.3	8.6	3.7	1.1	1.0	0.3	24	3	82	138
	65	32.6	22.9	9.1	4.0	1.1	1.1	0.3	24	3	70	140
	70	31.4	22.7	9.2	4.1	1.1	1.0	0.3	25	3	61	132
	75	32.5	22.8	8.9	3.9	1.1	1.1	0.3	24	3	76	143
80	31.5	21.8	9.9	4.3	1.2	1.3	0.3	26	3	62	136	
85	32.9	22.5	8.3	3.7	1.0	1.0	0.3	23	2	50	108	
90	30.7	22.1	9.5	3.9	1.1	1.1	0.5	25	3	76	113	

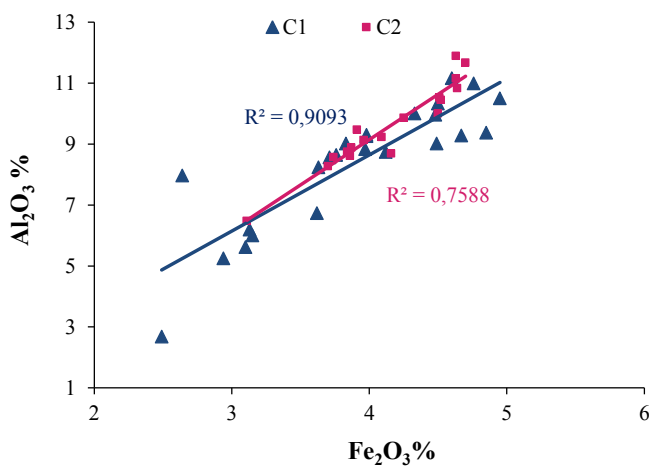


Fig. 3. Crossplot of Fe_2O_3 vs Al_2O_3 concentrations in C1 and C2 core samples.

I_{geo} values are calculated (5.9) which classify these sediments as “very highly polluted”. The Cd I_{geo} values do not exceed the value of 3 i.e. “moderately polluted”. Sediments at the base of the core are classified as “non-polluted”.

5.2. Comparison of heavy metal concentrations with natural background values and other river sites

The comparison of heavy metal concentrations with natural background values and other river sites shows that the heavy metal concentrations in C1 are clearly higher than those at the other contaminated sites listed in Table 2. The results suggest the presence of severe pollution in the Sidi Bou Said Valley sediments. Indeed, the comparison of these results with the UCC values (Wedepohl, 1995) clearly shows that concentrations of Cd, Pb, and Zn in C1 are up to 1245-fold, 730-fold and 441-fold, respectively.

In Tunisia, several studies have been carried out to estimate the metal contamination in sediments influenced by Pb–Zn mining activities. For example, in the Oued Medjerda sediments, maximum total concentrations are 265 mg kg^{-1} for Pb, 304 mg kg^{-1} for Zn, and 1.4 mg kg^{-1} for Cd (Moldenhauer et al., 2008). The Zn, Pb and Cd concentrations reported for the Oued Mellègue are roughly 17 mg kg^{-1} , 79 mg kg^{-1} and 0.3 mg kg^{-1} (Mlayah et al., 2009). Moreover, in sediments of the Oued, which drains the Bouaouane mining districts (where Pb and Zn are extracted), the concentrations of Pb, Zn and Cd reach 13065 mg kg^{-1} , 23695 mg kg^{-1} , 124 mg kg^{-1} respectively (Chakroun, 2012).

Compared to other sites affected by mining activities (Table 2),

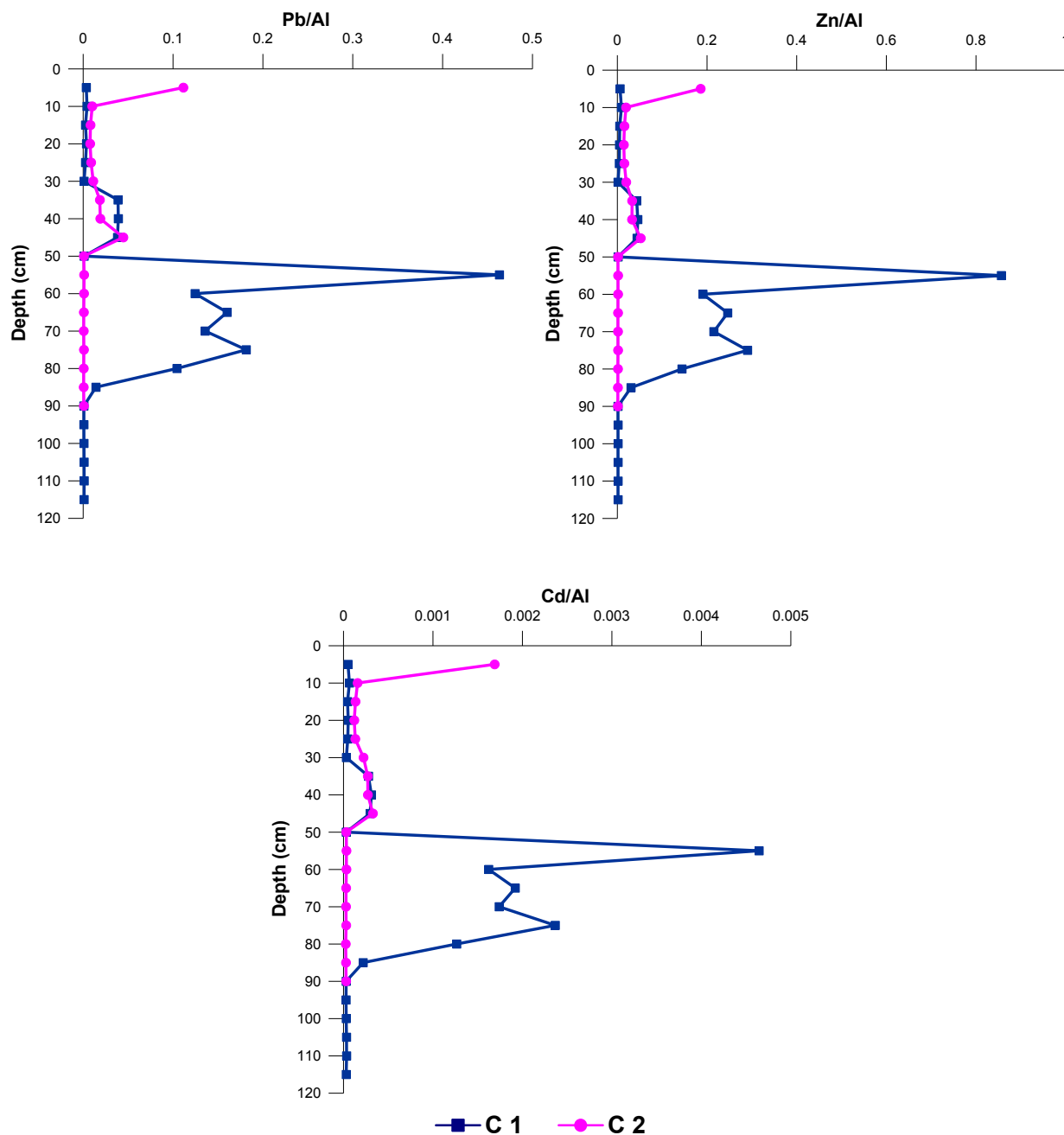
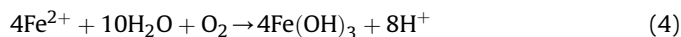
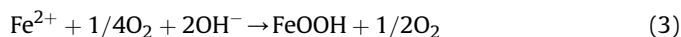


Fig. 4. Profiles of Al-normalized concentrations of Pb, Zn and Cd.

the maximum Cd, Pb and Zn concentrations observed in C1 are at least one order of magnitude higher. The maximum Pb concentration (12410 mg kg^{-1}) is about 11-fold higher than the concentrations observed in Spanish polluted rivers (Odiel and Tinto). The maximum Zn concentration ($23,000 \text{ mg kg}^{-1}$) is quite similar to those measured in the Kalimanci Lake (Macedonia). In contrast, the maximum Cd concentration (125 mg kg^{-1}) was about 2-fold lower than the results in the Lot River (France) at the Cajarc site (close to the confluence with a small mining- and smelting-affected watershed), but almost similar to those observed at another site, located at the outlet of the Lot River (Temple site, 185 mg kg^{-1}). According to the results obtained from other Tunisian mining sites, the metal concentrations in both cores are exceptionally high.

5.3. Metal bearing-phases and availability

The distribution of Fe (Fig. 5b) is similar for both C1 and C2. Fe is associated with three major bearing phases: (a) associated to crystallized oxy-hydroxide and amorphous Fe-oxides. They are typically secondary mineral phases resulting from the oxidation of mineral tailings, formed according to reactions:



(b) associated to the acid-soluble fraction (carbonates), explained by the substitution of Fe to Ca in calcite or the occurrence

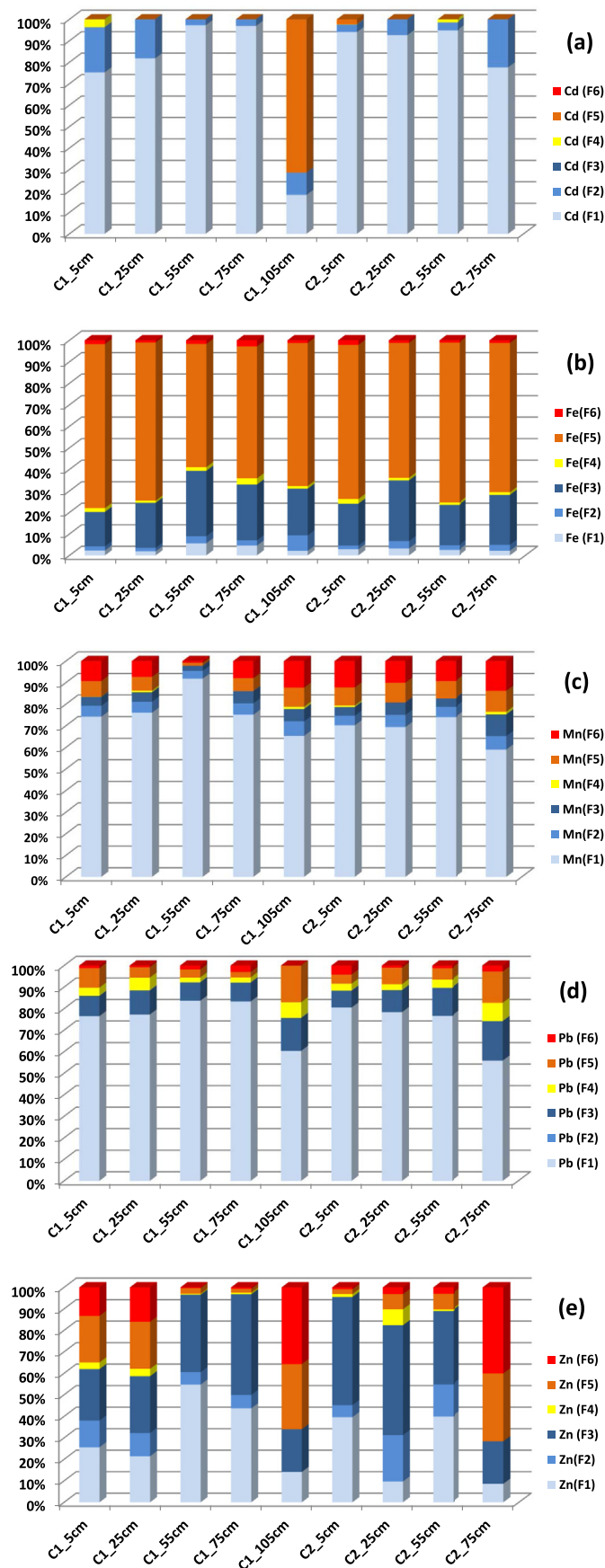


Fig. 5. Percentage of extraction of Cd, Fe, Mn, Pb and Zn in selected C1 and C2 core samples.

of Fe as siderite (FeCO_3); and (c) sulphides, corresponding to the residual fraction (associated to the primary mineralization mainly sulphides). Manganese is largely associated with the carbonated fraction and, to a lesser extent, with Mn-oxi-hydroxide and amorphous Fe-oxi-hydroxide. The higher availability of Mn in carbonate phase is consistent with the results of Wang et al. (2010) for Jinzhou bay.

These results highlight different solid state partitioning for Cd and Zn. Those obtained for Pb show that this element is associated to carbonated phases. Other researchers have found similar results: Denys et al. (2007) showed that Pb carbonate forms, and particularly cerussite, are highly bioaccessible; Palumbo-Roe et al. (2013) indicated that higher bioaccessible Pb fractions are related to samples where cerussite occurred in the Pb mineral assemblage of mine wastes, irrespective of the presence of other Pb minerals. An experimental study of dissolution of galena, carried out by this author, suggested the presence of carbonate and hydroxycarbonate of Pb. However, for pH values higher than 7, Carroll et al. (1998) suggested a competition between the sorption of Pb onto Fe oxyhydroxides and carbonated phases according to the Fe concentrations in the system. Plots point out a preferential Zn adsorption onto Fe oxyhydroxides and carbonated phases. This behaviour was observed by O'Day et al., 1998; Relic et al., 2005; Farkas et al., 2007; Nemati et al., 2011; Hamzeh et al., 2014 in sediments which are contaminated by mining activities where Zn showed a high affinity to hydrous iron oxides and carbonates. According to these authors, Cd is not associated with oxyhydroxides, while for the same samples, 50–75% of Zn is bound to oxyhydroxides. Bo-feng and Wei-ling (2014) shows that the Cd in sediments from the Xiangjiang River in China is mainly bound to non-residual fractions, mainly to the exchangeable (7.2%–54.4%), carbonate (7.6%–58.1%) and Fe–Mn oxides fractions (21.3%–62.3%), but rarely to the organic fraction (1.0%–28.6%). Similarly, Zhi-feng et al. (2009) and Jain (2004) showed that Cd in sediments of the Yamuna River and the Yangtze River are also primarily bound with the exchangeable and carbonate fractions. This distinctive behaviour between Zn and Cd can be explained in terms of competition of adsorption, either between Zn and Cd or between Cd and alkaline earth cations (such as Ca and Ba). Li-cheng et al., 1996; Sutherland et Tack, 2007; Farkas et al., 2007; Sundaray et al., 2011; Garcia-Pereira et al., 2014, reported that the high proportion of carbonate-bound Cd in sediments contaminated by heavy metals may be ascribed to the fact that carbonates are common in this area and that the similarity of the ionic radii of Ca and Cd favours the co-precipitation of Cd carbonate and its incorporation into the calcite lattice.

In binary adsorption experiments with transition metals and Cd, Benjamin and Leckie (1981) found that the competition rate depends on the specific combination of metallic cations. In particular, they show that the presence of Zn (but also Pb) in solution significantly reduces the adsorption of Cd by oxides due to the adsorption on mutually compatible sites. Using similar experiments, Cowan et al. (1991) showed that a significant decrease (up to 40% with pH 7.2) of Cd adsorption by amorphous Fe oxides in the presence of Ca in solution, compared to a solution containing only Cd. The presence of Ba can also influence the Cd adsorption onto the surface of Fe oxides (15% in pH 8 – Cowan et al., 1991).

In sediments, metals are mainly distributed between acid-soluble and reducible phases and, to a lesser extent sulphides. Sulphides are unstable species in surface conditions. Their oxidation will eventually result in metal release. Conversely, carbonates and (oxy) hydroxides of Fe are more stable under the Tuirref conditions, at the outlet of the upstream watershed. However, metals may become unstable if physicochemical conditions change,

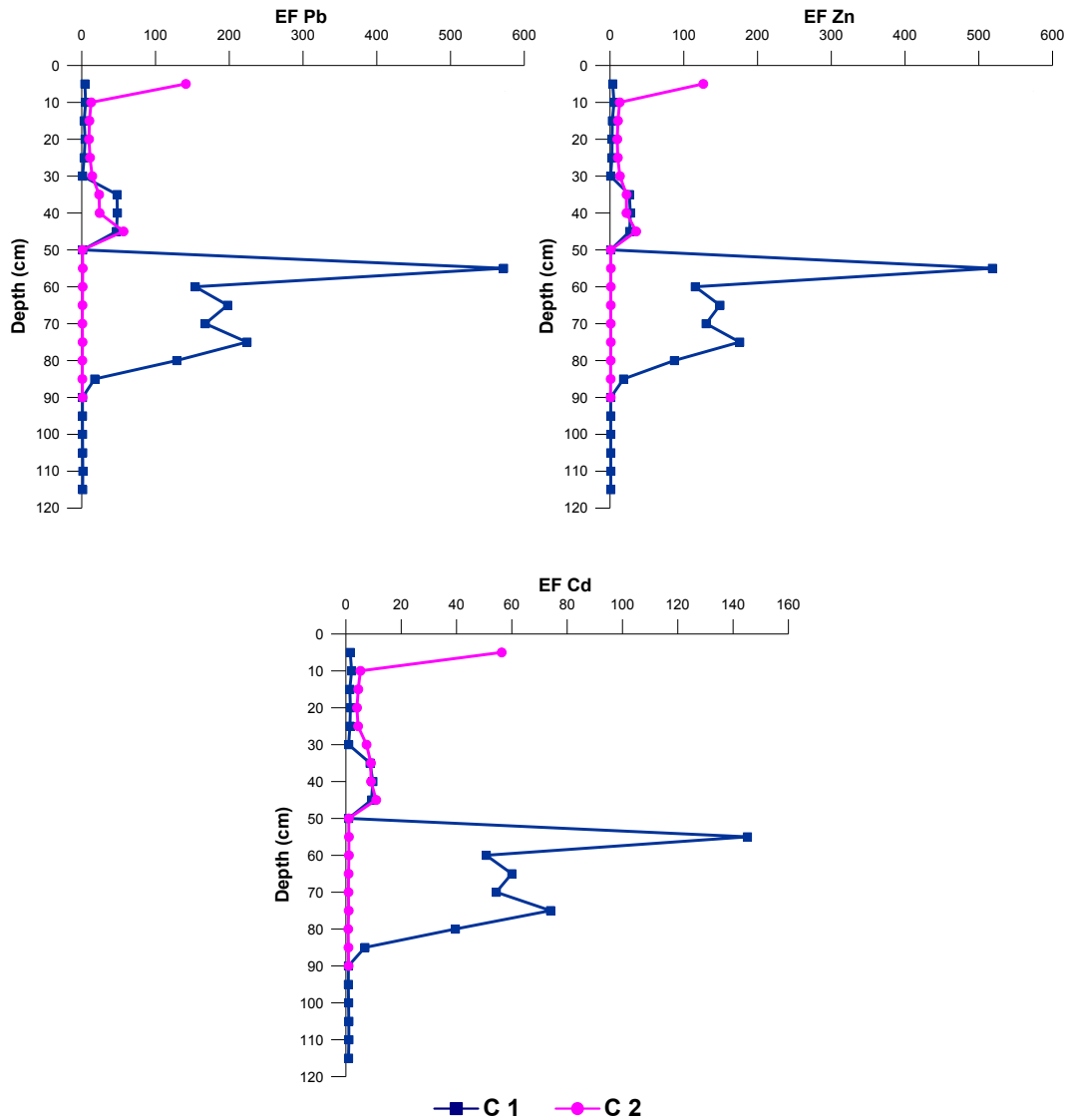


Fig. 6. Enrichment factor (EF) of Cd, Pb and Zn in selected C1 and C2 core samples.

particularly changes in pH or Eh. Sediments can act as metal storage and are a secondary source of reactive metal contamination.

5.4. Metal pollution and accumulation sedimentary record

It is possible to link the geochemical results and the accumulation sedimentary record of the two cores at El Goreaa with the events in mining production. These events can be summarized as follows:

- 1) Around 1900, the discovery of rich Pb/Zn veins in the district “St. Louis Jobard and St. Felix,” and the first mining operations triggered a large displacement of sediments and rocks in the downstream pool with a monthly output around 2000 tons (1889–1930). This is reflected in a concentration peak between 78 and 85 cm of C1 (Fig. 6a).
- 2) Economic downturn between 1931 and 1935 resulted in the collapse of Pb prices and an economic crisis in the mining industry. Metal ore extraction and mining-quarrying then continued with limited resources and is restricted to Ressay East with a monthly production of about 1000 tons. This is recorded

as a peak at 60–78 cm depth and explains the high EF values (Fig. 6a).

- 3) In 1948, the company mining in Tunisia was taken over by Pennaroya, a different mining company with a new philosophy. Research was actively pushed and important investments were made, resulting in the construction of a Laundromat flotation of 250 t/day. Production exceeded 4000 t/month, which is reflected in the two cores by the existence of very intense peaks for all the elements (Fig. 6a and b) in the range of 50–57 cm depth. During the early period of World War II, there were inflated international prices for metals (Pb, Cd and Zn). These peaks coincided precisely with the production capacity of major Touiref’s mine, following the construction of the new laundry, around 1951.
- 4) Significant research carried out produced disappointing results. In Ressay West, operating tests should have been stopped because of the high mining costs and the low-grade of ore extracted. This work in Ressay West stopped in November 1955. In Ressay East, the surface was mineralized and the concentrations decreased with depth, but most fractures were not heavily mineralized. Work in these areas stopped in May 1957. This can

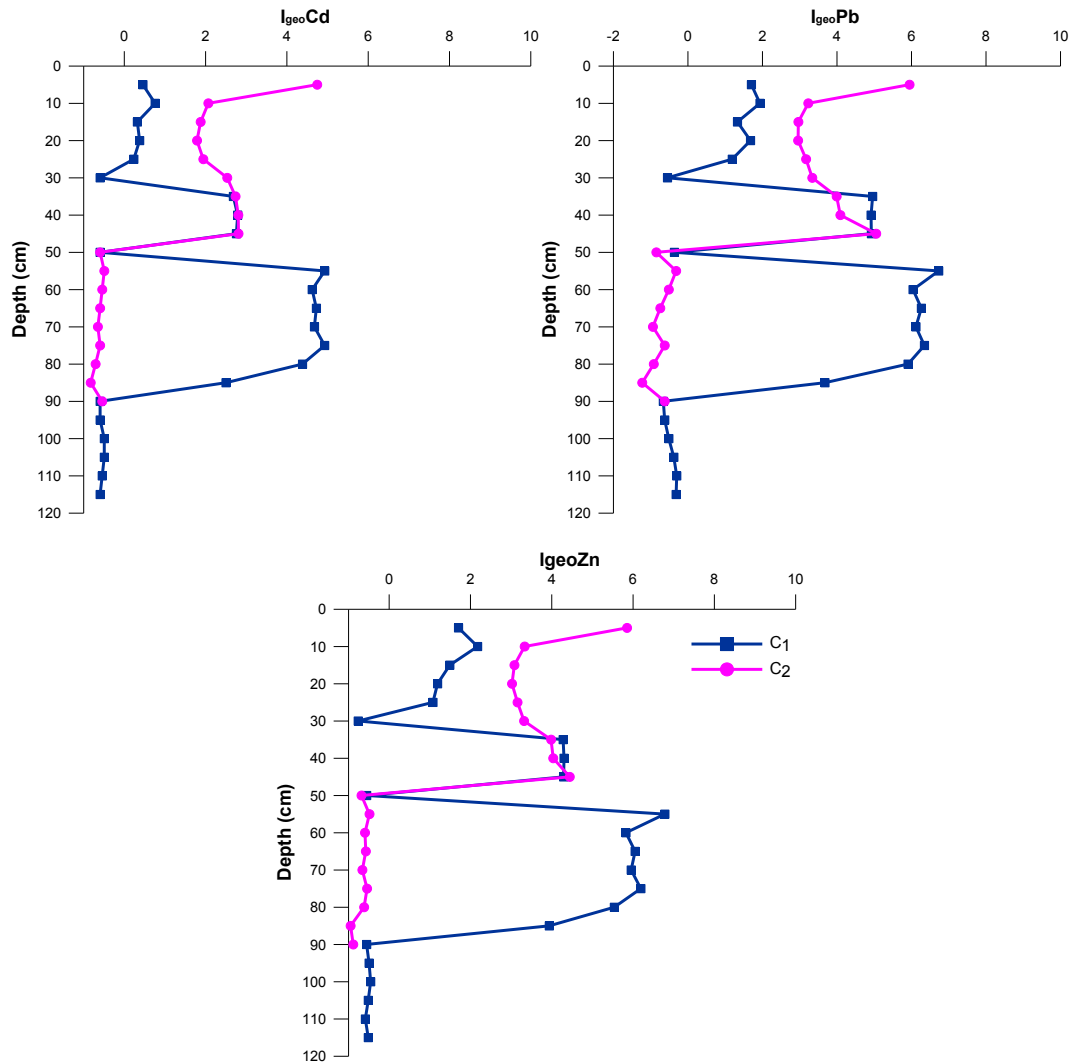


Fig. 7. Geoaccumulation index (I_{geo}) for Cd, Pb and Zn in selected C1 and C2 core samples.

Table 2

Maximum values of the trace elements (mg kg^{-1}) acquired in this study and comparison with other selected sites.

Location	Cu			Zn			Cd			Pb			References
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	
Core 1, Touiref	11	20	15	146	22957	4617	2.7	124	35	74	12414	2978	This study
Core 2, Touiref	12	19	14	107	12045	1890	2.3	95	16	50	7227	1153	This study
Geochemical background			12			140			2.7			77	This study
Cajarc site, Lot River	40.6	264	97.7	909	10,000	4430	12.6	294	125	111	1280	523	Audry et al. (2004)
Temple site, Lot River	16.7	78	30.7	81.5	7230	949	0.56	180	20.4	31.3	593	105	Audry et al. (2004)
UCC	–	–	14.3	–	–	52	–	–	0.10	–	–	17	Wedepohl (1995)
Oued Mellègue, Tunisia	7	12	9	49	110	43	01	03	0.4	33	49	7	Mlayah et al. (2009)
Jendouba Basin, Tunisia	18	23	–	74	108	–	–	–	–	31	51	–	Moldenhauer et al. (2008)
Oued Tessa, Tunisia ^a	8	50	24	29	3055	739	–	5	1	83	356	148	Sebei (2007)
Lake Kalimanci, Macedonia ^a	144.4	1162	415.1	295	20,900	8420	16.5	136	56.58	187	16,300	6059	Vrhovnik et al. (2013)
Malter Reservoir, Germany ^a	–	240	196	–	1900	1362	–	91	37.5	–	740	465	Müller et al. (2000)
Oued Kasseb, Tunisia ^a	–	–	–	–	5277	13,065	–	57	151	–	49,360	–	Chakroun (2012)
Odiel River, Spain ^a	54	2920	1282	143	3150	954	0.35	68	8.5	46	1140	649	Morillo et al. (2002)
Tinto River, Spain ^a	180	2650	846	110	6730	1754	<1	23	6.2	370	1650	870	Galán et al. (2003)
Guadiamar River, Spain ^a	98	265	165	590	2970	1421	1.8	9.5	3.9	51	250	127	Lacal et al. (2003)
Patroon Reservoir, NY, USA	–	–	–	–	–	–	–	25	–	–	3600	–	Arnason and Fletcher (2003)
Elbe River, Germany	7	283	–	34	1266	–	0.1	12.4	–	7	305	–	Schulz-Zunkel et al. (2013)
Elbe River, China	11.3	920	–	34.1	1050	–	00.9	29.4	–	15.9	535	–	Wang et al. (2014)

^a River draining mine sites.

be observed as the decrease in EF values for Pb, Zn, Cd and As in the depth range of 7–8 cm.

- 5) South of the concession (Touiref's mount and in the Jebel (mount) El Lafi), the tonnage of minerals remaining was low and the rate of extraction of 4000 t/month explains highest FE values in the sediments between 30 and 45 cm.
- 6) The decrease in metal concentrations at the surface of the core is likely to reflect the decrease in mining and its final activity in the 1960s. Consequently, surface values are now similar to those observed at the base of the core.

Finally, recent anthropogenic influence has been detected in C2; the peaks observed and the EF values in the most superficial sediment could be the result of the use of mine tailings for unpaved road base. Moreover, it is not a question of transportation by wind or water, but it is due to human transport. In this area, the mining wastes were stored directly (for almost 50 years) in agricultural lands without any measure of protection to avoid environmental and human health impact.

Given the mountainous landscape, the high-altitude of the Sidi Bou Said River, the climatic conditions (high-intensity precipitation is dominant during winter, 455 mm), the mode of deposit and the physical characteristics of the mine tailings, there is a severe hydraulic erosion of the mining residue. The presence of these metals in downstream sediments reveals the influence of the transported metal-contaminated, especially Pb and Zn. These concentrations could be explained by the erosion and transport of waste particles from the tailing impoundments through the river and the consequent settling of particles in endoreic plain.

6. Conclusion

Based on the study of major element compositions, vertical metal concentration profiles and solid state partitioning, the results have shown a significant human influence on the natural records of the Touiref region. Both cores show an impact of the mining development in the valley. In fact, the beginning of mining activity in the region began after World War II, with the installation of a gravimetric laundry, which is reflected in C1. The intensity of the metal pollution was evaluated by calculating enrichment factors that showed maximum values of 65, 524 and 550 for Cd, Pb and Zn, respectively. Furthermore, according to the Geo-accumulation Index (Igeo), the sediments are classified as "severely polluted". The relative importance of the pollution is as follows: Zn > Pb >> Cd.

The improvement of processing mineral ores by the upgrade of the flotation process during the late '40s is reflected in a maximum metallic contamination in both cores. Trace element concentrations measured in the core bottom layers (i.e. 140, 77 and 2.7 mg kg⁻¹ for Zn, Pb and Cd, respectively) are much lower than those found at the top and middle sections. These values could be representative of geochemical background concentrations before the period of industrialization in the Touiref watershed and the beginning of the ore processing plant activities, i.e. around 1900 (SERMI, 1965).

Finally, recent anthropogenic activity marked by an increase of metal EF and Igeo is recorded in surface C2 sediments. These concentrations do not seem to be directly related to mining activity, since it has fallen sharply in intensity during this period, but this could be due to the dispersion of tailing materials by water and wind and by the use of these materials in the s road pavements.

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References

- Andrades-Moreno, L., del Castillo, I., Parra, R., Doukkali, B., Redondo-Gómez, S., Pérez-Palacios, P., Caviedes, M.A., Pajuelo, E., Rodríguez-Llorente, I.D., 2014. Prospecting metal-resistant plant-growth promoting rhizobacteria for rhizoremediation of metal contaminated estuaries using *Spartina densiflora*. *Environ. Sci. Pollut. Res.* 5, 3713–3721.
- Arnason, J.G., Fletcher, B.A., 2003. A 40+ year record of Cd, Hg, Pb, and U deposition in sediments of Patroon Reservoir, Albany County, NY, USA. *Environ. Pollut.* 123, 383–391.
- Audry, S., Schafer, J., Blanc, G., Jouanneau, J.M., 2004. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). *Environ. Pollut.* 132, 413–426.
- Audry, S., Blanc, G., Schafer, J., 2006. Solid state partitioning of trace metals in suspended particulate matter from a river system affected by smelting-waste drainage. *Sci. Total Environ.* 363, 216–236.
- Audry, S., Blanc, G., Schäfer, J., Guérin, F., Masson, M., Robert, S., 2007. Budgets of Mn, Cd and Cu in the macrotidal Gironde estuary (SW France). *Mar. Chem.* 107, 433–448.
- Ayrault, S., Rianti, C., Evrard, O., Lefèvre, I., Bonté, P., 2010. Silver and thallium historical trends in the Seine River basin. *J. Environ. Monit.* 12, 2177–2185.
- Ayrault, S., Le Pape, P., Evrard, O., Priadi, C.R., Quantin, C., Bonté, P., Roy-Barman, M., 2014. Remanence of lead pollution in an urban river system: a multi-scale temporal and spatial study in the Seine River basin, France. *Environ. Sci. Pollut. Res.* 21, 4134–4148.
- Benjamin, M.M., Leckie, J.O., 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *J. Coll. Interf. Sci.* 79, 209–221.
- Bird, G., Brewer, P.A., Macklin, M.G., Balteanu, D., Driga, B., Serban, M., Zaharia, S., 2003. The solid-state partitioning of contaminant metals and As in river channel sediments of the mining affected Tisa drainage basin, northwestern Romania and eastern Hungary. *Appl. Geochem.* 18, 1583–1595.
- Bo-feng, J., Wei-ling, S., 2014. Assessment of heavy metal pollution in sediments from Xiangjiang River (China) using sequential extraction and lead isotope analysis. *J. Cent. South Univ.* 21, 2349–2358.
- Bruggemann, L., Paschke, A., Daus, B., Weiss, H., 2004. Characterization of sediments in an 405 abandoned mining area; a case study of Mansfeld region. *Ger. Environ. Geol.* 45 (6), 818–833.
- Callender, E., 2003. Heavy metals in the environment—Historical trends. In: Lollar, B.S. (Ed.), *Environmental*.
- Calvert, S.E., Pedersen, T.F., 1993. Geochemistry of recent oxic and anoxic marine sediments: implications for the geological record. *Mar. Geol.* 113, 67–88.
- Cardoso Fonseca, E., Ferreira da Silva, E., 1998. Application of selective extraction in metal-bearing phases identification: a South European case study. *J. Geochem. Explor.* 6, 203–212.
- Carroll, S.A., O'Day, P.A., Piechowski, M., 1998. Rock-water interactions controlling zinc, cadmium, and lead concentrations in surface waters and sediments. U.S. Tri-State Mining District. 2. Geochemical interpretation. *Environ. Sci. Technol.* 32, 956–965.
- Chakroun, H.K., 2012. Etude des rejets miniers et impact du transfert des métaux lourds vers le sol et la végétation dans le district de Jbel Hallouf- Sidi Bouaouane. Thèse Sci. Univ. Tunis, Tunisie, 218 p.
- Clark, E.V., Odhiambo, B.K., Ricker, M.C., 2014. Comparative analysis of metal concentrations and sediment accumulation rates in two Virginian Reservoirs, USA: lakes Moomaw and Pelham Ellyse. *Water Air Soil Pollut.* 225, 1860.
- Cowan, C.E., Zachara, J.M., Resch, C.T., 1991. Cadmium adsorption on iron oxides in the presence of alkaline-earth elements. *Environ. Sci. Technol.* 25, 437–446.
- Coynel, A., Schäfer, J., Blanc, G., Bossy, C., 2007. Scenario of particulate trace metal and metalloid transport during a major flood event inferred from transient geochemical signals. *Appl. Geochem.* 22, 821–836.
- Deycard, V.N., Schäfer, J., Blanc, G., Coynel, A., Petit, J.C.J., Lancelot, L., Dutruy, L., Bossy, C., Ventura, A., 2014. Contributions and potential impacts of seven priority substances (As, Cd, Cu, Cr, Ni, Pb, and Zn) to a major European Estuary (Gironde Estuary, France) from urban wastewater. *Mar. Chem.* 167, 123–134.
- Denimal, S., Bertrand, C., Mudry, J., Paquette, Y., Hochart, M., Steinmann, M., 2005. Evolution of the aqueous geochemistry of mine pit lakes-Blanzy-Montceau-les-Mines coal basin (Massif Central, France): origin of sulfate contents; effects of stratification on water quality. *Appl. Geochem.* 20, 825–839.
- Denys, S., Caboché, J., Tack, K., Delalain, P., 2007. Bioaccessibility of lead in high carbonate soils. *J. Environ. Sci. Health Part A Toxic/Haz. Subst. Environ. Eng.* <http://dx.doi.org/10.1080/10934520701435569>.
- Dhivert, E., Grosbois, C., Coynel, A., Lefèvre, I., Desmet, M., 2015. Influences of major flood sediment inputs on sedimentary and geochemical signals archived in a reservoir core (Upper Loire Basin, France). *Sci. Total Environ.* 505, 121–136.
- DIB, I., 2009. L'impact de l'activité agricole et urbaine sur la qualité des eaux souterraines de la plaine de Gadaine-Ain Yaghout (Est Algérien). Mémoire de magister en hydraulique, construction hydro-technique et environnement, faculté des sciences de l'ingénieur, département d'hydraulique, Université Hadj Lakhdar Batna, p. 127.

- Duarte, B., Caçador, I., 2012. Particulate metal distribution in Tagus estuary (Portugal) during a flood episode. *Mar. Pollut. Bull.* 64, 2109–2116.
- Duffa, C., Dufois, F., Coudray, S., 2011. An operational model to simulate post-accidental radionuclide transfers in Toulon marine area: preliminary development. *Ocean Dyn.* 61 (11), 1811–1821.
- EL Yaouti, F., Mandour, A.E.L., Khattach, D., Benavente, J., Kaufmann, O., 2009. Salinization processes in the unconfined aquifer of Bou-Areg (NE Morocco): a geostatistical, geochemical, and tomographic study. *Appl. Geochem.* 24, 16–31.
- Farkas, A., Erratico, C., Viganò, L., 2007. Assessment of environmental significance of heavy metal pollution in surficial sediments of the River Po. *Chemosphere* 68, 761–768.
- Fathollahzadeh, H., Kaczala, F., Bhatnagar, A., Hogland, W., 2014. Speciation of metals in contaminated sediments from Oskarshamn Harbor, Oskarshamn, Sweden. *Environ. Sci. Pollut. Res.* 21, 2455–2464.
- Fernández-López, C., Faz Cano, A., Aroca, J.M., Alcolea, A., 2014. Elemental and mineral composition of salts from selected natural and mine-affected areas in the Poopó and Uru-Uru lakes (Bolivia). *J. Great Lakes Res.* <http://dx.doi.org/10.1016/j.jglr.2014.08.003> 0380–1330.
- Frömmichen, R., Wendt-Potthoff, K., Friese, K., Fischer, R., 2004. Microcosm studies for neutralization of hypolimnetic acid mine lake water (pH 2.6). *Environ. Sci. Technol.* 38, 1877–1887.
- Galán, E., Gómez-Ariza, J.L., González, I., Fernández-Caliani, J.C., Morales, E., Giraldez, I., 2003. Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. *Appl. Geochem.* 18, 409–421.
- García-Pereira, F.J., Gimenez, R., García, de la Villa, R., Vigil, Procopio, J.R., 2014. Heavy metal fractionation in sediments from the Jarama River (central Spain). *Environ. Earth Sci.* <http://dx.doi.org/10.1007/s12665-014-3587-9>.
- Giuseppe, D.D., Bianchini, G., Antisari, L.V., Martucci, A., Natali, C., Beccaluva, L., 2014. Geochemical characterization and biomonitoring of reclaimed soils in the Po River Delta (Northern Italy): implications for the agricultural activities. *Environ. Monit. Assess.* 186, 2925–2940.
- Grosbois, C., Meybeck, M., Lestel, L., Lefèvre, I., Moatar, F., 2012. Severe and contrasted polymetallic contamination patterns (1900–2009) in the Loire River sediments (France). *Sci. Total Environ.* 435 (436), 290–305.
- Hamzaoui-Azaza, F., Ketata, M., Bouhila, R., Gueddari, M., Riberio, L., 2011. Hydro-geochemical characteristics and evaluation of drinking water quality in Zeuss-Koutine aquifer, southeastern Tunisia. *Environ. Monit. Assess.* 174, 283–298.
- Hamzeh, M., Ouddane, B., Daye, M., Halwani, J., 2014. Trace metal mobilization from surficial sediments of the Seine River Estuary. *Water Air Soil Pollut.* 225, 1878–1893.
- Heim, S., Schwarzbauer, J., 2013. Pollution history revealed by sedimentary records: a review. *Environ. Chem. Lett.* 11, 255–270.
- Helali, M.A., Oueslatia, W., Zaabou, N., Addeda, A., Abdeljaouad, S., 2013. Geochemistry of marine sediments in the Mejerda River delta, Tunisia. *Chem. Speciat. Bioavailab.* 25 (4), 247–257.
- Hernandez, L., Probst, A., Probst, J.L., Ulrich, E., 2003. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Sci. Total Environ.* 312 (1–3), 195–219.
- Hong, S., Candelone, J.P., Patterson, C.C., Boutron, C.F., 1994. Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations. *Science* 265 (5180), 1841–1843.
- INM (Institut National de Météorologie de Tunisie), 2004. Archives des données de pluviométrie, température, évaporation, précipitation et vent de la région d'El Kef. INM, Tunis.
- Jain, C.K., 2004. Metal fractionation study on bed sediments of river Yamuna. *India J. Water Res.* 38 (3), 569–578.
- Jeziorski, A., Keller, W., Paterson, A.M., Greenaway, C.M., Smol, J.P., 2013. Aquatic ecosystem responses to rapid recovery from extreme acidification and metal contamination in lakes near Wawa, Ontario. *Ecosystems* 16, 209–223.
- Lacal, J., Pilar da Silva, M., García, R., Sevilla, T.M., Procopio, J.R., Hernández, L., 2003. Study of fractionation and potential mobility of metal in sludge from pyrite mining and affected river sediments: changes in mobility over time and use of artificial ageing as a tool in environmental impact assessment. *Environ. Poll.* 124, 291–305.
- Lanceleur, L., Schäfer, J., Chiffolleau, J.F., Blanc, G., Auger, D., Renault, S., Baudrimont, M., Audry, S., 2011. Long-term records of cadmium and silver contamination in sediments and oysters from the Gironde fluvial estuarine continuum: evidence of changing silver sources. *Chemosphere* 85 (8), 1299–1305.
- Larrose, A., Coynel, A., Schäfer, J., Blanc, G., Massé, L., Maneux, E., 2010. Assessing the current state of the Gironde estuary by mapping priority contaminant distribution and risk potential in surface sediment. *Appl. Geochem.* 25, 1912–1923.
- Li-cheng, Z., Gui-jiu, Z., 1996. The species and geochemical characteristics of heavy metals in the sediments of Kangjiaxi River in the Shuikoushan Mine Area, China. *J. Appl. Geochem.* 11 (1/2), 217–222.
- Maanan, M., Landesman, C., Maanan, M., Zourarah, M., Fattal, P., Sahabi, M., 2013. Evaluation of the anthropogenic influx of metal I and metalloïd contaminants into the Moulay Bousseham lagoon, Morocco, using chemometric methods coupled to geographical information systems. *Environ. Sci. Pollut. Res.* 20, 4729–4741.
- Maftéi, A.E., Iancu, O.G., Buzgar, N., 2014. Assessment of minor elements contamination in Bistrița River sediments (upstream of Izvorul Muntelui Lake, Romania) with the implication of mining activity. *J. Geochem. Explor.* 145, 25–34. <http://dx.doi.org/10.1016/j.gexplo.2014.05.001>.
- Moldenhauer, K.M., Zielhofer, C., Faust, D., 2008. Heavy metals as indicators for Holocene sediment provenance in a semi-arid Mediterranean catchment in northern Tunisia. *Quat. Int.* 189, 129–134.
- Monteiro, F.F., Cordeiro, R.C., Santelli, R.E., Machado, W., Evangelista, H., Villar, L.S., Viana, L.C.A., Bidone, E.D., 2012. Sedimentary geochemical record of historical anthropogenic activities affecting Guanabara Bay (Brazil) environmental quality. *Environ. Earth Sci.* 65, 1661–1669.
- Mlayah, A., Ferreira da Silva, E., Rocha, F., Ben Hamza, Ch., Charef, A., Noronha, F., 2009. The Oued Mellègue: mining activity, stream sediments and dispersion of base metals in natural environments, North-western Tunisia. *J. Geochem. Explor.* 102, 27–36.
- Morillo, J., Usero, J., Gracia, I., 2002. Partitioning of metals in sediments from the Odiel River (Spain). *Environ. Int.* 28, 263–271.
- Müller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. *Geo J.* 2, 109–118.
- Müller, G., 1979. Schwermetalle in den sediment des Rheins, Veränderung seit 1971. *Umschau* 79, 778–783.
- Müller, J., Ruppert, H., Maramatsu, Y., Schneider, J., 2000. Reservoir sediments – a witness of mining and industrial development (Malter Reservoir, eastern Erzgebirge, Germany). *Environ. Geol.* 39, 1341–1351.
- Mwanamoki, P.M., Devarajan, N., Niane, B., Ngelinkoto, P., Thevenon, F., Nlandu, J.W., Mpiana, P.T.K., Prabakar, Kandasamy, Mubedi, J.L., Kabele, C.G., Wildi, W., Poté, J., 2015. Trace metal distributions in the sediments from river-reservoir systems: case of the Congo River and Lake Ma Vallée, Kinshasa (Democratic Republic of Congo). *Environ. Sci. Pollut. Res.* 22, 586–597.
- Nemati, K., Bakar, N.K.A., Abas Mhd, R., Sobhanzadeh, E., 2011. Speciation of heavy metals by modified BCR sequential extraction procedure indifferent depths of sediments from Sungai Buloh, Selangor, Malaysia. *J. Hazard. Mat.* 192, 402–410.
- Nieminen, T.M., Ukonmaanaho, L., Shoty, W., 2002. Enrichment of Cu, Ni, Zn, Pb and As in an ombrotrophic peat bog near a Cu-Ni smelter in Southwest Finland. *Sci. Total Environ.* 292 (1–2), 81–89.
- O'Neill, A., Phillips, D.H., Bowen, J.J., Sen Gupta, B.B., 2015. Contaminants in surface water and sediments near the Tynagh silver mine site, County Galway, Ireland. *Sci. Total Environ.* 512 (513), 261–272.
- Omanović, D., Pižeta, I., Vukosav, P., Kovács, E., Francisković-Bilinski, S., Tamás, J., 2015. Assessing element distribution and speciation in a stream at abandoned Pb-Zn mining site by combining classical, in-situ DGT and modelling approaches. *Sci. Total Environ.* 511 (2015), 423–434.
- Othmani, M.A., Souissi, F., Souissi, R., Mansouri, A., Jrad, A., Naouali, H., Ben Mammou, A., 2007. Les résidus miniers de Touïref: caractérisation et impact sur l'environnement. *Rev. Méditer. l'Environ.* 2, 313–327.
- Othmani, M.A., Souissi, F., Benzaazoua, M., Bouzahzah, H., Bussière, B., Mansouri, A., 2013. The geochemical behaviour of mine tailings from the Touïref Pb–Zn district in Tunisia in weathering cells leaching tests. *Mine Water Environ.* 32, 28–41.
- Othmani, M.A., Souissi, F., Bouzahzah, H., Bussière, B., Ferreira da Silva, E., Benzaazoua, M., 2014. The flotation tailings of the former Pb–Zn mine of Touïref (NW Tunisia): mineralogy, mine drainage prediction, base-metal speciation assessment and geochemical modeling. *Environ. Sci. Pollut. Res.* 22, 2877–2890.
- O'Day, P.A., Carroll, S.A., Waychunas, G.A., 1998. Rock–Water interactions controlling Zinc, Cadmium, and Lead concentrations in surface waters and sediments, U.S. Tri-State Mining District. 1. Molecular identification using X-Ray absorption spectroscopy. *Environ. Sci. Technol.* 32, 943–955.
- Palumbo-Roe, B., Wragg, J., Cave, M.R., Wagner, D., 2013. Effect of weathering product assemblages on Pb bioaccessibility in mine waste: implications for risk management. *Environ. Sci. Pollut. Res.* <http://dx.doi.org/10.1007/s11356-013-1515-2>.
- Pouget, F., Schäfer, J., Dutrich, L., Garnier, C., Tessier, E., Huy Dang, D.H., Lanceleur, L., Mullot, J.U., Lenoble, V., Blanc, B., 2014. Sources and historical record of tin and butyl-tin species in a Mediterranean bay (Toulon Bay, France). *Environ. Sci. Pollut. Res.* 21 (10), 6640–6651.
- Quevauviller, P., Lavigne, R., Cortez, L., 1989. Impact of industrial and mine drainage wastes on the heavy metal distribution in the drainage basin and estuary of the Sado River (Portugal). *Environ. Pollut.* 59, 267–286.
- Re, V., Sacchi, E., Mas-Pla, J.A., Menció, El Amrani, N., 2014. Identifying the effects of human pressure on groundwater quality to support water management strategies in coastal regions: a multi-tracer and statistical approach (Bou-Areg region, Morocco). *Sci. Total Environ.* 500–501 (2014), 211–223.
- Relic, D., Dordevic, D., Popovic, A., Blagojevic, T., 2005. Speciations of trace metals in the Danube alluvial sediments within an oil refinery. *Environ. Int.* 31, 661–669.
- Renberg, I., Persson, M.W., Emteryd, O., 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature* 368, 323–326.
- Rouvier, H., 1977. Géologie de l'extrême Nord tunisien : tectoniques et paléogéographies superposées à l'extrémité orientale de la chaîne maghrébine. Thèse Doctorat es Sci. Univ P et M Curie, Paris, France.
- Sainfeld, P., 1952. Les gites plombo-zincifères de la Tunisie. *Ann. Mines et Géologie, Tunis, Tunisie.*
- Sakan, S.M., Djordjevic, D.S., Manojlovic, D.D., Polic, P.S., 2009. Assessment of heavy metal pollutants accumulation in the Tisza river sediments. *J. Environ. Manage.* 90, 3382–3390.
- Salomons, W., 1995. Environmental impact of metals derived from mining activities: processes, predictions, prevention. *J. Geochem. Explor.* 52, 5–23.
- Sarmiento, A.M., Nieto, J.M., Olías, M., Cánovas, C., 2009. Hydrochemical characteristics and seasonal influence on the pollution by acid mine drainage in the Odiel river Basin (SW Spain). *Appl. Geochem.* 24, 697–714.

- Schulz-Zunkel, C., Krueger, F., Rupp, H., Meissner, R., Gruber, B., Gerisch, M., Bork, H.R., 2013. Spatial and seasonal distribution of trace metals in floodplain soils. A case study with the Middle Elbe River, Germany. *Geoderma* 211/212, 128–137.
- SERMI (Société d'Etudes et de Recherches Minières), 1965. Inventaire géologique et minier: Etude géologique et minière de la zone de Touiref. Rapport interne Office National des Mines, Tunis.
- Sebei, A., 2007. Impacts des rejets miniers sur l'environnement cas des bassins versants des oueds Mellegue et Tessa (Tunisie septentrionale). Thèse Sci. Univ. Tunis, Tunisie, 259 p.
- Serrano, O., Mateo, M.A., Dueñas-Bohórquez, A., Renom, P., López-Sáez, J.A., Martínez Cortizas, A., 2011. The *Posidonia oceanica* marine sedimentary record: a holocene archive of heavy metal pollution. *Sci. Total Environ.* 10. STOTEN-12818.
- Shaofeng Wang, S., Jia, Y., Wang, S., Wang, X., Wang, H., Zhao, Z., Liu, B., 2010. Fractionation of heavy metals in shallow marine sediments from Jinzhou Bay, China. *J. Environ. Sci.* 22 (1), 23–31.
- Shotyk, W., 1996. Peat bog archives of atmospheric metal deposition: geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. *Environ. Rev.* 4, 149–183.
- Shotyk, W., 2002. The chronology of anthropogenic, atmospheric Pb deposition recorded by peat cores in three minerogenic peat deposits from Switzerland. *Sci. Total Environ.* 292 (1–2), 19–31.
- Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A., Kramers, J.D., 1996. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. *Earth Planet. Sci. Lett.* 145 (1–4), E1–E7.
- Shotyk, W., Blaser, P., Grunig, A., Cheburkin, A.K., 2000. A new approach for quantifying cumulative, anthropogenic, atmospheric lead deposition using peat cores from bogs: Pb in eight Swiss peat bog profiles. *Sci. Total Environ.* 249 (1–3), 281–295.
- Simpson, S.L., Apte, S.C., Batley, G.E., 2000. Effect of short-term resuspension events on the oxidation of cadmium, lead, and zinc sulfide phases in anoxic estuarine sediments. *Environ. Sci. Technol.* 34, 4533–4537.
- Sinex, S.A., Helz, G.R., 1981. Regional geochemistry of trace elements in Chesapeake Bay sediments. *Environ. Geol.* 3, 315–323.
- Smuc, R., Vrhovnik, N., Dolenc, P., Serafimovski, T., Tasev, G., Dolenc, M., et al., 2009. Assessment of the heavy metal contamination in the surficial sediments of Lake Kalimanci (Macedonia): a preliminary study. *RMZ Mater. Geoenviron.* 56, 437–447.
- Sonke, J.E., Burnett, W.C., Hoogewerff, J.A., van der Laan, S.R., Vangronsveld, J., Corbett, R.D., 2003. Reconstructing 20th century lead pollution and sediment focusing in a peat land pool (Kemp, Belgium), via 210Pb dating. *J. Paleolimnol.* 29 (1), 95–107.
- Soua, M., Zaghib-Turki, D., Ben Jemia, H., Smaoui, J., Boukadi, A., 2011. Geochemical record of the Cenomanian–Turonian anoxic event in Tunisia: is it correlative and isochronous to the biotic signal? *Acta Geol. Sin. Engl. Ed.* 85 (6), 1310–1335.
- Sundaray, S.K., Nayak, B.B., Lin, S., Bhatta, D., 2011. Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments—a case study, Mahanadi basin, India. *J. Hazard. Mater.* 186, 1837–1846.
- Sutherland, R.A., Tack, F.M.G., 2007. Sequential extraction of lead from grain size fractionated river sediments using the optimized BCR procedure. *Water Air Soil Pollut.* 184, 269–284.
- ten Hulscher, T.E.M., Mol, G.A.J., Luers, F., 1992. Release of metals from polluted sediments in a shallow lake; quantifying resuspension. In: Hart, B.T., Sly, P.G. (Eds.), *Sediment/water Interactions; Proceedings of the Fifth International Symposium, Hydrobiologia*, vol. 235(236), pp. 97–105.
- Tessier, E., Garnier, C., Mullot, J.U., Lenoble, V., Arnaud, M., Raynaud, M., Mounier, S., 2011. Study of the spatial and historical distribution of sediment inorganic contamination in the Toulon Bay (France). *Mar. Pollut. Bull.* 62, 2075–2086.
- Tribouillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. *Chem. Geol.* 232 (1), 12–32.
- Valette-Silver, N.J., 1993. The use of sediment cores to reconstruct historical trends in contamination of estuarine and coastal sediments. *Estuaries* 16 (3B), 577–588.
- Van Den Berg, G.A., Loch, J.P.G., Van Der Heijdt, L.M., Zwolsman, J.J.G., 2000. Dredging-related mobilization of trace metals: a case study in the Netherlands. *Water Res.* 35, 1979–1986.
- Vrhovnik, P., Nastja, R.S., Dolenc, T., Serafimovski, T., Dolenc, M., 2013. An evaluation of trace metal distribution and environmental risk in sediments from the Lake Kalimanci (FYR Macedonia). *Environ. Earth Sci.* 70, 761–775.
- Walkley, A., Black, C.A., 1934. An examination of degradation method for determining soil organic matter: a proposed modification of the chromic acid titration method. *Soil Sci.* 37, 29–35.
- Wang, L., Wang, Y., Zhang, W., Xu, C., An, Z., 2014. Multivariate statistical techniques for evaluating and identifying the environmental significance of metal contamination in sediments of Yangtze River, China. *Environ. Earth Sci.* 71, 1183–1193.
- Wedepohl, K.H., 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta* 59, 1217–1232.
- Zhang, J., 1995. Geochemistry of trace metals from Chinese River/Estuary systems: an overview. *Estuar. Coast. Shelf Sci.* 41, 631–658.
- Zhang, Y., Huo, S., Zan, F., Xi, B., Zhang, J., Wu, F., 2014. Historical records of multiple heavy metals from dated sediment cores in Lake Chenghai, China. *Environ. Earth Sci.* <http://dx.doi.org/10.1007/s12665-014-3858-5>.
- Zhao, H., Xia, B., Qin, J., Zhang, Jiaying, 2012. Hydrogeochemical and mineralogical characteristics related to heavy metal attenuation in a stream polluted by acid mine drainage: a case study in Dabaoshan Mine, China. *J. Environ. Sci.* 24 (6), 979–989.
- Zhi-feng, Y., Wang, Y., Zhen-yao, S., Jun-feng, N., Zhen-wu, T., 2009. Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. *J. Hazard. Mater.* 166 (2/3), 1186–1194.