

Spatial assessment and source identification of trace metal pollution in stream sediments of Oued El Maadene basin, northern Tunisia

J. Ayari · Y. Agnan · A. Charef

Abstract An extensive spatial survey was conducted on trace metal content in stream sediments from Oued El Maadene basin, northern Tunisia. Our objectives were to evaluate the level of trace metal pollution and associated ecological risk and identify the major sources of metal pollution. A total of 116 stream sediment samples were collected and analysed for total As, Cd, Cr, Cu, Ni, Pb, V, Zn, and Zr concentrations. The results showed that concentrations of Cr, Ni, V, and Zr were close to natural levels. In contrast, As, Cd, Cu, Pb, and Zn had elevated concentrations and enrichment factors compared to other contaminated regions in northern Tunisia. Ecological risk to aquatic ecosystems was highlighted in most areas. Principal component analysis showed that Cr, Ni, V, and Zr mainly derived from local soil and bedrock weathering, whilst As, Cd, Pb, and Zn originated from mining wastes. Trace metals could be dispersed downstream of tailings, possibly due to surface runoff during the short rainy season. Surprisingly, Cu, and to a lesser extent As, originated from agricultural activities, related to application of Cu-based fungicides in former vineyards and orchards. This study

showed that, despite the complete cessation of mining activities several decades ago, metal pollution still impacts the local environment. This large pollution, however, did not mask other additional sources, such as local agricultural applications of fungicides.

Keywords Trace metals · Sediments · Enrichment factor · Ecological risk · Geochemical background · Source

Introduction

In northern Tunisia, there are tens of abandoned Pb-Zn mining sites, most of which were active during the last century (Sainfeld 1952). Extraction of trace metals from sulphide minerals generated significant amount of waste tailings with elevated concentrations of potentially toxic trace metals (e.g., Cu, Zn, Cd, and Pb; Alloway 1995; Klassen et al. 2010). Most of mining wastes were deposited in inadequate facilities or were simply released in the nearest water courses. Trace elements contained in the residues from mining and metallurgical processes are often dispersed as particles or dissolved forms after their disposal by the wind or runoff (Ghorbel et al. 2010; Mlayah et al. 2009; Othmani et al. 2013). In semiarid environments, such as in northern Tunisia, the spreading of trace metal contamination from mining waste is often enhanced by heavy winds and intense rainfall during the short rainy season (Khalil et al. 2013; Navarro et al. 2008; Oyarzun et al. 2011; Rodriguez et al. 2009). As a

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result, large pollution of surface water, sediments, and agricultural soils occurred.

Trace metal contamination of sediments is a serious environmental problem because sediments act either as sinks by accumulating trace metals or sources through releasing trace metals into water if conditions change (Webster and Ridgway 1994). Hence, the monitoring of trace metal levels in sediments is of great importance for protecting and ensuring future sustainability of aquatic environments. However, few environmental studies on spatial distribution, identification of pollution sources, and risk assessment of trace metals in stream sediments in entire basin were conducted in Tunisia (Jdid et al. 1999; Mlayah et al. 2009).

An extensive environmental survey of potentially toxic trace metals (As, Cd, Cr, Cu, Ni, Pb, V, Zn, and Zr) was therefore conducted in stream sediments of Oued El Maadene basin. Our main objectives were to evaluate the level of trace metal pollution and associated ecological risk and identify the major sources of metal pollution. For this purpose, enrichment and contamination levels of these trace metals and their potential risk to ecosystems were assessed using various geochemical methods (geochemical background threshold, enrichment factor, geoaccumulation index, and potential ecological risk index). Statistical analyses, including descriptive parameters and principal component analysis, were applied to study the spatial patterns of investigated trace metals and identify their possible sources.

Materials and methods

Study area

The Oued El Maadene basin is situated in Nefza region, northern Tunisia (Fig. 1), characterised by a humid Mediterranean climate with an average annual precipitation of 716 mm occurring mostly during winter and autumn as heavy storms. The average annual temperature is 19.9 °C, with minimum and maximum temperatures of 4.7 °C in February and 36.7 °C in August, respectively. The prevailing winds are from west-northwest with a mean speed of 2.7 m.s⁻¹. The main flow direction of drainage systems guided by the topographic slope is from southeast to northwest. The region is subjected to several agricultural activities (e.g., cereals, forage, and arboriculture).

The present study area belonged to the Nappe zone, characterised by allochthonous thrust sheets composed by Numidian clays and sandstones, resulting from a major Neogene tectonic event (Rouvier 1977). Nappe pile in the study area is formed by the Kasseb and Ed Diss thrust sheets (Upper Cretaceous to Eocene) which consist of alternating marls and limestones. The whole Nappe pile is crosscut by upper Miocene felsic and mafic magmatic rocks (Decrée et al. 2014; Jallouli et al. 2003). The Oued El Maadene basin, which belongs to Nefza mining district, has various metal-rich deposits (Fe, Pb, Zn, etc.; Abidi 2010; Decrée et al. 2008). There are two active iron mines (Tamera and Boukhchiba) and several abandoned Pb-Zn mines (Sainfeld 1952). These deposits are associated with middle to late Miocene magmatism of the Nefza area, especially in the Sidi Driss, Tamera, and Boukhchiba regions and hosted in hard carbonate of lower Maastrichtian formations in the Sidi Ahmed, Khanguet Kef Ettout, and Tabouna Pb-Zn mines. The original Pb-Zn deposits mainly consist of galena, sphalerite, cerussite, and smithsonite (Abidi 2010; Decrée et al. 2014; Sainfeld 1952). Pyrite occurs as accessory mineral. The ores valorisation process used, include crushing, grinding operations and flotation procedure using organic matter. The different Pb-Zn mines were extensively exploited during the last century. However, upon closure, tailings with elevated levels of potential toxic elements, including Pb, Zn, Cd, and As were dumped along local streams without any refinement. These toxic elements potentially contaminate soils, sediments, and water by clastic movement through wind and water.

Sampling and chemical analyses

In the spring of 2013, 116 stream sediment samples were collected from the Oued El Maadene river and its tributary streams, up and downstream of the different mining areas (Fig. 1). For each site, three subsamples were collected at 0–20-cm depth using a stainless steel shovel and then mixed to obtain a homogeneous composite sample. Geographic coordinates of each sampling site were reported on a field sheet.

To determine trace metals concentrations, the sediment samples were air-dried, sieved to <2 mm, and crushed manually in an agate mortar. Total As, Cd, Cr,

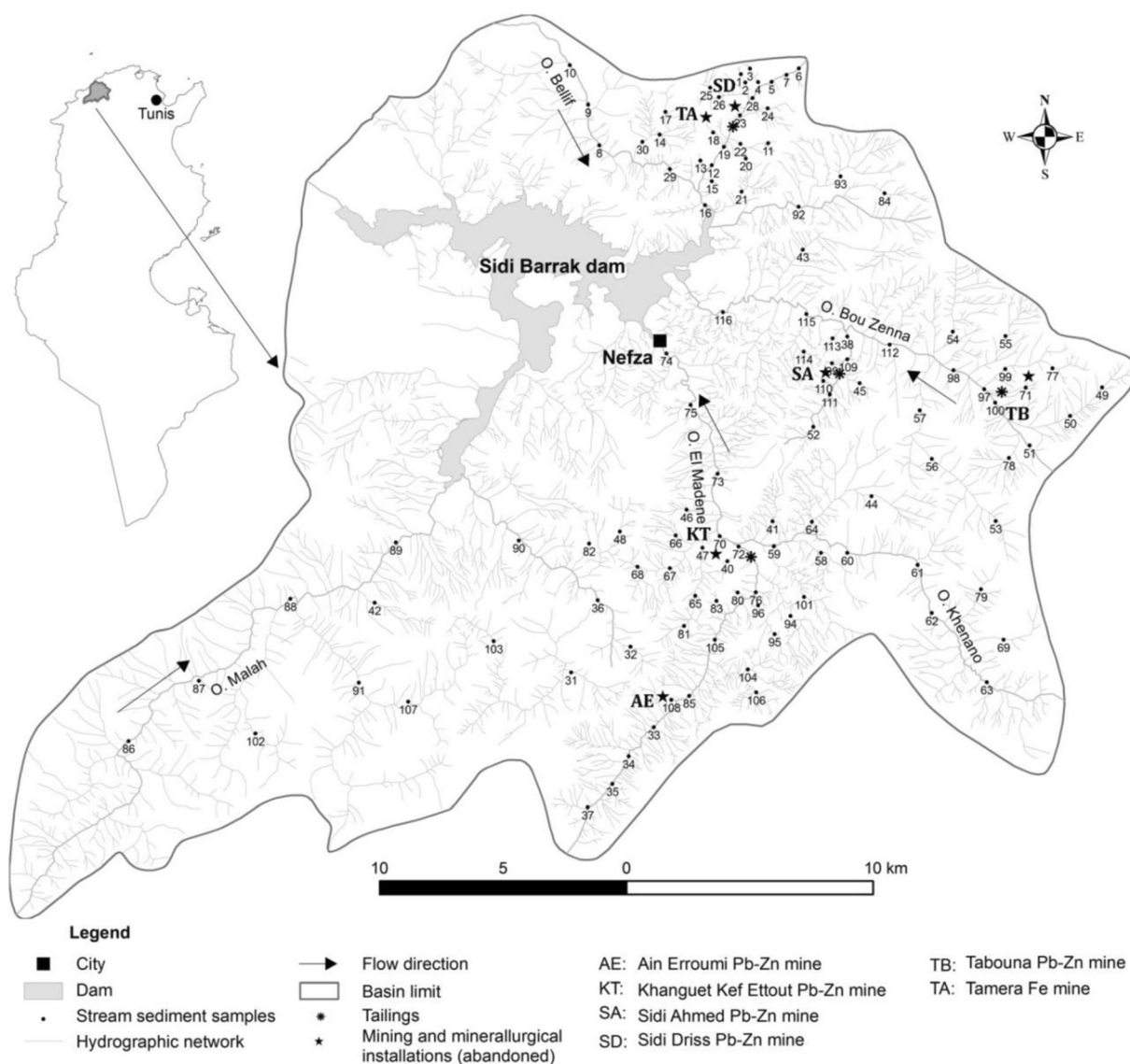


Fig. 1 Oued El Maadene basin and sampling sites

Cu, Ni, Pb, V, Zn, and Zr concentrations of stream sediment samples were determined after a strong acid mineralization method using a mixture of 5 mL of HNO_3 , 10 mL of HClO_4 , and 10 mL of HF. This method is commonly used to determine the total trace metal content in environmental samples (Khalil et al. 2013; Skordas and Kelepertsis 2005). The residue was further dissolved using 5 mL of HCl and diluted with distilled water to reach 100 mL. Then, total concentrations of As, Cd, Cr, Cu, Ni, Pb, V, Zn, and Zr were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Ultima C of HORIBA-JOBIN YVON) at the National Office of Mines in Tunis. The limits of

detection for examined trace metals were 0.05 mg kg^{-1} for Cd, 0.1 mg kg^{-1} for Cu, and 0.5 mg kg^{-1} for As, Cr, Ni, Pb, V, Zn, and Zr. Duplicates were performed for each sample.

Calculation of geochemical background threshold

Geochemical background is defined as the natural distribution of trace metal concentrations. The threshold of this geochemical background allows identifying anthropogenically influenced concentrations (Matschullat et al. 2000). Various statistical methods have been developed to estimate the background distribution,

including Lepeltier method, relative cumulative frequency curves, mode analysis, calculated distribution function, and regression analysis (Matschullat et al. 2000; Rowlatt and Lovell 1994). The application of such methods consists of elimination of outliers to obtain a Gaussian distribution.

In this paper, geochemical background distributions were obtained from the calculated distribution function method due to its robustness (Matschullat et al. 2000). This method is based on the assumption that the data set from the minimal value to the median value represents the first half of the natural distribution. The second half of the distribution was generated by ‘mirroring’ each value against the median by adding the distance from the value to the median. Geochemical background threshold was estimated using mean + 2 standard deviations of the new background distribution.

Indices of contamination and environmental risk

Enrichment factor (EF), geoaccumulation index (Igeo), and potential ecological risk index (RI) were applied to assess contamination levels of trace metals and their potential risk to soil and sediment ecosystems (Barbieri et al. 2014; Hakanson 1980; Muller 1969; Yuan et al. 2014; Zhang et al. 2014).

Enrichment factor of trace metals was frequently used to determine both natural and anthropogenic trace metal sources and to evaluate the degree of contamination (Bourennane et al. 2010; Reimann and de Caritat 2000). The EF of each trace metal in the sediment was calculated by the following equation:

$$EF = \frac{C_x/C_r}{B_x/B_r}$$

where C_x and C_r are concentrations of the trace metal of concern and the reference element in sediment samples, respectively; B_x and B_r are the geochemical background values of the trace metal of concern and the reference element, respectively. In this study, the values of the upper continental crust (UCC; Taylor and McLennan 1985) were used as background values for calculating EF. Zirconium was used as the reference element because of its high chemical stability on the earth and during weathering processes (Wang et al. 2008). The signification of EF values in terms of degree

Table 1 Degree of trace metal contamination according to different indices: enrichment factor (EF), geoaccumulation index (Igeo), and potential ecological risk index (RI)

Index	Value	Degree of contamination
<i>EF</i>	<2	Depletion to minimal enrichment
	2–5	Moderate enrichment
	5–20	Significant enrichment
	20–40	Very high enrichment
	>40	Extremely high enrichment
<i>Igeo</i>	<0	Uncontaminated
	0–1	Uncontaminated to moderately contaminated
	1–2	Moderately contaminated
	2–3	Moderately to strongly contaminated
	3–4	Strongly contaminated
	4–5	Strongly to extremely contaminated
	>5	Extremely contaminated
<i>RI</i>	<150	Low ecological risk
	150–300	Moderate ecological risk
	300–600	Considerable ecological risk
	>600	Very high ecological risk

of contamination was defined by Sutherland (2000) (Table 1).

Geoaccumulation index is used to evaluate the level of trace metal contamination in geological sample by comparing current and pre-industrial concentrations (Muller 1969). This index was calculated for each trace metal as follows:

$$I_{geo} = \log_2 \left(\frac{C_x}{1.5 \times B_r} \right)$$

where C_x is the concentration of trace metal of concern in sediment sample; B_r is the geochemical background value of the trace metal of concern using the UCC (Taylor and McLennan 1985); and the constant 1.5 is the geochemical background matrix correction factor, used to minimise possible variations in the background values due to lithospheric effects. Geoaccumulation index values were classified into seven classes of contamination level (Table 1), as described by Muller (1969).

Potential ecological risk index is used to assess the degree of trace metal pollution in sediments according to their toxicity and response of the environment Hakanson (1980). This index was calculated as the

sum of risk factors of individual trace metals (E_i), calculated by the following equation:

$$RI = \sum_{i=1}^n E_i$$

where E_i is the single risk factor for each trace metal i defined as:

$$E_i = T_i \frac{C_i}{B_i}$$

where T_i is the toxic-response factor for each trace metal i as calculated by Hakanson (1980), i.e., $Hg = 40$, $Cd = 30$, $As = 10$, $Pb = Cu = Ni = Co = 5$, $Cr = V = 2$, and $Zn = 1$; C_i is the measured concentration of the trace metal i ; and B_i is the background value of the trace metal i . Hakanson (1980) defined four levels of RI (Table 1).

Data treatment

Descriptive statistical parameters, including minimum, maximum, mean, standard deviation, and coefficient of variation, were implemented to characterise the distribution of trace metal contents in sediments. Box-and-whisker plots, representing medians and interquartile range, were generated for displaying the data distribution using the SPSS Statistics for Windows 20.0 (IBM Corp., Armonk, NY).

Pearson's correlation analysis and principal component analysis (PCA) were implemented to evaluate the trace metal concentration relations, and therefore, to identify potential natural and anthropogenic sources of trace metals in sediments (Candeias et al. 2011; Lui et al. 2013; Sun et al. 2010; Zhang et al. 2009). Principal component analysis was performed after a centred log ratio transformation using the *rgr* package in R 3.2.2 (R Foundation for Statistical Computing, Vienna), and elements were grouped using their relative axis scores (Berg and Steinnes 1997). The ArcGIS 9.3 software (Environmental Systems Research Institute, Redlands, CA) was used to map study site locations, as well as the spatial distribution of principal component scores using the inverse distance weighted (IDW) method.

Results and discussions

Trace metal contamination in stream sediments from the Oued El Maadene basin

Trace metal concentrations in stream sediments of the Oued El Maadene basin and descriptive statistics are summarised in Table 2. The results showed that Cr, Ni, V, and Zr concentrations exhibited generally low standard deviation and coefficient of variation values, suggesting a homogeneous spatial distribution. In contrast, As, Cd, Cu, Pb, and Zn contents showed heterogeneous spatial distribution, as reflected by high coefficient of variation and large standard deviation values. This is confirmed by the median concentrations of these trace metals that were lower than the mean concentrations. Both the difference between mean and median values and the high coefficient of variation of As, Cd, Cu, Pb, and Zn may be attributed to the extremely high values of these trace metals (cf. maximum values, Table 2). According to the box plots (Fig. 2), the outliers of previously cited elements were located downstream of the mine wastes.

Compared to the UCC (Taylor and McLennan 1985), mean concentrations of Cu, Cr, Ni, V, and Zr measured in stream sediments from the Oued El Maadene basin were in the same order of magnitude despite higher levels, whilst As, Cd, Pb, and Zn were much higher in our samples with mean concentrations of 28, 43, 20, and 8 times higher than UCC values, respectively. Median concentrations were even higher than regional bedrock (data from north-western Tunisia; Jdid et al. 1999; Mlayah et al. 2009) with, on average, 3 to 9 times literature data for As, Cd, Cu, Pb, and Zn. Assuming a similar geochemical composition in the Oued El Maadene basin, particularly for trace metals, these elements could not come from the natural bedrock weathering. Compared to stream sediments contaminated by mining from the Oued Mellègue in north-western Tunisia (Mlayah et al. 2009), our concentrations also showed higher values, especially for As and Cd with median concentrations 5 and 4 times higher, respectively.

Geochemical background thresholds, determined using the calculated distribution function (Matschullat et al. 2000), of As, Cd, Cu, and Pb exceeded 1.5 times the corresponding median values (Table 2). Moreover, they were lower for As, Cd, Pb,

Table 2 Descriptive statistics of trace metal concentrations in stream sediment samples and comparison to guideline and background values

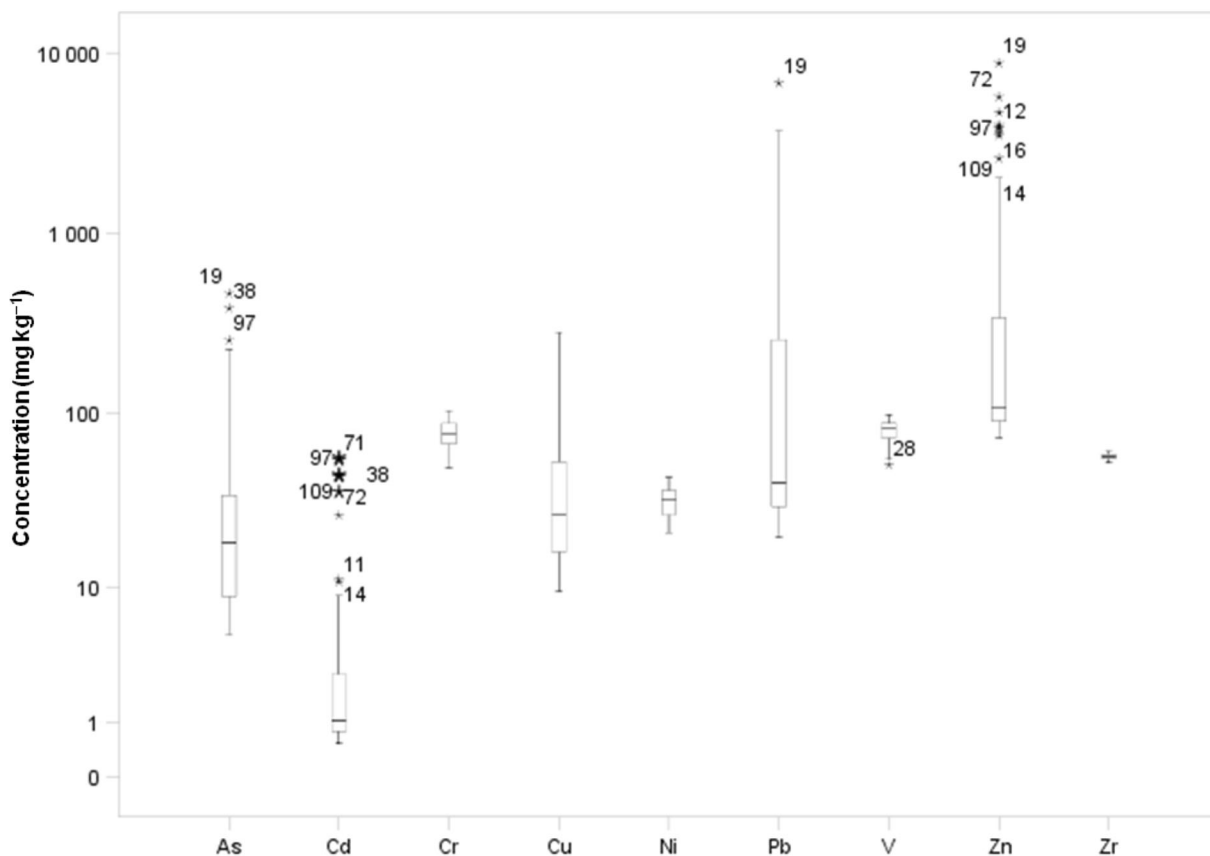
Element	Sample concentration (mg kg ⁻¹)						Geochemical background threshold ^a (mg kg ⁻¹)		Guideline values (mg kg ⁻¹)	
	Mean	SD	Median	Min.	Max.	CV			TED	PEC
<i>As</i>	41.2	70.3	18.8	5.10	467.80	171	37.5		9.79	33
<i>Cd</i>	4.24	10.0	1.03	0.52	57.40	235	1.59		0.99	4.98
<i>Cr</i>	77.2	13.4	77.3	50.10	103.70	17.4	104.6		43.3	111
<i>Cu</i>	42.9	41.3	27.1	9.60	283.20	96.1	49.6		31.6	149
<i>Ni</i>	32.1	5.95	33.0	21.30	44.10	18.5	46.7		22.7	48.6
<i>Pb</i>	401	979	41.5	20.10	6803.30	244	66.0		35.8	128
<i>V</i>	80.5	10.5	83.1	51.90	98.40	13.0	110			
<i>Zn</i>	567	1310	108	73.80	8756.60	231	144		121	459
<i>Zr</i>	57.8	2.19	57.7	53.60	61.90	3.79	62.0			

SD standard deviation, *CV* coefficient of variation, *TEC* threshold effect concentration, *PEC* probable effect concentration

^a Geochemical background threshold of the Oued El Maadene basin determined in this study

and Zn than mean values. This can be attributed to the wide distribution range due to local enrichments for these elements. Both past mining and metallurgical activities and geochemical weathering of parent

rock material characterised by various metal-rich deposits could contribute to these differences. This can also result in geochemical background thresholds that were 1.7 to 4.5 times the regional bedrocks.

**Fig. 2** Box plots of trace metal concentrations in stream sediments from in Oued El Maadene basin

To assess the quality of the stream sediments, we compared trace metal concentrations to literature data, including two indices (Table 2; MacDonald et al. 2000): threshold effect concentration (TEC, concentration below which harmful effects are unlikely to be observed) and probable effect concentration (PEC, concentration above which harmful effects are likely to be observed). The results showed that, in most sites, Cr, Ni, V, and Zn concentrations were below the TEC. Some sites, however, exceeded the PEC for As, Cd, Cu, Pb, and Zn; it is noteworthy that high concentrations likely due to trace metal contamination were measured for these elements in some locations.

Indices calculated for Cr, Ni, V, and Zr of stream sediments from the Oued El Maadene basin showed a moderate enrichment (EF mostly lower than 5; Fig. 3a) and low pollution levels (Igeo lower than 1; Fig. 3b) in the whole study area. These observations agreed with the lowest concentrations previously evoked (Fig. 2) and support the absence of contamination of these four trace metals in the study basin. In contrast, extremely high enrichments (EF higher than 40; Fig. 3a) and pollution levels (Igeo from -1 to 9; Fig. 3b) were

observed on average for As, Cd, Pb, and Zn. The high heterogeneity of EF and Igeo, as also observed in concentrations with coefficient of variation (Table 2), suggests that these trace metals may originate from point sources different from the diffuse origin implied for the first group. Copper, despite lower level of contamination compared to elements previously cited (EF from 2 to 40 and Igeo from -2 to 3), showed a non-negligible anthropogenic influence. In addition to the pattern defined by analogous behaviours, EF varied significantly across the studied basin; highest EF was reported for As, Cd, Pb, and Zn in sediments downstream of mining wastes. Surprisingly, the highest EF observed for Cu did not follow the same spatial pattern compared to the other trace metals and were heterogeneously distributed with enrichments both upstream and downstream sites.

Potential ecological risk index of all investigated samples varied from 21.4 to 22,500 (Fig. 3c). Only 6.9 % of all samples (8 samples) had a low to moderate ecological risk (RI lower than 300), whilst 53.4 % (62 samples) and 39.7 % (46 samples) had a considerable (RI between 300 and 600) to very high (RI higher than 600) ecological risk. These results revealed that most areas had a non-

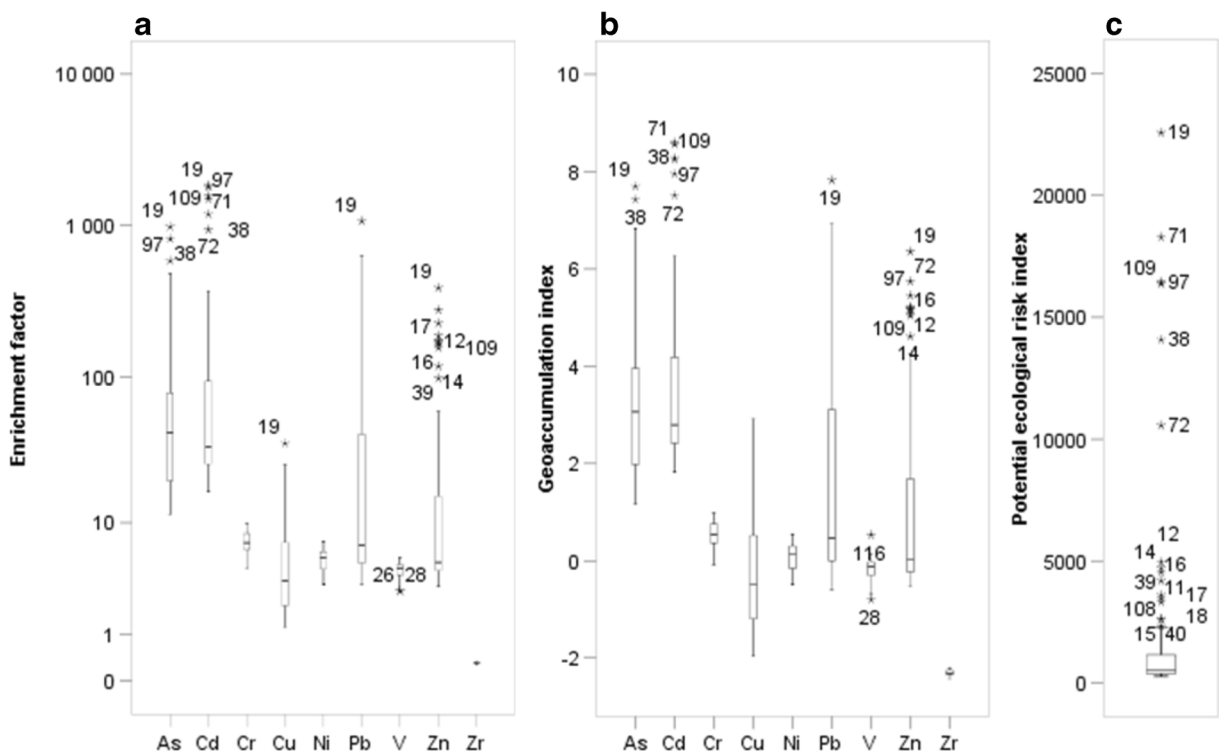


Fig. 3 Box plots of enrichment factors (a), geoaccumulation index (b), and potential ecological risk index (c) of trace metals in stream sediments

Table 3 Pearson's correlation matrix for trace metal in stream sediments

	As	Cd	Cr	Cu	Ni	Pb	V	Zn	Zr
<i>As</i>	1.000								
<i>Cd</i>	0.836**	1.000							
<i>Cr</i>	0.233	0.200	1.000						
<i>Cu</i>	0.669**	0.589**	0.359	1.000					
<i>Ni</i>	0.181	0.165	0.803**	0.290	1.000				
<i>Pb</i>	0.810**	0.791**	0.204	0.722**	0.134	1.000			
<i>V</i>	0.049	0.096	0.674**	0.177	0.671**	0.074	1.000		
<i>Zn</i>	0.797**	0.826**	0.215	0.672**	0.157	0.972**	0.078	1.000	
<i>Zr</i>	0.139	0.116	−0.154	0.075	−0.198	0.119	−0.124	0.103	1.000

*Correlation is significant at $p < 0.05$ (two-tailed) and **Correlation is significant at $p < 0.01$ (two-tailed)

negligible risk to aquatic ecosystems regarding the nine investigated trace metals (Hakanson 1980). The sediment samples with high RI were all located downstream of tailings, supporting the trace metal contamination of As, Cd, Pb, Zn, and to a lesser extent Cu.

Based on results described above (i.e., concentration, geochemical background threshold, EF, Igeo, and RI), three groups of trace metals could be distinguished with different behaviours: (1) Cr, Ni, V, and Zr showed homogeneous distributions amongst study sites with low concentrations compared to literature data in the whole study area and low pollution level; (2) As, Cd, Pb, and Zn showed highly variable distributions related to local pollution mainly downstream of mining wastes and presented a potential risk to aquatic ecosystems; and (3) Cu had a singular behaviour with locally high concentrations and enrichments both upstream and downstream sites.

Sources of trace metals in stream sediments from the Oued El Maadene basin

To better assess the origin of trace metals in the Oued El Maadene basin, we performed a Pearson's correlation matrix between the nine investigated elements (Table 3). Coefficients showed strong positive correlations between Cr, Ni, and V ($p < 0.01$), elements frequently found originate mainly from mineral weathering (Nriagu 1989; Pacyna 1986). Indeed, the low concentrations and enrichment factors found for these three elements in stream sediments (Figs. 2 and 3) indicated that their main source was bedrock and soil weathering. Despite any correlation between these trace metals and Zr, a similar lithogenic origin for Zr can be proposed since both concentrations and enrichments were low.

The absence of correlation may result from a different mineral chemical form; Zr is commonly found as silicates unlike Cr, Ni, or V (Newton 2010).

A second strong group highlighted by Pearson's correlations included As, Cd, Cu, Pb, and Zn ($p < 0.05$). This suggests that these trace metals had a different origin than for the first group of elements. Due to the high concentrations and enrichment factors for As, Cd, Pb, and Zn downstream of tailings (Figs. 2 and 3), a similar mining source of pollution was possible. No explanation can be provided for Cu case regarding the Pearson's correlation matrix.

A PCA was applied on trace metal concentrations in stream sediments from the Oued El Maadene basin. The resulting first two principal components explained 87 % of the data variance (Table 4). The nine trace metals

Table 4 Scores of the first two principal component of trace metal concentrations in stream sediments from the Oued El Maadene basin using a centred log ratio transformation

Variable	First component	Second component
Cr	0.984	−0.081
Ni	0.981	−0.083
V	0.981	−0.141
Zr	0.959	−0.193
Cu	0.232	0.907
As	−0.648	0.430
Cd	−0.854	−0.226
Zn	−0.888	−0.240
Pb	−0.937	−0.157
Eigenvalue	6.679	1.212
Variance (%)	74	13

studied are plotted for the first component (74 % of the data variance) versus the second component (13 % of the data variance), showing distinct groups of elements (Fig. 4). The first component included Cr, Ni, V, and Zr with high positive scores (>0.9) and As, Cd, Pb, and Zn with negative scores (>-0.6). Thus, the first component discriminated lithogenic elements (positive scores) from anthropogenic elements (negative scores). This anti-correlation showed that study sites were either mainly influenced by lithogenic or anthropogenic sources. The spatial distribution of this first component showed positive scores at upstream sites, whereas negative scores occurred downstream of tailings (Fig. 5a). This indicated that As, Cd, Pb, and Zn in stream sediments were mostly controlled by past mining and metallurgical activities of the Oued El Maadene basin, confirmed by elevated contents of Cd, Pb, and Zn in the Pb-Zn sulphide ore deposits and tailings in northern Tunisia (Boussen et al. 2013; Daldoul et al. 2015; Souissi et al. 2013). Tailings consisting of very fine ground barren rock with significant quantities of trace metals from the host ore are very susceptible to erosion caused by surface runoff, as observed with high pollution level for several kilometres after the point sources of pollution. The spreading of trace metal pollution from tailings is thus enhanced by climate factors including hydric transport of particles. These results were in complete accordance with numerous previous studies reporting that strong loadings of As, Cd, Pb, and Zn are associated to

mining (Anju and Banerjee 2012; Fernandez-Caliani et al. 2009; Ghorbel et al. 2010; González-Corrochano et al. 2014; Rodriguez et al. 2009).

The second principal component highlighted Cu (>0.9) and to a lesser extent As (>0.4). The difference of behaviour of Cu in stream sediments was already emphasised (Figs. 2 and 3) and might result from another source of pollution. The scores of the second component showed a heterogeneous distribution that we can attribute to the application of Cu-based fungicides in former vineyards and orchards (Fig. 5b). The use of Cu compounds appears to be very frequent in northern Tunisia since agriculture could be a significant source of income (Mlayah et al. 2011). Arsenic pollution may result from the agricultural use of arsenites and arsenates as herbicides and insecticides, respectively, explaining the slight relationship between Cu and As in the PCA (Henke and Atwood 2009). The higher relative score for the first component highlighted that weathering of mining wastes was, however, the main source of As.

Pearson's correlations and PCA allowed us to identify three main origin of trace metals studied: (1) natural lithogenic source from bedrock and soil weathering for Cr, Ni, V, and Zr; (2) mining source realising As, Cd, Pb, and Zn in streams from erosion of tailings; and (3) agricultural source for Cu and to a lesser extent As.

Conclusions

The presence of trace metals in stream sediments from Oued El Maadene basin, northern Tunisia, is an issue to ecosystem and human health. In this study, we investigated concentrations, enrichments, and risk assessment of nine elements (As, Cd, Cr, Cu, Ni, Pb, V, Zn, and Zr) in order to identify current levels and sources of metal pollution. It appeared that the study area was largely polluted compared to other contaminated sites in northern Tunisia, with a high risk to natural ecosystems and possibly to human health. Three major groups of trace metals were identified: (1) Cr, Ni, V, and Zr showed low concentrations and enrichments in the whole study area, they mainly originated from natural bedrock and soil weathering explaining the homogeneous concentrations amongst the study sites; (2) As, Cd, Pb, and Zn showed local high enrichment from several point sources related to tailings from past mining and metallurgical activities; and (3) Cu, and to a lesser extent As, originated from

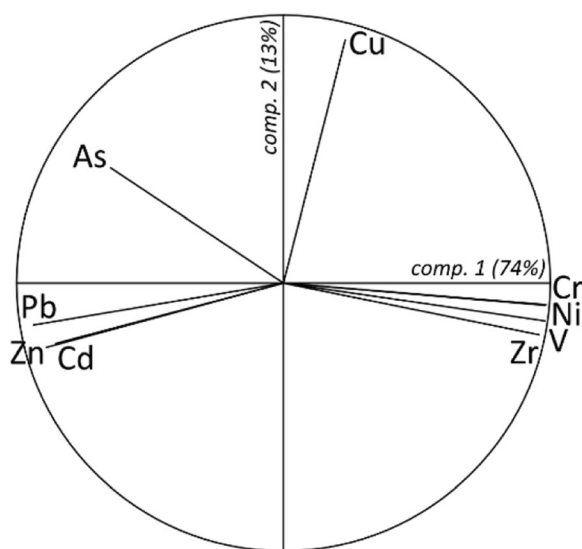


Fig. 4 Principal component analysis of trace metal concentrations in stream sediments from the Oued El Maadene basin using a centred log ratio transformation

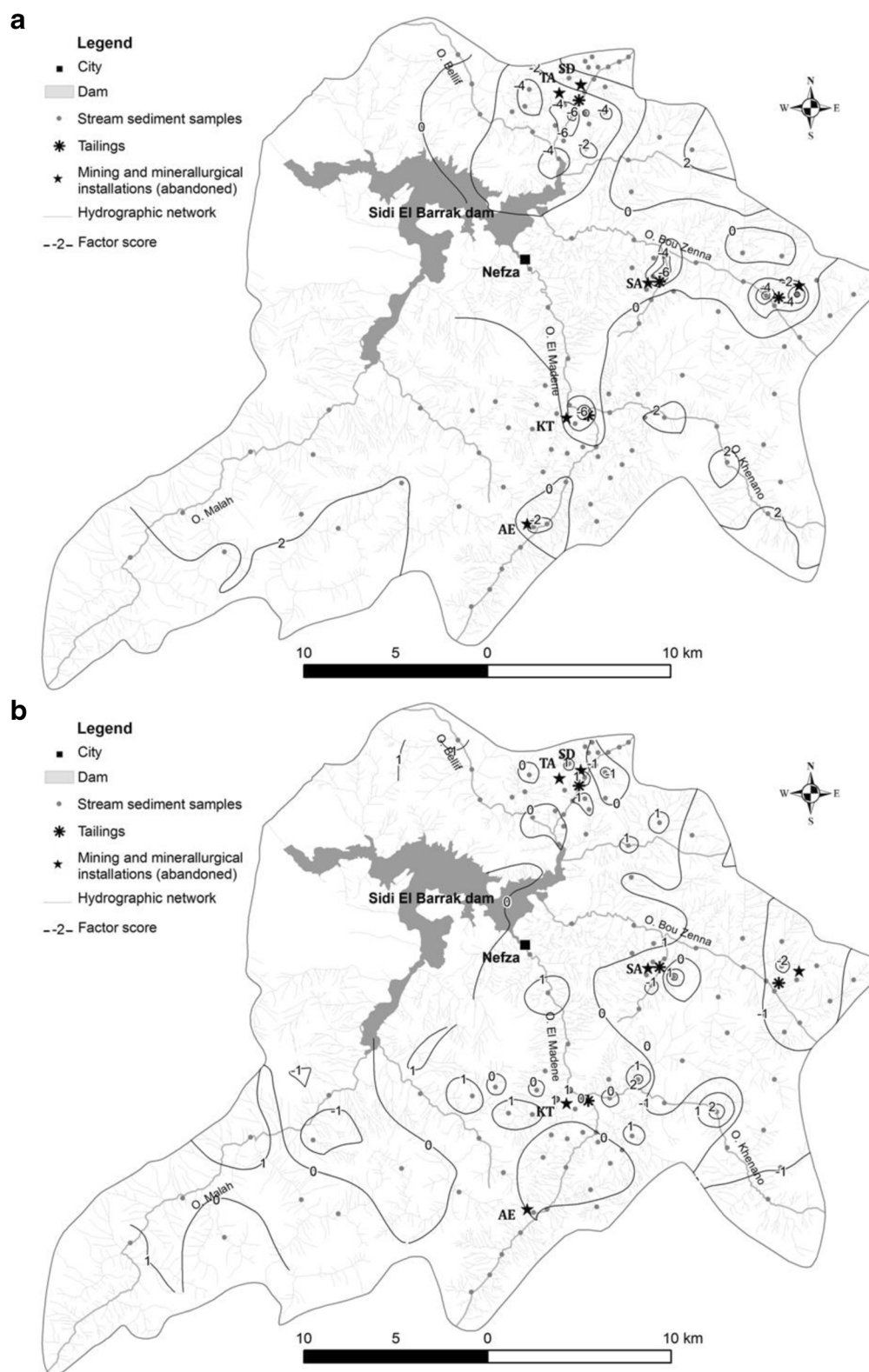


Fig. 5 Spatial distribution of the first two principal component scores of trace metal concentrations in stream sediments from the Oued El Maadene basin using a centred log ratio transformation: first (a) and second (b) components

agricultural activities controlled by the use of Cu-based fungicides in former vineyards and orchards. Despite the large mining pollution, it was possible to identify additional sources, such as local agricultural activities.

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