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TECHNICAL ARTICLE

Assessment of Trace Elements in Soils and Mine Water Surrounding a Closed Manganese Mine (Anti Atlas, Morocco)

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Abstract Five mine water samples, 23 topsoil samples, and four mine waste (tailings) samples were collected to assess the effects of a closed Moroccan Mn mine. Based on the pH, electrical conductivity, and concentrations of sulphate, Cu, Zn, As, Cd, Pb, and Mn, mining has not adversely influenced mine water quality. Soil samples were analyzed for 23 chemical elements and the results were interpreted by univariate and multivariate statistical techniques. Based on an enrichment factor (EF) calculation, only Cd, As, V, and Mn were selected for further study. Geochemical background (GB) and geoaccumulation index (I_{geo}) were determined for these elements to differentiate between geogenic and anthropogenic enrichment. The GB values showed that the Tiwiyyine soils contained a high geogenic content of Cd, As, V, and Mn that reflected the geochemistry of the parental rocks in this mineralized region. The I_{geo} calculation revealed that these soils were moderately influenced by anthropogenic activity, which had increased the concentrations of those elements. Finally, geochemical maps revealed that mining was likely responsible for the anthropogenic soil pollution.

Keywords Enrichment factor · Geoaccumulation index · Tiwiyyine mine · Geochemical background · GIS

Introduction

Morocco contains about 200 abandoned mines that cause serious environmental problems (Hakkou et al. 2008). The implementation of an appropriate reclamation program for these mines requires detailed site investigations for assessing pollution and highlighting its source (Acosta et al. 2011; Candeias et al. 2011; Kim et al. 2012). Therefore, many researchers have studied the environmental issues of these closed mines, such as soil contamination, water pollution, and landscape destruction (Argane et al. 2015; Bossé et al. 2013; Goumih et al. 2013; Iavazzo et al. 2012; Khalil et al. 2013, 2014; Ouakibi et al. 2013). We assessed the water quality and the trace elements of surface soil near the closed Tiwiyyine Mn mine site (Anti Atlas, Morocco) to statistically determine whether mining was responsible for the trace element content in the surrounding area by calculating the: enrichment factor (EF); geochemical background (GB), and geoaccumulation index (I_{geo}).

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Materials and Methods

Study Area

The closed Tiwiyyine mine is located approximately 40 km southwest of the city of Ouarzazate in the central Anti-Atlas Mountains of Morocco (Supplemental Figure 1a). There are about 1000 people living in the area. The climate of the region is classified as arid with average maximum and minimum temperatures ranging from 8 °C in January to 28.5 °C in July. The average rainfall is 120 mm $year^{-1}$. The study area is drained by the Iriri River; the Tiwiyyine dam was recently built for supplying drinking and irrigation water and for flood control.

The Tiwiyyine manganese mine was exploited between 1932 and 1961, mainly for braunite ($Mn^{2+}Mn^{3+}{}_6[O_8|SiO_4]$) and hollandite ($Ba(Mn^{4+}{}_6Mn^{3+}{}_2)O_{16}$). Afterwards, it was closed without implementation of any reclamation program. During its operation, the mine generated more than 0.5 Million t of Mn concentrate containing an average of 45 wt% of Mn. The ore enrichment process, which consisted of gravimetric separation (jigs) generated a large amount of mine tailings, which were stockpiled in piles over an area of about 24 ha (Supplemental Figure 1b and c).

Concerning the geological setting of the study area, the Precambrian III formations consist of volcanic series surmounted by sedimentary detrital series (conglomerates) where beds of manganese ore are interstratified (Supplemental Figure 2). The Mn mineralization (pyrolysite: MnO_2) also occurred in veins, which had impregnated ignimbrites and conglomerates (Supplemental Figure 2). The gangue mineralogy is represented by quartz, fibrous silica, and barite, which are found locally associated with hematite acting as the cement matrix of the conglomerates. Finally, the quaternary formations of the study area consist mainly of alluvial materials (Supplemental Figure 2).

Sampling and Analytical Methods

Five mine water samples (from W1 to W5) were collected from within the study area from existing farm water wells and watercourses (Fig. 1). The pH and EC were measured directly in the field using a portable pH and conductivity meter. The collected water samples were then divided into two subsamples, with one being acidified with $NHO_3$for

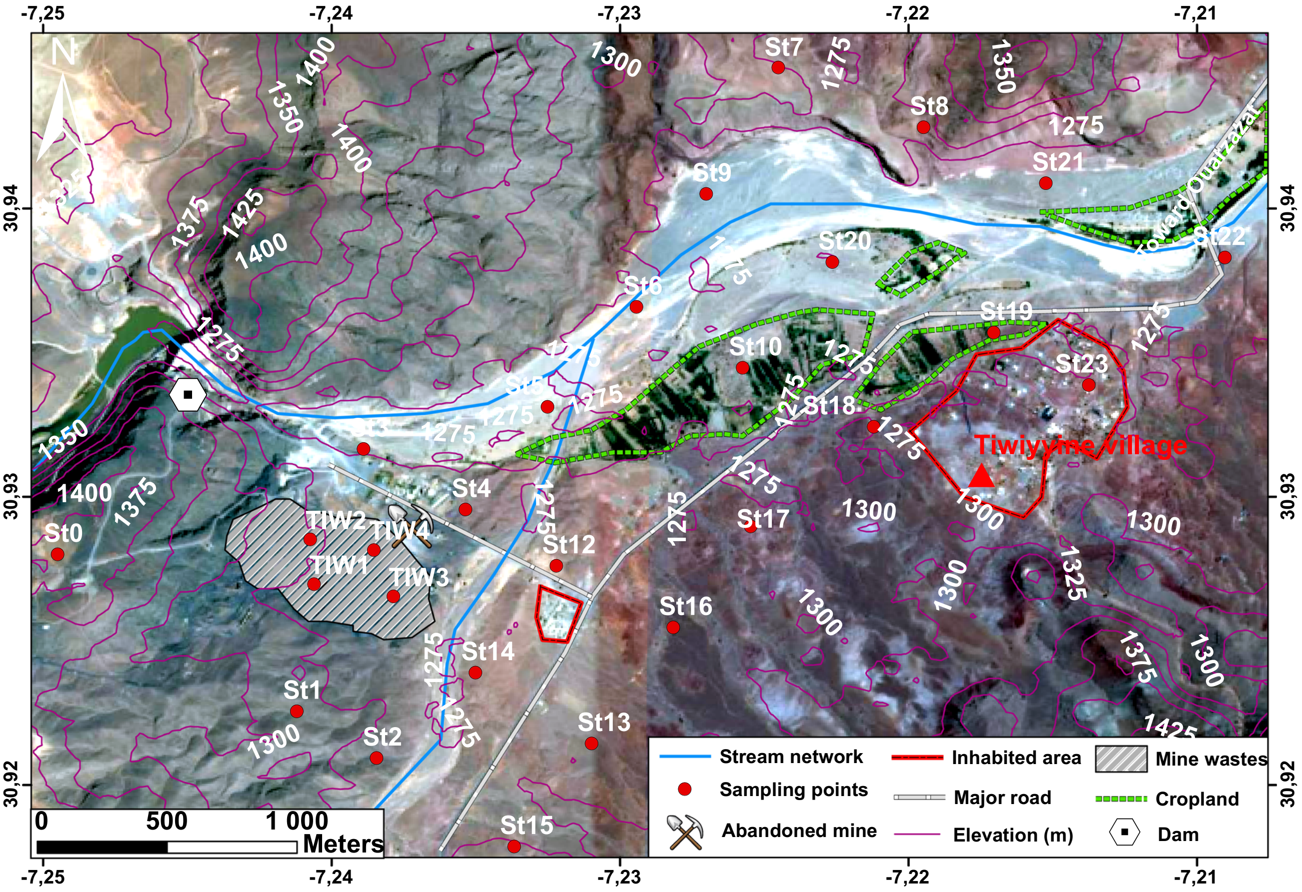

Fig. 1 Map of sampling point locations of soil and mine wastes (Google Earth image modified)

metal analysis, while the unacidified samples were analyzed for SO_4^{2-}. The collected samples were stored in polyethylene bottles that had been washed previously with dilute hydrochloric acid and then rinsed with distilled water. In the laboratory, the samples were filtered through 0.45 µm Millipore membrane filters to separate suspended sediment. Finally, SO_4^{2-} was analyzed using a Tomos spectrophotometer, while Cu, Zn, As, Cd, Pb, and Mn were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP–AES).

Additionally, 23 topsoil samples (St0 to St23) and four mine waste samples (TIW1 to TIW4) were collected from the Tiwiyyine mine and its surroundings over an area of approximately 25 km^2, using a partially randomized design (Fig. 1). The sampling locations were chosen according to their proximity to the mine site and tailings ponds as well as the hydrological network. The topographic and geographic profiles of the study area and human activities such as agriculture (croplands) and inhabited areas were also considered. The coordinate of the sampling locations were recorded with a global positioning system (GPS) within ±5 m accuracy. To minimize sampling variability, all samples were taken within the first 5 cm of the first soil horizon (A) using a stainless steel shovel. The samples were then quartered and stored in a polyethylene bag to avoid external contamination.

In the laboratory, all samples were dried for 24 h in an oven at 100 °C, and then sieved through a 2 mm mesh sieve. The total sample under 2 mm was ground in an agate mortar to less than 63 µm for subsequent chemical and mineralogical analysis. Afterwards, chemical analyses of both soil and mine waste samples were carried out using an x-ray fluorescence (XRF) analyzer (Thermo Scientific NITON 2008), which allowed analysis of the following elements: Zn, Mn, Fe, As, Sr, Cd, V, Ca, P, Cr, Mg, Ba, Ti, Al, K, Rb, Mo, Cu, Pb, Ag, Ni, Co, and Au. The data quality was assessed using duplicate sample analyses and the concentration measurement accuracy was estimated at ±5 % for all of these elements. Finally, the mineralogical assembly of mine waste samples was determined by x-ray diffraction (XRD) spectroscopy using a Bruker AXS D8 advance diffractometer, scanning over diffraction angle ranges from 5 to 60. Scan settings were 0.005_ 2 h step size and 1 s counting time per step. The "Diffrac Plus" EVA software was used to identify mineral species. "TOPAS" software implementing Rietveld refinement (Young 1995) was used to quantify the abundance of all identified mineral species.

Acid–Base Accounting Test

Acid–base accounting (ABA) is used to predict the potential of generating acid mine drainage (AMD) by mine waste materials. The ABA test was conducted according to Sobek et al. (1978), as modified by Lawrence and Wang (1997). This test evaluates the acid-generating potential (AP) of mine wastes as well as their neutralization potential (NP). The AP was calculated for the mine wastes samples assuming that the sulfide sulfur content was exclusively expressed as pyrite and that all pyrite was available for oxidation. Afterwards, the obtained results were converted to calcite equivalents (kg $CaCO_3$/t) by multiplying by a factor of 31.25. Then, the NP was determined for the mine wastes by a digestion of the samples with an excess of standardized acid (HCl), and NaOH back titration to a pH 8.3 endpoint. The obtained results were converted to calcite equivalents (kg $CaCO_3$/t) by multiplying by a factor of 83.33. Finally, to evaluate the potential of acid production, the net neutralization potential (NNP) was calculated using the following equation:

$$NNP = NP - AP \tag{1}$$

Three classes were recognized: (1) $NNP < -20$ kg $CaCO_3$/t indicates an acid-producing material; (2) $NNP > 20$ kg $CaCO_3$/t is considered to be acid consuming; (3) $20 > NNP > -20$ kg $CaCO_3$/t indicates an uncertainty zone (Miller et al. 1991).

Univariate and Multivariate Statistical Analysis

The results of the geochemical analysis of soil and mine waste samples were processed using the Statistical Package for Social Science (SPSS) program v. 17.0. First, descriptive statistic parameters (minimum, maximum, mean, median, and standard deviation) were determined for the considered chemical elements. These statistical parameters are very useful for summarizing and interpreting the obtained geochemical results (Cai et al. 2012; Khalil et al. 2013; Martínez et al. 2007). Afterwards, the data distribution of the soil samples was evaluated for normality using the Kolmogorov–Smirnov (K–S) test (Chakravarti et al. 1967) and by calculating the kurtosis and skewness parameters. Principal component analysis (PCA) was used to identify the relationship among the studied trace elements as well as their possible source. PCA has been applied in environmental studies to reduce data and extract a smaller number of independent factors (principal components) for analyzing relationships among the observed variables (Cai et al. 2012; Lu et al. 2010; Zhang et al. 2014). PCA was performed with Varimax rotation with Kaiser normalization.

Enrichment Factor and Geochemical Background

To highlight the chemical elements that were enriched in the Tiwiyyine soils, the enrichment factor (EF) was determined for the considered elements (Bourennane et al. 2010; Khalil et al. 2013; Li and Feng 2012; Martínez et al. 2007). The EF is widely employed to identify the anthropogenic source of elements (Li and Feng 2012). Based on EF, five contamination categories were recognized: (1) $EF < 2$ states deficiency to minimal enrichment; (2) $2 \leq EF < 5$ moderate enrichment; (3) $5 \leq EF < 20$ significant enrichment; (4) $20 \leq EF \leq 40$ very high enrichment, and; (5) $EF > 40$ extremely high enrichment (Han et al. 2006; Lu et al. 2009a, b). According to Chester and Stoner (1973), the EF calculation is expressed as Eq. (2):

$$EF_{El} = \frac{[El]_{sample}/[X]_{sample}}{[El]_{crust}/[X]_{crust}} \tag{2}$$

where "*El*" is the element under consideration, the square brackets indicate concentration (usually in mg/kg), "*X*" is the chosen reference element and the subscripts "sample" or "crust" indicate which medium the concentration refers to. Crust refers to the Earth's crust, most often continental or upper continental crust (UCC). The Clarke values corresponding to mean concentrations of chemical elements in the UCC, are given by McLennan (2001). Iron (Fe), yttrium (Y), and aluminum (Al) can all be used as reference elements to calculate the EF (Buat-Menard and Chesselet 1978; Martínez et al. 2007; Salomons and Förstner 1984). In the current study, Al was selected as the reference value. Indeed, Al is the most common reference value used to calculate the EF (Bourennane et al. 2010; Buat-Menard and Chesselet 1978; Khalil et al. 2013; Lu et al. 2009a, b).

The following equation shows an example for calculating the EF for Mn:

$$EF_{Mn} = \frac{1428/63780}{600/80400} = 3$$

where 1428 mg/kg corresponds to the mean concentration of Mn in the soil samples; 63,780 mg/kg corresponds to the mean concentration of Al (reference element) in the soil samples; 600 mg/kg is the mean concentration of Mn in the UCC; and 80,400 mg/kg is the mean concentration of Al in the UCC. Therefore, Mn has been enriched in the study area three-fold (moderate enrichment) and is considered an element of interest.

In addition to enrichment due to human activity, the EF also detects geogenic enrichment resulting from soil formation (Bourennane et al. 2010; Reimann and DeCaritat 2005). Therefore, to distinguish between geogenic and anthropogenic enrichment, geochemical background (GB), defined by Hawks and Webb (1962) as "the normal abundance of a chemical element in barren earth material", was determined for the enriched elements using the graphical test of normality: normal quantil–quantil (Q–Q) plot (Khalil et al. 2013; Martínez et al. 2007).

Geoaccumulation Index

Unlike the EF, the I_{geo} is a geochemical criterion that highlights soil contamination that is strictly related to anthropogenic activity (Chabukdhara and Nema 2012; Loska et al. 2004). Therefore, to measure trace element contamination in Tiwiyyine soils, the geochemical index (I_{geo}) was determined for the elements of interest (Mn, Cd, As, and V). The I_{geo} was first developed for assessing the contamination levels of bottom sediments (Maftei et al. 2014; Müller 1969, 1979), but it has since been widely used for measuring soil contamination by trace elements (Chabukdhara and Nema 2012; Chung and Chon 2014; Ji et al. 2003; Loska et al. 2004; Wei et al. 2011). Based on I_{geo}, seven quality classes were recognized: (0) $I_{geo} \leq 0$ states practically uncontaminated; (1) $0 < I_{geo} < 1$to moderately contaminated uncontaminated; (2) $1 < I_{geo} < 2$ moderately contaminated; (3) $2 < I_{geo} < 3$ moderately to heavily contaminated, (4) $3 < I_{geo} < 4$ heavily contaminated, (5) $4 < I_{geo} < 5$ heavily to extremely contaminated and (6) $5 < I_{geo}$ extremely contaminated (Müller 1981). The I_{geo} was calculated for the enriched chemical elements using Eq. (3):

$$I_{geo} = \log_2 \frac{C_n}{\,} 1.5B_n \tag{3}$$

where C_n is concentration of trace element in soil, B_n is the geochemical background value, and 1.5 is a correction factor due to changes that may occur in the lithology. The following equation is an example for calculating the I_{geo} for Mn in soil sample "St1":

$$I_{geo} = \log_2 \frac{2752}{1.5791} = 1.213$$

where 2752 mg/kg corresponds to the concentration of Mn in the St1soil sample; 791 mg/kg corresponds to the geochemical background of Mn in the study area, and; 1.5 is a correction factor due to changes that may occur in the lithology. Therefore, the St1 soil sample is uncontaminated to moderately contaminated.

Assessing Trace Element Distribution Using GIS

GIS is a powerful tool for studying environmental problems (Acosta et al. 2011; Khalil et al. 2014), and an effective way to research the spatial variability of pollutants (Sun et al. 2012). Therefore, GIS-based spatial mapping was used to study the spatial distribution of the enriched trace elements in the Tiwiyyine soils (Mn, Cd, As, and V). Consequently, a pollution map were generated by overlying graduated symbols that represented the concentrations of these contaminants in soils on a georeferenced Google earth satellite image using ArcGIS v.9.3 (Environmental System Research Institute Inc.). In addition to showing areas where the element concentrations are elevated, these pollution maps can reveal significant information on the source, and how the contamination spread (Chung and Chon 2014; Yenilmez et al. 2011).

Results and Discussion

Assessment of Mine Water Quality

Hydrochemical analysis of the mine water samples showed that all the analyzed trace elements were under the limit of detection. The pH of the water samples ranged from 7.2 to 7.8, the electrical conductivity (EC) ranged from 555 to 1188 μS cm^{-1}, and the sulfate ranged from 53 to 55 mg L^{-1}. The pH, EC, and SO_4^{2-} values of ground and surface water samples were generally in agreement (Table 1). Furthermore, they met the World Health Organization guidelines for drinking water (WHO 1997). Therefore, it appears that local anthropogenic activity has not influenced mine water quality, presumably because of the arid climate of the study area. Moreover, groundwater supplies most of the irrigation needs in the area, while drinking water is supplied, after treatment, by the nearby water dam.

Statistical Analysis of Geochemical and Mineralogical Data

Soils around the Tiwiyyine's mine site area had very high concentrations of Cd, As, V, and Mn compared to the Clarke values given by McLennan (2001), and thus high EFs (Table 2).

Cadmium was extremely enriched at 159.7 times the Clarke value. It was followed by As, which was very highly enriched at 25.7 times the Clarke values. Finally, V and Mn showed moderate enrichment at 4.6 and 3 times the

Table 1 Hydrochemical data of the Tiwiyyine groundwater and surface water samples

Parameters	Groundwater				Surface water				WHO (1997)[a]
	N	Min	Max	Mean	N	Min	Max	Mean	
pH	3	7.5	7.8	7.6	2	7.2	7.3	7.2	6.5–9.2
EC (μS/cm)	3	555	1188	875	2	560	583	571.5	1500
$S0_4^{-2}$ (mg/L)	3	53	55	54	2	53	54	53	600

[a] Guidelines for drinking water quality (WHO 1997)

Table 2 Descriptive statistics: clarke values and enrichment factors (compared to the upper continental crust) of the chemical elements of the examined Tiwine soils (23 samples)

	Min	Max	Mean	Median	SD	Skewness	Kurtosis	K–S test[a]	Clarke values[b]	Enrichment factor
Zn	13.3	73	36.7	32	14.45	1	1.12	0.056	71	0.7
Mn	746	4640	1428	1145	897	2.46	6.93	0.000	600	**3.0**
Fe	33,436	55,700	45,564	45,326	5788	−0.23	−0.60	0.200	35,000	1.6
As	16	58	30.6	26.7	11.55	1.04	0.10	0.012	1.5	**25.7**
Sr	43.4	160	75	63	278	1.41	2.50	0.035	350	0.3
Cd	4	19.6	12.7	13.4	5	−0.60	−1.05	0.051	0.1	**159.7**
V	258	1092	393	323	187	2.83	8.80	0.000	107	**4.6**
Ca	7501	87,814	25,196	17,873	20,934	1.86	3.14	0.000	30,000	1.1
P	161	2270	631	549	504	1.74	4.09	0.063	700	1.1
Cr	35	219	114	112	40	0.49	1.73	0.139	83	1.7
Mg	3918	13,903	9769	10,168	2652	−0.56	0.10	0.200	13,300	0.9
Ba	77	2452	354	172	522	3.34	12.44	0.000	550	0.8
Ti	3320	5165	4361	4486	539	−0.56	−0.65	0.185	4100	1.3
Al	47,367	82,179	63,780	64,599	9366	0.04	−0.65	0.200	80,400	1.0
K	23,814	57,442	38,177	38,115	7477	0.49	1.33	0.200	28,000	1.7
Rb	35	97	56	52	17	1.28	0.90	0.015	112	0.6

Bold in enrichment factor limit are superior values

SD standard deviation

[a] Shapiro–Wilk normality test (Shapiro and Wilk 1965)

[b] Clarke values = mean concentrations of the chemical elements in the upper continental crust (McLennan 2001); Geochemical data are expressed in mg/kg

Clarke values, respectively. However, EF values calculated for the rest of the considered elements indicate minimal enrichment, with EF values less than 2 (Table 2). Therefore, Cd, As, V, and Mn were selected as special elements of interest in Tiwiyyine mining area. Many authors have pointed-out potential health risks from the selected elements in other areas with high concentrations of these metals and metalloids (Chowdhury et al. 2000; Gummow 2011; Health Canada 1987; Tang et al. 2009).

The elements of interest show a wide range in concentrations in Tiwiyyine a mine soil, which explains the difference between the mean and the median values. The concentrations of Cd, As, V, and Mn varied between 4 and 19.6, 16 and 58, 258 and 1092, and 746 and 4640 mg/kg respectively, with a mean concentration of 12.7, 30.6, 393, and 1428 mg/kg, respectively (Table 2). The mean values of the total content in soils follow an ascending order: Cd > As > V > Mn. The median concentrations of As, V, and Mn were less than their mean concentrations (Table 2), while their skewness values were larger than 1. Therefore, As, V, and Mn were positively skewed toward lower concentrations. Finally, the K–S test showed that, among the selected elements, only Cd was normally distributed ($P > 0.05$), which is confirmed by the large standard deviation and kurtosis values, which indicate that As, V, and Mn were asymmetrically distributed (Table 2).

High concentration levels were also found for As, V, and Mn in the Tiwiyyine mine wastes (Table 3). The concentrations ranged between 130 and 291, 5230 and 9127 and 15, 1642 and 38,9624 mg/kg, respectively, and a mean concentration of 193, 6586, and 257,130 mg/kg, respectively. These concentrations indicate that the mine wastes were significantly enriched in these trace elements. However, Cd, which has been enriched in the surrounding soils, was absent in all of the analyzed mine waste samples. As illustrated in supplemental Fig. 3, the mine wastes contained high amount of pyrolusite (MnO_2), with concentrations ranging between 22 and 38 %, with a mean of 28 %. Moreover, the total iron sulfide content was not significant (Supplemental Figure 3).

Table 3 Descriptive statistics of the chemical elements of the examined Tiwiyyine mine wastes (4 samples)

Elements	Min	Max	Mean	Median
Mo	24.4	84.8	58.9	63.2
Cu	77	265	168	164
Pb	8293	13,309	10,520	10,238
Zn	32	109	55.7	41
Co	196	472	292	250
Mn	151,642	389,624	257,130	243,627
Fe	9022	29436	21,917	24,604
As	130	291	193	176
Sr	294	600	421	396
V	5230	9127	6586	5993
Ca	287	2283	1132	980
Mg	1650	5422	3794	4052
Ba	18,385	49554	31358	28746
Ti	10,371	16,371	12508	11,644
Al	36,400	60,517	52,128	55,797
K	23,895	42,638	35,184	37,101
Rb	39	80	62	64

Geochemical data are expressed in mg/kg

Acid–Base Accounting Test (ABA)

Table 4 summarizes the ABA test results. The AP values ranged from 1 to 2.7 kg $CaCO_3$/t for the mine wastes. This agreed with the mineralogical analysis, which had revealed the absence of sulphide minerals in most of the analyzed samples, except for TW1 (Supplemental Figure 3). However, all of the mine wastes had low NP values, ranging from 3.5 to 10 kg $CaCO_3$/t, indicating a deficiency of carbonates in the mine waste samples. According to Miller et al. (1991), the mine wastes were in the uncertainty zone (20 > NNP > −20 kg CaCO3/t).

Determination of Soil GB and Anomalous Values

The GB was determined using the Q–Q plots of the selected elements. Measured concentrations were plotted on the X axis and the expected values under a normal distribution were plotted on the Y axis (Fig. 2). This graphical representation provides a detailed visualization of the geochemical data; inflection points indicate the involvement of different processes (Zhang et al. 2008).

The As, V, and Mn curves reveal such an inflection point (Fig. 2a–c). This allows us to distinguish between the geochemical background (geogenic contribution), which can be deduced by calculating the mean concentration of the first bend of the plot, and the anthropogenic activity, which is depicted by high concentrations of subsequent populations (Bauer and Bor 1995; Khalil et al. 2013; Martínez et al. 2007). However, the plot curve of Cd exhibits only one

Table 4 Acid-base accounting analysis of the mine wastes samples

	Tiwiyyine mine wastes			
	TIW1	TIW2	TIW3	TIW4
AP (kg $CaCO_3$/t)	1	2.7	2.6	2.5
NP (kg $CaCO_3$/t)	6	3.8	10	3.5
Net NP (kg $CaCO_3$/t)	5	1.1	7.4	1
Classification	UZ	UZ	UZ	UZ

UZ Uncertainty zone

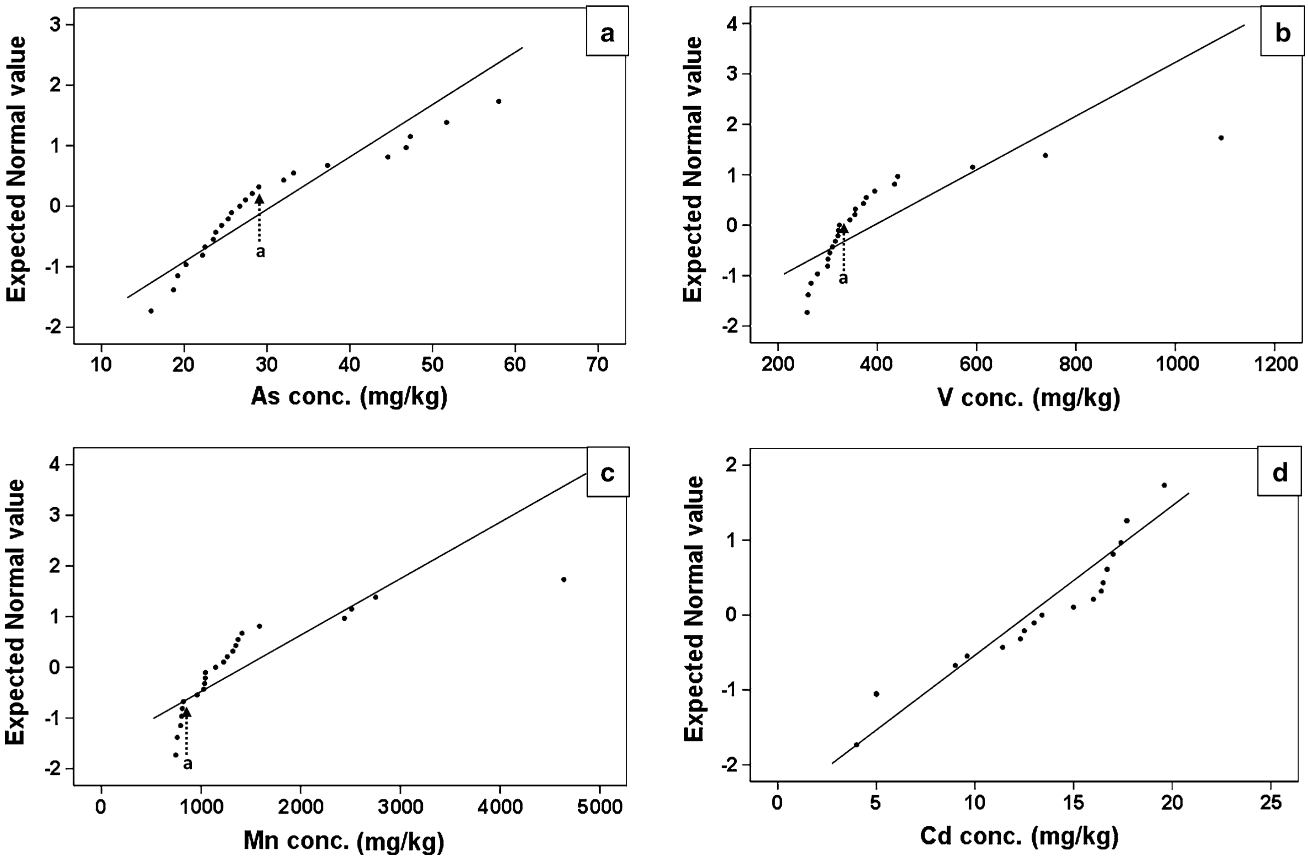

Fig. 2 Normal Q–Q plots for As, V, Mn, and Cd (*arrow* a indicates inflection point)

population of concentrations, represented by points that are close to the diagonal line (Fig. 2d). Therefore, the geochemical data of Cd are statistically normally distributed. This finding agrees with the result of the K–S numerical normality test. After separating the two populations of concentrations, the GB and the anomalous values of the soils were determined by calculating, respectively, the mean concentrations of the first and second populations, as represented in the Q–Q plots (Fig. 2a–d). The net anomalous values were deduced by subtracting the GB values from the anomalous values (Martínez et al. 2007).

The GB values, anomalous values, and net anomalous values are reported in Table 5. Because there are no Moroccan guidelines for assessing soil quality, the obtained values were compared with Canadian guidelines (CCME 2006), as was previously done in several Moroccan environmental studies (El-Khalil et al. 2008; Khalil et al. 2013). The Cd, As, and V GB values were much higher than the Canadian guideline values (Table 5), suggesting that these elements were naturally enriched in the study area; the soils contained a high natural geogenic content of Cd, As, V, and Mn. However, the anomalous As, V, and Mn values were 1.9, 1.7, and 2.1 times the GB values of the soils, respectively (Table 5); this demonstrates an anthropogenic source. Moreover, these elements showed significantly anomalous net values: As (20.5 mg/kg), V (204 mg/kg), and Mn (863 mg/kg). In contrast, the Cd concentrations were approximately equal to their GB, indicating that the Cd mainly originated from the geogenic natural enrichment. The amplitude and the origin of the anthropogenic contribution are discussed below.

Assessment of Cd, As, V, and Mn Contamination Using the Geoaccumulation Index

The I_{geo} values for Cd, As, V, and Mn are listed in supplemental Table 1. According to the I_{geo} classification system (Müller 1981), the I_{geo} values for Cd for the entire examined samples fell into class 0, indicating a lack of anthropogenic Cd pollution. This finding is in perfect agreement with the result of the GB calculation, discussed above. The I_{geo} values of As, V and Mn fell into three groups. The first group represents class 0 (practically uncontaminated soils); most of the soil sampled far from the mine wastes (from 1.5 to 4 km) fell into this category. The second group represents class 1 (uncontaminated to moderately contaminated soils) and contained few soil

Table 5 Geochemical background values, anomalous, and net anomalous values of the Tiwiyyine soils

	Tiwiyyine soils			Geochemical background of soils (1st population)			Anomalous content (2nd and 3rd populations)			Net anomalous values	Canadian soil quality guidelines[c]
	N	Mean	Median	N	Mean (a)	Median	N	Mean (b)	Median	(b–a)	
Mn	23	1428	1145	6	791	800	17	1654	1319	863	–
As	23	30.6	26.7	15	23.5	23.3	8	44	46	20.5	12
Cd	23	13	13.4	23	13	13.4	–	–	–	–	1.4
V	23	393	323	12	296	302	11	500	395	204	130

samples. However, the 3rd group, which represents class 2 (moderately contaminated soils) contained five samples from near (from 0.25 to 0.75 km) the deposited mine waste (Supplemental Table 1 and Fig. 1). Moreover, among the few contaminated samples, the I_{geo} values of As, V, and Mn never exceeded 1.96, 0.71, and 1.29, respectively, and these samples were located next to mine waste. In the light of these results, the I_{geo} calculation suggests that anthropogenic activity moderately contributed to the contamination of the studied soils.

GIS Analysis

GIS application facilitated our evaluation of trace element dispersion in the Tiwiyyine area. The adopted graduated symbols representation differentiating between the points affected by the geogenic contamination and the points which are affected by both the geogenic and the anthropogenic contamination. According to the pollution maps (Fig. 3), higher contamination of Cd, As, V, and Mn was recognized in the vicinity of the abandoned mine site and in the downstream direction of surface runoff pathways. However, these concentrations become lower with the increase of distance from the mine site.

The Cd pollution map shows that the studied soils present high Cd concentration levels ranging from 4 to 20 mg/kg (Fig. 3a). As discussed previously, the high Cd content in soil are derived from the parental rocks (mainly hematite), which explains the high GB of Cd in Tiwiyyine soil (13 mg/kg). However, for the locations where the Cd concentrations exceed the established GB, the Cd pollution map (Fig. 3a) shows that they are linked to zones where the products of parental rock erosion have accumulated.

Figure 3b illustrates that As concentrations ranged from 15 to 58 mg/kg. The related map shows that the highly polluted samples are located around the mine site and in the downstream direction of the surface runoff pathways and stream network. The high As content in these samples exceeds the established GB (23.5 mg/kg). This is due to two processes; the first is geogenic, due to erosion of parental rocks over the years, while the second is anthropogenic, apparently due to the abandoned mine. However, samples with intermediate concentration levels, which also exceeded the established GB of As in the soil, were located far from the mine site (Fig. 3b). It should be mentioned that the As content derived from the two processes was mainly dispersed over the years in the study area by surface runoff and a stream network.

Figure 3c shows a relatively similar distribution pattern for Mn, with Mn concentrations ranging from 746 to 4640 mg/kg. High Mn levels, widely exceeding the established GB of Mn in the soil (791 mg/kg), were also observed near the mine site, while intermediate Mn values were located downstream of the mine site (Fig. 3c).

Compared to As and Mn, the highest vanadium concentrations were only located near the mine waste, which are highly enriched in vanadium (Fig. 3d and Table 3). Furthermore, these concentrations significantly exceeded the established GB of vanadium in the soil (296 mg/kg). In the light of these findings, it can be concluded that mining is the anthropogenic source responsible for soil pollution in the contaminated area, especially when the rest of the examined areas exhibited intermediate concentration values that are close to the established GB (Fig. 3d).

The obtained results corroborate perfectly the findings of the I_{geo} calculation, which indicate that only points located near the mine site and in the downstream direction of surface run off present positive I_{geo} values, representing uncontaminated to moderately contaminated soils. This implies that mining is responsible for the anthropogenic soil pollution. However, the other points present values with negative I_{geo}, even if they contain an elevated geogenic content of Cd, As, V, and Mn, which infer that they reflect the geochemistry of the parental rocks. In contrast to other mine sites in Morocco and abroad (Bourennane et al. 2010; Khalil et al. 2013), the contamination from the Tiwiyyine mine site stayed near the mine, and did not spread over long distances.

Principal Component Analysis (PCA)

The results of the PCA obtained by applying Varimax rotation with Kaiser normalization for the obtained geochemical data of the Tiwiyyine soils are shown in

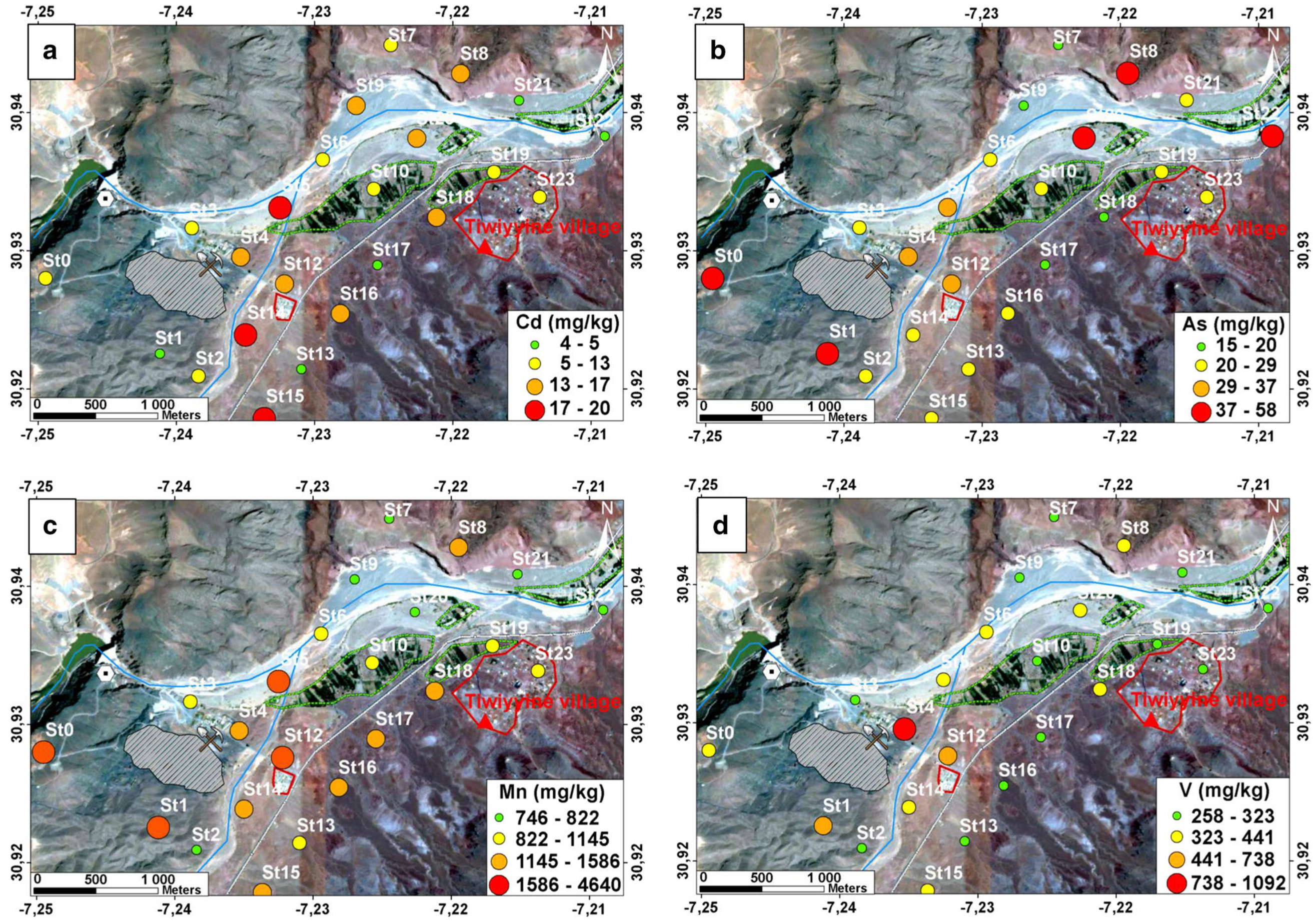

Fig. 3 Spatial distribution of Mn, As, Cd, and V concentrations in Tiwiyyine soils (Base map: Google Earth image modified)

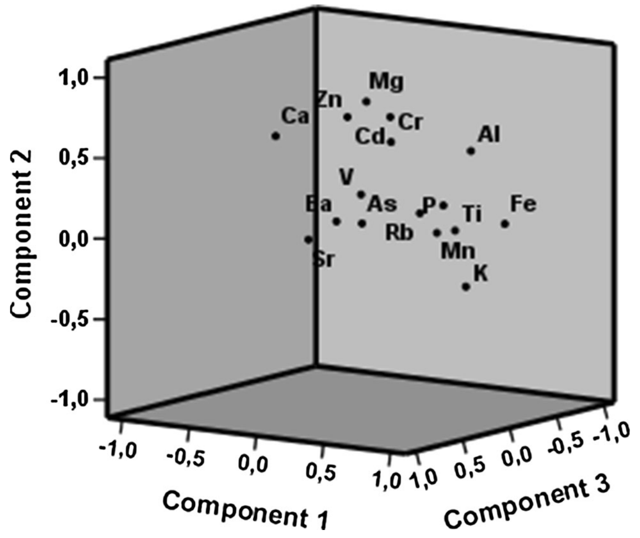

Fig. 4 Loading plot of PC1, PC2, and PC3.and relationships between the elements of interest

supplemental Table 2. Only the first three principal components (CP), with eigen values higher than 1 (before and after rotation), were selected. Figure 4 illustrates the graphic representation of the selected components and the associations between the analyzed elements. The results show that PCA has reduced the initial dimension of the geochemical dataset into three components that explain 55.4 % of the data variation. The first principal component (CP1) explains 21.1 % of the total variance and was influenced heavily by K, Fe, Rb, and Al, and moderately by Mn and As. The Mn loading (0.616) and As loading (0.485) are not as high as the K, Fe, Rb, and Al loadings (0.797, 0.792, 0760, and 0.714 respectively), which may imply quasi-independent behavior within the group (Cai et al. 2012). The second principal component (CP2), dominated by Mg and Zn, and also moderately by Cd, Ca, Cr, and Al, accounts for 19.1 % of the total variance. Finally, the third principal component (CP3) correlated moderately with As, Ca, and Rb, and accounted for 12.2 % of the total variance.

PCA results were consistent with the results of the GB determination and I_{geo} calculation because again two main sources can be identified: (1) Mn and As, which are loaded by CP1, originate mainly from an anthropogenic source; (2) Cd, which is loaded by the CP2, originates essentially from a natural source. As can have mixed sources (geogenic and anthropogenic).

Conclusions

There was no contamination of water resources due to mine water in the Tiwiyyine area. Therefore, mine water can be used for irrigation without any expected risk. Application of the enrichment factor (EF), geochemical background (GB), geoaccumulation index I_{geo}, and geographic information system (GIS) analysis made it possible to efficiently assess the soil contamination levels with some potentially toxic elements in the Tiwiyyine area of Morocco. This case study indicated that the Tiwiyyine soils are heavily enriched with Cd, As, V, and Mn, with mean concentrations of 13, 30.6, 393, and 1,428 mg/kg, respectively. Furthermore, the established GB of Cd, As, V, and Mn (13, 23.5, 296, and 791 mg/kg, respectively) revealed that the soils contained a naturally high geogenic content of these elements, derived from the parental rocks from which the soils developed. However, the I_{geo} calculation distinguished between anthropogenically contaminated samples, with $I_{geo} > 0$, and samples that contained naturally high geogenic metal and metalloid content, but had a negative I_{geo}. Finally, combining the results of the I_{geo} calculation with the GIS analysis showed that the anthropogenically contaminated samples were only located in the vicinity and downstream of the abandoned mine site, and that the mining was responsible for the soil pollution in the studied area.

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References

Acosta JA, Faz A, Martinez M, Zornoza R, Carmona DM, Kabas S (2011) Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation. J Geochem Explor 109:8–17

Argane R, Benzaazoua M, Bouamrane A, Hakkou R (2015) Cement hydration and durability of low sulfide tailings-based renders: a case study in Moroccan constructions. Miner Eng 76:97–108

Bauer I, Bor J (1995) Lithogene, geogene und anthropogene Schwermetallgehalte von Lößböden an den Beispielen von Cu, Zn, Ni, Pb, Hg und Cd. Mainzer Geowiss Mitt 21:47–70

Bossé B, Bussière B, Hakkou R, Maqsoud A, Benzaazoua M (2013) Assessment of phosphate limestone wastes as a component of a store-and-release cover in a semiarid climate. Mine Water Environ 32(2):152–157

Bourennane H, Douay F, Sterckeman T, Villanneau E, Ciesielski H, King D, Baize D (2010) Mapping of anthropogenic trace elements inputs in agricultural topsoil from Northern France using enrichment factors. Geoderma 157:165–174

Buat-Menard P, Chesselet R (1978) Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. Earth Planet Sci Lett 42:399–411

Cai L, Xu Z, Ren M, Guo Q, Hu X, Hu G, Wan H, Peng P (2012) Source identification of eight hazardous heavy metals in agricultural soils of Huizhou, Guangdong Province, China. Ecotoxicol Environ Saf 78:2–8

Candeias C, Ferreira da Silva E, Salgueiro AR, Pereira HG, Reis AP, Patinha C, Matos JX, Avila PH (2011) Assessment of soil contamination by potentially toxic elements in Aljustrel mining area in order to implement soil reclamation strategies. Land DegradDev 22:565–585

CCME (2006) Canadian soil quality guidelines for the protection of environment and human health. Canadian Council of Ministers of the Environment. http://www.ccme.ca/ourwork/soil.html

Chabukdhara M, Nema AK (2012) Assessment of heavy metal contamination in Hindon River sediments: a chemometric and geochemical approach. Chemosphere 87:945–953

Chakravarti IM, Laha RG, Roy J (1967) Handbook of methods of applied statistics, vol 1. Wiley, New York City, pp 392–394

Chester R, Stoner JH (1973) Pb in particulates from the lower atmosphere of the eastern Atlantic. Nature 245:27–28

Chowdhury UK, Biswas BK, Chowdhury TR, Samanta G, Mandal BK, Basu GC, Chanda CR, Lodh D, Saha KC, Mukherjee SK, Roy S, Kabir S, Quamruzzaman Q, Chakraborti D (2000) Groundwater arsenic contamination in Bangladesh and West Bengal, India. Environ Health Persp 108(5):393–397

Chung S, Chon HT (2014) Assessment of the level of mercury contamination from some anthropogenic sources in Ulaanbaatar, Mongolia. J Geochem Explor 147:237–244

El-Khalil H, El Hamiani O, Bitton G, Ouazzani N, Boularbah A (2008) Heavy metal contamination from mining sites in South Morocco: monitoring metal content and toxicity of soil runoff and groundwater. Environ Monit Assess 136:147–160

Goumih A, El Adnani M, Hakkou R, Benzaazoua M (2013) Geochemical behavior of mine tailings and waste rock at the abandoned Cu–Mo–W Azegour mine (Occidental High Atlas, Morocco). Mine Water Environ 32(2):121–132

Gummow B (2011) Vanadium: environmental pollution and health effects. Encyclopedia of environmental health. Elsevier, Amsterdam, the Netherlands, pp 628–636

Hakkou R, Benzaazoua M, Bussière B (2008) Acid mine drainage at the abandoned Kettara mine (Morocco): 1. environmental characterization. Mine Water Environ 27:145–159

Han Y, Du P, Cao J, Posmentier ES (2006) Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci Total Environ 355:176–186

Hawkes HE, Webb JS (1962) Geochemistry in mineral exploration. Harper & Row, New York

Health Canada (1987) Manganese. Technical document—chemical/physical parameters in www.hc-sc.gc.ca (accessed Nov 11, 2014)

Iavazzo P, Adamo P, Boni M, Hillier S, Zampella M (2012) Mineralogy and chemical forms of lead and zinc in abandoned mine wastes and soils: an example from Morocco. J Geochem Explor 113:56–67

Ji Y, Feng Y, Wu J, Zhu T, Bai Z, Duan C (2003) Assessment of arsenic enrichment of cultivated soils in southern Poland. PolJ Environ Stud 2:187–192

Khalil A, Hanich L, Bannari A, Zouhri L, Pourret O, Hakkou R (2013) Assessment of soil contamination around an abandoned mine in a semi-arid environment using geochemistry and geostatistics: pre-work of geochemical process modeling with numerical models. J Geochem Explor 125:117–129

Khalil A, Hanich L, Hakkou R, Lepage M (2014) GIS-based environmental database for assessing the mine pollution: a case study of an abandoned mine site in Morocco. J Geochem Explor 144:468–477

Kim SM, Choi Y, Suh J, Oh S, Park HD, Yoon SH, Go WR (2012) ArcMine: AGIS extension to support mine reclamation planning. Comput Geosci 46:84–95

Lawrence RW, Wang Y (1997) Determination of neutralization potential in the prediction of acid rock drainage. In Proceedings 4th international conferences on acid rock drainage (ICARD), Vancouver 1:451–464

Li X, Feng L (2012) Multivariate and geostatistical analyzes of metals in urban soil of Weinan industrial areas, Northwest of China. Atmos Environ 47:58–65

Loska K, Wiechula D, Korus I (2004) Metal contamination of farming soils affected by industry. Environ Int 30:159–165

Lu X, Loretta Li Y, Wang L, Lei K, Huang J, Zhai Y (2009a) a) Contamination assessment of mercury and arsenic in roadway dust from Baoji, China. Atmos Environ 43:2489–2496

Lu X, Wang L, Lei K, Huang J, Zhai Y (2009b) b) Contamination assessment of copper, lead, zinc, manganese and nickel in street dust of Baoji, NW China. J Hazard Mater 161:1058–1062

Lu XW, Wang LJ, Li LY, Lei K, Huang L, Kang D (2010) Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China. J Hazard Mater 173:744–749

Maftei AE, Iancu OG, Buzgar N (2014) Assessment of minor elements contamination in Bistriţa River sediments (upstream of Izvorul Muntelui Lake, Romania) with the implication of mining activity. J Geochem Explor 145:25–34

Martínez J, Llamas J, De Miguel E, Rey J, Hidalgo MC (2007) Determination of the geochemical background in a metal mining site: example of the mining district of Linares (South Spain). J Geochem Explor 94:19–29

McLennan SM (2001) Relationships between the Trace Element composition of sedimentary rocks and upper continental crust, Geochem Geophy Geosyst, 2: 2000GC000109. doi:10.1029/2000GC000109

Miller SD, Jeffery JJ, Wong JWC (1991) Use and misuse of the acid base account for AMD prediction. In: Proceedings, 2nd ICARD, Montreal, Canada, vol 3, p 489–506

Müller G (1969) Index of geoaccumulation in sediments of the Rhine River. Geojournal 2(3):108–118

Müller G (1979) Schwermetalle in den sedimenten des Rheins-Veränderungen seitt 1971. Umschan 79: 778–783 [**in German, with English abstract**]

Müller G (1981) Die Schwermetallbelastung der Sedimenten des Neckars und Seiner Nebenflüsse. ChemZtg 6:157–164

Ouakibi O, Loqman S, Hakkou R, Benzaazoua M (2013) The potential use of phosphatic limestone wastes in the passive treatment of AMD: a laboratory study. Mine Water Environ 32(4):266–277

Reimann C, De Caritat P (2005) Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Sci Total Environ 337:91–107

Salomons W, Förstner U (1984) Metals in the hydrocycle. Springer, Tokyo

Shapiro SS, Wilk MB (1965) An analysis of variance test for normality (complete samples). Biometrika 52:591–611

Sobek AA, Schuller W, Freeman JR, Smith RM (1978) Field and laboratory methods applicable to overburdens and minerals. US Environmental Protection AgencyTech Rept EPA-600/2–78–054, Washington DC

Sun H, Li J, Mao X (2012) Heavy metals' spatial distribution characteristics in a copper mining area of Zhejiang Province. J Geogr Inf Syst 4:46–54

Tang J, Xiao TF, Wang SJ, Lei JL, Zhang MZ, Gong YY, Li H, Ning ZP, He LB (2009) High cadmium concentrations in areas with endemic fluorosis: a serious hidden toxin? Chemosphere 76:300–305

Thermo Scientific NITON (2008) Thermo scientific NITON® XL3t 900 series product specifications. www.thermo.com/niton. Accessed 3 Nov 2014)

Wei Z, Wang D, Zhou H, Qi Z (2011) Assessment of soil heavy metal pollution with principal component analysis and geoaccumulation index. Procedia Environ Sci 10:1946–1952

WHO (1997) Guidelines for drinking-water quality. Recommendations, vol 1. World Health Org, Geneva, pp 1–4

Yenilmez F, Kuter N, Emil MK, Aksoy A (2011) Evaluation of pollution levels at an abandoned coal mine site in Turkey with the aid of GIS. Int J Coal Geol 86:12–19

Young RA (ed) (1995) The rietveld method. Oxford Univ Press, Oxford

Zhang CS, Fay D, Grath DM, Grennan E, Carton OT (2008) Statistical analyses of geochemical variables in soils of Ireland. Geoderma 146:378–390

Zhang S, Yang D, Li F, Chen H, Bao Z, Huang B, Zou D, Yang J (2014) Determination of regional soil geochemical baselines for trace metals with principal component regression: a case study in the Jianghan plain, China. Appl Geochem 48:193–206