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Ambient background and quality reference values for trace metals in soils from Algeria

Abdelkader Laribi[1]*, *Charles Shand*[2], *Renate Wendler*[2],
Brahim Mouhouche[3], *Stephen Hillier*[2,4], *Gilles Colinet*[5]

[1]*Département des Sciences du sol, Ecole Nationale Supérieure Agronomique (ENSA), El Harrach, Algiers, Algeria*
[2]*The James Hutton Institute, Craigiebuckler, Aberdeen, United Kingdom*
[3]*Département de Génie Rural, Laboratoire de Maîtrise de l'eau en Agriculture (LMEA), Ecole Nationale Supérieure Agronomique (ENSA), El Harrach, Algiers, Algeria*
[4]*Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), Uppsala, Sweden*
[5]*University of Liège, Gembloux Agro Bio-Tech, BIOSE Dpt, Gembloux, Belgium*

**Corresponding author: laribiabdelkader@hotmail.com*

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Abstract: The establishment of the reference ambient background concentrations (ABCs) and quality reference values (QRVs) for trace metal (TM) concentrations in soils are required for the environmental assessment and any implementation of a protective action. This information is lacking for soils of the eastern Mitidja plain, which is an important agricultural production area in Algeria. Data for the *aqua regia* extractable Cd, Cr, Cu, Fe, Ni, Pb and Zn concentrations from 180 composite topsoil samples taken across the Mitidja plain in a stratified random pattern were statistically analysed. Descriptive statistical methods and linear regression equations were applied to determine the upper limit of the ABCs for the TMs. After removal of outliers, the derived QRVs were: Cd 0.24, Cr 62.1, Cu 99.3, Fe 45 590, Ni 47.7, Pb 33 and Zn 115 mg/kg. Iron is a macro element in the soils, but is included as its concentration can be used to normalise the concentrations of the other elements. The derived QRVs are similar or less than those reported for other regions of the world, apart from Cu, where a wide range (36 to 206 mg/kg) is reported. These reference values can be used to identify areas that may require follow-up surveys or to identify priority sites for decision making.

Keywords: environmental assessment; Mitidja plain; potentially toxic elements; soil contamination; threshold value

Trace metals (TMs) in soils are inherited from the parent materials and modified by pedogenic evolution (Baize 1997, 2009) and anthropogenic activities (Lienard et al. 2014; Bocardi et al. 2020). Environmental soil contamination by TMs has become a serious problem worldwide due to their toxicity, persistence, and non-degradability (Zovko & Romic 2011). The presence of TMs at very high concentrations and their transfer from the soil solution to the plant may impact human health through the food chain. Monitoring and managing the impacts of the natural environment on public health require the establishment of geochemical background and reference values, as this will serve as a sound basis for soil protection and in outlining the environmental risk areas well (Kazapoe & Arhin 2021). In exploration and environmental geochemistry, the geochemical background values (GBVs) are used to distinguish between the natural and anthropic element concentrations (Matschullat et al. 2000). The GBV is defined as the concentration of the element in the soil without human influence, but truly uncontaminated soils are almost impossible to find due to the diffuse contamination of potentially trace elements (Reimann & Garrett 2005). A more realistic approach for the assessment of TM concentrations in soils is in the use ambient background concentration values (ABCs) and quality reference concentration values (QRVs). The ABCs or usual background concentration, also known as the usual agricultural content or commonly observed soil concentration, is now widely used to characterise the geogenic natural content and the contribution of the anthropogenic activities to the increases in the metal concentration in soils (Tume et al. 2006; Zhao et al. 2007). The anthropogenic fraction of the ABC consists of several components. These components include the diffuse, moderate input into the soil from sources such as atmospheric deposition and fertilisers and does not necessarily include local sources due to industrial activity and mining (ISO 19258:2005; Zhao et al. 2007). In our work, the ABC concept is used in the same sense as that of background noise defined by the ISO standard (ISO 19258:2005). The ABCs of TMs in soil varies according to the element, soil parent materials, pedogenesis and land use (Zhao et al. 2007). For the purpose of establishing regulatory reference values, the QRVs for TMs based on the ABC (Mathieu et al. 2008) can be used. The QRVs are defined as the upper limit of the ABCs of TMs.

A range of statistical approaches to determine the QRVs for TMs in soils exist. One approach is the use of the parametric method mean + two standard deviations (SD) (Matschullat et al. 2000; Reimann & Garret 2005). However, the application of this method requires the population concentration values to have a normal distribution. Geochemical soil data rarely show a normal distribution and are often skewed (Reimann et al. 2005). Another approach is the use of non-parametric methods such as the median + two median absolute deviations (MADs) and the point of inflection on a cumulative frequency plot to address the problem of normality (Reimann & de Caritat 2017; Yotova et al. 2018). Other approaches have used upper element concentration values according to the 90th, 95th or 98th percentile of a given dataset population (Baize et al. 2006; Zhao et al. 2007; Ander et al. 2013; Yotova et al. 2018). Another approach in geochemical research has used the Tukey's inner fence (TIF) or the upper whisker in the Boxplot method (Villanneau et al. 2008; Yotova et al. 2018) defined as the concentration value corresponding to 1.5 times the interquartile range (IQR) added to the value of the upper quartile. Alternatively, the correlations between the TMs and the selected soil component values, such as the clay and soil organic matter concentration, can be used to predict the soil background concentration values. For instance, De Temmerman et al. (2003) defined the upper concentration limit for As, Cd, Cr, Cu, Pb, Ni and Zn in soils of northern Belgium as a function of a 'standard soil' containing 10% clay and 2% organic matter.

QRVs using statistical approaches have been determined for the soils of Cuba (Alfaro et al. 2015), Australia (Reimann & de Caritat 2017), Europe (Reimann et al. 2018), Brazil (Nogueira et al. 2018) and Bulgaria (Yotova et al. 2018). However, these values cannot be used to assess levels of soil contamination in Algeria due to the different pedoclimatic factors. Indeed, QRVs are unique for each environment and their extrapolation to different locations is not generally feasible (Bocardi et al. 2020).

Knowledge of the QRV concentrations in soils at a local or regional scale is a prerequisite for assessing the state of soil contamination by TMs (ISO 19258:2005; Ballesta et al. 2010) and for defining action levels in environmental legislation, which are element concentration values above which further investigation or site clean-up needs to take place (Reimann & de Caritat 2017). No such QRV values for the diagnosis of soil pollution by potentially toxic elements are known for the vast expanse of soils of Algeria or indeed the vital, agriculturally productive Mitidja plain in the north of the county bordering the Mediterranean Sea. Any element concentration value that is very much greater than this QRV concentration may be considered as anomalous and suspected to be the result of either local contamination of anthropogenic origin or of an abnormally high natural origin because of its specific pedogeological context or due to the addition of both natural and anthropogenic sources. Therefore, the objective of our work was to determine the ABCs and QRVs of TMs (As, Cd, Cr, Cu, Pb, Ni and Zn) and Fe in the soils of the eastern Mitidja plain in order to enable the future assessment of the extent of contaminated sites and the sources of contamination. Iron is a macro element in soils, but is included here as its concentration can be used as a normalisation reference for trace element concentrations (Krami et al. 2013).

MATERIAL AND METHODS

Study area. The Mitidja plain in the north of Algeria has a sub-humid Mediterranean climate and covers an area of 1 400 km^2. The study concerned the eastern part with an area of 665 km^2 centred around 3°10'25.58''E and 36°39'47.73''N. Full details of the soils and climate are available elsewhere (Laribi et al. 2019).

Soil sampling and analysis. A total of 180 composite soil samples (0–20 cm deep) were previously collected using an auger, in a randomised stratified sampling pattern, where the study area was subdivided into homogeneous entities according to a regular 2 × 2 km grid. In brief, each composite sample (around 2.5 kg) was made up of 5 subsamples of soil taken from the corners and centre of a 10 × 10 m square. The distribution of the sampling points is shown in Figure 1.

The soil samples were dried at room temperature (approximately 20 °C) and passed through a sieve with 2-mm openings to remove the stones and any other debris. The amount of clay in the soil samples was determined by the Robinson pipette method. The calcium carbonate concentration was determined volumetrically using HCl and Bernard's calcimeter method. The carbon concentration was determined by combustion using an elemental analyser (Flash EA 1112, Thermo Fisher, Germany). The samples were analysed for Cd, Cr, Cu, Ni, Pb and Zn by inductively coupled plasma-mass spectrometry (ICP-MS) (model G3281A, 7700 series, Agilent Technologies, Santa Clara, CA), whereas the Fe was determined by inductively coupled plasma optical spectrometry (ICP-OES) (model Optima 5300 DV, Perkin Elmer, Shelton, CT) following a standard *aqua regia* digestion method (ISO 11466:1995). The accuracy of the elemental analysis was assessed using a certified, sludge-amended soil (BCR, CRM 143). The recovery rates of the elements from the certified reference material were between 88 and 98%. The variation between batches of the analysed soil was assessed using an in-house prepared soil reference sample known as an artificial test soil (ATS) (Laribi et al. 2019).

Statistical analysis. Statistical analyses were carried out using Minitab software (Ver. 17, 2010). The normality of the TM concentration data was assessed using the Ryan-Joiner test, histograms and boxplots. Linear regression models were used to relate the trace element (TE) concentrations to clay, soil organic matter (OM) and calcium carbonate concentrations ($CaCO_3$).

RESULTS AND DISCUSSION

Ambient background concentrations. The assessment of the ABCs is based on descriptive statistics and boxplot methods and is evaluated by calculating a tolerance interval providing a limit that contained the largest part of the samples. This approach excluded samples with anomalous concentration values (outliers), which fall more than 1.5 times outside the interquartile range, above the third quartile, or below the first quartile determined using boxplots and frequency distribution methods (Reimann et al.

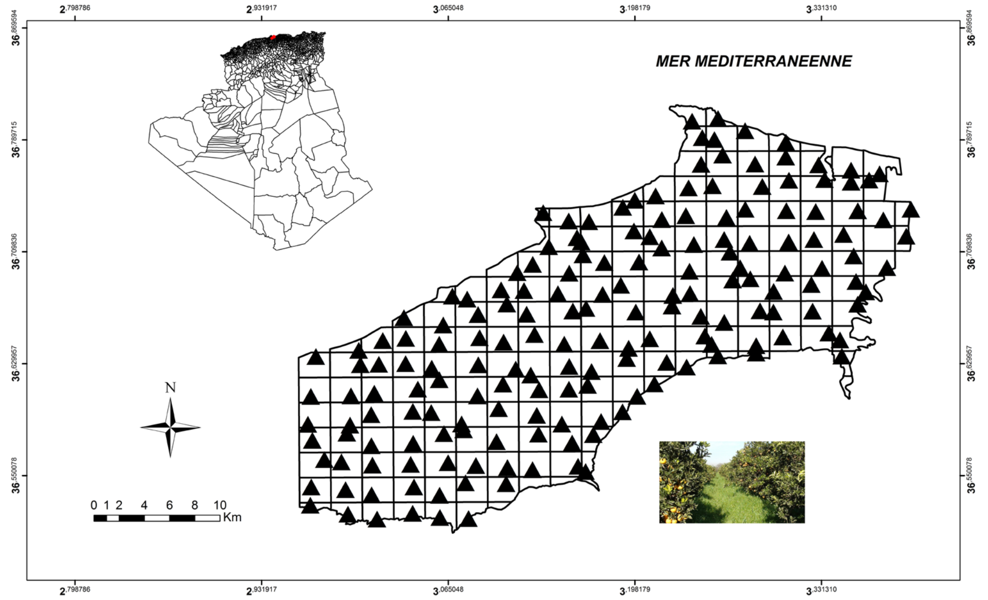

Figure 1. Location of the soil sampling points in the eastern Mitidja plain

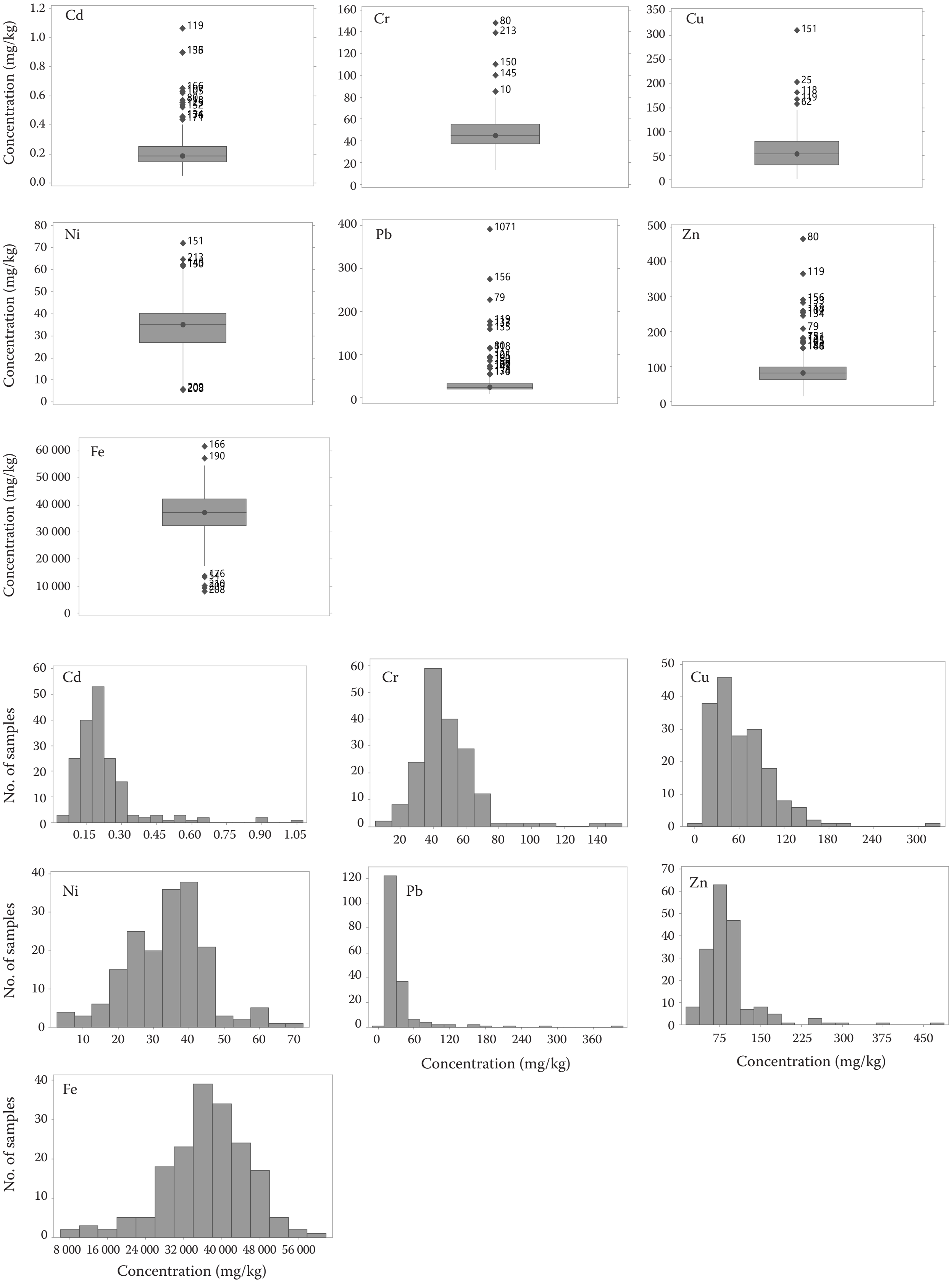

Figure 2. Distribution histograms and boxplots of the trace metal and Fe concentrations in the soils of the eastern Mitidja plain

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2005). For the soils from the eastern Mitidja plain, the most asymmetric distributions of trace element concentrations were observed for Pb followed by Zn, Cd, Cr and Cu (Figure 2). The distribution of the concentration values of these metals were strongly skewed, mostly towards higher concentrations.

The frequency distribution of the Cd concentrations showed thirteen outliers. The highest found concentration of Cd (1.07 mg/kg) was 10.7-fold higher than the GBV in the earth's crust. However, none of these samples had a Cd concentration more than the upper threshold values of 1.4 mg/kg set by the CCME (2007) or 1.5 mg/kg set by European legislation (Gawlik & Bidoglio 2006).

Five samples presented anomalously high Cr concentration values. The highest Cr concentration was 148 mg/kg and four samples exceeded the European legislation value of 100 mg/kg (Gawlik & Bidoglio 2006).

Five samples presented anomalously high Cu concentration values and had Cu concentration values higher than the European threshold value of 100 mg/kg (Gawlik & Bidoglio 2006). The highest Cu concentration (310 mg/kg) was 12.4-fold higher than the GBV in the earth's crust (McLennan 2001). The samples with relatively high Cu concentrations mainly came from the agricultural areas and may be associated with fertilisers or Cu-based fungicides used on crops (Khouli & Djabri 2011; Lebik & Ait-amar 2013).

Iron is a major element in soils and the Fe concentrations in soils are generally not subject to the magnitude of changes associated with trace elements. However, the graphical description of Fe showed seven outliers. Compared with the other elements in the study, the Fe concentrations in the soils are generally several orders of magnitude greater and the inputs of Fe by diffuse anthropogenic pollution are unlikely to be significant. Knowledge of the Fe concentrations in soils have been used as a reference to establish anthropogenic enrichment by trace metals (Krami et al. 2013). Most Fe in the soil is present in precipitated ferric forms, such as oxides and hydroxides, which have a high sorption capacity and may promote TE accumulation (Eze et al. 2010; Sipos et al. 2014).

In the case of Ni concentrations, six outliers (five high and one low concentration) were identified. Of all the soil samples, only one containing 71.9 mg per kg exceeded the upper threshold value of 70 mg per kg set for European soils (Gawlik & Bidoglio 2006).

The frequency distribution of Pb concentrations showed seventeen samples with anomalously high concentration values and out of these, eight exceeded the 100 mg/kg threshold value set for European soils (Gawlik & Bidoglio 2006). The highest concentration of Pb was 393 mg/kg. The soil samples with anomalously high Pb concentrations were mainly from the urbanised and industrialised area of the Mitidja plain and could be associated with traffic emissions and other anthropogenic activities (Aissa & Keloufi 2012). The high concentration of Pb in the soils of the Mediterranean cities of Algeria have previously been associated with the dense traffic and leaded gasoline still widely used in the country (Maas et al. 2010).

The frequency distribution for the Zn distribution showed sixteen extreme values. Eight samples exceeded the reference value of 200 mg/kg (Gawlik & Bidoglio 2006; CCME 2007). The highest Zn concentration was 466 mg/kg for a soil from the urban-industrial area. The main sources of Zn pollution are from industry and the use of liquid manure, composted materials and agrochemicals (Zovko & Romic 2011).

Table 1. Descriptive statistics of the trace metals and Fe (mg/kg) in the soils of the eastern Mitidja plain after elimination of the outliers

Element	No. of samples	No. of anomalous samples	Minimum	Maximum	Mean	SD	*CV* (%)
Cd	167	13	0.052	0.4	0.19	0.07	35.6
Cr	175	5	13.1	79.7	45.1	12.8	28.4
Cu	175	5	3.36	145	58.6	32	54.5
Fe	173	7	17 480	54 500	37 060	7 455	20.1
Ni	174	6	7.47	60.3	33.6	10.1	30.1
Pb	163	17	8.52	52.1	24.7	8.39	33.9
Zn	164	16	16.1	151	78.4	25.8	32.9

SD – standard deviation; *CV* – coefficient of variation

Table 2. Ambient background concentrations of the trace metals (mg/kg) in the soils of the eastern Mitidja plain

Element	Distribution	Population background	Arithmetic mean	Mean according to distribution	Background (world mean)[a]	Background (São Paulo State, Brazil)[e]	Background (Florida Urban Soil, USA)[f]
Cd	non-normal	0.052–0.4	0.19	0.18[c]	0.41	0.1	0.14
Cr	normal	13.1–79.7	45.1	45.1[b]	59.5	36	12.1
Cu	non-normal	3.36–145	58.6	51.9[c]	38.9	nd	6.76
Fe	normal	17 480–54 500	37 060	37 060[b]	nd	nd	nd
Ni	normal	7.47–60.3	33.6	33.6[b]	29	36	2.87
Pb	log-normal	8.52–52.2	24.7	23.4[d]	27	10	19
Zn	normal	16.1–151	78.4	78.4[b]	70	22	35.5

[a]Kabata-Pendias and Pendias (2011); [b]arithmetic mean; [c]median; [d]geometric mean; [e]Da Silva et al. (2020); [f]Nogueira et al. (2018); nd – not determined

Based on the frequency distribution results, the samples showing anomalous values require further investigations on their source, bioavailability and potential risks for human health (Alfaro et al. 2015). The descriptive statistics for the TE concentrations in the soils, including the outliers, are shown in Table 1. After excluding the outliers from the population, a characterisation of the type of distribution of the population (normal, log-normal and non-normal) was carried out for each element before calculating the ABC value. The statistical analysis showed that the concentrations of Cr, Fe, Ni and Zn had normal distributions, whereas the Cd, Cu and Pb concentrations did not. Therefore, the arithmetic mean was used for Cr, Fe, Ni and Zn; the geometric mean for Pb, which had a log-normal distribution; and the median for Cd and Cu, which had a non-normal distribution for both the untransformed and log-transformed concentrations. The ABC values determined in our study (Table 2) were lower or close to the world mean soil background values reported by Kabata-Pendias and Pendias (2011). The mean ABCs of the TMs in the soils were in the following order (in mg/kg): Zn 78.4 > Cu 51.9 > Cr 45.1 > Ni 33.6 > Pb 23.4 >> Cd 0.18.

Quality reference values. Different statistical methods were used to determine the QRVs (Table 3) for the TE concentrations in the soils. In the first method, the reference value was calculated from the ABC value using the statistical approach of Ballesta et al. (2010). In this approach, if the population follows a normal distribution, to determine the reference value, it is recommended to determine the QRV using the Mean + 2SD, which will, by definition, include 95% of the samples (Matschullat et al. 2000; Reimann et al. 2005). When the distribution is log-normal, the arithmetic mean is replaced by the Geometric Mean + 2SD. For those elements where the distribution of the element concentration data is not normal or log-normal, the median + 2 MAD was applied (Reimann et al. 2005, 2018), where the median is defined for sample X_1……, X_n as median$_i$ (X_i), and the MAD as:

$$\mathrm{MAD}_i(x_i) = \mathrm{median}_j(|x_i - \mathrm{median}_j(x_j)|) \qquad (1)$$

Table 3. Reference concentration values for the trace metals and Fe (mg/kg) in the soils of the eastern Mitidja plain

Element	Distribution	Mean + 2 SD	According to distribution	P90[a] this study	P90[e]
Cd	non-normal	0.33	0.26[b]	0.29	0.9
Cr	normal	71	71[d]	61.7	35.5
Cu	non-normal	123	99.3[b]	104	18.2
Fe	normal	51 970	51 970[d]	47 420	9 000
Ni	normal	53.8	53.8[d]	45.6	6.1
Pb	log-normal	41.5	40.2[c]	36.6	7.5
Zn	normal	130	130[d]	111	21

[a]ninetieth percentile; [b]median + 2 MAD; [c]GM+2 SD; [d]mean+2 SD; [e]Fernandes et al. (2018); SD – standard deviation

Table 4. Linear regression equations between the trace metals concentrations and Fe (mg/kg) and the selected soil components

Element	Clay (A)		Organic matter (% OM)		Calcium carbonate (% C)	
	equation	*r*	equation	*r*	equation	*r*
Cd	–	–	0.141 + 0.0234 OM	0.24^{**}	0.1728 + 0.00199 C	0.27^{**}
Cr	24.63 + 0.5422 A	0.55^{**}	37.80 + 3.419 OM	0.18^{*}	48.42 – 0.3832 C	-0.28^{**}
Cu	–	–	–	–	–	–
Fe	31 245 + 151.8 A	0.25^{**}	–	–	38 534 – 162.6 C	-0.2^{**}
Ni	22.96 + 0.2803 A	0.35^{**}	27.96 + 2.595 OM	0.19^{**}	–	–
Pb	18.55 + 0.1620 A	0.25^{**}	–	–	26.23 – 0.1725 C	-0.18^{*}
Zn	47.15 + 0.8224 A	0.41^{**}	64.79 + 6.463 OM	0.16^{*}	–	–

$^{*}P < 0.05$; $^{**}P \le 0.01$

In addition, the 90th percentile (Table 3) was also calculated to determine the upper limits of the ABC and/or to identify extreme high values (Baize et al. 2006; Zhao et al. 2007; Almeida et al. 2016). In Bulgarian soils, Yotova et al. (2018), using the 90th percentile, established QRVs (in mg/kg) for Cd (0.37) and Cr (90.3), which are higher than those obtained in the Mitidja plain. The QRVs for Cr, Cu, Fe, Ni, Pb and Zn obtained for this study were higher than those reported by Fernandes et al. (2018) for soils from the Eastern Amazon, Brazil.

In the second method, the QRVs were based on the correlations between the TM concentrations and soil parameters, such as the clay, organic matter, and calcium carbonate concentrations (Vegter 1995; Perez et al. 2000; Vazquez et al. 2000; Castillo Carrion et al. 2002). The regression models that described the TM concentrations as a function of clay, organic matter, and carbonate calcium concentrations are summarised in Table 4. Highly significant positive correlations were observed between the clay concentration and the Cr, Fe, Ni, Pb and Zn concentrations ($P \le 0.01$, $0.25 \le r \le 0.55$). The organic matter concentration had a very highly significant positive correlation ($P \le 0.01$) with Cd and Ni, and highly significant with Cr and Zn ($P < 0.05$). The calcium carbonate concentration was negatively and significantly correlated with Cr and Fe ($P \le 0.01$), negatively and significantly with Pb ($P < 0.05$), but positively and very significantly with Cd ($P < 0.01$). For a standard soil from the Netherlands, Vegter (1995) established reference values based on the regression equations between the TM and the clay and organic matter concentrations. In Mediterranean climates, other soil components, such as calcium carbonates are also important (Vazquez et al. 2000).

The concentration of the soil OM ranged from 0.54 to 5.99% (mean 2.15%) and was considered typical for the region. The clay contents of the soil were considerable ranging from 10.5 to 73% (mean 37.7%). The soil $CaCO_3$ ranged from 0 to 40.41% (mean 8.7%). From the linear regression parameters

Table 5. Linear regression equations and reference values (RV, mg/kg) for the trace element in the soils of the eastern Mitidja plain

Element	Equation	RV1^{a}	RV2^{b}	Proposed RV^{c}
Cd	0.18 + 0.011 OM + 0.000995 C	0.21	0.26	0.24
Cr	45.05 + 0.18 A + 1.14 OM – 0.13 C	53.2	71	62.1
Cu	–	–	99.3	99.3
Fe	37 060.1 + 75.9 A – 81.3 C	39 210	51 969	45 590
Ni	33.57 + 0.14 A + 1.3 OM	41.6	53.8	47.7
Pb	23.41 + 0.08 A – 0.09 C	25.7	40.2	33
Zn	78.42 + 0.41 A+3.23 OM	101	130	115

^{a}Reference values calculated from the regression equations; ^{b}reference values estimated according to the background distribution; ^{c}mean of RV1 and RV2

Table 6. Proposed reference values for the trace metals in the soils of the eastern Mitidja plain and a comparison with the reference values from other regions of the world (mg/kg)

Element	Cd	Cr	Cu	Fe	Ni	Pb	Zn
This study	0.24	62.1	99.3	45 590	47.7	33	115
Holland (Vegter 1995)	0.8	100	36	nd	35	85	140
Spain (Tobias et al. 1997)	2	103	206	nd	94	92	239
Spain (Castillo Carrion et al. 2002)	0.5	132	65	nd	58	69	132
Spain (Perez et al. 2002)	0.3	73	41	nd	43	30	192
Spain (Bech et al. 2005)	nd	120.2	111.6	nd	119	218	327
Cuba (Alfaro et al. 2015)	0.6	153	83	54 055	170	50	86
Australia (Reimann & de Caritat 2017)	0.5	149	109	nd	121	53	254
Europe (Reimann et al. 2018)	1.1	157	118	nd	216	87	239
Brazil (Nogueira et al. 2018)	0.2	63	nd	nd	57	15	38
Bulgaria (Yotova et al. 2018)	0.67	182	71.4	nd	71.9	46.3	112

nd – not determined

found between the TE concentrations and the OM, clay and calcium carbonate, the QRVs (Table 5, RV2) were calculated according to Equation (2) (Vazquez et al. 2000; Castillo Carrion et al. 2002), where *NF* is the ambient background value calculated from the arithmetic mean, median or geometric mean according to the distribution of the population; *A*, *B* and *C* correspond to the mean values of the considered soil components; and *a*, *b* and *c* are the slopes of the regression lines divided by the contribution factor according to the number of variables considered in the regression.

$$\mathrm{VR} = NF + aA + bB + cC \ldots \qquad (2)$$

Substituting the dependent variable with the mean values of these components in the study area (37.7%, 2.15% and 8.75% for clay, organic matter and calcium carbonate, respectively) yields the reference values for the different TMs in the eastern Mitidja plain as shown in Table 5, see RV1 (Vegter 1995; Castillo Carrion et al. 2002; De Temmerman et al. 2003).

Our proposed QRVs for the soils of eastern Mitidja were calculated as the mean of the reference values of both methods (Vazquez et al. 2000; Castillo Carrion et al. 2002), with the exception of Cu, where the reference value was calculated according to the equation median + 2 MAD (Table 5). The proposed QRVs are similar to those obtained with the 90th percentile method. The results of this study are consistent with those obtained by Baize et al. (2006) and Zhao et al. (2007) who proposed to use the 90th percentile as an alternative method for calculating the upper limit of the ambient background concentration of the TMs in soils. On the other hand, a comparison of the TM reference values obtained in this study with those recorded in other regions of the world are presented in Table 6. The QRVs for Cd, Cr, Ni and Pb concentrations were similar to those reported in the Murcia region of Spain by Perez et al. (2002) with the exception of Zn and Cu. In comparison to those of the eastern Mitidja plain, Tobias et al. (1997) and Bech et al. (2005) reported higher reference values for the soils of the Catalonia region in Spain. The QRVs of the TMs found for the Mitidja plain may be different from other regions of the world due to the different climatic, pedogenic processes and land use conditions which affect the ABCs (Nogueira et al. 2018).

CONCLUSION

Data from the analysis of 180 representative topsoil samples from across the Mitidja plain in Algeria were statistically analysed to determine the QRV concentrations for the *aqua regia* extractable Cd, Cr, Cu, Fe, Ni, Pb and Zn. Two methods were applied. The first used the ambient concentrations of the TEs alone applying statistical approaches including box and whisker plots to identify outliers. The second considered the linear correlation with the clay, OM and calcium carbonate concentrations. The proposed QRVs for the TMs taken as an average of the two methods are 0.24 Cd, 62 Cr, 99.3 Cu, 47.7 Ni, 33 Pb and for 115 Zn mg/kg. These reference values can be used to identify areas that may require follow-up surveys or identify priority sites for decision making and protect soil quality in the productive soils of the eastern Mitidja plain of Algeria.

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