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Concentrations and sources of Cd, Cr, Cu, Fe, Ni, Pb and Zn in soil of the Mitidja plain, Algeria

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ABSTRACT

In the last few decades, the Mitidja plain has undergone economic development which may have altered the concentrations of some trace metals in its soils. Therefore, this study was aimed at investigating the concentrations and sources of Cd, Cr, Cu, Fe, Ni, Pb and Zn in 180 composite topsoil samples using a combination of environmental quality indicators and multivariate statistical approaches with a geographic information system (GIS). Based on spatial distribution maps, various hot-spots have been identified. Enrichment factors (EFs) indicated that Cd, Cu, Pb and Zn were from anthropogenic sources, while Ni and Cr were controlled mainly by natural lithogenic source. Multivariate statistical analyses were in agreement, except for Cu which was classified as coming from both anthropogenic and lithogenic sources.

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Environmental quality indicators; Mitidja plain; multivariate statistics; topsoil; trace metals

1. Introduction

The accumulation of hazardous metals in agricultural soils is an important issue in Algeria, due to rapid economic development and industrialization (Gherbi 2012). Trace metals in soil are derived from lithogenic and anthropogenic sources. The concentration and distribution of trace elements in soil depend on many factors (Bech et al. 2008; Yan et al. 2016) but primarily on the composition of the geological parent material, which represent the geochemical background value (GBV) (Reimann and Garrett 2005). In environmental geochemistry, the mean concentrations of trace metals in the earth's crust, termed the GBV, are commonly used

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for the assessment of soil contamination (Lienard, Brostaux, and Colinet 2014; Wu et al. 2014). In addition, anthropogenic input of trace metals to soils is associated with numerous activities including the discharge of urban and industrial waste, traffic emission, atmospheric deposition, mining and smelting operations, the abusive use of agrochemicals, and other human activities (Huang et al. 2013; Lienard, Brostaux, and Colinet 2014; Zhao et al. 2015). The presence of trace metals at concentrations above the maximum allowable concentration can affect the fertility of soil and poses a toxicity risk to plants, animals and humans (McGrath and Zhao 2015). Understanding the sources of trace metals is important for environmental management and decision-making and also crucial for environmental risk assessment to distinguish between the natural and anthropogenic trace metal contents in soils (Baize 2010). In this respect, two categories of methods, quantitative and qualitative, are often cited in the literature. Quantitative methods or environmental quality indicators, also termed geochemical approaches, through the application of the enrichment factor (EF), the geochemical index and the contamination factor are widely used to assess the extent of contamination by comparing the current concentration of the metal with the GBV (Sulaiman, Mustaffa, and Khazaai 2016; Tume et al. 2018). Qualitative methods or multivariate statistical approaches such us correlation analysis and principal component analysis (PCA) are widely used to identify pollution sources and distinguishing between natural and anthropogenic contribution (Zhang et al. 2009; Huang et al. 2013; Lienard, Brostaux, and Colinet 2014). The combination of multivariate statistical geochemical data with a geographic information system (GIS) allows the examination of the spatial extent of trace metal contamination and provides evidence of their geogenic or anthropogenic origin (Kelepertsis, Argyraki, and Alexakis 2006) and can give more comprehensive and better assessment on potential sources of trace metals.

The Mitidja plain is an important agricultural production area in Algeria. In the last few decades, there has been economic development including the production of plastics, hydrocarbons, petrochemicals, steel, cement, building materials, pharmaceuticals and electronic components, which may have altered the concentration of trace metals in soil. Agricultural practices used in these soils, such as the use of agrochemical products and wastewater for soil irrigation could also result in contamination (Khouli and Djabri 2011; Lebik and Ait-amar 2013). Previous trace metal studies in the Mitidja plain have referred to a small local scale (Laribi and Saidani 2016) and to sediment (Laribi et al. 2017) and no published data are available at a regional scale.

The aims of the research reported here were: (1) to undertake a study of trace metal and Fe concentrations and their distribution in soils of the Mitidja plain, (2) to assess the concentration of trace metal contamination using environmental quality indicators (GBV and EF) and (3) to assess the potential sources of trace metals using multivariate statistical approaches. The results of this study are expected to be important not only for knowledge of the trace metal status of the soils of the Mitidja plain but also for the development of future strategies for soil protection and territorial decision-making (Hou et al. 2017).

2. Materials and methods

2.1. Study area

The Mitidja plain covers an area of 1400 km^2. Our study concerned the eastern part with an area of 665 km^2. The study site centered around 3° 10′ 25.58″ E and 36° 39′ 47.73″ N is limited geographically by the Mediterranean Sea to the north, the Blidean Atlas to the south, the Harrach River to the west and Reghaia River to the east. The area has a sub-humid Mediterranean climate, a mean annual temperature of 18.1 °C and a mean annual rainfall of 600 mm. The main agriculture uses of the plain are the production of vegetable crops, arboriculture and annual crops, which occupy 50% of the area (Khouli and Djabri 2011). The plain has a geological formation that has gone through folding and backfilling. The main geological formations of the plain are of active sedimentation whose alluvial materials come from the Piememont of the Blidean Atlas, which is an intracontinental chain mainly composed of thick calcareous marl series and continuous subsidence areas. These materials, which date from the Neogene and Quaternary periods rest on metamorphic crystallophyllian Paleozoic basement (mostly gneiss). The facies dating from the recent and present quaternary deposits consists of marine and lacustrine deposits, recent alluvium, gravel and silt, consolidated dunes, sandstone, clayey sands and ancient quaternary alluvium. The main soils of the region are weakly developed soils, calcimagnesic soils, iron sesquioxides soils, vertisols and raw mineral soils (Ecrement 1971).

2.2. Soil sampling and preparation

A total of 180 composite topsoil samples (0–20 cm deep) were collected in a randomized stratified pattern (Figure 1), equivalent to one composite soil sample per 2×2 km grid. Each composite sample (around 2.5 kg) was a mixture of five subsamples taken from the corners and center of a

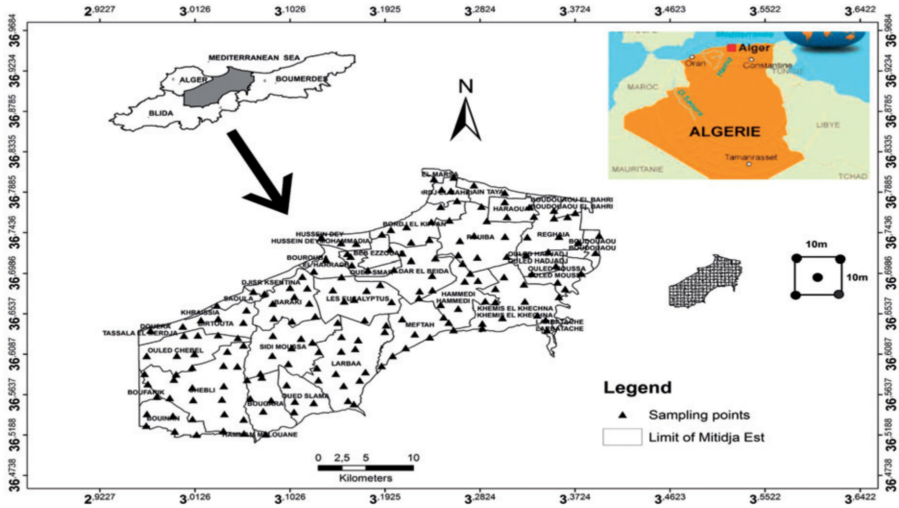

Figure 1. Location of the Mitidja plain and distribution of soil sampling sites.

10 × 10 m square using a hand auger. Sampling locations were recorded with a portable global positioning system device (model Etrex 10, Garmin Europe Ltd., Southampton, UK). The samples were air-dried at approximately 20 °C for 7 d and passed through a polyethylene 2-mm sieve with mm openings to remove stones, coarse materials and other debris.

2.3. Analytical procedures

For trace metal and Fe analysis, a representative sample of each soil, obtained by coning and quartering, was milled using an agate ball mill (model MM200, Retsch GmbH, Haan, Germany). The milled soil (2 g) was refluxed with 28 mL of aqua regia (prepared from concentrated HCl and HNO_3 from Fisher Scientific, Loughborough, UK) for 2 h using water-cooled condensers (ISO (International Standards Organization) 1995). The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the extracts were determined by inductively coupled plasma-mass spectrometry (ICP-MS) (model G3281A, 7700 series, Agilent Technologies, Santa Clara, CA), whereas Fe was determined by inductively coupled plasma optical spectrometry (ICP-OES) (model Optima 5300 DV, Perkin Elmer, Shelton, CT). Results were expressed as mg kg^{-1} dry weight on the basis of soil dried at 105 °C. Each batch of aqua regia digests comprised of 17 soil samples, two blanks and an in-house prepared quality assurance and quality control soil known as the analytical test soil. The data for the analytical test soil sample were previously validated against certified sludge amended soil (BCR, CRM 143, Institute for Reference Materials and Measurements, Geel, Belgium) for which recoveries between 88 and 98% for the elements studied have been found. The concentrations of aqua regia extractable elements found in the analytical test soil sample measured in successive batches ($n = 13$) showed satisfactory variations between batches although Zn concentration had slightly elevated values in two batches. The coefficients of variation were Cd 9.4, Cr 6.9, Cu 4.9, Fe 7.6, Ni 4.4, Pb 7.0 and Zn 9.2%. The limits of detection (LOD) of the ICP analyses for individual elements in solution were Cd 0.00003, Cr 0.003, Cu 0.0006, Fe 0.002, Ni 0.0005, Pb 0.002 and Zn 0.003 mg L^{-1}. Accounting for the 50-times dilution of the soil in the extract analyzed by ICP, these solutions LOD values are equivalent to Cd 0.0015, Cr 0.15, Cu 0.03, Fe 0.1, Ni 0.025, Pb 0.1 and Zn 0.15 mg kg^{-1} in soil.

2.4. Statistical analysis

Statistical analyses were performed using Minitab version 17 (Minitab Inc., State College, PA, USA) (Minitab Inc, 2010) and Past version 3 software (Oyvind Hammer, University of Oslo, Norway) (Hammer, Harper, and Ryan 2001). Basic statistical parameters for raw data were calculated and the Kolmogorov–Smirnov (K–S) test applied to test the normality of the data, which were log-transformed prior to multivariate analysis to reduce the influence of extreme values (Reimann, Filzmoser, and Garrett 2005; Kelepertzis 2014). PCA was used to identify geochemical associations between trace metals and to distinguish between natural and anthropogenic inputs (Prasse et al. 2012; Huang et al. 2013). Principal components analysis was conducted using the eigenvalue >1 (Kaiser Criterion) after a varimax rotation. The interpretation of PCA was performed in accordance with the hypothetical sources of trace metals (lithogenic, anthropogenic or mixed). Linear correlations between the element concentrations were assessed using the Pearson method on the log transformed data.

2.5. Spatial analysis based on GIS

The geochemical maps showing the overall spatial distribution of trace metals were elaborated using the Spatial Analyst tool for ArcMap (ArcGIS version 10.1, Esri Inc., Redlands, CA, USA). The inverse distance weighted interpolation method was performed to predict local features of soil contamination, especially local hot-spots (Kelepertzis 2014; Wu et al. 2014). Based on the quantile method, eight classes of intervals were defined.

Table 1. Statistical summary of aqua regia soluble metal concentrations in soils from the Mitidja plain ($n = 180$).

Variable	Minimum	Maximum	Mean mg kg^{-1}	Median	25th Percentile	75th Percentile	SD	CV (%)	Skewness	Kurtosis	K–S test
Cd	0.05	1.07	0.22	0.19	0.15	0.25	0.14	64	3.00	11.91	0.183
Cr	13.1	148	47	45	37.4	55.7	18	38	2.14	9.67	0.094
Cu	3.36	310	63	55	31.9	80.5	41	65	1.94	7.49	0.105
Ni	5.40	71.9	34	35	26.7	40.2	11	34	0.09	0.70	0.060*
Pb	8.52	393	35	24	19.2	32.4	43	120	5.28	33.79	0.324
Zn	16.1	466	92	82	64	99.4	56	61	3.21	14.71	0.207
Fe	7934	61690	37000	37190	32272	42217	8800	24	−0.56	1.16	0.076*

SD: standard deviation; CV: coefficient of variation.
*p value $> .15$.

Table 2. Comparison of the mean concentration (mg kg^{-1}) of aqua regia soluble trace metals and Fe in soils from the Mitidja plain with other regions of the world and some published guidelines.

Localization	Cd	Cr	Cu	Fe	Ni	Pb	Zn	References
This study. Mitidja plain	0.22	47.0	63	37000	34.0	35.2	92.1	–
Algeria (Annaba)	0.44	30.9	39	24270	NA	53.1	67.5	Maas et al. (2010)
Algeria (Rhumel wadi)	1.1	63	20	NA	26	31	98	El-Hadef El-Okki et al. (2016)
Spain (Catalonia)	0.35	24.6	24	21278	22.8	23.3	76	Tume et al. (2011)
Greece (Argolida basin)	0.54	83.1	74.7	26500	147	19.7	74.9	Kelepertzis (2014)
Scotland	NA	44.7	9.4	25500	20.5	31.8	53.8	Paterson, Campbell, and Shand (2011)
England & Wales	0.52	68	24	29000	23	81	91	Rawlins et al. (2012)
France	0.39	41.6	17.4	NA	24.1	30.4	68	Baize, Deslais, and Saby (2007)
World soils	0.41	59.5	38.9	NA	29	27	70	Kabata-Pendias (2011)
Canadian guidelines	1.4	64	63	NA	50	70	200	CCME (2007)[a]
European guidelines	1.5	100	100	NA	70	100	200	Gawlik and Bidoglio (2006)[b]
Earth́s crust	0.1	83	25	35000	44	17	71	McLennan (2001)

NA: not available
[a]Canadian soil quality guidelines for the protection of environment and human health;
[b]threshold or guideline values in European soil and sewages sludges (pH > 7).

3. Results and discussion

3.1. Trace metal concentrations

The magnitude of the mean concentration values of the metal concentrations (Table 1) indicated the following order: Fe $\ggg$ Zn > Cu > Cr > Pb > Ni $\gg$ Cd. Based on these results all the metals, except Cr and Ni, exceeded their corresponding GBV in the earth́s crust (McLennan 2001), but were lower than the European guideline values (Table 2). Maximum concentration of Cd, Cr, Cu, Pb and Zn were about 10.7, 1.78, 12.4, 23.1 and 6.5 fold higher than their corresponding GBV, respectively, which suggest a possible risk to the ecosystem in these areas.

3.2. Contamination assessment based on EF

The EF approach is widely used to assess the magnitude of soil contamination and to identify the potential sources as originating from either natural or anthropogenic sources (Sulaiman, Mustaffa, and Khazaai 2016). Basically, as the EF value increases, the contribution from anthropogenic sources also increases (Ali and Malik 2011). The EF index (Equation 1) is calculated as follows, where $(C_x/C_{Fe})_{soil}$ is the ratio of the concentration of a test element to that of Fe in soil sample and $(C_x/C_{Fe})_{reference}$ is the same ratio of the concentration with respect to reference material (earth crust).

$$EF = \frac{(C_x/C_{Fe})\ \text{soil}}{(C_x/C_{Fe})\ \text{reference}} \tag{1}$$

In the absence of data for the concentration of metals in deeper soil layers at the sampling points and because the bedrock in the area is terrigenous sedimentary, it was not possible to calculate a local GBV, and the assessment of EF in the surface layers was made using GBV (McLennan 2001) (0.1 for Cd, 83 for Cr, 25 for Cu, 35000 for Fe, 44 for Ni, 17 for Pb and 71 for Zn mg kg^{-1}). Iron was used as a reference element of normalization because of its high abundance in the earth's crust (Krami et al. 2013) and low occurrence variability.

The EF for the elements was in the following ranges: Cd 0.63–11.55, Cr 0.14–2.05, Cu 0.35–12.80, Ni 0.26–1.68, Pb 0.58–25.45 and Zn 0.44–7.54. According to Hussain et al. (2015) and Sun et al. (2016) the mean EF of Cd, Cu and Pb was in the range of 2–5, indicating moderate enrichment; Zn was in the range of 1–2, suggesting minimal enrichment, while the mean EF of Ni and Cr was ≤ 1, suggesting that the metal is derived from crustal materials or natural processes. These results suggested that Cd, Cu, Pb and Zn concentrations have been enhanced by anthropogenic sources, while Ni and Cr were predominately from natural sources. These observations are consistent with data by Wu et al. (2014) who reported that the area of Jiangxi, China to be similarly enriched with Cd, Cu, Pb and Zn. The distribution of the mean concentration values of the trace metals in the soils from the Mitidja plain indicate the following order of EF:

$$\mathrm{Cu}\ (2.47) > \mathrm{Cd}\ (2.22) > \mathrm{Pb}\ (2.08) > \mathrm{Zn}\ (1.26) > \mathrm{Ni}\ (0.74) > \mathrm{Cr}\ (0.56).$$

Based on the results of the coefficient of variation (CV), Han et al. (2006) and Zhang et al. (2009) reported that high concentrations accompanied by high CVs suggest anthropogenic sources for the trace metals; in contrast, the element dominated by a natural source can be expected to have a low CV. The CV can be classified into three categories (Cui et al. 2011): $CV < 50\%$, weak variation; $50\% < CV < 100\%$, moderate variation; $CV > 100\%$, strong variation. The CV of the metal concentrations in the studied area ranged from 24.2% for Fe to 122% for Pb. According to the classification, the metals studied could be divided into three groups: Pb ($CV > 100$), Zn, Cu and Cd ($50 < CV < 100$) and Fe, Ni, Cr ($CV < 50$). Accordingly, Pb, Zn, Cd and Cu tend to be affected by anthropogenic activities, while Fe, Ni and Cr may more likely be associated with natural sources.

3.2. Spatial distribution

The spatial distribution patterns of the trace metals and Fe in soils of the Mitidja plain (Figure 2) were used for identifying the enriched areas. Based on the geochemical maps of trace metals, various hot-spots were identified. The spatial distribution pattern of Cd showed that a hot-spot area is located in the north part of the Mitidja plain (Figure 2(a)).

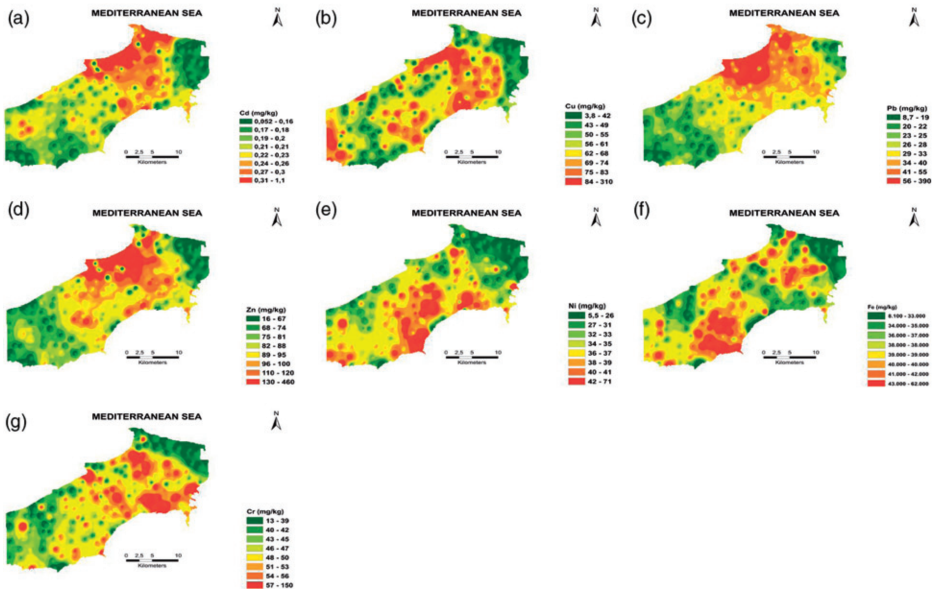

Figure 2. Spatial distribution maps of aqua regia soluble a Cd, b Cu, c Pb, d Zn, e Ni, f Fe and g Cr in soils from the Mitidja plain.

Copper distribution mapping revealed some peak values with high variability in agricultural soils in both rural and urban areas (Figure 2(b)). The highest concentration of Cu (310 mg kg^{-1}) was found at the southern part of the plain in the junction between Meftah and Hammedi districts, and could be attributed to the massive use of fertilizers and pesticides in the area (Khouli and Djabri 2011; Lebik and Ait-amar 2013). However, some industrial activities observed in the Meftah districts, such as the cement production could also contribute to the concentration of Cu in soil (Laribi and Saidani 2016).

The distributions of Pb and Zn concentrations showed similar trends to that of Cd, with high concentrations in areas surrounding the industrial and urban areas of El Harrach, Dar El Baida and part of Rouiba districts (Figure 2(c,d)). The high concentrations of Pb in soils of Annaba city of Algeria have been associated with the dense traffic and leaded gasoline still widely used in the country (Maas et al. 2010). Nickel and Fe concentrations showed a similar distribution pattern over a large area (Figure 2(e,f)). The area to the east of the plain revealed the lowest concentrations of these metals. With regard to Cr (Figure 2(g)), hot-spots are mainly distributed between Bordj El Kiffan, Dar El Beida and Rouiba districts, and between Khemis El Khechna and Hammedi districts (Figure 1). The highest concentration of Cr appeared in the center of El Harrach district. As observed for Ni and Fe, the lowest concentrations of Cr were observed to the east of the plain.

Table 3. Pearson correlation coefficients between aqua regia soluble metal concentrations in soils from the Mitidja plain.

	Cd	Cu	Ni	Pb	Zn	Cr	Fe
Cd	1						
Cu	0.36**	1					
Ni	0.19*	0.45**	1				
Pb	0.66**	0.18*	0.04^{ns}	1			
Zn	0.75**	0.37**	0.48**	0.64**	1		
Cr	0.19*	0.35**	0.80**	0.15*	0.48**	1	
Fe	0.31**	0.32**	0.72**	0.22**	0.53**	0.57**	1

^{ns}not significant
$^{*}p < .05$; $^{**}p < .01$.

3.3. Assessment of trace metal sources

The Pearson correlation coefficients between the metal concentrations (Table 3) provide information on trace metals sources and pathways. A strong, significant positive correlation at $p < .01$ was found between Ni and Fe ($r = 0.72$), and a significant, moderate correlation between Cr and Fe ($r = 0.57$), Zn and Fe ($r = 0.53$), and a significant, low correlation between Cd and Fe ($r = 0.31$), Cu and Fe ($r = 0.32$), and Pb and Fe ($r = 0.22$) at $p < .01$, suggesting that their distributions were controlled in part by the same factor. Tume et al. (2011) found a good correlation between the same trace metals (Cd, Ni, Zn, Pb, Cu and Cr) and Fe concentrations in surface soils of Catalonia and suggested that the trace metals are associated with Fe-oxides.

The strong, significant, positive correlation between the concentrations of Ni and Cr ($r = 0.80$; $p < .01$) reflect their natural pedogenic characteristic and that they are associated mostly with a single source. Lead showed no correlation with Ni, indicating different sources for Pb and Ni. The correlation observed between Cr, Ni and Fe could be associated with their similar geochemical behavior as they form the group of siderophile elements. This result is consistent with previously published data by Sipos et al. (2014) for soils in Hungary, which showed a lithogenic control over the distributions of Cr and Ni in soils. On the other hand, a low, significant correlation was found between Cd and Cr ($r = 0.19$) and Cd and Ni ($r = 0.19$) at the $p > .05$, suggesting that the concentrations of Cd in some sampling points came from the different sources than Ni and Cr. In contrast, Cd had a strong positive significant correlation with Pb ($r = 0.66$; $p < .01$) and Zn concentrations (0.75; $p < 0.01$). These results could be attributed to the common influential factors or sources for the three metals as they form the group of chalcophile elements. These findings are in accordance with those found by Zhang et al. (2009) who reported that Cd presented a strong correlation with Pb and Zn in soils of Fuyang County.

Element	Component matrix			Rotated component matrix		
	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3
Cd	0.681	−0.609	−0.080	0.094	−0.879	−0.244
Cu	0.589	0.099	−0.791	0.244	−0.171	−0.945
Ni	0.765	0.567	0.053	0.920	−0.028	−0.250
Pb	0.550	−0.699	0.151	0.015	−0.902	0.024
Zn	0.863	−0.322	0.123	0.465	−0.793	−0.137
Cr	0.735	0.470	0.151	0.869	−0.099	−0.139
Fe	0.761	0.315	0.236	0.818	−0.247	−0.054

[a]Extraction method: principal component analysis; Rotation method: varimax

The rotated factor loadings, communalities and the proportion of the variance explained, obtained by PCA with varimax for the studied metal concentrations are presented in Table 4; loadings having a value >0.70 are marked in bold. The results indicate that three components explain 84.7% of the total variance of the parameters. The first principal component (PC1) explained 36.5% of the total variance and has positive loadings on Ni (0.92), Cr (0.86) and Fe (0.81), indicating that the distribution and concentration of Ni, Cr and Fe in the studied area is probably dependent on lithogenic and pedogenic control. Chromium is defined as a lithophile element and Ni and Fe as siderophile elements. A high strong positive correlation was found between Ni-Cr and Ni-Fe ($r > 0.7$; $p < .01$) and this association is often used to distinguish natural concentrations of trace elements from anthropogenic ones. Overall, the variability of Cr, Fe and Ni in the topsoil of the Mitidja plain appeared to be controlled mainly by the soil parent materials. These results are in agreement with the previous results of the EF and those reported by Huang et al. (2013) and Kelepertzis (2014) and reinforce their pedogenic origin. Relatively lower loadings of Cd, Cu, Pb and Zn in the PC1 reflect that they might be the result of other sources. The second principal component (PC2) included Pb, Cd and Zn, and explained an additional 33.1% of the total variance and negative loadings on Cd (−0.87), Pb (−0.90) and Zn (−0.79), suggesting that the status of these metals was affected by the anthropogenic activities from the industrialization and urbanization of the Mitidja plain. The mean concentrations of Cd, Pb and Zn were higher than their corresponding GBV in the earth's crust and they had high coefficients of variation ($CV > 60\%$). In addition, this group of trace metals showed moderate contamination in soils of the Mitidja plain. The atmospheric deposition of particles from industrial and vehicular emissions could be the sources of these trace metals. The third principal component (PC3) explained an additional 15% of the total variance and was dominated by Cu (−0.94), and could be related to agriculture inputs. The EF of Cu ranged from 0.35 to 12.8 with a mean of 2.47 and was classified as moderately enriched element in the soil studied. The high CV of Cu ($CV = 65\%$) indicated that the distribution of Cu in soils was not homogenous (Figure 2(b)). These results suggested that in addition to natural sources, anthropogenic activities contributed to the accumulation of Cu in surface soils. The anthropogenic sources of Cu concentration in the study area could be due to the massive use of fertilizers and pesticides (Khouli and Djabri 2011; Lebik and Ait-amar 2013). El-Hadef El-Okki et al. (2016) reported that Cd, Cu, Pb and Zn are commonly found to be anthropogenically enriched in the soils of Rhumel wadi in Algeria.

4. Conclusion

The concentrations and potential sources of Cd, Cu, Cr, Fe, Ni, Pb and Zn in 180 composite soil samples collected from the Mitidja plain have been studied. The degree of contamination and sources of trace metals in soils of the Mitidja plain were assessed using EF in combination with multivariate statistics and GIS. The concentration of selected trace metals and Fe showed the following order: $Fe \ggg Zn > Cu > Cr > Pb > Ni \gg Cd$. The mean concentrations of Cd, Cu, Pb and Zn, except for Cr and Ni, in the top soils were higher than the GBV, suggesting human influence. Various hot-spots were observed within the studied area. Among the studied trace metals, Cr and Ni were depleted, while Cd, Cu, Pb and Zn were enriched in the study area. Based on multivariate statistical analyses and spatial distribution patterns of trace elements, the results indicated that Cd, Pb and Zn in topsoil were affected mainly by anthropogenic activities, whereas Cr, Ni and Fe were controlled by natural lithogenic sources. Copper was impacted by both lithogenic and anthropogenic components. Given the potential human health risk related to anthropogenic trace metals accumulation, strategies are needed to achieve better environmental soil quality and safe agricultural production.

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Disclosure statement

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References

Ali, S. M., and R. N. Malik. 2011. "Spatial Distribution of Metals in Top Soils of Islamabad City, Pakistan." *Environmental Monitoring and Assessment* 172 (1–4): 1–16. doi:10.1007/s10661-010-1314-x.

Baize, D. 2010. "Concentrations of Trace Elements in Soils: The Three Keys." Paper presented at the 19th congress of soil science, soil solutions for a changing world. Brisbane, Australia: International Union of Soil Sciences (IUSS).

Baize, D., W. Deslais, and N. Saby. 2007. *Teneurs en Huit Éléments en Traces (Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn) Dans Les Sols Agricoles en France. Résultats D'une Collecte de Données à L'échelon National [Content of Eight Trace Metals (Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn) in French Arable Topsoils. Results of Data Collection at the National Level].* Angers, France: ADEME.

Bech, J., P. Tume, M. Sokolovska, F. Reverter, P. Sanchez, L. Longan, J. Bech, A. Puente, and T. Oliver. 2008. "Pedogeochemical Mapping of Chromium, Nickel and Copper in Soils of the Barcelona Province (Catalonia, Spain): Relationship with Soil Physico-Chemical Characteristics." *Journal of Geochemical Exploration* 96 (2–3): 106–116. doi:10.1016/j.gexplo.2007.03.005.

CCME (Canadian Council of Ministers of the Environment). 2007. "Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health: Summary of A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines." Chapter 7. *Canadian Environmental Quality Guidelines*. Winnipeg, Canada: Canadian Council of Ministers of the Environment.

Cui, Z. A., S. Y. Qiao, Z. Y. Bao, and N. Y. Wu. 2011. "Contamination and Distribution of Heavy Metals in Urban and Suburban Soils in Zhangzhou City, Fujian, China." *Environmental Earth Sciences* 64 (6): 1607–1615. doi:10.1007/s12665-011-1179-5.

Ecrement, Y. 1971. "Etude Agropédologique de la Plaine de la Mitidja [Agropedological Study of the Mitidja Plain]. ANRH." *Echelle* 1/50.000e.

El-Hadef El-Okki, M., L. Sahli, A. Bentellis, R. Azzoug, G. D. Laing, and W. Rached. 2016. "Assessment of Metal Contamination in Soil Banks of the Rhumel Wadi (Northeast Algeria)." *Toxicological and Environmental Chemistry* 98 (1): 53–63. doi:10.1080/02772248.2015.1101115.

Gawlik, B. M., and G. Bidoglio. 2006. *Background Values in European Soils and Sewage Sludges*. 33. Brussels, Belgium: European Commission.

Gherbi, M. 2012. "Problematic of Environment Protection in Algerian Cities." *Energy Procedia* 18:265–275. doi:10.1016/j.egypro.2012.05.038.

Hammer, Ø., D. A. T. Harper, and P. D. Ryan. 2001. "Past: Paleontological Statistics Software Package for Education and Data Analysis." *Palaeontologia Electronica* 4 (1): 9.

Han, Y. M., P. X. Du, J. J. Cao, and E. S. Posmentier. 2006. "Multivariate Analysis of Heavy Metal Contamination in Urban Dusts of Xi'an, Central China." *Science of the Total Environment* 355: 176–186. doi:10.1016/j.scitotenv.2005.02.026.

Hou, D., D. O'Connor, P. Nathanail, L. Tian, and Y. Ma. 2017. "Integrated GIS and Multivariate Analysis for Regionale Scale Assessment of Heavy Metal Soil Contamination: A Critical Review." *Environmental Pollution* 231: 1188–1200. doi:10.1016/j.envpol.2017.07.021.

Huang, L. M., C. B. Deng, N. Huang, and X. J. Huang. 2013. "Multivariate Statistics Approach to Identify Heavy Metal Sources in Agricultural Soil around an Abandoned Pb-Zn Mine in Guangxi Zhuang Autonomous Region, China." *Environmental Earth Sciences* 68 (5): 1331–1348. doi:10.1007/s12665-012-1831-8.

Hussain, R., S. A. Khattak, M. T. Shah, and L. Ali. 2015. "Multistatistical Approaches for Environmental Geochemical Assessment of Pollutants in Soils of Gadoon Amazai Industrial Estate, Pakistan." *Journal of Soils and Sediments* 15 (5): 1119–1129. doi:10.1007/s11368-015-1075-9.

ISO (International Standards Organization). 1995. *ISO 11466:1995. Soil Quality- Extraction of Trace Elements Soluble in Aqua Regia*. London, UK: BSI Standards Publication.

Kabata-Pendias, A. 2011. *Trace Elements in Soils and Plants*. 4th ed. Boca Raton, FL: CRC Press.

Kelepertsis, A., A. Argyraki, and D. Alexakis. 2006. "Multivariate Statistics and Spatial Interpretation of Geochemical Data for Assessing Soil Contamination by Potentially Toxic Elements in the Mining Area of Stratoni, North Greece." *Geochemistry: Exploration, Environment, Analysis* 6: 349–355. doi:10.1144/1467-7873/05-101.

Kelepertzis, E. 2014. "Accumulation of Heavy Metals in Agricultural Soils of Mediterranean: Insights from Argolida Basin, Peloponnese, Greece." *Geoderma* 22: 82–90. doi:10.1016/j.geoderma.2014.01.007.

Khouli, M. R., and L. Djabri. 2011. "Impact of Use of Agricultural Inputs on the Quality of Groundwater, Case of Mitidja Plain (Algeria)." *Geographia Technica* 2: 35–44.

Krami, L. K., F. Amiri, A. Sefiyanian, A. R. B. M. Shariff, T. Tabatabaie, and B. Pradhan. 2013. "Spatial Patterns of Heavy Metals in Soil under Different Geological Structures and Land Uses for Assessing Metal Enrichments." *Environmental Monitoring and Assessment* 185 (12): 9871–9888. doi:10.1007/s10661-013-3298-9.

Laribi, A., B. Mouhouche, T. Benayad, and Z. Dehnoun. 2017. “Contamination Assessment and the Risk Associated with the Accumulation of Trace Metals in Sediments of the Mitidja Plain, Algeria.” *Environmental Progress and Sustainable Energy* 36: 1650–1657. doi:10.1002/ep.12620.

Laribi, A., and N. Saidani. 2016. “Assessment of Cu, Fe and Zn Contamination in Agricultural Soils around the Meftah Cement Plant, Algeria.” *Works of the Faculty of Forestry University of Sarajevo* 21: 271–278.

Lebik, H., and H. Ait-Amar. 2013. “Pesticides Occurrence in Groundwater Sources of Mouzaia (Algeria).” *African Journal of Agricultural Research* 8: 4269–4279. doi: 10.1016/j.jhydrol.2007.10.002.

Lienard, A., Y. Brostaux, and G. Colinet. 2014. “Soil Contamination near a Former Zn-Pb Ore-Treatment Plant: Evaluation of Deterministic Factors and Spatial Structures at the Landscape Scale.” *Journal of Geochemical Exploration* 147 (S1): 107–116. doi: 10.1016/j.gexplo.2014.07.014.

Maas, S., R. Scheifler, M. Benslama, N. Crini, E. Lucot, Z. Brahmia, S. Benyacoub, and P. Giraudoux. 2010. “Spatial Distribution of Heavy Metal Concentrations in Urban, Suburban and Agricultural Soils in a Mediterranean City of Algeria.” *Environmental Pollution* 158 (6): 2294–2301. doi:10.1016/j.envpol.2010.02.001.

McGrath, S. P., and F. J. Zhao. 2015. “Concentrations of Metals and Metalloids in Soil That Have the Potential to Lead to Exceedance of Maximum Limit Concentrations of Contaminants in Food and Feed.” *Soil Use and Management* 31: 34–45 doi:10.1111/sum.12080.

McLennan, S. M. 2001. “Relationships between the Trace Element Composition of Sedimentary Rocks and Upper Continental Crust.” *Geochemistry Geophysics Geosystems* 2: 1021–1024. doi:10.1029/2000GC000109.

Minitab Inc. 2010. *Minitab Reference Manual PC Version Release 17.* State College, PA: Minitab, Inc.

Paterson, E., C. Campbell, and C. Shand. 2011. *Geochemical Atlas for Scottish Topsoils.* Aberdeen, UK: The Macaulay Land Use Research Institute.

Prasse, C., W. Zech, F. Itanna, and B. Glaser. 2012. “Contamination and Source Assessment of Metals, Polychlorinated Biphenyls, and Polycyclic Aromatic Hydrocarbons in Urban Soils from Addis Ababa, Ethiopia.” *Toxicological and Environmental Chemistry* 94: 1954–1979. doi:10.1080/02772248.2012.737794.

Rawlins, B. G., S. P. McGrath, A. J. Scheib, N. Breward, M. Cave, T. R. Lister, M. Ingham, C. Gowing, and S. Carter. 2012. *The Advanced Soil Geochemical Atlas of England and Wales. British Geological Survey*. Nottingham, UK: British Geological Survey.

Reimann, C., P. Filzmoser, and R. G. Garrett. 2005. “Background and Threshold: Critical Comparison of Methods of Determination.” *Science of the Total Environment* 346 (1–3): 1–16. doi:10.1016/j.scitotenv.2004.11.023.

Reimann, C., and R. G. Garrett. 2005. “Geochemical Background-Concept and Reality.” *Science of the Total Environment* 350 (1–3): 12–27. doi:10.1016/j.scitotenv.2005.01.047.

Sipos, P., C. Choi, T. Nemeth, Z. Szalai, and T. Poka. 2014. “Relationship between Iron and Trace Metal Fractionation in Soils.” *Chemical Speciation and Bioavailability* 26: 21–30. doi:10.3184/095422914X13887685052506.

Sulaiman, F. R., N. F. S. Mustaffa, and S. N. M. Khazaai. 2016. “Preliminary Assessment of Selected Metals in Agricultural Soils in Jengka, Pahang, Malaysia.” *Environmental Earth Sciences* 75: 223. doi:10.1007/s12665-015-4926-1.

Sun, C., W. Zhao, Q. Zhang, X. Yu, X. Zheng, J. Zhao, and M. Lv. 2016. “Spatial Distribution, Sources Apportionment and Health Risk of Metals in Topsoil in Beijing, China." *International Journal of Environmental Research and Public Health* 13 (7): 727. doi:10.3390/ijerph13070727.

Tume, P., J. Bech, F. Reverter, J. Bech, L. Longan, L. Tume, and B. Sepulveda. 2011. "Concentration and Distribution of Twelve Metals in Central Catalonia Surface Soils." *Journal of Geochemical Exploration* 109 (1–3): 92–103. doi:10.1016/j.gexplo.2010.10.013.

Tume, P., E. González, R. W. King, L. Cuitiño, N. Roca, and J. Bech. 2018. "Distinguishing between Natural and Anthropogenic Sources for Potentially Toxic Elements in Urban Soils of Talcahuano, Chile." *Journal of Soils and Sediments* 18 (6): 2335–2349. doi:10.1007/s11368-017-1750-0.

Wu, J., Y. Teng, S. Lu, Y. Wang, and X. Jiao. 2014. "Evaluation of Soil Contamination Indices in a Mining Area of Jiangxi, China." *PLoS One* 9: e1129117. doi:10.1371/journal.pone.0112917.

Yan, W., D. Liu, D. Peng, Q. Mahmood, T. Chen, Y. Wang, S. Li, and J. Chen. 2016. "Spatial Distribution and Risk Assessment of Heavy Metals in the Farmland along Mineral Product Transportation Routes in Zhejiang, China." *Soil Use and Management* 32 (3): 338–349. doi:10.1111/sum.12268.

Zhang, X. Y., F. F. Lin, M. T. Wong, X. L. Feng, and K. Wang. 2009. "Identification of Soil Heavy Metals Sources from Anthropogenic Activities and Pollution Assessment of Fuyang County, China." *Environmental Monitoring and Assessment* 154 (1–4): 439–449. doi:10.1007/s10661-008-0410-7.

Zhao, K., W. Fu, Z. Ye, and C. Zhang. 2015. "Contamination and Spatial Variation of Heavy Metals in the Soil-Rice System in Nanxun County, Southeastern China." *International Journal of Environmental Research and Public Health* 12 (2): 1577–1594. doi:10.3390/ijerph120201577.