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Characterization of metal pollution in soils under two landuse patterns in the Angouran region, NW Iran; a study based on multivariate data analysis

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ABSTRACT

The study presents the application of selected multivariate statistical methods (multivariate analysis of variance, discriminant analysis, principal component analysis) and geostatistical techniques to evaluate soil pollution status in arable lands of the Angouran region, NW Iran. Two representative landuse patterns, cropland and grassland, were selected for the purpose of this study. Seventy soil samples (35 topsoils and 35 subsoils) were collected from the two landuse types and 21 soil parameters including total element content and physicochemical properties were also determined. Results from application of the multivariate analysis of variance showed that the two landuse patterns were not statistically differentiated by subsoil variables, whereas significant differences existed between the two landuse patterns with respect to topsoil variables. Discriminant analysis rendered seven variables (Cu, As, Cd, OM, P, K and total N) as indicator parameters responsible for the discrimination between the two landuse types. Using the principal component analysis (PCA), two main components (PCs) explaining 71.71% of total variance were extracted. PC1, with a high contribution of Ni, Cr, Fe, Mn and clay content was hypothesized as lithogenic component and PC2, with high loadings for the seven discerning variables (Cu, As, Cd, OM, P, K and total N), was considered as an agrogenic component. Geostatistical analyses, including the calculation of semivariogram parameters and model fitting, further supported the PCA results. PC1 was generally characterized by moderate spatial dependence and long-range spatial variation (8000 m) influenced by soil parent martial composition, while PC2 was modelled by pure nugget effect probably reflecting the influences of agrogenic activities. The findings of this study could not only expand our knowledge regarding the soil pollution status in the study area, but would also provide decision makers with the information to manage the agrochemical application in the arable lands to improve the sustainability and safety of intensive-farming activities in the study area.

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1. Introduction

Soil plays a vital role in the environment and acts like a pivot for material and energy exchanges among the atmosphere, hydrosphere, biosphere and lithosphere. Once pollutants are introduced into the soil they can be transferred from the soil to other ecosystem compartments such as underground water or crops and consequently can affect human health through the water supply and food web [1]. Among numerous soil pollutants, heavy metals (Cd, Cu, Pb, Zn and As) are especially dangerous due to their toxicity and persistence in the environment and public health concern [2,3]. (Arsenic is, strictly speaking, not a heavy metal although it shares many toxic characteristics with heavy metals and goes through similar environmental processes.) The natural concentration of heavy metals in arable soil depends primarily on the geological parent material composition [4,5]. In addition to this natural origin, some heavy metals may be supplied to soils by human activity. In recent decades, the natural inputs of several heavy metals in soils due to pedogenic processes have been exceeded by human input [3]. Agricultural activity is one of the most important human inputs of potentially hazardous metals in arable soils [6]. These activities not only contribute to the enrichment of heavy metals in agricultural soil, but also directly affect the soil physicochemical properties through the long-term application of either liquid or solid manure or chemical fertilizers [7]. Since agricultural soil has both direct and indirect influences on public health via food production, it is of great importance to have a good knowledge of the accumulation and the variability in space of heavy metals in soils.

Heavy metal accumulation in soil, the distribution of these metals and their controlling factors are priority objectives in many environmental assessment studies. Statistical and geostatistical techniques can provide such knowledge and assist the interpretation of soil research data.

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In recent years, statistical methods (univariate or multivariate) have been widely applied to investigate heavy metal concentration and distribution in soils. This is documented by a large number of reported studies which applied statistical methods to metal accumulation in soils [8–12]. These methods are also used to estimate the variability of soil properties and the related controlling factor(s), and to assess the influence of the soil management system on the soil properties. As data sets of soil research normally contain many objects and many features, the analysis by univariate statistical methods is complicated and usually insufficient [11]. Alternatively, the multivariate statistical methods, taking into account many variables simultaneously give much more information about the characteristics of a soil. Moreover, a multivariate approach usually reduces Type I errors that occur in univariate tests [13]. Therefore, from the methodological point of view, multivariate statistical methods offer more robust and better integrated ways to study all aspects of soil quality. In spite of these advantages, classical multivariate statistical approaches ignore the spatial relationships between soil variables which include important information. On the other hand, the concentrations of heavy metals in soil are a spatial phenomenon [14]. Geostatistics, as a spatial interpretation tool, can be used to quantify the spatial dependency (features) of soil properties including heavy metal concentrations. These methods have been widely applied in soil surveys and other environmental research programs [15–20]. Understanding the variations of soil characteristics and their controlling factors and how soil attributes vary spatially can be helpful in the characterization of complex relationships between soil properties, environmental factors and contamination sources. From an environmental management point of view, these findings may be useful in achieving a better understanding of soil quality and thereby adopting appropriate management strategies for guaranteeing the maintenance or even improvement of soil quality.

The Angouran region located in the northwest of Iran is characterized by widespread arable and cultivated lands. There is very little information about the heavy metal pollution status in the arable soils of this region. Although different sources may contribute to the soil pollution in the Angouran region, agricultural activities are so widespread that it is reasonable to hypothesize that these practices are the major contributor to the soil pollution in the study area. The evaluation and differentiation of anthropogenic and lithogenic inputs are an important and difficult task in this area since soils here are naturally enriched in metals.

In order to evaluate the impacts of agronomic practices on soil characteristics (metal contents and physicochemical properties), we have chosen two main landuse patterns (cropland and grassland) and assessed, by means of multivariate statistics, (1) whether these two main landuse patterns are statistically different from each other or not and if they are then what specific soil variables best differentiate these from each other. Using unsupervised multivariate statistics (PCA) and geostatistical methods (variogram analysis), we also investigated the spatial variability (structure) of the soil variables and infer (indirectly) the factors (soil parent material, agricultural practices) that can promote this variability.

2. Materials and methods

2.1. Site description

The study area is located in Zanjan province about 90 km west of Zanjan city and 450 km northwest of Tehran. Geologically, it is part of the Takab mineralization zone. The Takab area is characterized by several sediment-hosted mineralizations which are usually associated with volcanic–plutonic rocks [21]. The intensive volcanic (epithermal) activity and presence of carbonate rock sequences or their metamorphosed equivalents (host rocks) have resulted in a series of mineral deposits of which some are also mined. The main rocks that are exposed in the outcrop are limestone and marl of Miocene age and metamorphosed rock units (marble and micaschist) of Precambrian age. Volcano-sedimentary rocks of Oligomiocene age are also exposed to the west of the study area.

Topographically, the region is surrounded by mountains, particularly in the northern part. The gradient of the terrain trends from north to south gradually with elevation from 5 m (in the middle plain) to 3500 m (in the northern mountains). The Angouran region has a semiarid and cold climate with annual temperatures ranging from −22 °C in winter to 36 °C in summer, with an average annual rainfall over 350 mm.

The soils in the study area, developed predominately on Pleistocene alluvial sediments, are mainly composed by loam and gravels. Principally, the soils are shallow and calcareous with an alkaline pH because of their calcium-carbonate rich parent material. According to soil taxonomy [22], these soils are mainly classified as Entisols. As a definition, they are poorly developed, immature and shallow soils containing low organic content.

The two representative main landuse patterns in the study area include cropland (50%) and grassland (44.5%) with an overall area of >20 ha. The major differences between grassland and cropland are the kind of vegetation and level of management that each land area receives. In the study area, grassland supports native vegetation (*Spartina pectinata*) that is extensively managed through the control of livestock rather than agronomy (cultivation) practices such as fertilization or pesticide application. In contrast, the cropland is intensively managed using agronomy practices and rotational cultivation of crops. According to the survey, an average of 500 kg ha^{-1} yr^{-1} of commercial fertilizers and manure are used in the agricultural area. Wheat, alfalfa and barley are being cultivated rotationally in the cropland.

2.2. Soil sampling and chemical analysis

Considering the uniformity of the soil samples distribution over the study area, a total of 70 uniformly distributed samples (35 samples for both topsoils and subsoils) were collected from the two different landuse patterns (Fig. 1). Each site was divided into a 2 × 2 km grid using topographic maps at 1:50,000 scale. At each plot, two initial subsamples were taken at 0–20 cm (topsoils) and 20–60 cm (subsoils). These subsamples were mixed to obtain a bulk sample that provides an estimate of the concentrations of that site. The density of sampling was generally one sample every 2 km^2 and the total area sampled was 50 km^2 (12.1 km × 4.1 km). At each sampling location, the related information such as landuse history, vegetation and soil type were also recorded in detail.

The soil samples were dried for 7 days at 40 °C, sieved to less than 2 mm in a plastic sieve and ground to fine powder using agate and a pestle. The soil samples were then submitted for total heavy metal concentration analysis (by ICP-OES) in an accredited Australian laboratory (Amdel Limited's Labs ISO 9001). Major elements (K, Na, P, Mg, Al and Fe) were analyzed by X-ray fluorescence (XRF). Total nitrogen was measured by Kjeldhal procedure [23]. Replicated measures of internal references materials, reagent blanks and duplicated soil samples randomly selected from the set of available samples were used to assess contamination and precision during analysis. The quality control gave good precision (SD < 10%).

Selected soil properties were also determined. The TOC content of the soil was determined by loss on ignition at 550 °C in a muffle furnace [24]. Soil pH was determined by mixing soil and distilled water in a 1:2.5 (g:ml) ratio and shaking for 15 min before measuring pH. Clay content was also determined using the hydrometer method after pretreatment with Na-hexametaphosphate [25].

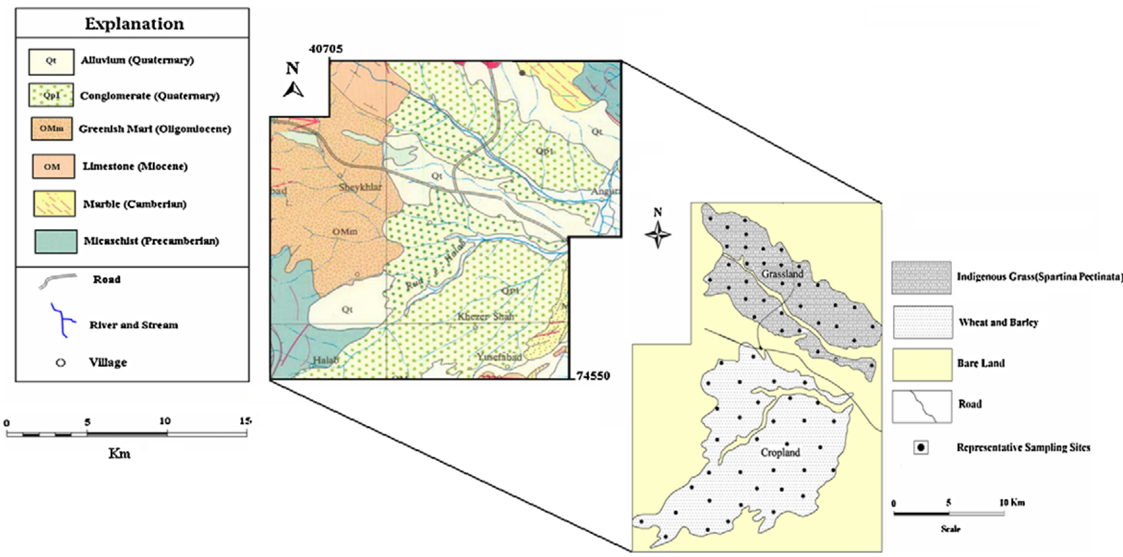

Fig. 1. Map of the study area showing sampling points, landuse patterns and geological rock units.

2.3. Statistical and geostatistical analysis

Descriptive statistics including mean, maximum, minimum, median and coefficient of variation (CV) were calculated for topsoil and subsoil samples from the two sampling locations. We adopt the CV as an indicator of the variability of soil properties.

The distribution of the data was tested for normality by Kolmogorov–Smirnov (K–S) test. When statistical distribution was not normal, the variables were transformed by applying neperian logarithms to obtain a normal distribution. Pearson correlation matrix was also used to identify the relationship between soil variables.

2.3.1. Multivariate analysis of variance (MANOVA)

To assess significant differences in total metal concentration and soil physicochemical properties among top/sub soil samples from the two sampling sites, MANOVA was used. In the MANOVA, the overall mean of the groups (partitioned to a series of sum of squares) is compared by Test Statistics (Wilks' Lambda, Lawley-Hotelling, Pillai's Trace and Roy's Largest Root) and between-group variance is expressed as *F*-statistics.

Once the MANOVA tests established that at least one of the variables was different between landuse types, means for individual soil properties were subjected to discriminant analysis (as post-hoc univariate test).

2.3.2. Discriminant analysis (DA)

The MANOVA technique gives the overall test of the equality of mean vectors of several groups but it does not provide information as to which variables are responsible for the differences in mean. For this purpose, discriminant analysis was performed on each of the mean of variables individually to add support to the results of MANOVA.

DA is a method of analyzing dependence that is a special case of canonical correlation. In this study, the DA was first used to reveal whether the two sampling sites (landuse patterns) differ significantly in terms of heavy metal concentrations and soil properties. After elucidating the differences between the two sites, the DA determines the variables that discriminate between the two sites.

If many measures (variables) are included in the model, stepwise DA (in the modes of standard, forward and backward) can be used to determine the variables that discriminate between the groups.

2.3.3. Principal component analysis (PCA)

Principle component analysis is a technique widely used for reducing the dimensions of multivariate problems. As a non-parametric method of classification, it makes no assumptions about the underlying statistical data distribution. It reduces the dimensionality of the data set by explaining the correlation amongst a large number of variables in terms of a smaller number of underlying factors (principal components or PCs) without losing much information [26].

All statistical treatments mentioned above were performed using SPSS for Windows (release ver.11 Inc., Chicago, IL).

2.4. Geostatistical analysis

Geostatistics is based on the theory of regionalized variable [27] which is distributed in space and shows spatial autocorrelation such that samples close together in space are more alike than those that are further apart [20]. In this study, the results of PCA were used to calculate the autocorrelation value and to produce a minimum unbiased variance estimate. This variance is calculated as a function of a semivariogram, which is a measure of the dissimilarity between a pair of regionalized variables ($Z(x_i)$, $Z(x_i+h)$) with respect to the spatial separation, h:

$$\gamma(h) = \frac{1}{2n(h)}\sum_{i=1}^{n(h)}[Z(x_i) - Z(x_i+h)]^2$$

where $n(h)$ is the number of pairs of differences with the distance h. No anisotropy was evident in the directional semivariograms of any of the soil properties, thus isotropic semivariogram models (spherical, exponential, Gaussian, linear, or pure nugget effect) were fitted to the data. Each of the models can be described on three parameters; nugget variance (the y-intercept of the model, C_0), sill (the model asymptote, C_0+C) and range (the distance over which spatial dependence is apparent, A_0) [6]. Selection of semivariogram models was made based on the regression coefficient of determination (R^2), residual sum squares (RSS) and the goodness-of-fit (*gof*) index [28]. It should be noted that in the variography of the original data, we restricted semivariance estimation to half the maximum lag distance to better estimate the semivariogram within the spatial correlation range (minimum lag distance was 1000 m and each lag distance had at least 200 pairs of points in this study).

Table 1
Descriptive statistics of element concentration of soil and some soil properties.

Subgroup	Descriptive statistics	Mg	Na	K	Al	Cr	Ni	Cd	Cu	As	Zn	Pb	Clay content (%)	OM (%)	$[H]^{+}$ [a] (mol)	P	N
Cropland (topsoil)	Geometric mean	3.24	4330	12605	51225	33.46	36.23	3.61	884.6	241	2501	2862	223.89	5.18	8.1×10^{-9}	25527	14003
	Arithmetic mean	3.49	4410	17967	51467	33.95	36.65	5.3	1100	649	1403	1175	220.14	4.79	6.4×10^{-8}	3165.7	19646
	Min	2.2	3257	923	42315	22.16	33.19	1.19	125	45	385	2143	15	1.2	6.1×10^{-8}	928	275
	Max	5.22	6259	25970	57290	42.15	52.16	10.13	3250	1100	4256	3525	3342	22.41	7.5×10^{-10}	72935	57400
	Median	3.25	4337	19637	53083	34.37	36.76	4.46	1598.5	323.5	3335.5	2854.5	40	11.3	4.4×10^{-9}	52109	33875
	SD	0.86	893	8981	5060	5.73	6.14	2.66	1587.9	420.6	1186.8	437.31	853.04	4.45	0.68	25584	18707
	CV × 100	0.25	0.2	0.51	0.09	0.16	0.15	0.6	0.75	0.92	0.4	0.15	3.2	0.58	0.08	0.57	0.62
	K–S test	0.14	0.11	0.19	0.17	0.21	0.22	0.16	0.02	0.03	0.19	0.01	0.52	0.14	0.17	0.27	0.13
Cropland (subsoil)	Geometric mean	4.08	3815	299	51455	31.24	34.97	0.32	114.37	28.66	1062.2	2358	33.24	0.95	1.4×10^{-8}	185.81	427.94
	Arithmetic mean	4.53	3753	283	5112	29.41	30.31	0.32	110.25	27.21	969.08	2337	30.58	0.91	1.7×10^{-8}	238.83	430.16
	Min	1.232	2123	217	37960	26	22.12	0.23	95	22.3	700	1754	17	0.11	2.5×10^{-7}	128	275
	Max	12.3	5354	473	69750	40.32	56.9	0.45	152	35.96	1752	3740	65	5	5.1×10^{-10}	275	525
	Median	4.54	3838	320	52450	33.15	34.2	0.32	101	29.53	1125	2210	37	1.1	5.1×10^{-8}	200	423
	SD	4.21	1143	79	10679	4.31	9.06	0.09	23.49	4.46	307.54	629.72	15.3	1.26	0.91	54.23	74.2
	CV × 100	0.21	0.29	0.25	0.2	0.13	0.25	0.27	0.2	0.15	0.27	0.25	0.19	0.13	0.11	0.27	0.17
	K–S test	0.28	0.14	0.18	0.22	0.15	0.32	0.25	0.27	0.17	0.21	0.22	0.11	0.23	0.23	0.14	0.21
Grassland (topsoil)	Geometric Mean	18.83	3666	698	47588	18.11	22.38	0.959	23.04	12.1	306.86	546.07	26.83	3.72	7.5×10^{-9}	146	189.83
	Arithmetic mean	12.2	3710	676	41178	19.8	22.59	1.1	22.19	9.94	288.41	596.16	25.27	3.3	1.6×10^{-8}	138	173.75
	Min	13.61	2750	500	29730	13.4	15.51	0.68	19.62	7.9	225	475	10	2.2	7.7×10^{-8}	115	151
	Max	25.8	5740	975	57540	25.7	30.42	1.3	29.31	17.3	425	925	72	6.31	4.7×10^{-10}	230	220
	Median	20.31	3642	720	48185	18.11	22.75	1.03	23.32	13.1	300	533.51	34	2.2	7.1×10^{-9}	142.5	197.53
	SD	4.24	1112	145	11273	5.06	6.19	0.22	3.23	3.34	82.62	177.91	17.31	1.82	0.82	44.59	23.22
	CV × 100	0.21	0.27	0.2	0.25	0.27	0.26	0.23	0.13	0.26	0.26	0.28	0.27	0.19	0.1	0.27	0.12
	K–S test	0.16	0.21	0.24	0.25	0.21	0.18	0.19	0.16	0.16	0.21	0.38	0.1	0.15	0.16	0.26	0.19
Grassland (subsoil)	Geometric mean	22.17	1754	854	41995	41.46	23.88	0.63	174.11	140.78	366.08	920.43	32.81	0.68	2.1×10^{-9}	81.51	197.63
	Arithmetic mean	20.01	1856	758	42685	40.86	20.75	0.57	167.21	68.29	380.16	723.33	30.15	1.12	7.9×10^{-9}	81.92	197.5
	Min	17.5	1150	710	24750	35.81	17.32	0.32	110	125	220	747	15	0.16	6.1×10^{-8}	59.6	170
	Max	25.5	2275	1250	61150	47.9	39.91	0.98	200	154	500	1000	72	2.91	7.9×10^{-10}	110	231
	Median	22.85	1951	746	43855	41.75	21.4	0.62	174	146	367.51	922.5	38	1.11	4.4×10^{-9}	80.75	194
	SD	2.71	472	219	12607	4.22	7.86	0.22	42.81	12.1	101.92	82.21	19.21	0.69	0.68	17.8	23.84
	CV × 100	0.12	0.26	0.25	0.28	0.1	0.31	0.34	0.26	0.08	0.28	0.09	0.49	0.13	0.08	0.21	0.11
	K–S test	0.14	0.26	0.3	0.16	0.16	0.27	0.19	0.27	0.26	0.2	0.2	0.1	0.11	0.17	0.15	0.19

All values in $mg\,kg^{-1}$ unless otherwise mentioned.
[a] $pH = -\log[H]^{+}$.

All the geostatistical analyses were carried out with GS+ (Version 3.1a Demo).

3. Results and discussion

Descriptive statistics for element and physicochemical characteristics of the analyzed soils are summarized in Table 1. The application of the K–S test confirmed that most variables are normally distributed with the exception of Cu, Pb and As in the cropland topsoil samples. For non-normal variables, a neperian transformation was used to get a more symmetric (normal) distribution.

The mean concentrations of heavy metals in the cropland topsoils were higher than those in grassland topsoils. Physicochemical properties of the cropland topsoil were generally more variable than those of the grassland topsoil as well. Soil pH, as an exception, varied narrowly from 8.00 (for cropland topsoil) to 7.83 (for grassland topsoil), indicating a moderately alkaline condition.

Comparing the mean values of heavy metal concentration in the cropland topsoil of the Angouran region with the values available from literature [29,30], Fe and Mn exhibit lower contents than the mean values established for arable soils worldwide, Ni and Cr are roughly comparable with mean global values, while Cu, Cd, Pb, Zn and As are significantly higher than average world values.

3.1. Multivariate analysis of variance

A priori assumption advanced in this study is that cropland and grassland sites are statistically different from each other in terms of soil attributes (i.e. soil attributes were expected to be influenced by landuse types). To test whether mean values of soil attributes (element concentrations and soil properties) differ between the defined groups (two sites), MANOVA was applied to the data set. For statistical analysis, data from the upper (topsoil) and underlying layer (subsoil) were treated separately. Table 2a brings out the results of the MANOVA for the subsoils. According to the results, the two sites (cropland and grassland) are not significantly different from each other with respect to all variables ($p > 0.01$, F values = 0.448). In spite of the high concentration levels, the coefficient of variation values varied from 8% (for As in grassland subsoil) to 29% (for Na in cropland subsoil), indicating slight variations for the subsoil variables. Therefore, the spatial distributions of these variables are remarkably similar over a large area. As one can see in Table 1, for all the subsoil variables the median is very close to the arithmetic and geometric mean, indicating a similar statistical distribution. The relatively small variability and the lack of significant differences between the two sites suggest that subsoils of the two sites were derived from a single or uniform parent material (geologic substrate). Since no statistical significance was found between the two landuse patterns (sites) in terms of subsoil variables, the statistical analyses were restricted to the topsoil variables.

The results obtained from application of the ANOVA method for topsoil samples (Table 2b) show that there are strong differences between the two sites with regard to all determined variables at level $p < 0.01$. The F values, as the ratio of the between-groups variance to within-group variance are relatively high (191.374), indicating significant differences between the two landuse patterns. In cropland topsoil, for some variables (As, Cu, Cd, OM, N, K and P) the CVs exceed 50%, representing considerable variability. This indicates that some soil attributes are being affected by anthropogenic (agrogenic) activities rather than by geogenic (parent material) factors. Based on the MANOVA results, the mean values of As, Cu, Cd, N, K, P, OM and Zn in cropland topsoil are remarkably larger than those found in grassland (Fig. 2). The fact that these elements are most strongly enriched in the cultivated soils suggests that these soils have been subjected to a high input of anthropogenic metals most likely related to the application of agrochemicals used to improve production and quality.

Table 2a
Results of multivariate tests (MANOVA) for subsoil samples of the two landuse types.

Test	Value	*F*	Hypothesis d.f.	Error d.f.	Sig.
Pillai's Trace	0.956	0.448	48.000	1.000	0.858
Wilks' Lambda	0.044	0.448[a]	48.000	1.000	0.858
Hotelling's Trace	21.499	0.448	48.000	1.000	0.858
Roy's Largest Root	21.499	0.448[b]	48.000	1.000	0.858

[a] Exact statistic.
[b] The statistic is an upper bound on *F* that yields a lower bound on the significance level.

Table 2b
Results of multivariate tests (MANOVA) for topsoil samples of the two landuse types.

Test	Value	*F*	Hypothesis d.f.	Error d.f.	Sig.
Pillai's Trace	0.989	191.374	16.000	34.000	0.000
Wilks' Lambda	0.011	191.374[a]	16.000	34.000	0.000
Hotelling's Trace	90.058	191.374	16.000	34.000	0.000
Roy's Largest Root	90.058	191.374[b]	16.000	34.000	0.000

[a] Exact statistic.
[b] The statistic is an upper bound on *F* that yields a lower bound on the significance level.

3.2. Discriminant analysis

The results of the MANOVA are statistically too general, i.e. they only tell us whether or not two or more groups are significantly different from each other with respect to the means of all variables. To determine which variables contribute to the separation between groups, discriminant analysis was used. In order to ensure the results of the MANOVA evaluation we carried out DA on each of the variables determined in the topsoil samples. Since the objective of the execution of discriminant analysis was to determine whether the two sites differ significantly in terms of soil attributes, the two sites were entered as the grouping variables and the soil attributes were entered as the independent variables.

The discriminant analysis results are presented in Table 3. The obtained results clearly indicate the two landuse patterns (sites) exhibit different levels of soil variables (parameters) in the top layer. It is evident that for each variable under investigation, a high degree of between-groups variations exist (canonical correlations have values between 0.663 and 0.983), whereas there is a lower degree of within-group variations (Wilks' Lambda statistics range from 0.002

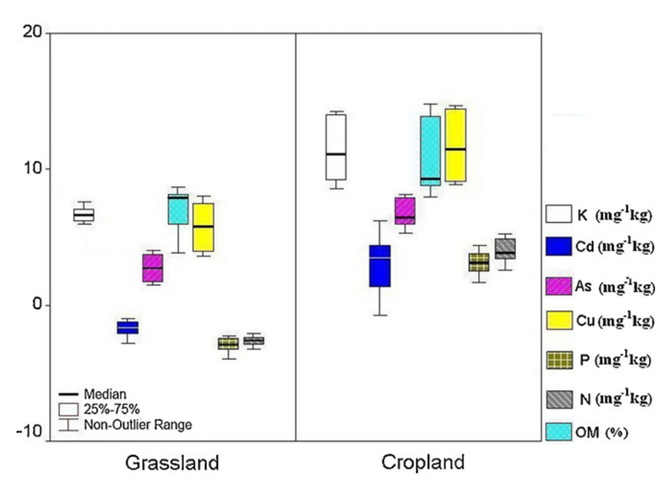

Fig. 2. Box plot showing difference between landuses in terms of seven discerning variables in topsoil samples.

Table 3
Results of discriminant analysis for topsoil variables of the two landuse types.

Variable	Canonical correlation	Wilks' Lambda statistic	d.f.	Sign.	Percentage of grouped cases correctly classified
pH	0.752	0.108	1	0	72
OM	0.871	0.01	1	0	99
Clay content	0.666	0.287	1	0	75
Pb	0.785	0.086	1	0	82
Zn	0.78	0.538	1	0	85
As	0.852	0.127	1	0	92
Cu	0.925	0.378	1	0	90
Cd	0.902	0.203	1	0	100
Ni	0.741	0.211	1	0	79
Cr	0.75	0.238	1	0	72
Al	0.726	0.229	1	0	72
K	0.854	0.184	1	0	95
Na	0.663	0.187	1	0	95
Mg	0.701	0.002	1	0	98
Fe	0.821	0.137	1	0	70
Mn	0.742	0.12	1	0	78
P	0.983	0.174	1	0	97
N	0.902	0.103	1	0	98

The level of significance was set at $p < 0.01$ (two-tailed).

to 0.538). The statistically significant results also show a very high percentage of correct classification, ranging from 72% to 100%.

To discover in detail which variable(s) make(s) the highest contribution to the discrimination between the two sites, stepwise discriminant analysis modes were performed on the original data (Table 4). The standard DA mode constructed DFs including all variables. In forward mode stepwise mode, variables are included step-by-step beginning with the more significant until no significant changes are obtained; in backward stepwise mode, variables are removed step-by-step with the less significant until no significant changes are obtained.

Table 4
Results of the stepwise discriminant analysis for all data measurements in topsoils and classification matrix showing percentage of correctly cases for the two landuse types.

Parameters	Standard mode		Forward/backward mode	
	Cropland	Grassland	Cropland	Grassland
pH	0.280	0.339		
OM (%)	0.871	0.730	0.731	0.621
Clay content (%)	0.123	0.676		
Pb	0.989	0.227		
Zn	0.664	0.926		
As	0.736	0.623	0.531	0.712
Cu	1.721	0.932	1.521	0.802
Cd	0.636	0.287	1.745	0.985
Ni	0.261	0.632		
Cr	1.254	1.023		
Al	1.2127	1.036		
K	1.23	1.14	0.977	0.873
Na	0.308	0.452		
Mg	0.492	0.412		
Fe	0.231	0.425		
Mn	0.368	0.450		
P	1.17	0.925	1.27	0.975
N	0.923	0.714	1.10	0.727

Classification matrix	%Correct
Standard mode	
Cropland	96.61
Grassland	92.33
Total	94.47
Forward/backward mode	
Cropland	99.11
Grassland	97.24
Total	98.17

The standard mode yielded the corresponding correlation matrixes (CMs) assigning 94.47% correctly using 18 discriminant variables (Table 4). The forward/backward stepwise modes yielded the corresponding CMs, assigning more than 97% of cases correctly using only seven discriminant variables. Therefore, based on the results of the discriminant analysis, there are significant differences between the two sampling sites which are expressed in terms of seven discriminating variables (As, Cd, Cu, K, N, P and OM). As seen, some metals with high total concentrations (such as Pb, Zn, Fe and Mn) did not contribute to the discrimination between the two landuse types, as the topsoil concentration of these metals is very close to their corresponding subsoil concentration. This indicates a close relation between the horizons and consequently the same origin for these metals in both horizons. In contrast, the separation of topsoil and subsoil element concentration (as for As, Cd, K and Cu) is caused most probably by the fact that the prevailing origin of these metals in the topsoil is different from the principal origin in the subsoil. It is noteworthy that these discerning variables are also known to be associated with agronomic practices (manure application and fertilization) and as previously mentioned, the mean concentrations of the variables were considerably larger in cropland.

The Pearson correlation matrix (PCM) presented in Table 5 showed the high interdependence between particular variables. For instance, some metals such as Ni, Cr, Fe, Mn or Zn showed a higher correlation with soil clay content. This result suggests that adsorption and retention of these elements in the cropland soils are mainly influenced by clay minerals. This is in agreement with the results obtained in studies conducted worldwide which have shown that the fine grained soils fraction exhibit a higher tendency for metal adsorption than the coarse grain fraction. On the other hand, some other elements such as As, Cu and Cd exhibited a significant relationship with soil organic matter probably as a consequence of their different (external) sources. It is well-established in the literature that organic matter content plays a fundamental role in the control of metal sorption by soils [31,32]. Organic matter, both in the dissolved and solid states, has a large specific surface area and elevated negative charge, thus attracting metals. According to McBride [33], most transition metals in soils tend to form stable complex with organic ligands. Similar results have also been reported by other authors in agricultural soils (e.g. Rodriguez et al. [5]).

Other soil property (soil pH) did not present any obvious correlation with heavy metal concentrations. This could be due to the narrow internal of pH values in the study area confirmed by the low standard deviation of this parameter.

Table 5
Pearson correlation coefficient (r) between some element concentrations and soil properties.

N	P	pH	OM	Clay content	Pb	Zn	As	Cu	Cd	Ni	Cr	Al	K
N	0.726*	−0.034	0.666*	−0.057	0.436	0.482	0.640*	0.996**	0.991**	0.041	−0.050	0.136	0.747*
	P	0.088	0.816**	0.097	0.657*	0.667*	0.731*	0.998**	0.960*	−0.215	−0.124	−0.027	0.713*
		pH	0.365	0.190	0.278	0.329	0.028	−0.125	0.060	−0.205	−0.253	0.350	0.106
			OM	−0.197	0.169	−0.232	0.827**	0.869**	0.994**	−0.216	−0.260	0.033	0.651*
				Clay Content	0.526*	0.686*	−0.135	−0.060	0.051	0.868**	0.858**	0.943**	0.013
					Pb	0.848**	−0.036	−0.116	−0.113	0.701**	0.555*	0.611*	−0.030
						Zn	0.196	−0.064	0.126	0.687*	0.792*	0.669*	0.213
							As	0.948**	0.846**	0.029	−0.023	0.039	0.264
								Cu	0.953**	0.091	−0.057	−0.259	0.938**
									Cd	−0.078	−0.091	−0.241	0.862**
										Ni	0.997**	0.825**	0.074
											Cr	0.804**	−0.302
												Al	−0. 257
													K

* Correlation is significant at the 0.05 level (two-tailed).
** Correlation is significant at the 0.01 level (two-tailed).

Inter-element relationships can also provide information on metal sources and pathways. The 14 metals were grouped according to correlation levels among elements. Elements in Group 1 (Ni, Cr, Al, Fe, Mn, Mg, Zn and Pb) strongly correlated with each other ($p < 0.01$). The results indicate that these elements had the same input sources and similar geochemical behavior. Those in Group 2 (Cu, As and Cd) displayed a positive correlation of different levels with each other, suggesting the possibility that a common origin exists for these elements in the analyzed soils. It should be noted that Pb and Zn had moderate to strong correlations with elements of both groups showing that these metals may be supplied to soils by two possible sources. To better understand the relationships among soil variables, principal component analysis was applied.

3.3. Principal component analysis

This analysis was applied to the autoscaled data matrix and standardized to zero mean and unit variance, aiming at assuring that all variables contribute equally to the model. The components were also rotated using a Varimax normalized rotation [34] which maximizes the variances of the squared normalized factor loadings across variables for each component. A screen test was performed to corroborate primer results, only principal components with eigenvalues >1 and that explain >10% of the total variance were retained (Table 6). Therefore, the most explanatory first components with more than 71% of the observed variance were selected. PC3 was not taken into account as it contained no relevant information to distinguish the landuse patterns. The association of metals with these two components can indicate the hypothetical source of these elements (lithogenic, anthropogenic or mixed).

3.3.1. PC1

The largest loadings for the first component which accounts for more than 45% of observed variance were observed for topsoil Cr, Ni, Fe, Mn, Pb and Zn (loadings greater than ±0.5 were considered). Except for Zn and Pb, other soil variables with high loading factors in this component are characterized by low variability and narrow range (see Table 1). Rodriguez et al. [5] and Brumelis et al. [35] found a similar metal grouped (Pb, Zn, Cr, Ni, Fe and Mn) in the same factor and explained the results as arising from the same source. Among the metals, Ni and Cr are ferrofamily transition elements which have similar geochemical behavior and are known to be added geogenically [36]. Generally, anthropic inputs of Cr and Ni in fertilizers or manures are lower than the concentration already present in the soil. The parent material of the study area (alluvial and colluvial sediments), particularly that of calcareous nature, determines Cr and Ni contents in the soil. In natural soils, Cr and Ni are derived mainly from weathering of parent material and subsequent pedogenesis. In the study area these metals appear in precipitated forms in sedimentary carbonate rocks (limestone and marl). Similar chemical behavior is presented by Fe and Mn, partly in oxide form and partly present as hydroxides which appear in precipitated forms in the parent materials (sediments). These metals also showed significantly positive correlations with clay content ($r = 0.6–0.7$), suggesting their strong association with products of parent rock weathering. Zn–Pb can also have a geogenic source as they form a number of insoluble compositions (e.g. silicates, carbonates, . . .) according to the prevailing pedogenic process [2]. Zn–Pb mineralization (as $ZnCO_3$, smithsonite and calamine ore) in the study area may contribute to the enrichment of topsoils in these metals. The remaining elements (Na, Mg and Al) are principally lithogenic and as such appeared in the PC1.

The above findings were further evidenced by the Top Enrichment factors (TEF), defined as the concentration ratio between the upper layer and underlying layer. A natural pedogenic enrichment is unlikely to produce TEF values exceeding 2, while higher values point to an important anthropic input from the top. As expected, all the metals positively associated with the PC1 had TEF values lower than 2, suggesting a natural input of these metals from parent rocks. Therefore, we interpret the first component as a geogenic (lithogenic) factor because of (i) high (dominant) loading factors of the typical lithogenic elements in this component; (ii) the large positive correlation of this group of elements with soil properties (clay content), and (iii) low level of total metal concentrations in the topsoil (TEF < 2). Relatively lower and negative loading factors for other elements in the PC1 suggested other effects and also other influences on the status of elements in the soils. The elements have large positive loadings on the second component as will be discussed below.

3.3.2. PC2

The second component (PC2) contributes Cu, K, As, Cd, Pb, Zn, total N, P and OM at 26.22% total variance. This component seems to have arisen from a different source such as agrochemical products or solid manures. Chemical or commercial (N–K–P) fertilizers are an important source of metals entering agricultural soils, especially Cd, Pb, Zn and K [8]. As seen, Zn and Pb have the following loading factors in the first and second components indicating a mixed source both from lithogenic and from anthropogenic inputs. High Cu and As values can also come from metal-based agrochemicals (especially sulfate and arsenate containing pesticides) related to specific agricultural practices. Therefore, PC2 can be hypothesized as an anthropogenic component with high loadings of Cu, As, Pb, Zn, and Cd. These results are in broad agreement with other studies

Table 6
Total variance explained and component matrix for topsoil variables.

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative%	Total	% of variance	Cumulative%	Total	% of variance	Cumulative%
1	8.189	45.497	45.497	8.189	45.497	45.497	7.900	43.887	43.887
2	4.720	26.220	71.717	4.720	26.220	71.717	3.284	18.247	62.134
3	1.743	9.683	81.400	1.743	9.683	81.400	2.891	16.062	78.197
4	1.241	6.895	88.295	1.241	6.895	88.295	1.818	10.098	88.295
5	.930	5.165	93.459						
6	.464	2.579	96.039						
7	.253	1.405	97.444						
8	.193	1.074	98.517						
9	.152	.844	99.361						
10	.040	.223	99.584						
11	.035	.192	99.777						
12	.020	.109	99.886						
13	.012	.066	99.952						
14	.004	.025	99.977						
15	.003	.018	99.995						
16	.001	.003	99.998						
17	.000	.001	100.000						
18	8.742E−05	.000	100.000						

	Component matrix		Rotated component matrix[a]	
	1	2	1	2
Cr	.970	−.073	.971	.005
Ni	.983	−.113	.973	.082
Fe	.936	−.146	.964	.019
OM	−.456	−.537	−.426	.621
P	−.263	.668	−.273	.768
As	−.415	.694	−.309	.760
Cu	.358	.759	.202	.764
Mn	.936	.021	.900	.100
Pb	.774	.446	.929	.577
Zn	.852	.425	.976	.521
Clay	.893	.078	.859	.086
Al	.897	−.167	.928	.028
Mg	.595	.187	.631	.404
Cd	−.052	.842	−.194	.882
pH	.271	.306	.141	−.178
N	.333	.865	−.433	.862
K	.197	−.812	−.153	.875
Na	.528	−.102	.658	−.116

Extraction method: principal component analysis, rotation method: Varimax with Kaiser normalization.
[a] Rotation converged in five iterations.

which report that metal concentrations significantly increased in fertilized soils [37]. Nicholson et al. [7] also found that an important percentage of several metals contained in agricultural soils of England was due to chemical fertilizers or solid manure. Except for Pb and Zn, other elements loaded in the PC2 show a higher average topsoil concentration with TEF values ranging from 4.1 for Cd to 6.7 for Cu and As. This suggests the local surface addition of Cu, Cd and As of agrogenic origin. In the case of Zn and Pb, TEF has a mean value of 1.42 (for Zn) to 1.90 (for Pb) suggesting anthropogenic and geogenic inputs.

Among the soil properties studied here, OM showed the highest loading for the PC2 which to some extent represents the special relationships of the metals to this soil property. This also indicates that long-term agricultural activity has increased the TOC content of the surface layer. Similar results were observed by Huang et al. [38], who found that long-term fertilization acts to enhance the TOC content of agricultural lands. The strong affinity of metals from anthropogenic sources to organic matter has been shown in the literature [31,39]. Organic matter can provide a large number of sorption sites facilitating metal accumulation in the top layer of soils. In agricultural land receiving organic matter from an agrogenic source, OM acts as the major adsorbent for the metals. According to these results, the bioavailability of metals would be expected to be low in the topsoils analyzed. It should, however, be stressed that under changing environmental condition, metals from anthropogenic sources can be more easily mobilized than those derived from parent materials, and this may be a matter of concern due to the risks of metal transfer into food plants.

In addition to the metals, we found exceptionally high concentrations of nutrient elements (P, K and N) in the top layer of cropland soils. To increase crop production, large quantities of N–P–K composite fertilizers are applied. According to the survey, an average of 500 kg composite fertilizer is used per ha per year. Table 5 shows that the nutrient elements (N–P–K) are positively correlated with metals such as Cd and Cu which further supports our hypothesis about the agrogenic source of the metals. It is interesting to mention that the variables with high loading factors in the second component also have a high contribution in the discrimination between the two sites. This is confirmed by projecting the PC scores of both sites (cropland and grassland fields) into the component plot. As can be seen in Fig. 3, most cropland topsoils are located on the positive side of the axis for component 2 (PC2 scores >0) which represents soils with higher amounts of elements originating mainly from anthropogenic sources. Grassland topsoils are also almost uniformly distributed with respect to the axis of component 1 and show a tendency to this axis. The distinction between crop-

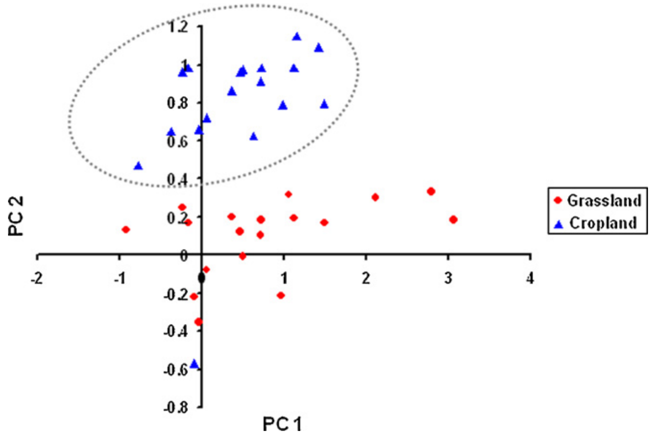

Fig. 3. Projection of mean principal component scores for the two landuse patterns.

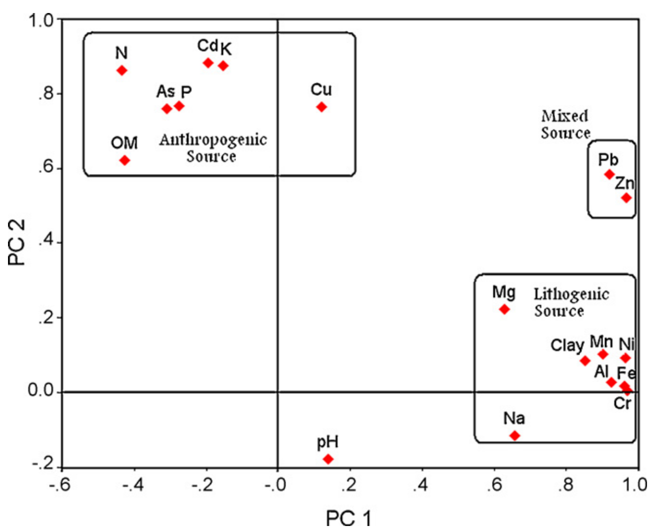

Fig. 4. Principal component analysis loading plot for the two rotated components showing different sources for the soil variables.

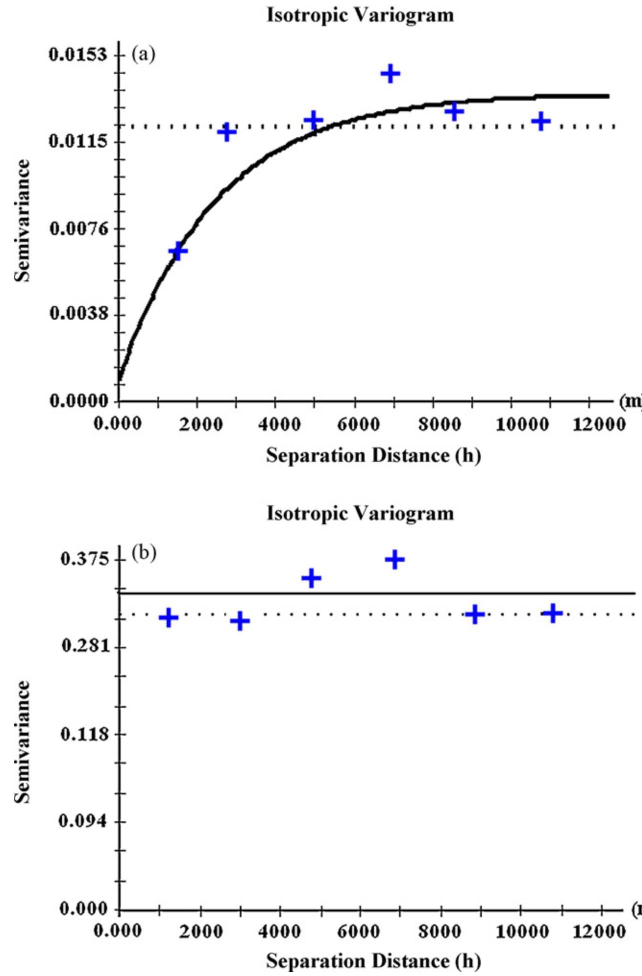

Fig. 5. (a, b) Experimental semivariogram of PC1 (a) and PC2 (b) with fitted models.

land and the grassland topsoils matches the results obtained from the execution of the discriminant analysis.

Based on earlier discussions we can classify the metal sources into three groups (Fig. 4): (i) Fe, Mn, Cr, Ni and Al with natural levels; (ii) Pb and Zn with moderate topsoil enrichment due to mixed inputs from natural and anthropogenic (agrogenic) sources and (iii) Cu, As and Cd with highly elevated topsoil concentrations resulting primarily from agricultural activities.

3.4. *Multivariate geostatistical analysis (variography)*

Variogram analysis was carried out in this study to further substantiate the results from multivariate analysis. The attributes of the semivariogram for PC1 and PC2 data are tabulated in Table 7. It is clear that the semivariograms parameters (model types, nugget, sill, effective range and nugget to sill ratio) are different for the two components. PC1 was characterized by relatively low nugget to sill ratio (13%), long effective range (8000 m) and small nugget effect. This factor was also well-fitted to the exponential model (Fig. 5a) that had a relatively higher coefficient of determination and lower residual sum of squares ($R^2 = 0.723$, RSS = 0.4 and *gof* = 0.805). The nugget to sill ratio (NSR = $C_0/(C_0 + C)$) can be regarded as cri-

Table 7
Semivariogram models for PC1 and PC2 and their parameters.

Component	Model	Nugget	Sill	Range (m)	Nugget to sill ratio (NSR)	R^2	RSS	*gof*
1	Spherical	0.0013	0.0145	8000	0.0896	0.310	0.427	0.458
	Exponential	**0.0010**	**0.0139**	**8200**	**0.0719**	**0.723**	**0.420**	**0.712**
	Linear	0.0031	0.0150	8521	0.206	0.406	0.219	0.221
	Nugget effect	0.0020	0.0140	8540	0.142	0.597	0.432	0.610
	Gaussian	0.0035	0.0150	8438	0.233	0.300	0.431	0.102
2	Spherical	0.328	0.374	2000	0.877	0.582	0.044	0.252
	Exponential	0.310	0.361	1500	0.858	0.470	0.022	0.433
	Linear	0.285	0.320	200	0.890	0.523	0.197	0.417
	Nugget effect	**0.328**	**0.327**	–	**1.00**	**0.719**	**0.031**	**0.718**
	Gaussian	0.325	0.370	800	0.878	0.123	0.029	0.412

Regression coefficient of determination (R^2) passed F test method at 0.05 significance level. RSS: residual sum squares; *gof*: goodness-of-fit.

terion to define the spatial dependence of soil properties. If the ratio is less than 25%, the variable has strong spatial dependence; between 25% and 75%, the variable has moderate spatial dependence; and greater than 75%, the variable shows only weak spatial dependence [40]. The strong spatial dependence for the PC1 indicates that (Table 7) the soil variables loaded on this factor depend mainly upon the bedrock from which the soil parent material was derived. This is confirmed by the continuous variation in the variable contents over a large effective range, reflecting the continuity seems to be derived originally from the spatial distribution of metals (elements or variables) in parent materials. As we have already noted, Cr and Ni are typical lithogenic elements and are well known to be geogenically influenced. The rocks in this region are composed of limestone and dolomites (or their metamorphosed equivalents) with high concentrations of these metals [41]. The Pb–Zn mineralization in the study area can also explain the association of these metals in the first components. There are significant occurrences of Pb–Zn mineralization in the lithology of the study area, thus the main source of these metals would originate from the lithogenic source. From our findings it is evident that the spatial variability of heavy metals loaded in PC1 was mainly affected by intrinsic factors (soil formation process). It should be noted that the first component has high loadings of clay content (about 0.8) and typical lithogenic elements (Na, Mg, Co, Fe and Mn). This suggests that the parent material and subsequent pedogenic process are major factors in the amounts and distribution of these metals. This conclusion is in agreement with other studies [1,5].

As shown in Fig. 5b, the second component with high proportions of Cu, K, OM and As was modelled by a pure nugget effect ($R^2 \approx 1$), i.e. the nugget (small scale spatial variability) was equal to the variance of the data, indicating this component to be spatial independent with purely random variance. The weak to no spatial dependence for the second component means quite probably that extrinsic factors such as fertilization or other agricultural practices affected the spatial distribution of the elements. We must point out that there is very likely small scale correlation occurring at intervals less than the distance between sampling locations (<2000 m) that cannot be detected with this dataset. While it may be difficult to obtain reliable estimates from small sample sets, geostatistics can be applied to undersized datasets provided caution is used during development and interpretations. From the semivariogram analysis presented here, it may be said that the spatial variation of soil properties has different patterns in the study area, reflecting that different sources of variability exist at the regional scale.

4. Conclusions

The results obtained in this study increase our knowledge of the metal contents and their possible sources in the arable soils of the Angouran area. This study also demonstrated multivariate data analysis methods can provide a valid (useful) method for the evaluation of the impacts of landuse practices on soil characteristics and for the identification of their controlling factors in the landuse scale.

Our study generally concludes that site-specific management policies such as *precision agriculture* (integrated into other management components of agronomic systems) need to be conducted in the study area. These sustainable strategies can increase profits by maximizing yield, while simultaneously decreasing environmental impacts by managing inputs (e.g. fertilization or pesticides). In this sense, the findings of this preliminary study can also provide decision makers with the information needed to improve the sustainability and safety of intensive-farming activities.

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