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Characterization of soil samples according to their metal content

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Abstract Soil samples were collected from two small agricultural fields located in Médanos and Hilario Ascasubi, Bahía Blanca, Argentina and analyzed for Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sc, Th, U, Yb, and Zn by instrumental neutron activation analysis (INAA). In order to evaluate the contribution of anthropogenic sources and the similarity/dissimilarity between the samples, the database was studied by means of enrichment factors (EF) and discriminant analysis (DA), respectively. In addition to identifying redundant variables without losing essential information, the data set was studied using forward stepwise discriminant analysis.

Keywords Soil · Instrumental neutron activation analysis · Discriminant analysis · Procrustes analysis

Introduction

Soil is the source for most of the biologically active trace elements which reach man through plants and animals and can affect human health. The concentration levels of trace elements in soil can occur in concentrations that are toxic or deficient, both leading to weakened health. Several trace elements are considered essential such as Fe, Mn, Ni, Zn, Cu, V, Co, Cr, Mo, Sn, Se, I and F [1], although they can all be toxic if the concentrations exceed certain limits. Each has its specific role in the human metabolism, and they cannot be replaced by any other elements.

The trace elements in soil are linked to the determination of the geographic origin of foodstuff. This is one of the most important issues in the quality control of food and its traceability, because this may contribute to enforcing existing importation laws and regulations [2–10].

In this project, INAA was applied to determine the elemental composition of soil samples from two agricultural fields (45 ha each) being used for cultivating garlic. In order to identify compositional groups and anthropogenic sources, the data set was analyzed using discriminant analysis (DA) and enrichment factor (EF), respectively.

Experimental

The fields are located in Médanos and Hilario Ascasubi 39 km and 85 km away respectively, from Bahía Blanca, Argentina. The location was chosen due to its distance from local sources of pollution. The area receives about 584 mm of rainfall per year and the mean annual temperature is about 15 °C. In all, 200 soil samples were collected at different levels and the depth varied from 10 to 15 cm. The precise coordinate sampling points were determined during the sampling by using a GPS device. Figure 1 shows the two sampling locations.

The samples were prepared by manually grinding them into an agate mortar and pestle until a thin enough

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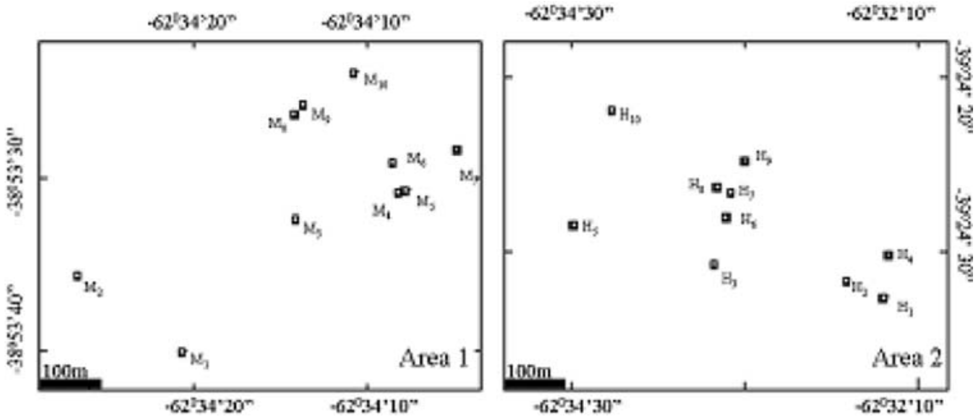

Fig. 1 Sampling points

granulometry was obtained. This was done in order to pass it through a 100 mesh sieve. These materials were dried in an oven for 24 h, at 105 °C and stored in a desiccator. Constituent Elements in Coal Fly Ash (NIST-SRM-1633b) were used as a standard and the International Atomic Energy Agency—IAEA-Soil-7 (Trace Elements in Soil) were used to check the samples throughout the analysis. These materials were dried in an oven for 2 h, at 105 °C and stored in a desiccator until weighing [11].

About 100 mg of soil samples, one standard (NIST-SRM-1633b) and one IAEA-Soil-7, were weighed in polyethylene bags and wrapped in aluminum foil. Groups of 8 samples and one reference material were packed in aluminum foil and irradiated in the research reactor's pool, IEA-R1, located at IPEN-CNEN/SP, Brazil. It was performed with a thermal neutron flux of about 5×10^{12} n cm^{-2} s^{-1} for 1 h.

Two measurement series were carried out, using a Ge (hyperpure) detector; model GX 2519 from Canberra, with a resolution of 1.90 keV, using a 1332.49 keV gamma peak of ^{60}Co and an S-100 MCA from Canberra. This contained 8192 channels. K, La, Lu, Na, U, and Yb were measured after 7 days cooling time and Co, Cr, Cs, Eu, Fe, Hf, Sc, Ta, Tb, Th, and Zn after 25–30 days. Gamma ray spectra analysis and the concentrations were carried out using the Genie-2000 Neutron Activation Analysis Processing Procedure from Canberra. The program calculates elemental concentrations by comparing integrated peak areas in the samples and the standards.

Results and discussion

Throughout this paper, a determination of all parameters in the analyses were measured and quantified [12], in order to make corrections before applying the method to real samples.

In order to evaluate the accuracy and the precision of the analytical process the IAEA—Soil—7 reference material elemental concentrations were statistically compared with the certified values. The elements, with an accurate and relative standard deviation (RSD) of less than 10%, were Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sc, Th, U, Yb and Zn. Afterwards, these elements were used in the subsequent data analyses.

Basic statistical parameters for the determined elements in the two fields, which included the arithmetic mean, minimum and maximum values, standard deviation, median, as well as the distribution's skewness and kurtosis, which was done for all of the samples, were calculated in order to describe the central tendency and variation of the data. In both fields the comparison of the variables' mean values with their median values showed that there were small variations for all the variables. According to the Shapiro-Wilk W statistic [13], the distribution parameters of all the variables were approximately normal in both fields. Skewness >1 occurred occasionally and was mainly caused by one or more outliers in the data set, rather than by significant deviations from normal distribution.

In order to evaluate the contribution of anthropogenic sources in the soil, the enrichment factors (EF) for each field were calculated. Fe was used as a conservative component and the average concentration of the earth's crust reported by Mason and Moore [14] was used as a reference. The EF values were in the same order of magnitude as those obtained in slightly polluted soil, so, anthropogenic sources have little influence on the chemical composition of soil. This is not surprising, because the study area is far from the city center and besides, there are no other roads in the vicinity with heavy traffic. The results show that there is no evidence of any chemical element fertilizer contribution. According to other authors, elevated values were found in cultivated soil samples and they are connected with pesticide and fertilizer usage. Comparing our database with the crustal average of Masson and Moore, our results were less than or of the same order of magnitude as the authors', showing clearly that the soil is free of contamination of trace elements.

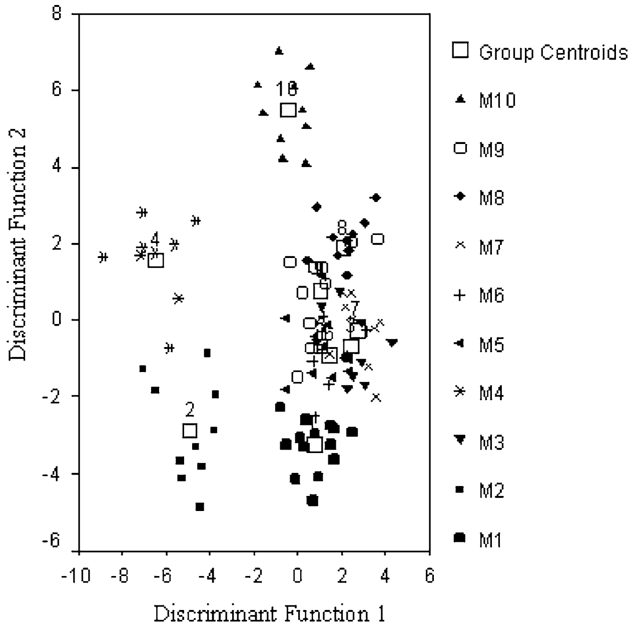

Fig. 2 Discriminant functions for all variables in Médanos

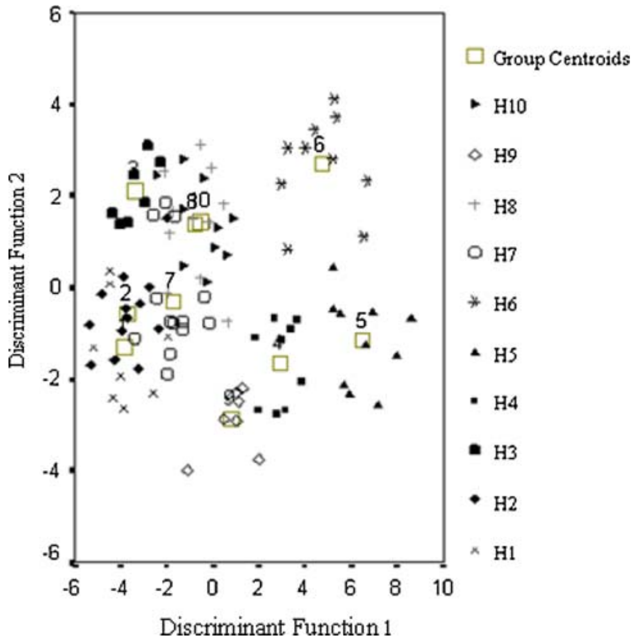

Fig. 3 Discriminant functions for all variables in Hilário Ascasubi

With the purpose of studying the similarities and the dissimilarities between the soil samples, the results were submitted to discriminant analysis. Initially the results were transformed to a log base of 10 in order to compensate for the large difference of percentage in magnitude between the measured elements and the trace level. Another reason for this is that a logarithmic transformation tends to stabilize the variance of the variables and would thus give them approximately equal weight in a non- standardized multivariate statistical analysis. Figures 2 and 3 show discriminant function 1 versus discriminant function 2 for all the soil samples from fields 1 and 2. As shown in Fig. 2, field 1 (Médanos) reveals five different chemical groups that are well separated from one another. At this location, the results show that the samples in positions M_1, M_2, M_4 and M_{10} are clearly different in their chemical compositions to other soil samples in the area. The samples collected at position M_3, M_5, M_6, M_7, M_8 and M_9 form only one cluster with a similar chemical composition.

As can be seen in Fig. 3, in field 2 (Hilario Ascasubi), the samples in positions H_4, H_5, H_6 and H_9 have a different chemical compositions. The samples at positions H_1, H_2 and H_7 and H_3 and H_8 show a high degree of chemical similarity between them and form a very tight homogeneous group, with similar chemical compositions.

Variable selection

In general when characterizing samples by means of chemical elements for the first time, the analyst measures several variables, many of which may not be very informative. In subsequent studies the analyst may wish to measure fewer variables without losing essential information.

A procedure for the identification of redundant soil variables was used, as well as the selection of variable subsets, preserving a multivariate data structure. Forward stepwise discriminant analysis and the fundamental partition equation was used by selecting those variables, which are in some sense adequate for characterization purposes [15–19].

The variable with the small partial *F* statistic was compared with a 95% critical value confidence level [19]. Thus the variables selected for field 1 (Médanos) were Fe, Sc, Na, U, Zn, Th, La, Ce, Cr, Yb, Eu and Hf and for field 2 (Hilario Ascasubi) were Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sc, Th, U and Yb.

To determine how well these subsets captured all the information of the soil samples, Figs. 2 and 3 show the plotting for discriminant function 2 versus discriminant function 1 for all the variables of fields 1 and 2, respectively. Figs. 4 and 5 show the plot of discriminant function 2 versus discriminant function 1 using the selected variables. The comparison of Figs. 2, 3, 4 and 5 confirm that forward stepwise discriminant analysis based on selected variables produced similar results to a discriminant analysis using all the variables. So, when doing an elemental characterization of this area of study, the use of selected variables was found to be appropriate for this research and could be applied to similar studies.

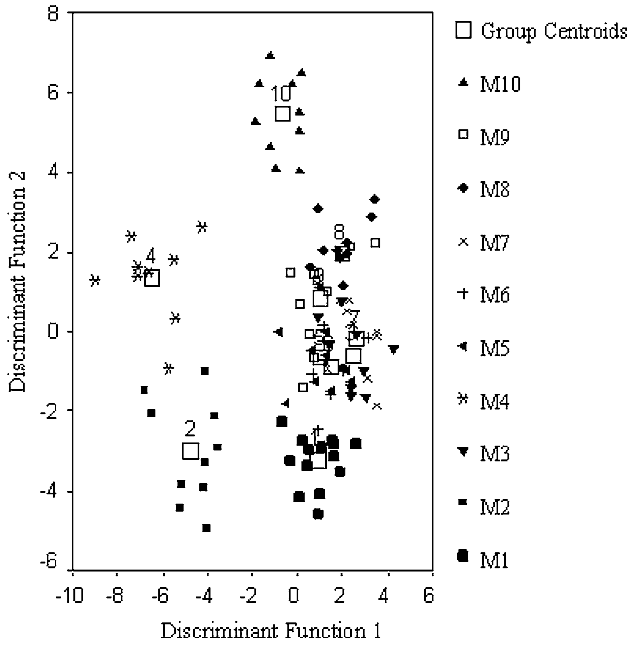

Fig. 4 Discriminant functions for selected variables in Médanos

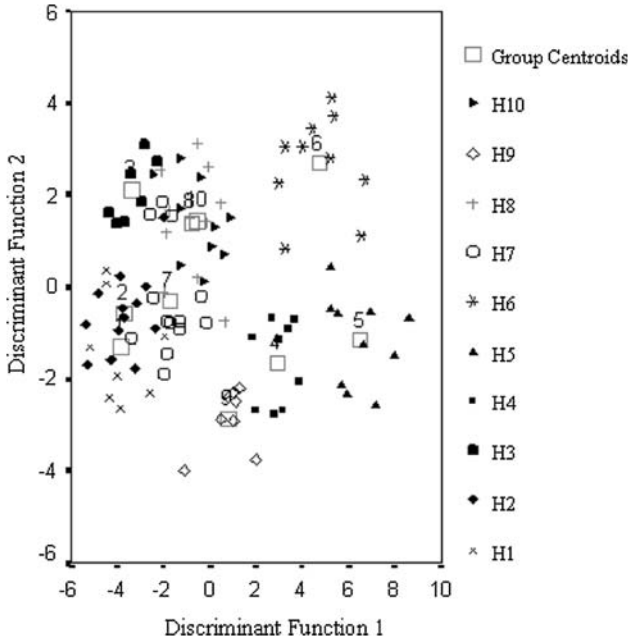

Fig. 5 Discriminant functions for selected variables in Hilário Ascasubi

Conclusion

This study showed the ability of the trace elements spatial variability in soil samples from two agricultural fields, which were used for garlic cultivation. The study was done in Médanos and Hilario Ascasubi in Bahía Blanca, Argentina. Although differences do exist in the elements' concentrations, simple inspection of the data set cannot be used to differentiate the chemical groups. Discriminant analysis revealed the occurrence of groupings between the analyzed samples according to their geographical positions. The trace elements showed that the studied area is free of anthropogenic sources, including the chemical elements from fertilizer. In field 1 (Médanos) there were 5 chemical groups in the M_1, M_2, M_4, M_8 and M_{10} geographical positions, with different chemical compositions. In the area located in Hilario Ascasubi, the statistical analysis revealed 5 groups that were different from the chemical elements. The plots of the discriminant functions, which use all the variables or with the selected variables obtained via forward stepwise discriminant analysis, display reasonably good visual separation of the samples.

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