Spatial Distribution of Metal Contents in Soil

K. P. Nunes(1), C. S. Munita(1), M. B. A. Vasconcellos(1), P. M. S. Oliveira(1), C. A. Croci(2)
F. M. Faleiros(3)

[1] Instituto de Pesquisas Energéticas e Nuclerares, IPEN-CNEN/SP, A. Prof Lineu Prestes 2242, CEP05508-000, São Paulo, BRAZIL.

[2] Laboratório de Radioisótopos, Depto de Química e Ing. Química, Universidad Nacional del Sur, Avda. Alem 1253, B 8000 FWB, Bahía Blanca, Argentina.

[3] CPRM – Brazilian Geological Survey. R. Costa, 55, CEP 01304-010 São Paulo/SP, BRAZIL.

Soil samples were collected in 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 INAA to study the spatial distribution. This agricultural area is used for garlic cultivation. The soil samples and the standards were irradiated in the swimming pool research reactor at IPEN-CNEN/SP, Brazil. The data sets were studied using several statistical methods. In order to evaluate the contribution of anthropogenic sources in the soil, enrichment factors were calculated. The similarity/dissimilarity between the samples was studied by discriminant analysis in order to explore the feasibility of classifying soils samples according to geographic position. In addition, to identify redundant variable without losing essential information, the data set was studied by

means of stopping rule for variable selection using forward stepwise discriminant analysis.

Introduction

Soil is the source of the most biologically active trace elements that reach man through plants and animals and which can affect human health. Elements from soil pass through the food chain and also get into the water supply. They can occur in concentrations that are either toxic or deficient, both leading to ill health. In general, it is the trace elements that are important, many of which are considered essential, although they can all be toxic if the concentrations exceed certain limits. For example, Na is required in the diet, but in excess it causes hypertension, this is a problem where saline soil affects the quality of the water.

Essential elements for health are the first row transition elements: Fe, Mn, Ni, Zn, Cu, V, Co and Cr, together with Mo, Sn, Se, I and F.[1] Each has its specific role in the metabolism, and it cannot be wholly or partially replaced by any other element. Their roles range from weak ionic effects to highly specific associations with metalloenzymes.[1] For example, Cr acts as cofactor for insulin, and I makes the hormone thyroxine active.[1] Potentially harmful trace elements include As, Cd, Pb, Hg and U.

Deficiency can result from small concentrations of trace elements or their unavailability in the soil, i.e. absolute, or induced. For example, decreased Zn availability is induced by the presence of Cu, Fe and Ca.[2] If the water is alkaline it decreases the availability of Zn and enhances plant uptake of Mo and Se, and iron-rich water restricts Se uptake.[3] In general the more acid the soil the more available Fe, Al, Mn and heavy metals such as Pb and Cd. In addition, where the soil is acid I and Se are less available.

The trace elements in soil are linked with the determination of the geographic origin of foodstuff using trace elements or chemical compounds and it is one of the most important issues in food quality control and traceability because it may contribute to enforce existing importation laws and regulations.[4] There are many studies attempting to elucidate the link between composition and geographic origin using a variety of analytical techniques, in general coupled with sophisticated data classifying techniques as multivariate statistical methods. Several studies determined the origin of some foodstuffs with some precision in several kinds of samples such as garlic,[5] wines,[6] olive oil,[7] asparagus varieties,[8] potatoes,[9] coffee,[10] orange juice[11] and pistachios.[12]

The analytical methods used can be categorized into two types: the physicochemical techniques and biological techniques. However, this kind of study is not an easy task not even with the availability of modern analytical techniques because the trace elements mobility in soil depends on their chemical speciation,[13] physicochemical conditions,[13] spatial distribution with respect to water, roots, micro-organism[14] and other factors such as rainfall, sunshine, temperature, soil characteristics, agricultural practice, and plant species that have important roles in the uptake of trace elements. It is the combination of these factors that influence the uptake of trace elements creating a fingerprinting where the plant grows.

The purpose of this study was to characterize by means of some trace elements soil samples from two agricultural fields (45 ha each) determined by means of INAA. Both areas in study are used for garlic cultivation. Garlic (genus *Allium*, family Alliaceae) is one of the oldest cultivated plants distributed worldwile and it has been an integral part of human health and diet. The health-beneficial properties are attributed to several sulfur-containing compounds derived from amino acid secondary metabolites.[15] Alliin is one of the most important secondary metabolites and is also a precursor to the flavor compounds that are unique to *Allium*. To identify compositional groups the data set were analyzed using discriminant analysis.

Experimental

Sample preparation and standard

The fields are located in Médanos and Hilario Ascasubi 39 km and 85 km away, respectively, from Bahia Blanca, Argentina. The precise coordinate sampling points were determined during the sampling by using GPS device. The topography is plane and horizontal. The place was chosen because it was far from local sources of pollution. The area receives about 584 mm/year of rainfall and the mean annual temperature is about 15ºC. Since the early 1995s the main crop grown on the studied area is garlic. Figure 1 shows the two sampling places used in this study. At each sampling location (area 1 and 2) the soil sample were collected at different levels, the depth varied from 10 to 15 cm and were placed in plastic bag for transportation to the laboratory.

In this study 200 samples of soil were analyzed using INAA. The samples were prepared by manual grinding in an agate mortar and pestle, until a thin enough granulometry was obtained in order to pass through a 100-200 mesh sieve. The material became more homogenous, considering that it would be predominantly used in a trace analysis. The large contamination, which could have been originated from agate, is silicon, which is not a serious problem, since this element was not determined. Finally, these materials were dried in an oven 105°C for 24h and stored in desiccator. Constituent Elements in Coal Fly Ash (NIST-SRM-1633b) was used as standard and International Atomic Energy Agency – IAEA-Soil-7, Trace Elements in Soil, was used as check samples in all analysis. These materials were dried in an oven at 105^{o}C for 2h and stored in desiccator until weighing.[16]

About 100 mg of soil sample, standard (NIST-SRM-1633b and 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 swimming pool, IEA-R1, from the IPEN-CNEN/SP, Brazil, at a thermal neutron flux of about 5 x 10^{12} n$\cdot$ cm$^{-2}\cdot$ s^{-1} for 8h.

Two measurement series were carried out using Ge (hyperpure) detector; model GX 2519 from Canberra, resolution of 1.90 keV at the 1332.49 keV gamma peak of ^{60}Co, with S-100 MCA of Canberra with 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 sample and standards.

Results and Discussion

NAA is a sensitive technique and it can determine the elements, which are found in very low concentrations, such as ppm (parts per million) or ppb (parts per billion). This characteristic has contributed to NAA being recognized as the preferred technique by various researchers who analyzed different kind of samples for trace levels. Because NAA is a highly sensitive technique, it is possible to quantify the small differences that may occur between the samples.

Another parameter related to the analytic properties of methods is about accuracy and precision. Accuracy is related to the real concentration of the sample element, a value that does not depend on the method used. The accuracy of the analytical methods is determined by means of the reference materials, where the concentration was determined by various analytical methods.

The determination of the analytic precision is of great importance and must be quantified. Precision is related to the capacity that the method has to reproduce the same result. The precision limitations can result from the sample inadequate preparation, either due to contamination with the same element that we want to determine, or due to inhomogenity problems.

In this paper the determination of all parameters in the analyses were measured and quantified to make corrections before applying the method in real samples, because these small variations may affect the power capacity to distinguish between the sample groups.

To evaluate the analytical process the elemental concentrations for the reference material IAEA – Soil – 7 Trace Elements in Soil were statistically compared with the certified values. Close agreement among replicate measurements is usually a pre-requisite in analysis for achieving good data comparability. The analytes with relative standard deviation, RSD, less than 10% were Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sc, Th, U, Yb and Zn. Then those elements were used in subsequent data analyses.

All possible sources of error in the gamma-ray spectrometry were considered and checked. A possible source of error in the determination of REE elements is the presence of significant amounts of fissible nuclides (^{235}U and ^{233}U). As it is well known, REE nuclides, especially among the light REE element (La to Sm), are produced both by activation and by fission. In the present work no interferences were expected in the samples due to the fact that very low uranium fission in the determination of La and Ce is negligible when uranium concentration does not exceed 5 ppm.[17]

Table 1 shows the basic statistical parameters for the elements determined in the two fields, including the arithmetic mean, minimum and maximum values, standard deviation, median, as well as distribution´s skewness and kurtosis for all samples used to describe the central tendency and variation of the data. In both fields the comparison of mean values of variables with their median values shows that there are small variations for all the variables. According to the Shapiro-Wilk W statistic[18] the distribution parameters of all variables were approximately normal in both fields. Skewness >1 occurred occasionally and was mainly caused by one or few outliers in the dataset rather than by significant deviations from the normal distribution.

In order to evaluate the contribution of anthropogenic sources in the soil, the enrichment factors (EF) for each field were calculated of a given element according to the following formula:

$$EF = (X/R)_{sample}/(X/R)_{reference}$$

where X and R represent concentrations of any element X normalized to a selected element R. In this paper Fe was used as conservative component and the average concentration of earth crust reported by Mason and Moore[19] as reference. The EF values are presented in last column in the Table 1. These values are of the same order of magnitude as those obtained on a weakly 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 not roads in the vicinity with heavy car traffic. On top of that the results show that there is not evidence of chemical element fertilizer contribution. In other places elevated values are found in cultivated soil samples and they are connected with pesticide and fertilizer usage. Comparing our database with the crustal average from Masson and Moore, our results are of less or of the same order of magnitude than the authors, showing clearly, that the soil is free of contamination.

The application of statistical methods in experimental results aims to classify and order the objects related to each other in function, exclusively, from its chemical composition. Various multivariate statistical techniques have been developed. However, discriminant analysis maximizes the difference between two or more groups and it is based on the fact that principal variance-covariance matrix is an accurate representation of the total variance and covariance. In addition, multivariate statistical methods are recognized methods to study data set to determine if the geographic origin of a sample could be characterized by the proportion of its trace element constituents.

With the purpose of studying the similarities and the dissimilarities between the soil samples, the results were submitted to discriminant analysis. The data were analyzed to explore the feasibility of classifying soil samples according to geographic origin. Initially the results were transformed to log base 10 to compensate for the large differences of magnitude between the measured elements in percent and for the trace level. The log base 10 transformation of data before a multivariate statistical methods is common. One 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 an unstandardized multivariate statistical analysis. Discriminant analysis was used to isolate those variables which could most effectively reveal the differences between cluster and to establish a discriminant function for this purpose. Figures 2 and 3 shows the discriminant function 1 versus discriminant function 2 for all the soil samples from fields 1 and 2. As shown in Figure 2 field 1 reveals five different chemical groups that are well separated from one another. In this place the result show that the sample analyzed in positions M_1, M_2, M_4 and M_{10} have a clear difference in the chemical composition between the 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 similar chemical composition.

As it can be seen in Figure 3 in the field 2 the soil samples collected at the positions H_4, H_5, H_6 and H_9 have different chemical composition. The samples at positions H_1, H_2 and H_7 and H_3 and H_8 show a high degree of chemical similarity among them and form a very tight homogeneous group with similar chemical composition.

Variable selection

In general when characterizing samples by means of chemical elements for the first time, such as soil samples, the analyst measures a large number of variables, many of which may not be very informative. In fact, some may even be unrelated to the issue at hand, and blur the picture instead of making it clearer. In subsequent studies the analyst may wish to measure fewer variables for several reasons such as to save time, in cases where measurement time is important or in order to reduce cost or effort; etc. Therefore, hopefully those variables, which are most relevant, will be determined without losing essential information and the less productive information will be removed.

A procedure for the identification of redundant variables for the soil is presented here as well as the selection of variable subsets preserving multivariate data structure. Forward stepwise discriminant analysis, was used by selecting those variables which are in some sense adequate for characterization purposes.

Assuming that p variables have been measured on each of n samples, and that the essential dimensionality of the data to be used in any comparison, is k, then the procedure is based on the fundamental partition equation[20,21]

$$T = B + W$$

where T is the matrix of the total variation in the data set, consisting of B, variation between the groups, and W, the variation within the groups. A formal discussion of these matrix components is given by Cooley and Lohnes.[22] By using these relationships one can use minimum trace-W, determinant-W, or maximization of trace W^{-1} B.[23] In this paper the minimum trace-W was used to determine which variable is important by comparison with the critical value at 95% confidence level. A criterion for assessing a particular variable x_{p+1} increases the separation provided by the variables x_1 ......x_p which is obtained by means of an analysis of covariance, treating x_{p+1} as the response, and x_1.....x_p as covariants. Then x_{p+1} provides significant additional information at level α if the partial F statistic for the value of the (p + 1)th variables is given by[23]

$$F = \frac{\boldsymbol{n-k-p}}{\boldsymbol{k}-1}\left(\frac{\boldsymbol{A_p}}{\boldsymbol{A_{p+1}}} - 1\right)$$

where A_p is the value of Wilk´s Lambda for MANOVA based on the first p variables[24] with F distribution with (k – 1) and (n – k – p) degrees of freedom if the (p + 1)th variable does not bring about a significant improvement in discrimination among the groups.

In others words, for each variable, the F statistic is computed. The variable corresponding to the lowest of these statistics is first selected. Variables are then added one at a time based on an examination of partial F statistic. The procedure terminates when none of the selected variables can be excluded, and no further variables can be included.

The procedure was applied on the data set. The partial F statistic involved in the database for forward selection procedure is shown in Table 2 and 3 for fields 1 and 2 respectively. The variable with the small partial F statistic was selected. In Table 2 the smallest value in the first column was 0.3008 corresponds to the variable Fe. For the sake of discussion, this is compared with the critical value at 95% of confidence level (0.0301). Hence Fe can be selected. The smallest partial F statistic in the second column is 0.0909 and it corresponds to the variable Sc. The comparison of this with the critical value at 95% of confidence level 0.0909 leads to the selection of Sc. The procedure terminates at step 13 when the smallest partial F statistic is higher than the critical value at 95% of confidence level (0.0020). Thus the variables selected are Fe, Sc, Na, U, Zn, Th, La, Ce, Cr, Yb, Eu and Hf for field 1 (Médanos). The same procedure was applied for field 2. The results are shown in Table 3. For field 2 the variable selected are Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sc, Th, U and Yb.

To determine how well these subsets capture all the information of the soil samples, Figures 2 and 3 show the plot for discriminant function 2 versus discriminant function 1 for all the variables for fields 1 and 2, respectively. Figures 4 and 5 show the plot of discriminant function 2 versus discriminant function 1 using the variables selected. The comparison of Figures 2, 3, 4 and 5 confirms that forward stepwise discriminant analysis based on selected variables produce similar results to a discriminant analysis using all variables. Then, to do elemental characterization of this area of study the use of selected variable is enough.

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 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 the 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 a different chemical composition. 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 variables or with the selected variables obtained via forward stepwise discriminant analysis, display reasonably good visual separation of the samples.

Acknowledgements

We thanks to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Process nº 06/57343-3 for the financial support.

References

1. J.A. PLANT, J.W. BALDOCK, B. SMITH, The role of geochemistry in environmental and epidemiological studies in developing countries: a review. In *Environmental Geochemistry and Health*. J.D. Appleton, R. Fuge, G.J.H. McCall, (eds), pp. 7-22. Special Publication No 113, Geological Society, London, 1996.

2. L. KIEKENS, Zinc. In *Heavy Metals in Soil*, 2nd edn. Alloway, B.J. (ed), pp. 284-305. Blackie Academic and Professional, Glasgow, 1995.

3. C.F. MILLS, Geochemical aspects of the aetiology of trace element related diseases, In *Environmental Geochemistry and Health*. J.D. Appleton, R. FUGE, G.J.H. MCCALL, (eds), pp. 1-5, Special Publication No 113, Geological Society, London, 1996.

4. R.S. SCHWARTZ, L.T. HECKING, J. Anal. At. Spectrosc., 6(1991)637.

5. R.G. SMITH. J.Agric, Food Chem., 53(2005)4041.

6. D. COZZOLINO, H.E. SMYTH, M. GISHEN, J. Agric. Food Chem., 51(2003)7703.

7. G. DOWNEY, P. MCINTYRE, A.N. DAVIES, J. Agric. Food Chem., 50(2002)5520.

8. D.P. PEREZ, M.T. SANCHEZ, G. CANO, A. GARRIDO, J. Agric. Food Chem., 66(2001)323.

9. K.A. ANDERSON, B.A. MAGNUSON, M.L. TTSCHIRGI, B. SMITH, J. Agric. Food Chem., 47(1999)1568.

10. K.A. ANDERSON, B.W. SMITH, J Agric. Food Chem., 50(2000)2068.

11. S. NIKDEL, S. NAGY, J. ATTAWAY, Sci. Toxicol., 596(1988)81.

12. K.A. ANDERSON, B.W. SMITH, J. Agric. Food Chem., 53(2005)410.

13. G. SPOSITO, The chemistry of soils. Oxford University Press, 1989.

14. B.J. ALLOWAY, A.P. JACKSON, Sci. Tot. Environ., 100(1991)151.

15. M. ICHIKAWA, K. RYU, J. YOSHIDA, J. N.B. IDE, Y. KODERA, T. SASSAOKA, R.T. ROSEN, J. Agric. Food Chem., 51(2003)7313.

16. C.S. MUNITA, R.P. PAIVA, M.A. ALVES, P.M.S. OLIVEIRA, E.F. MOMOSE, J. Trace Micropr. Techn. 21(2003)697.

17. M.D. GLASCOCK, Characterization of archaeological ceramics at MURR by NAA and multivariate statistics. In *Chemical characterization of ceramic paste in archaeology*; H. Neff, Ed.; Prehistory Press: New York, 1992; 11-26, Monographs in World Archaeology, Section 1.

18. STATSOFT. STATISTICA W, Vol. 1-3. Statsoft, Tulsa, OK, 1994.

19. B. MASON, C.B. MOORE, Principles of Geochemistry. Fourth Edition, John Wiley & Sons, 1982.

20. S.S. WILKS, Mathematical Statistics. Wiley and Sons, New York, 1962.

21. W.R. DILLON, M. GOLDSTEIN, Multivariate Analysis. Methods and Applications. John Wiley & Sons, Inc. New York, 1984.2

22. W.W. COOLEY, T.R. LOHNES, Multivariate data analysis. Wiley and Sons, New York, 1971.

23. J. RUBIN, H.P. FRIEDMAN, A cluster and analysis and taxonomy system for grouping and classification data. IBM, Scientific Center, New York, 1967.

24. J.D. JOBSON, Applied Multivariate data analysis. Vol. II, Spinger-Verlag, New York, 1984.

Captions

Table 1. Descriptive statistic for the elements in soil samples from Médanos and Hilario Ascascubi, field 1 and 2, respectively.

Table 2. Partial *F*- statistic for variable selection. in Médanos.

Table 3. Partial *F* - statistic for variable selection in Hilário Ascasubi.

Figure 1. Map of Médanos and Hilario Ascasubi showing the sampling points.

Figure 2. Discriminant functions for all variables in Médanos.

Figure 3. Discriminant functions for all variables in Hilário Ascasubi.

Figure 4. Discriminant functions for selected variables in Médanos.

Figure 5. Discriminant functions for selected variables in Hilário Ascasubi.

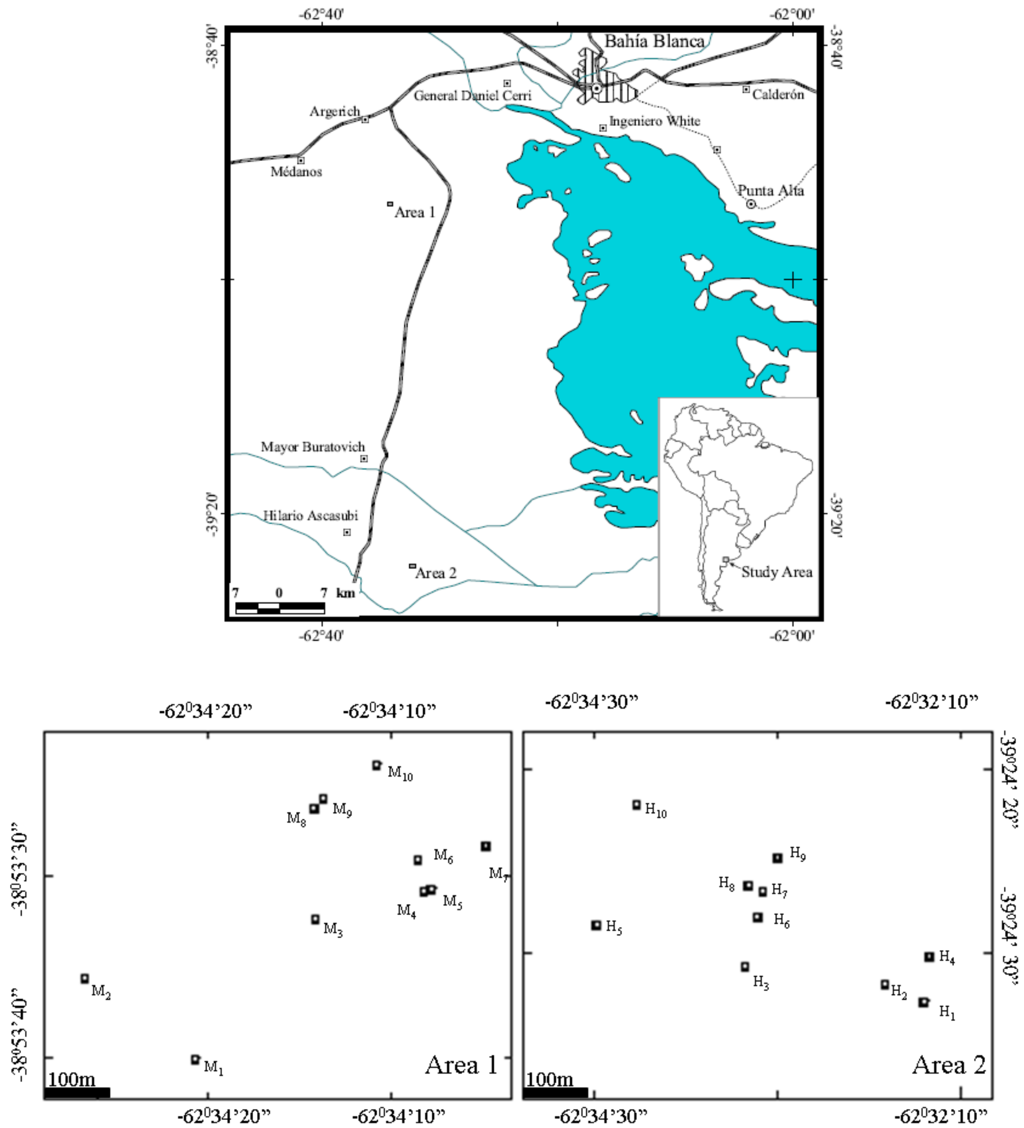

Figure 1 (Nunes et al)

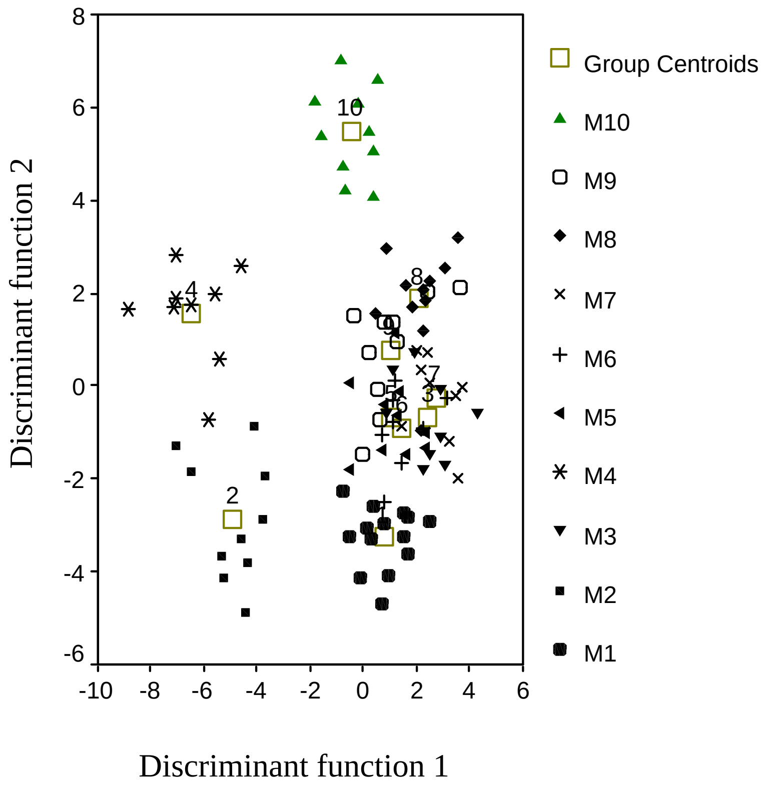

Figure 2 (Nunes et al)

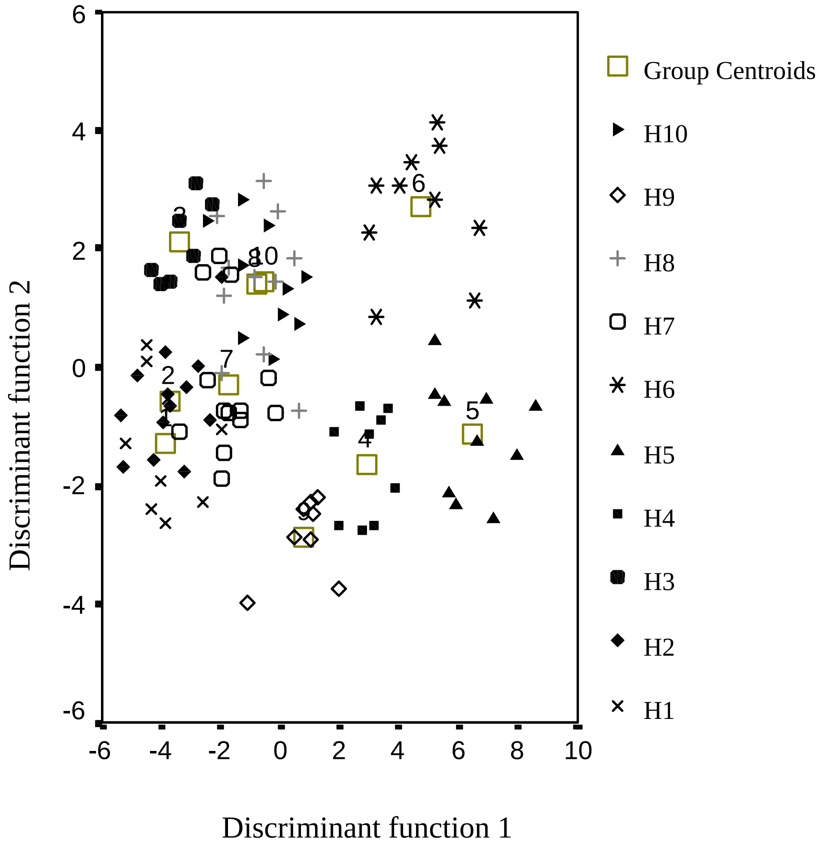

Figure 3 (Nunes et al)

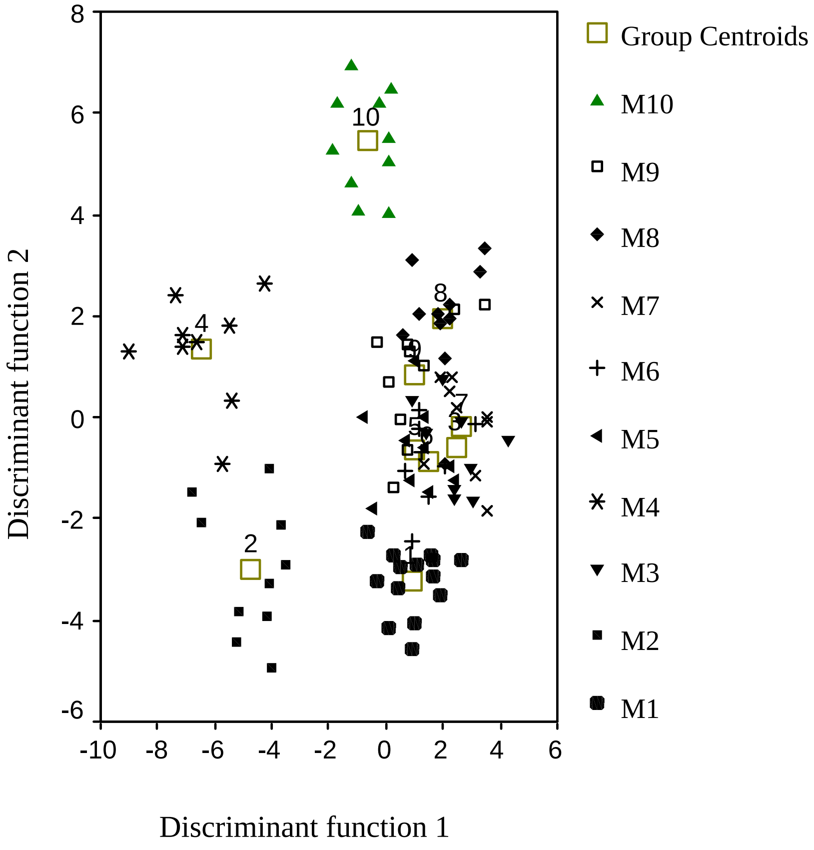

Figure 4 (Nunes et al)

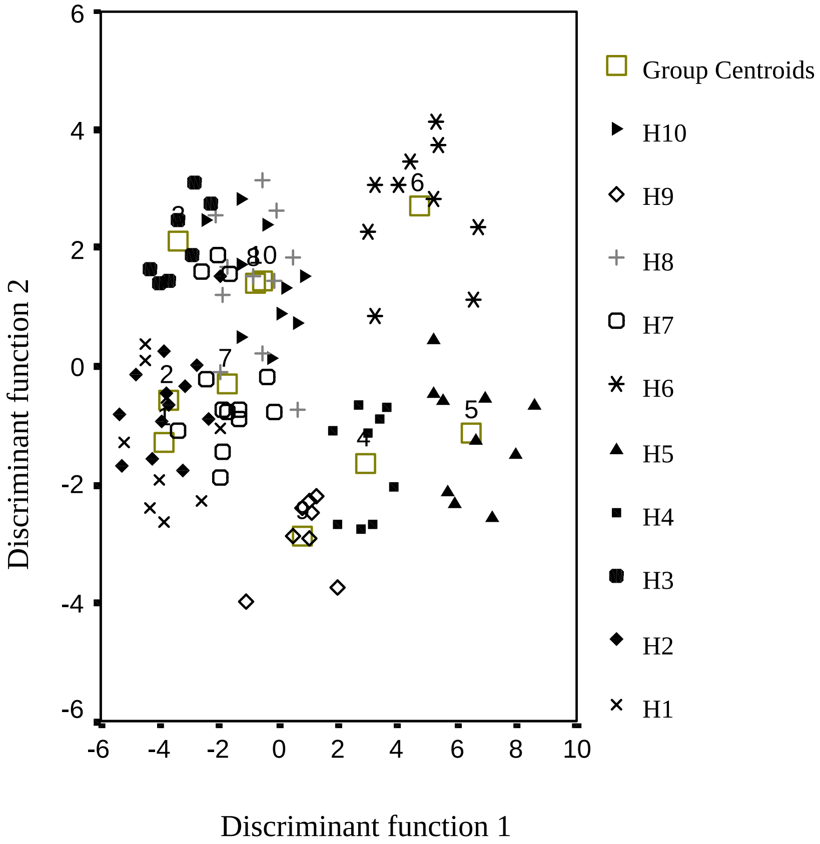

Figure 5 (Nunes et al)

Table 1 (Nunes et al)

	Mean	Min.	Max.	Median	Std. Dev.	Skewness	Kurtosis	EF
Médanos								
Ce	35.30	29.10	44.20	35.00	2.71	0.54	1.03	0.85
Co	10.07	8.60	11.60	10.10	0.61	-0.21	-0.22	0.58
Cr	28.80	20.00	39.00	28.30	3.63	0.26	0.21	0.42
Cs	3.01	1.50	4.30	3.00	0.49	0.01	0.28	1.45
Eu	1.08	0.80	1.30	1.10	0.10	-0.04	0.34	1.30
Fe,%	3.45	2.90	3.90	3.45	0.20	-0.09	-0.01	1.00
Hf	4.56	3.30	6.00	4.60	0.46	0.10	0.48	2.20
K,%	1.93	0.50	4.10	1.80	0.75	1.11	1.07	1.08
La	19.42	17.00	24.20	19.30	1.42	0.75	0.83	0.94
Na,%	2.66	2.40	3.00	2.60	0.12	0.61	0.42	1.36
Rb	65.98	27.00	98.90	66.30	12.93	-0.56	1.67	1.06
Sc	11.52	10.10	13.30	11.60	0.61	0.05	0.20	0.76
Th	6.36	5.30	8.50	6.30	0.57	0.81	1.63	1.28
U	1.54	0.60	2.70	1.60	0.51	0.02	-0.81	1.24
Yb	1.77	1.30	2.30	1.80	0.20	0.02	-0.09	0.76
Zn	60.49	41.30	81.10	59.25	7.67	0.23	0.51	1.25
Hilario Ascasubi								
Ce	43.52	38.80	50.80	43.15	2.58	0.62	0.05	1.05
Co	10.29	9.20	11.90	10.25	0.55	0.60	0.43	0.60
Cr	25.48	18.40	35.20	25.30	3.42	0.64	0.69	0.37
Cs	4.11	2.90	5.60	4.10	0.51	0.10	0.43	1.99
Eu	1.14	0.90	1.40	1.10	0.10	0.07	-0.13	1.38
Fe,%	3.27	3.10	3.50	3.30	0.11	0.29	-0.72	0.95
Hf	4.90	3.70	6.50	4.85	0.59	0.43	-0.17	2.37
K,%	2.24	1.10	3.90	2.10	0.65	0.68	-0.27	1.25
La	22.98	20.60	26.60	22.80	1.20	0.61	0.17	1.11
Na,%	2.49	2.30	2.60	2.50	0.09	-0.49	-0.29	1.27
Rb	70.90	30.20	97.60	72.40	14.07	-0.48	-0.01	1.14
Sc	11.83	10.90	12.90	11.80	0.45	0.29	-0.40	0.78
Th	7.45	6.40	8.90	7.40	0.53	0.26	-0.02	1.50
U	2.01	1.00	3.60	2.00	0.48	0.70	1.08	1.62
Yb	2.15	1.50	2.80	2.20	0.21	-0.22	1.15	0.92
Zn	67.74	46.00	89.40	68.05	8.37	-0.10	0.10	1.40

Table 2 (Nunes et al)

Variable	Steps												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Ce	0.6761	0.1957	0.0777	0.0194	0.0116	0.0072	0.0048	0.0038*					
Co	0.5119	0.2442	0.0840	0.0215	0.0130	0.0080	0.0058	0.0044	0.0035	0.0028	0.0024	0.0021	0.0019
Cr	0.6889	0.2317	0.0725	0.0181	0.0110	0.0068	0.0050	0.0038	0.0030*				
Cs	0.7984	0.2380	0.0747	0.0194	0.0117	0.0074	0.0055	0.0042	0.0034	0.0027	0.0023	0.0020	0.0018
Eu	0.7955	0.2564	0.0742	0.0196	0.0120	0.0073	0.0053	0.0040	0.0032	0.0027	0.0023*		
Fe	0.3008*												
Hf	0.8309	0.2558	0.0775	0.0193	0.0116	0.0074	0.0055	0.0042	0.0033	0.0027	0.0023	0.0020*	
La	0.7032	0.2066	0.0705	0.0180	0.0110	0.0068	0.0047*						
Na	0.5449	0.1137	0.0227*										
Rb	0.8999	0.2744	0.0837	0.0209	0.0126	0.0078	0.0059	0.0044	0.0035	0.0029	0.0024	0.0021	0.0019
Sc	0.3966	0.0909*											
Th	0.6998	0.1940	0.0598	0.0170	0.0100	0.0062*							
U	0.6157	0.1853	0.0521	0.0137*									
Yb	0.7018	0.2242	0.0733	0.0183	0.0111	0.0069	0.0051	0.0039	0.0032	0.0025*			
Zn	0.5253	0.2076	0.0602	0.0149	0.0085*								
Critical value **		0.0301	0.0909	0.0227	0.0137	0.0085	0.0062	0.0047	0.0038	0.0030	0.0025	0.0023	0.0020

* Variable entered at each step.
** Nominal 5% test

Table 3 (Nunes et al)

Variable	Steps														
	1	2	3	4	5	6	7	8	9	10	11	12	13	15	15
Ce	0.5747	0.1926	0.0321	0.0207	0.0141	0.0101	0.0075	0.0053	0.0040	0.0031	0.0023	0.0020	0.0015	0.0014*	
Co	0.4847	0.1713	0.0259	0.0175*											
Cr	0.8692	0.2024	0.0334	0.0227	0.0155	0.0108	0.0076	0.0056	0.0042	0.0033	0.0026	0.0020	0.0016*		
Cs	0.8169	0.1930	0.0321	0.0210	0.0145	0.0099	0.0070	0.0054	0.0038	0.0029	0.0023	0.0018*			
Eu	0.6723	0.1617	0.0274	0.0181	0.0124	0.0088*									
Fe	0.5772	0.1881	0.0292	0.0200	0.0134	0.0094	0.0067	0.0049	0.0037*						
Hf	0.5952	0.1541	0.0258	0.0178	0.0121*										
La	0.5072	0.2016	0.0330	0.0210	0.0142	0.0099	0.0070	0.0051	0.0039	0.0030	0.0023*				
Na	0.2599	0.0389*													
Rb	0.6698	0.1575	0.0255*												
Sc	0.2350*														
Th	0.6207	0.1820	0.0293	0.0191	0.0133	0.0092	0.0066	0.0048*							
U	0.8248	0.1879	0.0315	0.0210	0.0139	0.0094	0.0070	0.0051	0.0037	0.0028*					
Yb	0.6950	0.1902	0.0310	0.0199	0.0137	0.0095	0.0065*								
Zn	0.7709	0.2163	0.0359	0.0235	0.0161	0.0113	0.0082	0.0060	0.0044	0.0034	0.0026	0.0021	0.0017	0.0014	0.0013
Critical value **		0.2350	0.0389	0.0255	0.0175	0.0121	0.0088	0.0065	0.0048	0.0037	0.0028	0.0023	0.0018	0.0016	0.0014

* Variable entered at each step.
** Nominal 5% test