Assessing the agronomic and environmental effects of the application of cattle manure compost on soil by multivariate methods

María Victoria Gil, Luis Fernando Calvo*, Daniel Blanco, Marta Elena Sánchez

Department of Chemical Engineering, Institute of Natural Resources, University of León, Avenida de Portugal, 41, 24071 León, Spain

Abstract

Multivariate analysis was used for interpreting data from a pot experiment using samples of three Spanish soils. Samples of soil fertilized with compost were compared with untreated control samples. We also compared the effect of adding the compost to soil with a controlled moisture content of 50% of its water holding capacity (WHC), and to a near-saturated soil (95% WHC). Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used; they perfectly differentiated sample groups both as a function of the treatment applied and by sampling date. The compost samples were characterized by higher pH, electrical conductivity (EC), organic matter (OM) content and cation exchange capacity (CEC), together with nutrient concentrations than the control pots. The pots with a soil-compost mixture at 95% WHC presented lower values of EC, CEC, inorganic N, K, Na and B than the mixtures at 50% WHC. Multivariate methods may therefore be useful for the analysis and interpretation of a large number of data in soil research.

Keywords: Bovine manure; Compost; Multivariate analysis; Hierarchical cluster analysis; Principal component analysis

---

* Corresponding author: Luis Fernando Calvo. Tel.: +34 987 291844; fax: +34 987 291839.

E-mail address: lfcalp@unileon.es (L.F. Calvo).

1. Introduction

One of the most important aims of soil study is to assess its physical, chemical and biological properties, which are the main indicators of soil quality and fertility. Nevertheless, no isolated measurement, whether physical, chemical or biological, can give a complete picture of the quality of a soil (de Sena et al., 2000). Thus, an integrated analysis of the different parameters defining soil characteristics will offer more information than an individual analysis of such parameters. The above mentioned authors show chemometric data analysis to be a useful tool in the evaluation of soil research data, as it gives an integrated analysis of the data with improved extraction of the information contained. The univariate statistics normally used are too limited for this objective, while a multivariate analysis takes into account many variables analysed simultaneously to give much more information about the characteristics of a soil. Therefore, the consideration of several properties and multivariate analytical methods will be necessary for a greater understanding of soil processes.

Although in general these methods are underutilized in soil research, in recent years, some authors have begun to use multivariate analytical tools (Wander and Bollero, 1999; Ball et al., 2000; Lucho-Constantino et al., 2005). According to Sena et al. (2002), a better understanding of all aspects of soil quality is necessary in soil research. Particularly necessary is the development of better indicators of trends in changes resulting from different management systems and improved techniques for recognizing different patterns in the data. These authors also mention the possible usefulness of multivariate methods in assessing the effects of alternative soil amendments on soil properties. In this sense, we wanted to check if these techniques were really a useful tool for obtaining conclusions.

Several works have assessed the effect of the application of organic materials and wastes to the soil by the analysis of a few soil chemical properties, studied in isolation at the end of the growth cycle, with one or a few sampling dates throughout the experiment. However, we propose the use of multivariate analysis for an overall and more complete assessment of the effect of organic residues application to the soil. These techniques simultaneously analyse a large number of chemical parameters. Therefore, we were able to carry out exhaustive monitoring of soil evolution in an extended experiment with a high number of sampling dates. The multivariate methods chosen for analysing the data were hierarchical cluster analysis (HCA) and principal component analysis (PCA). These methods take into account the correlation between different variables, which are analysed simultaneously. They allow easier interpretation of the results and, according to Sena et al. (2002), offer new possibilities for soil research.

In this work, we will assess the use of multivariate analysis for the study of the effect of bovine manure compost application on the chemical properties and nutrient contents of samples of three agricultural soils in a pot experiment. On the one hand, pots containing soil treated with compost were compared with pots containing untreated soil, the latter as control, over 300 days of incubation. On the other hand, pots containing samples of soil treated with compost at a controlled medium moisture content (50% of its water holding capacity (WHC)) were compared with other, almost saturated (95% WHC), similar ones. Thus, the aims of this study were: (i) to check if the use of multivariate methods (HCA and PCA) is useful to differentiate soil samples in groups based on the treatment applied and the sampling time, (ii) to determine which variables characterize each of the sample groups, (iii) to evaluate the effects of the compost application on the soil chemical characteristics according to the results of HCA and PCA and (iv) to compare the effects of maintaining the soil-compost mixture at a moisture content of 50% WHC with another at 95% WHC, using the results of the multivariate methods.

2. Material and methods

2.1. Soil and compost samples

The experiments were carried out on soils taken from the top 15-20 cm of three plots in the province of León in northwest Spain, from a vineyard (V soil), a potato field (P soil) and a pear tree orchard (F soil). These soils were chosen because they belong to three of the most representative croplands of this region of Spain. The vineyard plantation was fifteen years old and the pear tree orchard was eleven years old. The potato field had been cultivated with a 2-year rotation of potato-winter wheat for the last five years. These soils had been conventionally managed; they had been fertilized with mineral nutrients and had not received organic fertilizers for the last seven years prior to the study. The texture was sandy clay loam in all places. Selected chemical properties of the soils at the beginning of the experiment are shown in Table 1.

Table 1
Properties of the soils and compost used in the study (means of three replicates) (dry matter basis)

Parameter	Soil or compost			
	V soil (vineyard)	P soil (potato)	F soil (pear trees)	Compost
pH	5.8 ± 0.2	6.1 ± 0.3	6.4 ± 0.3	9.6 ± 0.2
EC (dS/m)	0.010 ± 0.002	0.110 ± 0.020	0.109 ± 0.019	3.352 ± 0.089
Organic matter (%)	0.38 ± 0.05	1.53 ± 0.09	2.37 ± 0.13	56.96 ± 1.92
CEC (meq/100g)	1.5 ± 0.1	5.5 ± 0.3	6.2 ± 0.3	nd[a]
N total (g/kg)	0.5 ± 0.1	1.4 ± 0.1	1.6 ± 0.2	21.3 ± 2.5
NH_4^+-N (g/kg)	0.0010 ± 0.0004	0.0020 ± 0.0006	0.0020 ± 0.0004	0.80 ± 0.12
NO_3^--N (g/kg)	0.0020 ± 0.0007	0.0100 ± 0.0020	0.0120 ± 0.0030	1.10 ± 0.18
P Olsen (mg/kg)	6.3 ± 0.5	55.7 ± 2.4	79.8 ± 5.1	nd
P total (mg/kg)	nd	nd	nd	10400 ± 662
K (mg/kg)	43 ± 5	125 ± 13	371 ± 32	21700 ± 793
Ca (mg/kg)	275 ± 34	834 ± 29	808 ± 52	23700 ± 752
Mg (mg/kg)	34 ± 4	89 ± 6	153 ± 16	5680 ± 959
Na (mg/kg)	1.0 ± 0.2	14 ± 2	7 ± 2	4480 ± 426
B (mg/kg)	0.9 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	21,2 ± 0.3
Fe (mg/kg)	12 ± 1	138 ± 20	110 ± 12	1030 ± 175
Mn (mg/kg)	11.9 ± 0.6	6.6 ± 0.2	13.2 ± 1.3	176.2 ± 11.1
Cu (mg/kg)	3.0 ± 0.3	2.3 ± 0.4	6.9 ± 1.2	53.8 ± 1.6
Zn (mg/kg)	1.7 ± 0.1	2.4 ± 0.1	5.3 ± 0.7	182.3 ± 15.7
Cr (mg/kg)	9.6 ± 0.9	15.3 ± 1.4	0.7 ± 0.1	2.6 ± 0.3
Ni (mg/kg)	5.6 ± 0.6	11.5 ± 0.2	22.7 ± 0.5	<5.0
Pb (mg/kg)	8.9 ± 1.6	16.7 ± 0.4	19.3 ± 0.5	1.5 ± 0.2
Cd (μg/kg)	142 ± 12	154 ± 15	139 ± 12	88 ± 6
Hg (μg/kg)	<100	<100	<100	<200

[a] Not determined

The compost was produced from bovine manure. The composting system used was the turned bed or channel, beds being covered with a roof and force-aerated from below. After the thermophilic stage, the materials were placed in turned windrows, under a roof, until the end of the process. Compost samples were obtained from a local industrial composter. Selected chemical properties of the compost are shown in Table 1. The heavy metal concentrations were below the maximum permissible levels set out in Spanish Royal Decrees 824/2005 and 1310/1990 and European Council Directive 86/278/EEC.

2.2. Experimental design

Two experiments were carried out with each of the three soils (V, P and F) in 34 cm diameter and 29 cm deep pots with a hole in the bottom for drainage. The pots were filled with the respective soils, previously evenly mixed with compost in the case of the amended pots. Each of the amended pots (V1, P1 and F1) and the untreated control (V0, P0 and F0) soils were prepared in triplicate. The experiments were performed outside at ambient temperature.

In the first experiment, we compared pots of compost-treated soil (pots V1, P1 and F1) with controls (pots V0, P0 and F0). The amount of compost applied was 82 g DM per pot (115.7 g fresh weight per pot, equivalent to 9 Mg DM/ha), meeting the needs of N according to normal farming practice in the area. In the second experiment, we compared the effect of applying the same compost to soils with different controlled moisture content, 50% WHC (pots V1, P1 and F1) and 95% WHC (pots V2, P2 and F2). We wanted to compare the behaviour of the compost mixed with soil at a medium moisture content (50% WHC) used as control, which would be normal in the soil under usual conditions, with a near-saturated soil (95% WHC), because the latter condition would be usual after an episode of rain. The WHC of the V soil was 10% (m/m) and the WHC of the P and F soils was 18%. Therefore, to reach the value of 50% WHC, the moisture of pots V0 and V1 was kept at around 5% and the moisture of pots P0, F0, P1 and F1 was kept at 9%. On the other hand, in order to reach the value of 95% WHC, the moisture of pot V2 was kept at around 9,5% and the moisture of pot P2 and F2 was kept at around 17,1%. The water content was maintained by adding distilled water throughout the experiment after measuring the pot weight every two or three days.

Soil samples were obtained by extracting cores (1.2 cm in diameter and 20 cm in length) from each pot. The holes caused by soil sampling from pots were filled using a plastic bar having exactly the same diameter as the soil sampler. The bars avoided significant modifications in the pot, which could have meant that the samplings were not representative. The sampling was designed in such a way that the mass sampled was only 1.12% of the total mass of the pot. Such low ratio minimizes biases. Twenty-one parameters were determined for each soil sample: pH, electrical conductivity (EC), organic matter (OM) content, cation exchange capacity (CEC), organic N content, inorganic N concentration (NH_4^+-N + NO_3^--N), Olsen bicarbonate-extractable P concentration, ammonium acetate-extractable K, Ca, Mg and Na concentrations, B, Fe, Mn, Zn, Cu, Ni, Cr, Pb,Cd, and Hg concentrations. These parameters were monitored over 300 days and samples were taken at 0, 5, 10, 20, 40, 60, 80, 100, 120, 140, 180, 220, 260 and 300 days after the beginning of the experiment.

2.3. Chemical analyses

The soils in each pot were allowed to air dry and then passed through a 2 mm mesh screen before analysis. Bouyoucos' densimeter method was used to determine soil texture, which was obtained by fitting the percentages of sand, silt and clay fractions to the U.S.D.A. soil texture classification triangle (MAPA, 1994). Soil WHC was determined according to Sangnark and Noomhorm (2003). The moisture content of the samples was determined by drying a sample at 105ºC until constant weight was reached

(MAPA, 1994). The pH and EC were measured in 1:2.5 (m/v) soil and water ratio or 1:25 (m/v) compost and water ratio (MAPA, 1994). The organic carbon content of the compost samples was analysed by loss on ignition at 430ºC for 24h (Navarro et al., 1993). The Walkley-Black wet digestion method was used for the determination of soil organic matter (Walkley and Black, 1934). CEC was determined in $BaCl_2$ extracts by ICP-AES spectrophotometry, according to Hendershot and Duquette (1986). Organic nitrogen concentrations for soils and compost were determined according to the Kjeldahl method (Bremner, 1965). Ammonium-N concentrations of soils and compost were determined in KCl extracts using a pH ion-meter coupled with an ammonium ion selective electrode (APHA et al., 1992). Nitrate-N concentrations were determined in $CaSO_4$ extracts using a UV-visible spectrophotometer, according to the method described by Sempere et al. (1993). Available phosphorus was determined by Olsen method in HCO_3Na extracts using a UV-visible spectrophotometer. Concentrations of K, Ca, Mg and Na were determined in ammonium acetate extracts by atomic absorption spectrometry. Concentrations of Fe, B, Zn, Cu and Mn were determined in DTPA and CaCl by ICP-AES spectrophotometry. Concentrations of total P, Cr and Ni were determined by ICP-AES spectrophotometry after digestion in HNO_3 65% in a pressurized microwave. Lead and cadmium concentrations were determined using a graphite chamber atomic spectrophotometer. Mercury concentrations were determined with hydride generation by atomic absorption.

2.4. Multivariate statistical analysis

Hierarchical cluster analysis and principal component analysis were used to analyse the relationships between the applied treatments and the soil properties and nutrient concentrations. Multivariate methods were applied to the mean values of three replicates from each treatment. The initial variable values were standardized, mean centred and autoscaled to variance 1 prior to analysis to avoid any effects of scale of units with which they were measured.

The Hierarchical Cluster Analysis, HCA, is a technique used for classifying objects, which have been characterized by the values of a set of variables, into different groups. The clusters are formed by grouping objects according to similarity, and the results are presented in the form of dendrograms, which allow us to visualize the distances between objects. Data may be clustered in a variety of ways. We adopted the between-groups linkage or Unweighted Pair Group Method with Arithmetic mean (UPGMA) technique, which defines the distance between two clusters as the average of all the pairs of distances between elements of both clusters (Visauta and Martori, 2003). Similarities and dissimilarities were quantified by Square Euclidean distance measurements.

The Principal Component Analysis, PCA, is used in order to reduce the initial data from linear combinations of original variables. PCA breaks down the matrix of initial data, **X**, to express them as a least-square model (Geladi et al., 2003):

$$\mathbf{X} = \mathbf{A} \cdot \mathbf{F} + \mathbf{U} \tag{1}$$

where **X** is the original data matrix, **A** is the matrix of loadings of the original variables in the new reduced space, **F** is the matrix of scores of objects or samples and **U** is the matrix of residuals. The aim of PCA is the reduction of an original set of variables into a smaller set of non-correlated components which represent most of the information found in the original variables. The new calculated variables are called "principal components" (PCs), and are mutually orthogonal and not correlated. Usually, only the first few PCs in a descending order explain the maximum of the total variance of all original variables (Zbytniewski and Buszewski, 2005). PCA allows the whole data set to be represented in a way that is easy to interpret. The eigenvalue-one criterion, which is based on the fact that the average eigenvalue of autoscaled data is just one, was used to estimate the number of principal components. In this case only eigenvalues greater than 1 are considered significant. The principal component loadings of the data were analysed after the application of Varimax normalized rotation of the PCs coordinate system. The score plots of the first PCs may be used to investigate the interrelationships among the objects, as they allow the observation of clusters of objects. The interrelationships among variables may also be studied through the respective loading plots.

Data analysis was carried out using the SPSS v. 10.0 statistical package (SPSS, 1999).

3. Results and discussion

HCA and PCA were applied to the data of the three soils studied. In the first experiment, data were analysed for soils with and without compost (pots V0 and V1, P0 and P1, and F0 and F1) in order to study the effect of the treatment. In the second experiment, data were analysed for soils with low and high moisture content (pots V1 and V2, P1 and P2, and F1 and F2) to compare the effect of maintaining the soil-compost mixture at medium moisture content with other, near-saturated, soil.

PCA was made for all the parameters analysed (n =21) for each soil (data not shown). In PCA, loadings near to the origin of the coordinates will represent unimportant features. This determined that heavy metals (Ni, Cr, Cd, Cu, Pb and Hg) could be excluded from the analysis, as they did not contribute to the model. We had therefore fifteen variables for the later study: pH, EC, OM, CEC, inorganic N, organic N, Olsen bicarbonate-extractable P, ammonium acetate-extractable K, Ca, Mg and Na, B, Fe, Mn and Zn.

3.1. Effect of the application of compost to the soil

With the fifteen variables mentioned, separations of the samples according to the treatment applied and sampling day were found. In general, the results were similar for the three soils analysed.

With HCA, for soils V and P (Fig. 1a and 1b), the samples with compost (V1 and P1) were clearly clustered and distant from the compost-free controls (V0 and P0). The samples of the last days of the experiment (180-300 d) were nearer to those of the first days (0-60 d) than those in the middle (80-140 d). For soil F (Fig. 1c) there is also a separation of samples except for days 180-300, when both samples (with and without compost, F1 and F0) form a single cluster.

With PCA, a clear differentiation of groups of objects was also observed (Fig. 2), on one hand due to the presence/absence of compost, and on the other hand, depending on the sampling times. The graphs for the first two principal components (PC1 and PC2) are shown.

For soils V (Fig. 2a) and P (Fig. 2b) there is differentiation of the samples with compost (V1, P1) and those without compost (V0, P0). Furthermore, both groups have the same subgroups defined by the sampling times: 0-60 days, 80-140 days and 180-300 days. PC1 separates the sampling days; the first days have negative loadings on this axis, while the central days of the experiment show positive loadings, with the final days taking an intermediate position. On the other hand, PC2 separates the samples by treatments (compost/no compost); the samples with compost have positive Y axis values, while the control samples have negative ones. Even so, samples with compost have the highest values for both axes, meaning that the compost/no compost separation would also be influenced to some extent by PC1.

If the object graphs (Fig. 2a and 2b) and the component loadings of the different variables for the soils (Table 2) are analysed together, the importance of each variable in the discrimination of samples can be deduced. Most of the variables have positive loadings on the two axes, the same that the compost samples, meaning that these variables had greater values in the compost samples than in the controls.

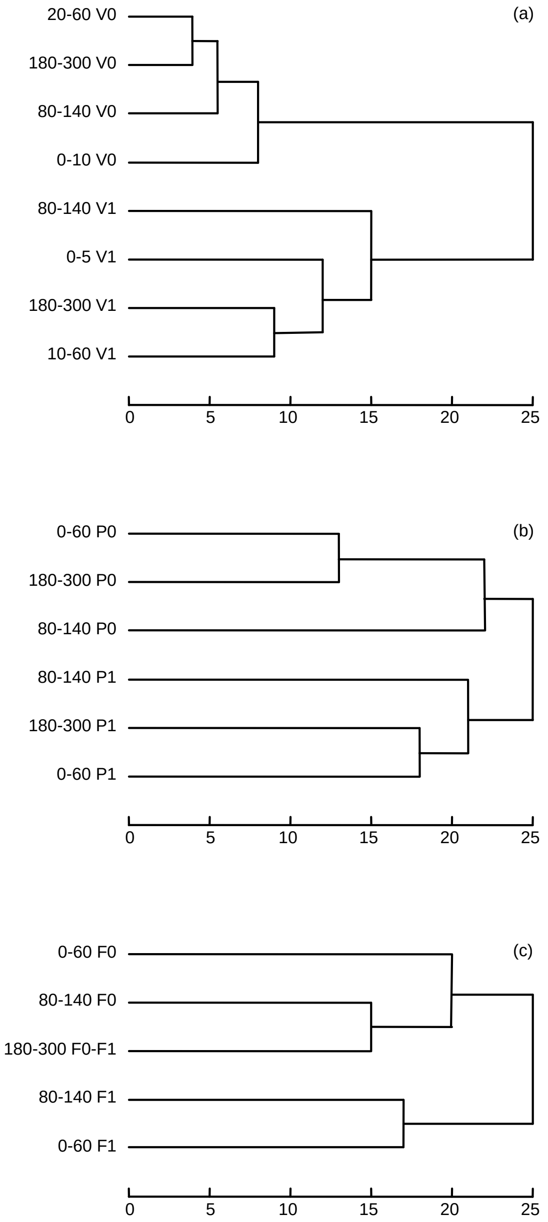

Fig. 1. Dendrograms obtained by HCA based on data of the effect of compost application to the soil from day 0 to day 300: (a) V soil (vineyard, pots V0 and V1); (b) P soil (potato field, pots P0 and P1) and (c) F soil (pear trees, pots F0 and F1). Pots 0 = without compost and pots 1 = with compost. The *x*-axis represents the Square Euclidean distances.

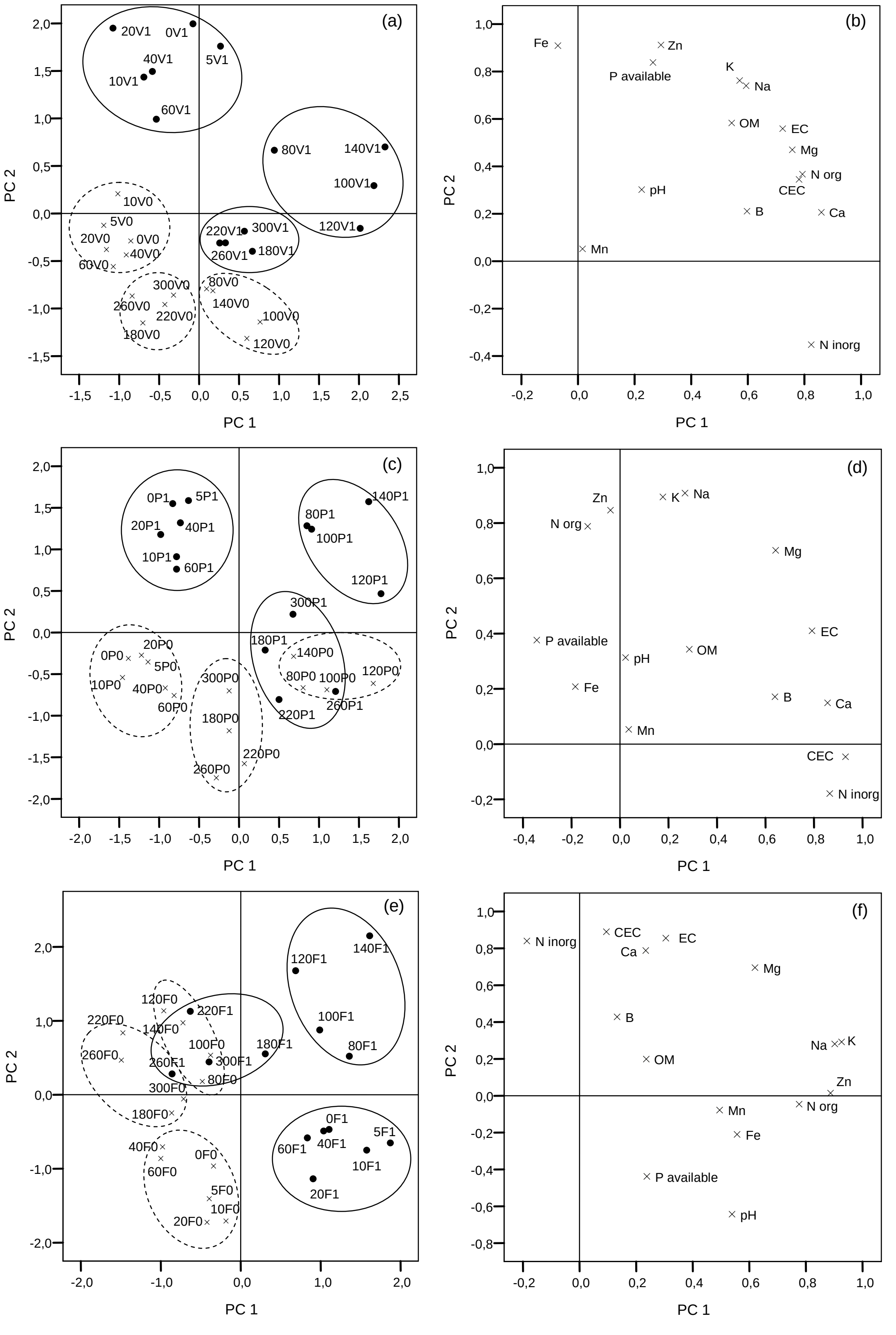

Fig. 2. Results of PCA based on data of the effect of compost application to the soil from day 0 to day 300: (a) score plot for V soil (vineyard, pots V0 and V1); (b) loading plot for V soil; (c) score plot for P soil (potato field, pots P0 and P1); (d) loading plot for P soil; (e) score plot for F soil (pear trees, pots F0 and F1) and (f) loading plot for F soil. Pots 0 = without compost (- -) and pots 1 = with compost (—).

Table 2
PCA component loadings for soil variables of the data based on the effect of compost application to the soil (pots 0 = without compost and pots 1 = with compost).

Parameter	V soil (vineyard)			P soil (potatoes)				F soil (pear trees)			
	PC1	PC2	PC3	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
Explained variance (%)	35.305	32.808	14.805	27.669	27.388	13.971	12.850	30.752	29.190	11.556	11.158
Cumulative Variance (%)	35.305	68.113	82.918	27.669	55.057	69.027	81.877	30.752	59.942	71.498	82.657
pH	0.225	0.302	0.731	0.023	0.313	-0.741	0.375	0.539	-0.643	-0.222	-0.207
EC	0.723	0.559	0.115	0.792	0.410	0.207	0.009	0.305	0.855	-0.070	0.209
OM	0.543	0.583	0.395	0.286	0.343	0.635	0.312	0.236	0.199	-0.622	-0.182
CEC	0.781	0.345	0.428	0.930	-0.046	-0.108	0.186	0.095	0.890	-0.038	-0.292
N organic	0.793	0.367	-0.138	-0.133	0.788	-0.186	-0.352	0.776	-0.046	-0.025	0.509
N inorganic	0.824	-0.352	0.128	0.865	-0.179	0.296	0.067	-0.186	0.840	-0.178	0.311
K	0.571	0.762	0.257	0.177	0.894	0.065	0.316	0.926	0.292	-0.123	-0.079
P Olsen	0.265	0.838	0.337	-0.343	0.376	-0.384	0.618	0.238	-0.438	0.143	-0.754
Ca	0.860	0.206	0.381	0.856	0.149	-0.119	-0.337	0.234	0.788	0.102	0.027
Mg	0.757	0.470	0.375	0.642	0.701	-0.075	0.011	0.620	0.695	-0.032	0.130
Fe	-0.071	0.909	0.032	-0.184	0.208	0.794	-0.056	0.557	-0.210	0.603	-0.078
Mn	0.016	0.052	-0.905	0.036	0.053	0.031	-0.932	0.495	-0.078	0.396	0.700
B	0.597	0.211	-0.063	0.639	0.171	-0.190	-0.199	0.133	0.428	0.781	-0.137
Na	0.594	0.740	0.093	0.268	0.908	0.028	0.134	0.902	0.281	-0.043	-0.075
Zn	0.293	0.912	-0.015	-0.039	0.846	0.356	-0.033	0.887	0.014	0.281	0.006

For V and P soils, PC1 was associated with CEC, inorganic N, EC, ammonium acetate-extractable Ca and B (variables with loadings > 0.5). For soil V, organic N and ammonium acetate-extractable Mg were also associated to PC1. However, PC2 was associated with Zn and ammonium acetate-extractable K and Na. The loadings of OM variable are similar in the two PCs. For soil V, Fe and Olsen bicarbonate-extractable P were also associated to PC2. For soil P, organic N was also associated to PC2 and the loadings of the ammonium acetate-extractable Mg were similar on the two axes.

The variables associated with PC1 in the two soils are mainly characterized by having higher values on the central days of the experiment because the groups of 80-140 days also have higher values of the PC1 in the object graphs. This is true both for composted samples and controls, although the values are much higher for the former. In soil P, the ammonium acetate-extractable Mg had high loadings for both axes, the same as the amended samples for the central days. This general increase in the values of most parameters in the central days can be explained because these days fell in the months of June, July and August. At this time of the year, in León (northwest Spain) the temperature is higher and less variable between day and night. This has a direct effect on the processes of microbial activity in the soil, which becomes faster and more constant, leading to an increase in the availability of elements in the soil. In this regard, Khalil et al. (2005) stated that high temperatures and favourable environmental conditions speed up the decomposition of organic materials, and Genxu et al. (2002) found that high temperatures in the summer months of the year promoted soil microbial activity. This is important from the agricultural point of view as it is thus possible to plan the application of nutrients, especially inorganic N, and so avoid its loss by leaching and consequent groundwater pollution.

The parameters that define PC2 had higher concentrations in the samples with compost, but these concentrations showed little variation over time, as they had low loadings for PC1, i.e. these variables did not increase during the central days. Regarding available P, Guerrero et al. (2001) observed that the levels of this nutrient remained constant or with slight fluctuations throughout one year of experiment.

On the other hand, OM in both soils, ammonium acetate-extractable K and Na in soil V and ammonium acetate-extractable Mg in soil P had similar loadings for both axes. These variables increased considerably in amended pots, but did not show such a sharp increase over the central days as the others. Soil pH was also increased with the use of compost, as it had positive loadings for both axes, but the values of these loadings were low, its value remaining therefore constant throughout the experiment. Olsen bicarbonate-extractable P, Fe in soil V, Zn and organic N in soil P also increased with compost, but did not affect discrimination of sampling days because their loadings for the PC1 were very low or even negative, i.e., they did not increase on the central days of the experiment. Mn in both soils and Fe in soil P, however, did not affect the model because of the low loadings on both axes, which means that their concentrations in the soil were not modified by the addition of compost.

Inorganic N had a negative loading for PC2 for both soils. If the data are observed, the values for this variable were only higher in the amended samples after the midpoint of the experiment, and in fact, its loading for PC1 was very high and positive and its loading for PC2 was low and negative. Therefore, the inorganic N would be in the area of separation of the samples of both treatments in the last days of sampling, confirming the slow mineralization of the organic nitrogen applied with the compost and the delay in nitrogen availability after compost application. In the same way, Erhart et al. (2005) found that compost could act as a slow-release nitrogen source.

Finally, in soil F (Fig. 2c), the same groups are present according to treatment, compost/no compost, as are the same subgroups regarding sampling days, but the situation is different for the first PCs. It is PC2 that discriminates the sampling days, having negative values over the first days, positive ones in the central period, and intermediate ones towards the end. PC1 now separates samples according to treatments, amended samples (F1) remaining on the positive side of this axis and the controls (F0) on the negative side. Over the final days (180-300 days) the samples with and without compost were fairly close, which was observed on the corresponding dendrogram, where they formed a cluster. In the PCA they did form two separate groups, with the amended samples towards the higher values of the PCs.

For soil F (Table 2), PC1 was associated with ammonium acetate-extractable K, ammonium acetate-extractable Na, Zn and organic N, and to a lesser extent with Fe. PC2 was associated with CEC, EC, inorganic N, ammonium acetate-extractable Ca, and, less so, with B. The loadings of ammonium acetate-extractable Mg were similar for the two axes. These variables are exactly the same as those explaining the two PCs for soil P, but the opposite way round, so that, although these two groups of samples take opposing places, the results for soil F are similar to those for soil P.

The variance explained by the PC1 and PC2 is quite similar in the three soils (Table 3) and we can not attribute a major significance to the treatment applied or to the sampling date in the discrimination of samples for the three soils.

If the loadings of variables (Table 2) are observed, a slightly different behaviour is noted for the soil V from that of the other two. Thus, all parameters in soil V, except pH and Mn, are significant in the discrimination of groups. It could be due to the fact that the soil V (vineyard) was poorer than the others, because its nutrient contents (N, P, K, Ca, Mg, Na, Fe) were lower and also its pH, EC, OM and CEC values were smaller (Table 1); therefore, the effect of the compost application was rather more noticeable. This is particularly important in the organic matter content, because the soil V initially only had a value of 0.38%, which indicates a great deficit of organic matter in this soil.

The multivariate analysis allowed us to reach same practical conclusions on the application of compost to the soil. Thus, we could conclude that this compost increased the pH and EC of the soil, along with its OM content, organic N and CEC. On the other hand, this compost was a source of nutrients, as it raised the concentrations of inorganic N (though not from the beginning of the experiment), Olsen bicarbonate-extractable P, ammonium acetate-extractable K, Ca, Mg and Na, B and Zn. Other authors had also found increases after organic fertilization in the values for EC (Stamatiadis et al., 1999), CEC (Ouédraogo et al., 2001) and OM content (Mantovi, 2005). On the other hand, other authors recorded that compost contributed nutrients such as K and available P (Guerrero et al., 2001; Ouédraogo et al., 2001).

3.2. Comparison of medium and high moisture content in the soil-compost mixture

Firstly, an HCA and a PCA were carried out with the fifteen variables selected, but the formation of groups of objects in the three soils analysed was not clear. We eliminated the parameters with low loading, since they did not contribute to the model, allowing a clearer discrimination (data not shown). Thus, the elimination of OM, organic N, Olsen bicarbonate-extractable P, ammonium acetate-extractable Ca and Mg permitted the distinction of groups separated by treatments over the central and final days of the study. We were left with 10 variables for the analysis: pH, EC, CEC, inorganic N, ammonium acetate-extractable K, ammonium acetate-extractable Na, B, Fe, Mn and Zn.

The HCA showed some differences in the three soils analysed (Fig. 3). In the PCA (Fig. 4), the separation of objects was generally clearer than with the HCA. The graphs are also shown for the first two principal components (PC1 and PC2), which explain most of the data variance.

In soil V (Fig. 4a), the separation of samples was similar to that obtained with the HCA. The subgroups defined by sampling days are the same as for the previous experiment, i.e., 0-60, 80-140 and 180-300 days. Over the first period there was no difference between the samples with high and low moisture content (V2 and V1), while between days 80 and 300, they were separate, with samples being closer for both treatments in the final days of the experiment (180-300 d) than over the central days (80-140 d). PC1 was associated with ammonium acetate-extractable K, ammonium acetate-extractable Na, EC, Fe and Zn, and that PC2 was associated with CEC, inorganic N and B (Table 3). As in the previous experiment, some variables (inorganic N, B) were situated in the same area as the samples of the central days, indicating that these variables had higher values than in the rest of the study, owing to the better ambient conditions.

Comparing pots V1 and V2 over the first 60 days reveals no difference, and these samples were highly correlated with the variables Mn, Fe and Zn, which also have negative loading for PC2. Therefore, these variables were not significantly different between the two considered soil moisture contents and their concentrations were not increased over the central days. From day 80 to day 300, however, the values were higher for V1 pots than V2 for both axes, which would seem to show that the values for CEC, inorganic N, EC, ammonium acetate-extractable K and Na and B were higher over this period when moisture is low. As for pH, a variable with negative loadings for both PC, it had a higher value in the V2 pots, that is, it increased more after compost application when moisture was high.

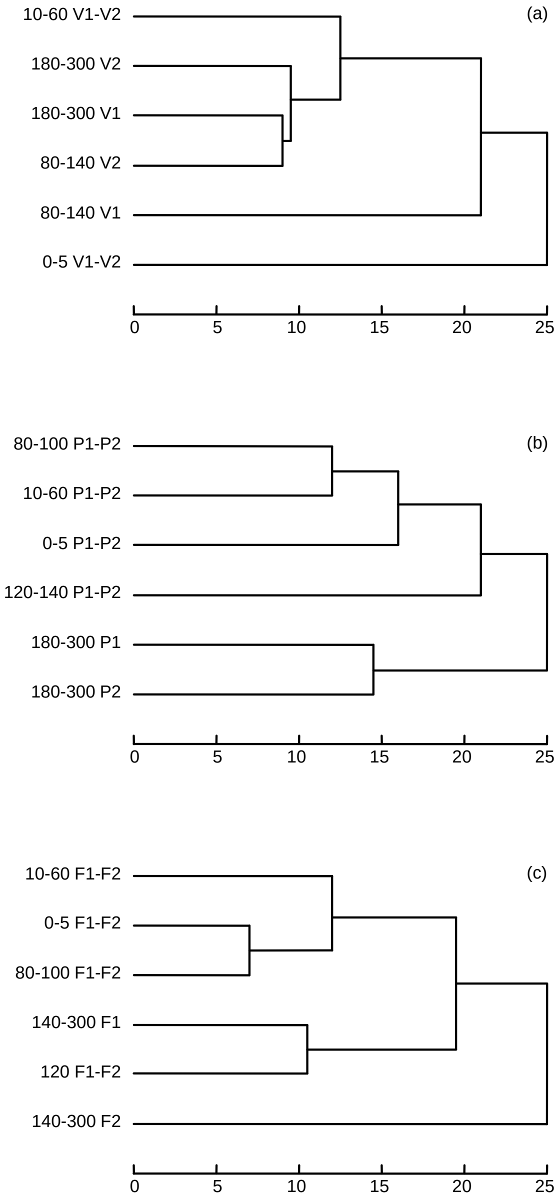

Fig. 3. Dendrograms obtained by HCA based on data of the effect of soil moisture content on the application of compost from 0 to day 300: (a) V soil (vineyard, pots V1 and V2); (b) P soil (potato field, pots P1 and P2) and (c) F soil (pear trees, pots F1 and F2). Pots 1 = 50% WHC moisture and pots 2 = 85% WHC moisture. The *x*-axis represents the Square Euclidean distances.

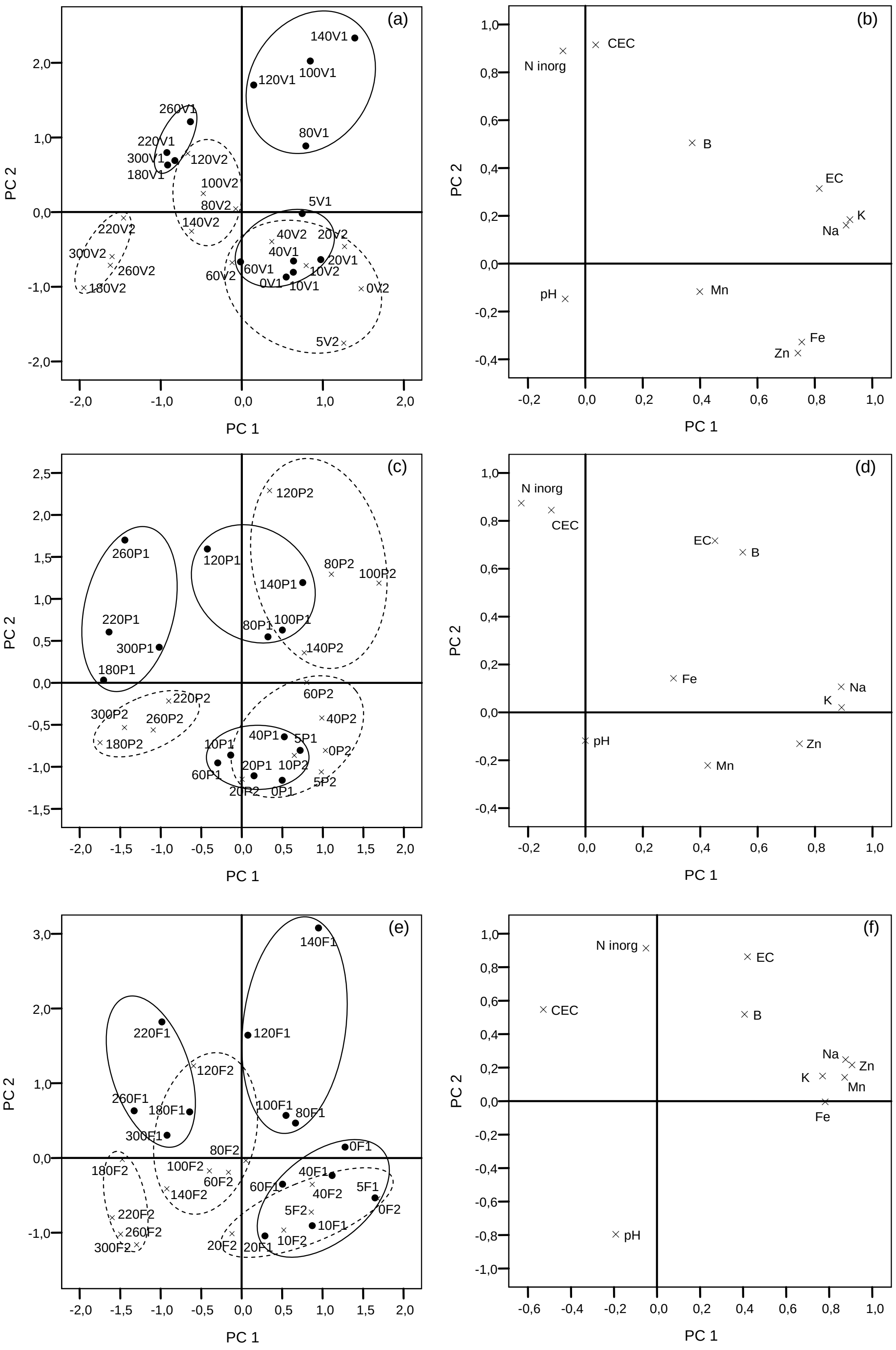

Fig. 4. Results of PCA based on data of the effect of soil moisture content on the application of compost from 0 to day 300: (a) score plot for V soil (vineyard, pots V1 and V2); (b) loading plot for V soil; (c) score plot for P soil (potato field, pots P1 and P2); (d) loading plot for P soil; (e) score plot for F soil (pear trees, pots F1 and F2) and (f) loading plot for F soil. Pots 1 = 50% WHC moisture (—) and pots 2 = 85% WHC moisture (- -).

Table 3
PCA component loadings for soil variables of the data based on the effect of soil moisture content on the application of compost (pots 1 = 50% WHC moisture and pots 2 = 85% WHC moisture).

Parameter	V soil (vineyard)			P soil (potatoes)			F soil (pear trees)	
	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2
Explained variance (%)	37.709	23.237	18.095	29.900	25.510	24.566	42.130	29.289
Cumulative Variance (%)	37.709	60.946	79.042	29.900	55.410	79.977	42.130	71.420
pH	-0.070	-0.147	-0.879	0.000	-0.118	-0.930	-0.192	-0.796
EC	0.816	0.314	0.335	0.451	0.717	0.388	0.420	0.863
CEC	0.036	0.915	-0.070	-0.119	0.845	-0.266	-0.528	0.547
N inorganic	-0.078	0.889	0.289	-0.224	0.874	0.268	-0.051	0.913
K	0.922	0.184	-0.072	0.892	0.020	0.060	0.769	0.149
Fe	0.755	-0.328	0.110	0.307	0.142	0.709	0.782	-0.005
Mn	0.399	-0.117	0.682	0.426	-0.221	0.780	0.872	0.141
B	0.372	0.505	-0.297	0.548	0.669	-0.006	0.407	0.518
Na	0.909	0.160	0.236	0.891	0.107	0.340	0.876	0.248
Zn	0.741	-0.374	0.457	0.746	-0.131	0.261	0.906	0.216

For soil P (Fig. 4b), the separation of samples was also similar to that obtained with HCA, so there was no separation between the high and low moisture samples (P2 and P1, respectively) in the first 140 days, while separate groups did appear between days 180 and 300. The loadings associated with PC1 were ammonium acetate-extractable K, ammonium acetate-extractable Na and Zn, while those associated with PC2 were inorganic N, CEC, EC and B. In soil F (Fig. 4c) there was also a discrimination of samples into groups according to sampling days and treatments, but in this case, the separation between high moisture (F2) pots and low moisture ones (F1) began from day 100-120. The variables associated with PC1 are Zn, ammonium acetate-extractable Na, Mn, Fe and ammonium acetate-extractable K, and those associated with PC2 are inorganic N, EC, pH and B. CEC have similar loadings for both axes.

Therefore, for the soils P and F, some variables had higher values over the central days (inorganic N, EC and B), as in the previous study, owing to the better ambient conditions. Inorganic N and CEC, with positive loadings for the PC2 but negative loadings for the PC1, was higher for pots P1 and F1, that is, with low moisture content, between days 100 and 300. Regarding the period 180-300, the samples with least moisture are on the positive side of the Y axis, and those with high moisture on the negative side, which shows that these soils also lost elements in the central and final stages of the study, with lower values for CEC, inorganic N, EC, B, ammonium acetate-extractable Na and ammonium acetate-extractable K, which all have positive values for the Y axis. There is no increase in pH over the central days, as it has a negative value for the Y axis, being higher when moisture is higher (P2 and F2).

Soils P and F retained more moisture than soil V due to the better conditions of these soils in relation to organic matter content, whose deficit leads to loss of soil structure and reduction in the water and nutrient retention. Therefore, soils P and F retained elements longer, and no separation of samples was observed between low and high moisture content until after the middle of the experiment, so moisture did not decrease or cause leaching before that.

Certain parameters appear to have been noticeably affected by soil moisture which may, therefore, decrease their values through leaching when it is above a certain level: inorganic N, EC, ammonium acetate-extractable K, ammonium acetate-extractable Na and B. Stamatiadis et al. (1999) also found a low soil EC explained by the leaching of soluble salts contained in compost, and emphasized the need to detect such adverse management effects, especially in soils of low cation exchange capacity. On the other hand, Debosz et al. (2002) stated that in the absence of a crop, inorganic N will probably leach down to deeper layers during irrigation. Mendham et al. (2003) stated that potassium is easily leached from soil, and Covelo and Gallardo (2002) say the same for Na.

Other variables, like OM, organic N, Olsen bicarbonate-extractable P, ammonium acetate-extractable Ca and ammonium acetate-extractable Mg do not seem to be affected in this way, and are not leached down to lower layers after the addition of more water. These elements would, then, mean a lower pollution risk. The latter nutrients could be associated with OM or the clay-humus complex and remain in the soil for this reason. Haileslassie et al. (2005) also stated that P is not susceptible to leaching, owing to adsorption to soil particles, while, on the other hand, K and inorganic N are subject to leaching. Mendham et al. (2003) found that Ca was leached through the soil more slowly than other cations.

Once again, with the multivariate methods the data were simultaneous and globally analysed avoiding multiple analyses of variance which must be carried out with all the variables. Sena et al. (2002) also stated that the multivariate methods largely enhance the capacity of extraction and interpretation of data information from soil analysis in relation to univariate and bivariate methods.

5. Conclusions

In this study, the multivariate methods allowed us to obtain conclusions about the application of compost to soil. The two utilized methods perfectly differentiated sample groups both as a function of the treatment applied, compost/no compost and medium/high moisture, and by sampling date, through the integrated evaluation of fifteen chemical parameters. In these experiments, the PCA showed a clearer differentiation of groups of samples than the HCA, allowing to answer the aims formulated in this study.

Therefore, the results allow to conclude that multivariate techniques, HCA and PCA, can help us extract important information from soil data when a high number of soil properties are analysed. These techniques also allow to know the most important variables for the discrimination of samples as a function of the factors which are considered. Multivariate techniques provided us with plots giving summarized information which can be globally visualized and they improved and facilitated the interpretation of soil data, making the identification of the key parameters affected by the treatments easier. Therefore, we have shown multivariate statistical methods to be a powerful tool for the integrated evaluation of soil properties and we think they should be more widely utilized in soil research in the future.

References

APHA, AWWA, WPCF, 1992. Métodos normalizados para el análisis de aguas potables y residuales. American Public Health Association, American Water Works Association and Water Pollution Control Federation. Ediciones Díaz de Santos, S. A., Madrid.

Ball, B.C., Campbell, D.J., Hunter, E.A., 2000. Soil compactibility in relation to physical and organic properties at 156 sites in UK. Soil Till. Res. 57, 83-91.

Bremner, J.M., 1965. Total nitrogen. In: Black, C.A. et al. (Eds.), Methods of Soil Analysis. Part 2. Agronomy 9. Am Soc. Agron. Inc., Madison, WI, pp. 1149–1178.

Covelo, F., Gallardo, A., 2002. Effect of pine harvesting on leaf nutrient dynamics in young oak trees at NW Spain. Forest Ecol. Manag. 167, 161-172.

Debosz, K., Petersen, S.O., Kure, L.K., Ambus, P., 2002. Evaluating effects of sewage sludge and household compost on soil physical, chemical and microbiological properties. Appl. Soil Ecol. 19, 237-248.

de Sena, M.M., Poppi, R.J., Frighetto, R.T.S., Valarini, P.J., 2000. Avaliação do uso de métodos quimiométricos em análise de solos (Evaluation of the use of chemometric methods in soil analysis). Quim. Nova 23, 547-556.

Erhart, E., Hartl, W., Putz, B., 2005. Biowaste compost affects yield, nitrogen supply during the vegetation period and crop quality of agricultural crops. Eur. J. Agron. 23, 305-314.

Geladi, P., Manley, M., Lestander, T., 2003. Scatter plotting in multivariate data análisis. J. Chemometr. 17, 503-511.

Genxu, W., Ju, Q., Guodong, C., Yuanmin, L., 2002. Soil organic carbon pool of grassland soils on the Qinghai-Tibetan Plateau and its global implication. Sci. Total Environ. 291, 207-217.

Guerrero, C., Gómez, I., Moral, R., Mataix-Solera, J., Mataix-Beneyto, J., Hernández, T., 2001. Reclamation of a burned forest soil with municipal waste compost: macronutrient dynamic and improved vegetation cover recovery. Bioresource Technol. 76, 221-227.

Haileslassie, A., Priess, J., Veldkamp, E., Teketay, D., Lesschen, J. P., 2005. Assessment of soil nutrient depletion and its spatial variability on smallholders' mixed farming systems in Ethiopia using partial versus full nutrient balances. Agr. Ecosyst. Environ. 108, 1–16.

Hendershot, W.H., Duquette, M., 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. Soil Sci. Soc. Am. J. 50, 605-608.

Khalil, M.I., Hossain, M.B., Schmidhalter, U., 2005. Carbon and nitrogen mineralization in different upland soils of the subtropics treated with organic materials. Soil Biol. Biochem. 37, 1507-1518.

Lucho-Constantino, C.A., Álvarez-Suárez, M., Beltrán-Hernández, R.I., Prieto-García, F., Poggi-Varaldo, H.M., 2005. A multivariate analysis of the accumulation and fractionation of major and trace elements in agricultural soils in Hidalgo State, Mexico irrigated with raw wastewater. Environ. Int. 31, 313-323.

Mantovi, P., Baldoni, G., Toderi, G., 2005. Reuse of liquid, dewatered, and composted sewage sludge on agricultural land: effects of long-term application on soil and crop. Water Res. 39, 289-296.

MAPA, 1994. Métodos oficiales de análisis (Tomo III). Ministerio de Agricultura, Pesca y Alimentación. Dirección General de Política Alimentaria, Madrid.

Mendham, D. S., O'Connell, A. M., Grove, T. S., Rance, S. J., 2003. Residue management effects on soil carbon and nutrient contents and growth of second rotation eucalypts. Forest Ecol. Manag. 181, 357–372.

Navarro, A.F., Cegarra, J., Roig, A., García, D., 1993. Relationships between organic matter and carbon contents of organic waste. Bioresource Technol. 44, 203-207.

Ouédraogo, E., Mando, A., Zombré, N.P., 2001. Use of compost to improve soil properties and crop productivity under low input agricultural system in West Africa. Agr. Ecosyst. Environ. 84, 259-266.

Sangnark, A., Noomhorm, A., 2003. Effect of particle sizes on functional properties of dietary fibre prepared from sugarcane bagasse. Food Chem. 80, 221-229.

Sempere, A., Oliver, J., Ramos, C., 1993. Simple determination of nitrate in soils by second-derivative spectroscopy. J. Soil Sci. 44, 633-639.

Sena, M.M., Frighetto, R.T.S., Valarini, P.J., Tokeshi, H., Poppi, R.J., 2002. Discrimination of management effects on soil parameters by using principal component analysis: a multivariate analysis case study. Soil Till. Res. 67, 171-181.

SPSS, 1999. SPSS Base 10.0, Manual del usuario. SPSS Inc, Chicago, Illinois, EE.UU.

Stamatiadis, S., Werner, M., Buchanan, M., 1999. Field assessment of soil quality as affected by compost and fertilizer application in a broccoli field (San Benito County, California). Appl. Soil Ecol. 12, 217-225.

Visauta, B., Martori, J.C., 2003. Análisis Estadístico con SPSS para Windows. Volumen II. Estadística multivariante. Segunda edición. Ed. McGraw-Hill, Madrid.

Walkley, A., Black, I.A., 1934. An examination of the Degtjareff method for determining soil O.M. and a proposed modification of the chromic acid titration method. Soil Sci. 37, 29-38.

Wander, M.M., Bollero, G.A., 1999. Soil Quality Assessment of Tillage Impacts in Illinois. Soil Sci. Soc. Am. J. 63, 961-971.

Zbytniewski, R., Buszewski, B., 2005. Characterization of natural organic matter (NOM) derived from sewage sludge compost. Part 2: multivariate techniques in the study of compost maturation. Bioresource Technol. 96, 479-484.