ASSESSMENT OF HEAVY METALS IN SOILS OF A VINEYARD REGION WITH THE USE OF PRINCIPAL COMPONENT ANALYSIS

Gustavo Souza Valladares[1]*; Otávio Antônio de Camargo[2]; José Ruy Porto de Carvalho[3]; Alessandra Maria Cia Silva[4]

[1]UFC/CCA, Depto. de Ciências do Solo, Campus do Pici, Bloco 807, C.P. 12168 - 60021-970 - Fortaleza, CE - Brasil.
[2]Instituto Agronômico de Campinas, Av. Barão de Itapura, 1481 - 13012-970 - Campinas, SP - Brasil.
[3]Embrapa Informática Agropecuária, Av. André Tosello, 209 - C.P. 6041 - 13083-886 - Campinas, SP - Brasil.
[4]PUC - R. Marechal Deodoro, 1099 - 13010-920 - Campinas, SP - Brasil.
*Corresponding author <g_souza_valladares@yahoo.com.br>

ABSTRACT: Agricultural management with chemicals may contaminate the soil with heavy metals. The objective of this study was to apply Principal Component Analysis and geoprocessing techniques to identify the origin of the metals Cu, Fe, Mn, Zn, Ni, Pb, Cr and Cd as potential contaminants of agricultural soils. The study was developed in an area of vineyard cultivation in the State of São Paulo, Brazil. Soil samples were collected and GPS located under different uses and coverings. The metal concentrations in the soils were determined using the DTPA method. The Cu and Zn content was considered high in most of the samples, and was larger in the areas cultivated with vineyards that had been under the application of fungicides for several decades. The concentrations of Cu and Zn were correlated. The geoprocessing techniques and the Principal Component Analysis confirmed the enrichment of the soil with Cu and Zn because of the use and management of the vineyards with chemicals in the preceding decades.
Key words: PCA, GIS, soil pollution, copper, zinc

AVALIAÇÃO DE METAIS PESADOS EM SOLOS DE REGIÃO DE VINHEDOS COM O USO DA ANÁLISE DOS COMPONENTES PRINCIPAIS

RESUMO: O manejo agrícola com agroquímicos pode levar a contaminação dos solos por metais pesados. O objetivo deste trabalho foi aplicar a Análise dos Componentes Principais e técnicas de geoprocessamento para identificar a origem dos metais pesados Cu, Fe, Mn, Zn, Ni, Pb, Cr e Cd como contaminantes potenciais em solos agrícolas. O estudo foi desenvolvido em uma área cultivada com vinhedos no Estado de São Paulo, Brazil. Amostras de solos foram coletadas e georeferenciadas por GPS sob diferentes usos e coberturas. As concentrações dos metais nos solos foram obtidas pelo método de extração com DTPA. As concentrações de Cu e Zn foram consideradas altas na maioria das amostras pesquisadas, sendo maiores nas áreas cultivadas com vinhedos sob aplicações de fungicidas por décadas. As concentrações de Cu e Zn apresentaram correlação. As técnicas de geoprocessamento e a Análise dos Componentes Principais indicaram enriquecimento do solo com Cu e Zn devido ao uso e manejo dos vinhedos com agroquímicos nas décadas anteriores.
Palavras-chave: ACP, SIG, poluição do solo, cobre, zinco

INTRODUCTION

Soil conservation is fundamental for the sustainable development and preservation of ecosystems and biodiversity. Soil contamination by heavy metals, exposes a risk to the productive capacity and the balance of the ecosystems. The soil is exposed to contamination by several anthropic activities, mainly by agriculture (Facchinelli et al., 2001).

The soil has a diverse heavy metal concentration that is dependent on the parent material on which it is formed, the formation processes, and the composition and proportion of the components of the solid phase (Fadigas, 2002; Alleoni et al., 2005a). This concentration may be affected by several anthropic activities such as: irrigation, fertilizer and chemical applications, and industrial or urban sewage incorporation (Facchineli, 2001; Costa, 2002; Nicholson et al.,

2003). The soil type, topography, geology, and the erosive processes influence the concentration and distribution of heavy metals in the environment, including their bioavailability (Ramalho et al., 2000; Costa, 2002).

Cultivation may cause soil contamination by heavy metals, and specifically, by copper in vineyard areas (Deluisa et al., 1996; Giovannini, 1997; Brun et al., 1998; Facchinelli et al., 2001; Parat et al., 2002; Alleoni et al., 2003; Chaignon & Hinsinger, 2003; Chaignon et al., 2003; Eijsackers et al., 2005; Felix, 2005). The effect of this contamination may be reflected in the plant behavior, microbiological processes and the transfer of toxic levels of the elements to man and animals (Nicholson et al., 2003).

Principal component analysis (PCA) is a multivariate statistical method in which each principal component (factor) is a linear combination of the original variables. It is useful for simultaneous analysis of several factors and is a technique that explains the variability of the data during the reduction of a great number of variables to a few unrelated components.

The objective of this study was to apply the PCA method to assess the origin of the metals Cu, Fe, Mn, Zn, Ni, Pb, Cr, and Cd, potentially toxic elements of agricultural soil pollution.

MATERIAL AND METHODS

The study was performed in a 59.8 ha catchment area in Jundiaí, São Paulo state, Brazil (23º11' S, 46º53' W), occupied by 2.9 ha vineyard, ten to sixty years old, with natural vegetation, pastures and other kinds of orchards in the vicinity, at 672 to 755 m altitude, with a rolling and hilly landscape in a geomorphological province dominated as 'half-orange' type relief. The soil types in the area are Inceptisols, Ultisols and Oxisols (Valadares et al., 1971), and the main original rock is the schist. The basic characteristics, pH, sum of bases, CEC, base saturation, C, sand, silt, and clay contents are presented in Table 1.

The spatial data was made uniform and GPS located based on satellite images of high spatial resolution. An interpretation of land use/cover was made

Table 1 - Descriptive statistics of the element concentrations in the soils.

Measure	Cu	Fe	Mn	Zn	Cd	Cr	Ni	Pb
0-0.15 m	--- mg dm^{-3} ---							
Maximum	18.5	481.0	66.1	41.6	0.2	0.2	3.2	16.2
Minimum	0.6	19.0	2.7	0.3	0.0	0.0	0.1	0.0
Mean	3.9	113.4	17.4	7.6	0.1	0.1	0.6	1.5
Standard deviation	3.5	94.5	12.2	6.5	0.0	0.0	0.4	1.7
Coefficient of variation	89.5	83.4	69.8	85.6	64.4	75.0	71.1	111.7
Measure	pH	Sum of bases	CEC	Bases saturation	C	Sand	Silt	Clay
0-0.15 m	----- mmol$_c$ dm^{-3} -----			%	---------------- g kg^{-1} ----------------			
Maximum	6.5	298	313	95	60.9	816	357	450
Minimum	3.6	6	41	6	7.5	218	74	75
Mean	4.8	49	91	50	19.7	613	147	240
Standard deviation	0.6	49	44	23	8.2	101	49	72
Coefficient of variation	13.2	99.3	48.4	45.4	41.8	16.4	33.6	29.9
Measure	Cu	Fe	Mn	Zn	Cd	Cr	Ni	Pb
0.15-0.30 m	--- mg dm^{-3} ---							
Maximum	15.5	438.0	70.3	261.7	0.1	0.2	4.7	7.0
Minimum	0.4	10.0	0.7	0.3	0.0	0.0	0.0	0.1
Mean	3.2	87.2	12.7	7.4	0.0	0.1	0.5	1.3
Standard deviation	3.2	81.2	11.6	26.2	0.0	0.0	0.5	1.0
Coefficient of variation	99.3	93.2	91.4	353.0	77.0	76.9	106.8	77.6
Measure	pH	Sum of bases	CEC	Bases saturation	C	Sand	Silt	Clay
0.15-0.30 m	----- mmolc dm^{-3} -----			%	---------------- g kg^{-1} ----------------			
Maximum	6.4	333	347	96	46.4	820	349	600
Minimum	3.7	5	33	5	4.1	139	63	75
Mean	4.7	33	75	42	12.6	603	142	254
Standard deviation	0.6	37	37	22	6.4	105	46	83
Coefficient of variation	12.9	113.3	49.3	52.0	50.5	17.4	32.0	32.7

with detailed field checking based on an IKONOS II mosaic, represented in Figure 1 (orbital point 159539, on 04/07/2001 at 13h19 min and 08/11/2001 at 13h24 min). The land use/ land cover map and the topographic data (Melo & Lombardi Neto, 1999) were utilized to plan soil sampling establishing a total of one hundred sample points. These points were georeferenciated and integrated in a vectorial format in the GIS -geographic information system (Figure 1).

At this stage the area was traversed and, with the help of an auger, georeferenciated perturbed soil samples at 0–0.15 and 0.15–0.30 m depths were collected, making up 200 samples. Samples were air dried, crushed and passed through a 2 mm sieve. The extraction of the heavy metals (Cu, Fe, Zn, Mn, Cr, Ni, Cd, and Pb) was carried by the DTPA method, considered the best extractor for the conditions under study to determine the bioavailable forms, and that is the most used extractor for soils from São Paulo State (Raij, et al., 2001; Abreu et al., 2002). Extracted metals in solution were determined by ICP-OES.

The descriptive statistics for the soil analysis are presented in Table 1. A Pearson correlation analysis was performed among the metals, for each soil layer. For the PCA the amount of metal in each layer was considered. The data were standardized to an average of 0 and a variance of 1 and the analyses were performed on the data matrix. The first four components were rotated using the Varimax program according to the scheme applied by Boruvka et al. (2005).

In the PCA, the factors that refer to the information on all eight of the variables that were estimated. Each soil sample, which was defined by the eight variables, is discribed by the new variables (factors) that make it possible to localize them as a point in a bi/tridimensional graph, where those that are closest together are the most similar; this can be utilized to group individuals. In this case study GIS tools were used to interpret the results of the PCA.

RESULTS AND DISCUSSION

The mean values for all the elements were slightly superior at the surface layer as compared to the subsurface layer (Table 1). With respect to the elements, according to Raij et al. (1997), high levels of Cu were present in the majority (95%) of the samples. These values indicate that Cu for the soils of the region is naturally high. There are soils under vineyards in the South of Brazil with very high levels of Cu, evaluated by the DTPA method, after decades of chemical cupric applications, e.g. a Lithic Odorthents
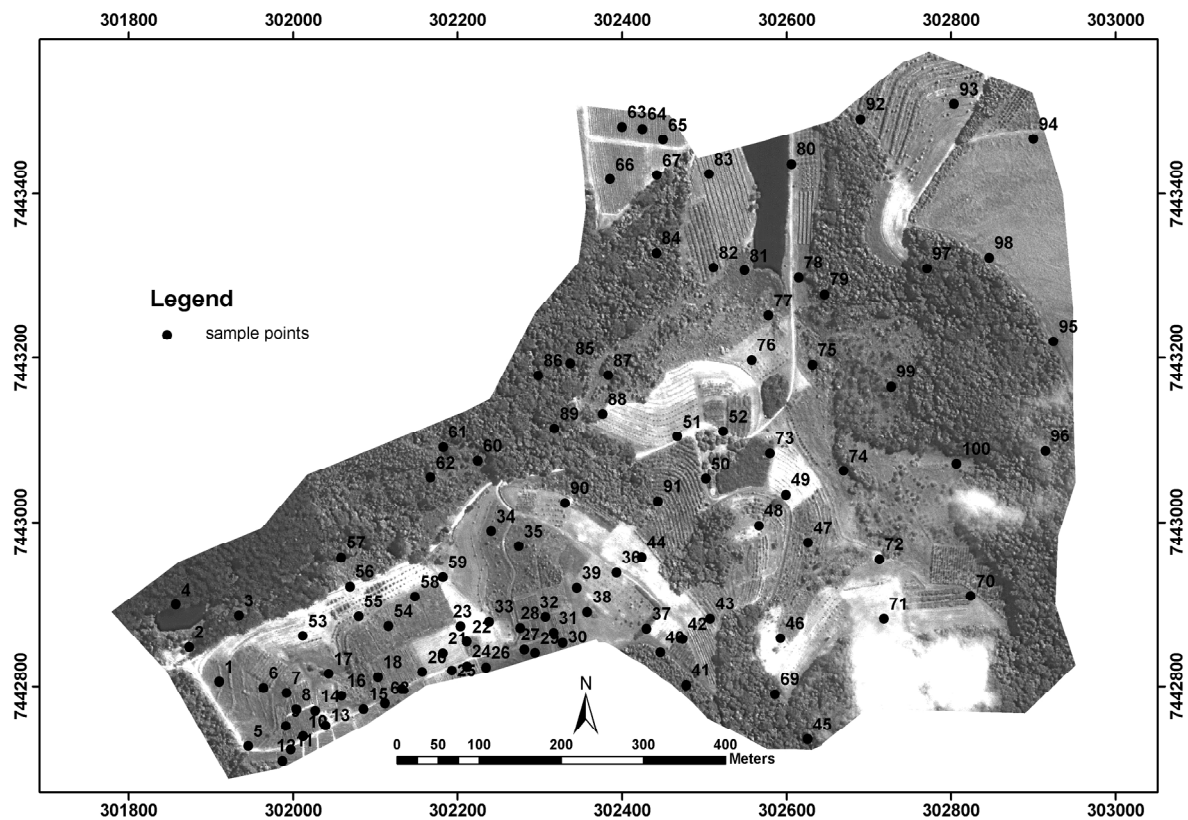

Figure 1 - IKONOS II image of the area in CAPTA-Frutas with georeferenciated sample points.

with 522 mg kg^{-1} and a Humic Dystrudepts with 475 mg kg^{-1} (Alleoni et al., 2003). For soils from Rio de Janeiro State, 29.1% of the samples had high levels of Cu (Pereira et al., 2001). Outside Brazil, a differentiated behavior of the Cu concentrations in vineyards was also observed, e.g. the verification of Cu contamination in mountain surface layer samples and Cu translocation to the lower layers (Deluisa et al., 1996).

Geoavailability of Cu is strongly influenced by the amount of organic matter and the nature of the humic substances in the soil (Wu et al., 2002). Soluble humic and fulvic acids may increase the solubility and mobility of the elements; once in a neutral to alkaline reaction environment they form stable complexes with the carboxyl, hydroxyl and amino groups of these compounds (Wu et al., 2002; Schnitzer & Kahn, 1972). However, copper toxicity depends on the soil organic matter, pH, organo-metalic complexes, the interaction between these complexes and the Cu ion with soil minerals and the CEC (Giovannini, 1997; Wu et al., 2002).

The average amount of Fe (Table 1) may be considered high, larger than 12 mg dm^{-3}, for the whole area, as found by Pereira et al. (2001) for soils of the Rio de Janeiro State. For Mn 87% and 72%, and for Zn 97% and 83% of the surface and subsurface layers samples, respectively, may be considered high (Raij et al., 1997). The levels of Cr, Ni, Cd, and Pb are normal in the area according literature (Bowen, 1979; Kabata-Pendias & Pendias, 1992; Casarini et al., 2001; Fadigas, 2002).

The anthropic addition of elements in the soil is made evident by the Top Enrichment Factor (TEF), defined as the ratio between the surface and subsurface layer concentrations of the element (Facchinelli et al., 2001). These authors assert that a natural surface pedogenetical enrichment does not exceed a value of 2. Most soils presented average values between 1 and 2, and just Zn had values of TEF around 2.1. Copper had the highest variability among the 100 points, 27 of them located in vineyards presented an average value of 1.76 and the others only 1.29. The Student t test indicated that they were different ($p < 0.05$), indicating an enrichment caused by the management of the vineyards.

A correlation analysis amongst all elements can be observed in Table 2. It is worth to point out the correlation between Cu and Zn, both in surface and subsurface layers. This fact may be linked to the use of micronutrients or chemicals during the agricultural use of the soil. The other correlations were quite complex and difficult to be explained. A better understanding may be achieved with the use of the PCA.

Cadmium adsorption by iron oxides and the correlation between Cd and Fe in soils are reported in the literature (King, 1998; Pierangeli et al., 2003; Alleoni et al., 2005b). In the soil, the Cd adsorption first occurs with a fast adsorption on iron oxide surfaces, and after a slow reaction that change the matrix ion for Cd, that undergoes a recrystalization.

Table 2 - Correlation matrix of the metal concentrations in the surface and subsurface layers.

	Cu[a]	Fe[a]	Mn[a]	Zn[a]	Ni[a]	Pb[a]	Cr[a]	Cd[a]
Cu[a]	1							
Fe[a]	-0.033	1						
Mn[a]	-0.098	0.135	1					
Zn[a]	0.305*	-0.037	0.207*	1				
Ni[a]	-0.102	0.323*	0.569*	0.191	1			
Pb[a]	-0.101	0.071	0.090	-0.032	0.096	1		
Cr[a]	-0.090	0.366*	0.057	0.109	-0.027	0.058	1	
Cd[a]	0.026	0.871*	0.184	0.104	0.273*	0.082	0.388*	1
	Cu[b]	Fe[b]	Mn[b]	Zn[b]	Ni[b]	Pb[b]	Cr[b]	Cd[b]
Cu[b]	1							
Fe[b]	0.183	1						
Mn[b]	-0.056	0.059	1					
Zn[b]	0.370*	0.044	0.073	1				
Ni[b]	-0.012	0.193	0.677*	0.144	1			
Pb[b]	-0.010	0.358*	0.107	0.162	0.168	1		
Cr[b]	-0.074	0.306*	-0.249*	-0.059	-0.130	-0.096	1	
Cd[b]	0.301*	0.861*	0.145	0.347*	0.312*	0.373*	0.226*	1

Coefficient of correlation $p < 0.05$. Letters "a" and "b" after element symbol identify, respectively, surface (0 – 0.15 m) and subsurface (0.15 – 0.30 m) layers.

Principal components analysis

PCA has been utilized to identify the origin of heavy metals (HM) in soils, and was shown to be as an efficient tool to define anthropic sources of HM (Facchinelli et al., 2001; Boruvka et al., 2005).

Both the eigenvalues and the percentage of variance calculated by PCA are shown in Table 3. According to these, for the surface layer (0–15 cm) the first four principal components or factors were considered (F1, F2, F3, and F4) and they explain 76.7% of the variation. In other studies, just the three first components were sufficient for the explanation (Facchinelli et al., 2001; Boruvka et al., 2005).

Early results showed an association between Fe, Cd, Mn, Ni, and Cr, with high values for F1, Mn and Ni are directly proportional and inversely related to Cr in F2, Cu and Zn in F3, Pb in F4 is isolated (Table 4), with ambiguity for Mn and Ni in F1 and F2, and Cr is positive in F1, and negative in F2. The matrix of rotation contributed to explain these ambiguities.

The subsurface layer data were treated in the same way (Table 3). The first four factors, which explained 81.1% of the variation, were considered. The

initial results showed an association between Fe, Cd, Ni, and Pb with high values in F1, Mn, Ni, and Cr in F2 like in the surface layers, Cu and Zn in F3, and Pb in F4 is isolated (Table 4), with ambiguity for Ni in F1 and F2, and Pb in F1 and F4. The rotation matrix was also here helpful for the explanation of these ambiguities.

Among all samples, 27 came from vineyards and 14 from native forests or forest plantations. In the vineyards the highest values were found for Cu in both depths and, for Zn in the surface layer. Applying the Student t test, a difference for Cu was found ($p < 0.05$) and for Zn ($p < 0.1$). These results suggest that there is soil contamination of these elements in vineyards. Based in the PCA the high values in F3 for Cu and Zn for surface/subsurface layers confirm this enrichment due to soil management practices and chemical applications.

It was mentioned previously that F3 explained the variability of Cu and Zn, and it was confirmed that high values of F3 of the samples also represent the highest values for these elements. The factor F3 of the rotated matrix was plotted in Figure 2,

Table 3 - Eigenvalue and variance estimated by PCA for the surface and subsurface layers.

|			F1	F2	F3	F4
Surface	Initial	Eingenvalue	2.416	1.453	1.321	0.948
		% Variance	30.200	18.163	16.513	11.845
		% Cumulative	30.200	48.363	64.876	76.722
	Rotation	% Variance	26.114	21.744	16.379	12.485
		% Cumulative	26.114	47.858	64.237	76.722
			F1	F2	F3	F4
Subsurface	Initial	Eigenvalue	2.530	1.712	1.305	0.939
		% Variance	31.630	21.401	16.312	11.742
		% Cumulative	31.630	53.030	69.342	81.084
	Rotation	% Variance	24.646	22.367	18.878	15.193
		% Cumulative	24.646	47.013	65.891	81.084
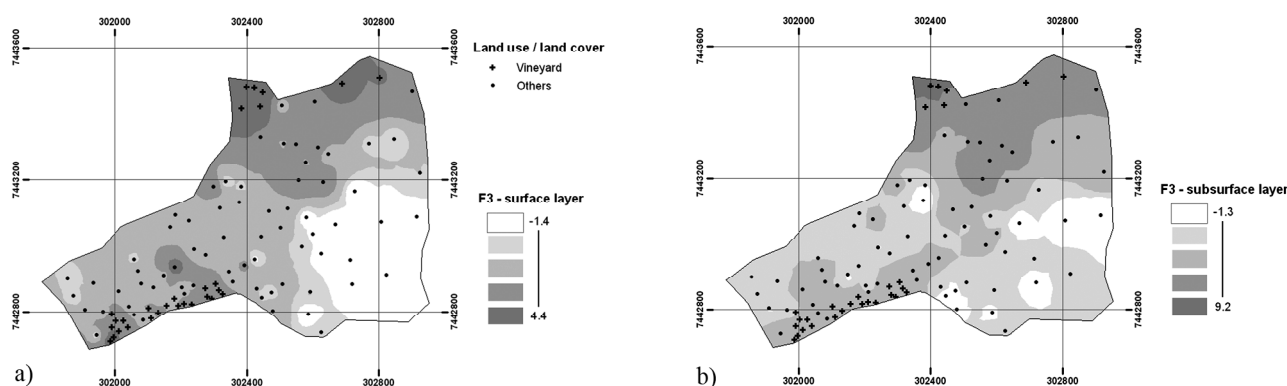
Figure 2 - Graphs of the scores obtained by the PCA for the collected samples. (a) Surface layer with factor F3; and (b) subsurface layer with factor F3.

Table 4 - Factors estimated by PCA for both layers based on the matrix of the amounts of the elements.

Variable	F1	F2	F3	F4
PCA Factors				
Cu[a]	-0.081	0.154	0.806	0.128
Fe[a]	0.851	-0.363	0.054	-0.142
Mn[a]	0.503	0.654	-0.234	-0.068
Zn[a]	0.213	0.508	0.609	0.245
Ni[a]	0.600	0.586	-0.238	-0.166
Pb[a]	0.187	0.018	-0.368	0.876
Cr[a]	0.495	-0.416	0.155	0.217
Cd[a]	0.865	-0.307	0.165	-0.067
PCA Factors - *Varimax Rotation*				
Cu[a]	0.005	-0.218	0.825	-0.071
Fe[a]	0.892	0.229	-0.033	0.019
Mn[a]	0.061	0.861	0.021	0.042
Zn[a]	0.028	0.277	0.780	0.006
Ni[a]	0.128	0.877	0.013	0.028
Pb[a]	0.063	0.056	-0.056	0.994
Cr[a]	0.702	-0.113	-0.032	0.037
Cd[a]	0.881	0.193	0.124	0.036
PCA Factors				
Cu[b]	0.354	-0.210	0.723	-0.208
Fe[b]	0.801	-0.376	-0.300	0.006
Mn[b]	0.383	0.789	-0.153	-0.225
Zn[b]	0.436	0.015	0.674	-0.040
Ni[b]	0.543	0.664	-0.178	-0.263
Pb[b]	0.533	0.039	-0.106	0.767
Cr[b]	0.119	-0.627	-0.411	-0.430
Cd[b]	0.913	-0.263	-0.054	-0.046
PCA Factors - *Varimax Rotation*				
Cu[b]	0.110	-0.078	0.842	-0.086
Fe[b]	0.874	0.103	0.097	0.298
Mn[b]	-0.059	0.915	-0.014	0.046
Zn[b]	0.020	0.100	0.788	0.127
Ni[b]	0.139	0.900	0.047	0.064
Pb[b]	0.193	0.052	0.007	0.919
Cr[b]	0.705	-0.253	-0.197	-0.401
Cd[b]	0.799	0.218	0.360	0.304

Letters "a" and "b" after element symbol identify, respectively, surface and subsurface layers.

developed using GIS software (Arcview), with the data interpolated by the inverse square distances method (Figure 2a, for surface layer, and Figure 2b, for subsurface layer). The higher values for F3 interpolated data for surface and subsurface layers show the spatial correlation with soils cultivated as vineyards, that the management contributes to soil enrichment with Cu and Zn. Enrichment of the subsurface layers was only observed in the oldest vineyards, with heavier chemical applications, like mancozeb, that contains high concentrations of Cu and Zn.

CONCLUSIONS

The PCA and the survey of metal concentrations in two soil layers (0–0.15 and 0.15–0.30 m) allowed an interpretation of complex phenomena that interfere with the enrichment of such metals in the soil. An enrichment of Cu and Zn in vineyards, as well as correlations among the different elements were observed.

REFERENCES

ABREU, C.A.; ABREU, M.F.; BERTON, R.S. Análise química de solo para metais pesados. **Tópicos em Ciência do Solo**, v.2, p.645-692, 2002.

ALLEONI, L.R.F.; BORBA, R.B.; CAMARGO, O.A. Metais pesados: da cosmogênese aos solos brasileiros. **Tópicos em Ciência do Solo**, v.4, p.1-42, 2005a.

ALLEONI, L.R.F.; IGLESIAS, C.S.M.; MELLO, S.C.; CAMARGO, O.A.; CASAGRANDE, J.C.; LAVORENTI, N.A. Atributos do solo relacionados à adsorção de cádmio e cobre em solos tropicais. **Acta Scientiarum Agronomy**, v.27, 729-737, 2005b.

ALLEONI, L.R.F.; NACHTIGALL, G.R.; CAMBRI, M.A.; NOGUEIROL, R.C.; LOPES, C.M. Disponibilidade de cobre em solos de vinhedos após aplicação de calda bordalesa por vários anos. In: CONGRESSO BRASILEIRO DE CIÊNCIA DO SOLO, 29., Ribeirão Preto, 2003. **Proceedings**. (CD-ROM).

BORUVKA, L.; VACEK, O.; JEHLICKA, J. Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils. **Geoderma**, v.128, p.289-300, 2005.

BOWEN, H.J.M. **Environmental chemistry of the elements**. London: Academic Press, 1979. 333p.

BRUN, L.A.; MAILLET, J.; RICHARTE, J.; HERRMANN, P.; REMY, J.C. Relationships between extractable copper, soil properties and copper uptake by wild plants in vineyard soils. **Environmental Pollution**, v.102, p.151-161, 1998.

CASARINI, D.C.P.; DIAS, C.L.; LEMOS, M.M.G. Relatório de estabelecimento de valores orientadores para solos e águas subterrâneas no Estado de São Paulo. São Paulo: CETESB, 2001. 73p.

CHAIGNON, V.; HINSINGER, P. A Biotest for evaluating copper bioavailability to plants in a contaminated soil. **Journal of Environmental Quality**, v.32, p.824-33, 2003.

CHAIGNON, V.; SANCHEZ-NEIRA, I.; HERMANN, P.; JAILLARD, B.; HINSINGER, P. Copper bioavailability and extractability as related to chemical properties of contaminated soils from a vine-growing area. **Environmental Pollution**, v.123, p.229-238, 2003.

COSTA, M.C.R. Avaliação da contaminação ambiental por metais pesados em áreas rurais próximas a uma indústria de reciclagem de chumbo no vale do rio Paraíba do Sul – SP. Seropédica: Universidade Federal Rural do Rio de Janeiro, 2002. 234p. Tese (Doutorado).

DELUISA, A.; GIANDON, P.; AICHNER, M.; BORTOLAMI, P.; BRUNA, L.; LUPETTI, A.; NARDELLI, F.; STRINGARI, G. Copper pollution in Italian vineyard soils. **Communications in Soil Science and Plant Analysis**, v.27, p.1537-1548, 1996.

EIJSACKERS, H.; BENEKE, P.; MABOETA, M.; LOUW, J.P.E.; REINECKE, A.J. The implications of copper fungicide usage in vineyards for earthworm activity and resulting sustainable soil quality. **Ecotoxicology and Environmental Safety**, v.62, p.99-111, 2005.

FACCHINELLI, A.; SACCHI, E.; MALLEN, L. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. **Environmental Pollution**, v.114, p.313-324, 2001.

FADIGAS, F.S. Estimativas das concentrações naturais (pseudo-total) de Cd, Co, Cr, Cu, Ni, Pb e Zn em solos brasileiros e proposição de valores de referência utilizando técnicas da estatística multivariada. Seropédica: Universidade Federal Rural do Rio de Janeiro, 2002. 94p. Tese (Doutorado).

FELIX, F.F. Comportamento do cobre aplicado no solo por calda bordalesa. Piracicaba: USP/ESALQ, 2005. 85p. Tese (Mestrado).

GIOVANNINI, E. Toxidez por cobre em vinhedos. **Pesquisa Agropecuária Gaúcha**, v.3, p.115-117, 1997.

KABATA-PENDIAS, A.; PENDIAS, H. **Trace elements in soils and plants**. 2 ed. Boca Raton: CRC Press, 1992. 315p.

KING, L.D. Retention of metals by several soils of the Southeastern United States. **Journal of Environmental Quality**, v.17, p.239-246, 1988.

MELO, A.R.; LOMBARDI NETO, F. Planejamento agroambiental do Centro Avançado de Pesquisa do Agronegócio de Frutas. Campinas: IAC/APTA, 1999. (CD-ROM).

NICHOLSON, F.A.; SMITH, S.R.; ALLOWAY, B.J.; CARLTON-SMITH, C.; CHAMBERS, B.J. An inventory of heavy metals inputs to agricultural soils in England and Wales. **The Science of the Total Environment**, v.311, p.205-219, 2003.

PARAT, C.; CHAUSSOD, R.; LÉVÊQUE, J.; DOUSSET, S.; ANDREUX, F. The relationship between copper accumulated in vineyard calcareous soils and soil organic matter and iron. **European Journal of Soil Science**, v.53, p.663-669, 2002.

PEREIRA, M.G.; PÉREZ, D.V.; VALLADARES, G.S.; SOUZA, J.M.P.F.; ANJOS, L.H.C. Comparação de métodos de extração de cobre, zinco, ferro e manganês em solos do Estado do Rio de Janeiro. **Revista Brasileira de Ciência do Solo**, v.25, p.655-660, 2001.

PIERANGELI, M.A.P.; GUILHERME, L.R.G.; OLIVEIRA, L.R.; CURI, N.; SILVA, M.L.N. Efeito da força iônica da solução de equilíbrio na adsorção de cádmio em latossolos brasileiros. **Pesquisa Agropecuária Brasileira**, v.38, p.737-745, 2003.

RAIJ, B. van; CANTARELLA, H.; QUAGGIO, J.A.; FURLANI, A.M.C. **Recomendação de adubação e calagem para o Estado de São Paulo**. 2.ed. Campinas: IAC, 1997. 285p. (Boletim Técnico, 100).

RAIJ, B.van; ANDRADE, J.C.; CANTARELLA, H.; QUAGGIO, J.A. **Análise química para avaliação da fertilidade de solos tropicais**. Campinas, IAC, 2001. 285p.

RAMALHO, J.F.G.P.; AMARAL SOBRINHO, N.M.B.; VELLOSO, A.C.X. Contaminação da microbacia de Caetés com metais pesados pelo uso de agroquímicos. **Pesquisa Agropecuária Brasileira**, v.35, p.1289-1303, 2000.

SCHNITZER, M.; KHAN, S.U. Humic substances in the environment. New York: Marcel Dekker, 1972. 368p.

VALADARES, J.; LEPSCH, I.F.; KÜPPER, A. Levantamento pedológico detalhado da estação experimental de Jundiaí, SP. **Bragantia**, v.30, p.337-386, 1971.

WU, J.; WEST, L.J.; STEWART, D.I. Effect of humic substances on Cu(II) solubility in kaolin-sand soil. **Journal of Hazardous Materials**, v.94, p.223-238, 2002.