



Geochemical assessment of soil potentially toxic elements from Copou – Iași vineyard area (NE Romania)

Doina-Smaranda Sirbu-Radasanu¹, Ramona Huzum^{1,2}, Simona Petronela Iftode², Gabriel Ovidiu Iancu², Nicolae Buzgar²

¹ “Alexandru Ioan Cuza” University of Iași, Department of Research, 20A Carol I Blv, 700505 Iași, Romania

² “Alexandru Ioan Cuza” University of Iași, Department of Geology, 20A Carol I Blv, 700505 Iași, Romania

Abstract

The Copou-Iași area is one of the oldest from the well-known vineyard region of Moldavian Platform (Eastern Romania). A number of 36 plots soil samples were systematically collected from a 0–40 cm depth. Soil profiles nearby the plots were sampled for the geochemical assessment of potentially toxic elements (PTE), using deep soil layers as controlled reference samples. The collected samples were analyzed for a series of 18 elements using ED-XRF method. The assessment of soil contamination was carried out by PCA multivariate statistic method and some geochemical indices (EF, AC, CF, CD) were calculated in addition. The obtained data shows an enrichment of PTE for the upper soil layer and denote an anthropogenic source due to the specifically disturbance of vineyards soils. Comparing to the Romanian legislation in force Cr, Ni, Pb and As exceed the normal values, but are within the alert threshold. Only Cu content exceed the Romanian alert threshold. A special attention is required in case of Cu and Cd due to their largest anthropogenic fraction, which increase the toxicity risk. The interaction between organic matter and PTE as result from PCA suggest that the toxicity risk is controlled by the stability of physico-chemical properties of vineyard soil.

Keywords: vineyard soil, Copou-Iași, PTE, PCA, contamination, geochemical index, ED-XRF.

1. Introduction

Viticulture causes the most intense soil deterioration due to land use for many years (sometimes almost a century) and

management practices. The regular viticulture practices such as pesticide and fungicide application, periodical tillage and green pruning can give rise to the change of the natural physico-chemical

characteristics and soil biodiversity (Komárek et al., 2010; Herrero-Hernández et al., 2012; Salome et al., 2014). The soil complex system is disturbed from its natural equilibrium and becomes susceptible to contamination once the anthropogenic impact increases.

The continuously interaction between natural soil components (e.g. organic matter, Fe- and Mn-hydro-oxides, clays minerals), pH and biota control the behavior of trace elements in soil, which result in their binding to different fractions, from where they can be released (mobile forms) or retained. Mobile forms are required for plant nutrition (Cu and Zn) or induce toxic effects on plants even at low concentration (Cr, Cd, Pb, As) or only at high concentration (Cu and Zn). Therefore, these trace elements are known as potentially toxic elements (PTE) and usually surveyed in soil composition. The regular use of fertilizers and pesticides enhance the PTE content in agricultural soil. This anthropogenic input generally presents a greater mobility in soil comparatively to a natural origin where the PTE are stronger associated with mineral fraction (Fernández-Calviño et al., 2009; Komárek et al., 2010). When the PTE are taken up by plant, the toxicity risk increases, the illness problems can occur and the crop can be damaged. Consequently, the pedogeochemical and biogeochemical processes are responsible for the natural management of soil trace element budget and their accumulation in the upper layer of soil profiles (Komárek et al., 2008; Ruyters et al., 2013).

More often the vineyard soils are mainly enriched with Cu (Komárek et al., 2010) due to the intensive use of Bordeaux mixture ($\text{CuSO}_4 + \text{Ca}(\text{OH})_2$) or others, like

manganese based fungicides (Mancozeb). Data summarized by Komárek et al. (2010) concerning the studies of vineyard soils indicates a potential contamination risk also for: Zn from fungicide and fertilizer, As from herbicides or insecticides, Pb from atmospheric deposition or lead arsenate insecticide and Cd from phosphate fertilizers.

The total trace elements concentrations of agricultural soils generally point out only the presence of contamination possible derived from the anthropogenic sources and cannot reflect the toxicity risk induced to the agro-system. Therefore, the purpose of present study is given by the assessment of soil contamination for a classic vineyard area located in the Northern part of Iași city.

The common methods used for the environmental geochemistry studies are based on the distribution of total trace element contents along soil profiles or in comparison with control soil sites located nearby investigated area. The contamination degree induced by one or more elements also can be achieved by the means of different geochemical indexes often used in the literature (Hakanson, 1980; Abraham and Parker, 2008; Teng et al., 2010; Martínez-Martínez et al., 2013).

As long as the land use category continuously changes through the development of new residential zone in the northern area of Iași city, the PTE loading in soil should be carefully monitored.

2. Materials and methods

2.1. Description of the area and soil sampling

The viticulture practices of Iași city area (NE Romania) have a long history and it was systematically developed and

diversified over the last century. The first testimonies come from 1496 and 1608, respectively mentioning about Bucium and Copou as small vineyards surrounding the old town. Since 1938, the Iași area is divided in four vineyard centers: Bucium, Miroslava, Copou and Șorogari (Cotea et al., 2000; Savin et al., 2008).

The Copou vineyard center is located in Northern part of Iași and nowadays is integrated in the urban area. The temperate climate and landform dominated by hills with moderate to smooth and sunny slopes fulfills the perfect terroir.

The geologic setting is typical of Moldavian Platform which represents South-Western section of the East-European Platform. The soil evolved on the top of sedimentary deposits consisting of Sarmatian formation overlaid by Quaternary units, developed mainly from Sarmatian rocks (Ionesi and Pascariu, 2011; Dill et al., 2012).

According to previously studies, the Copou vineyards soil is represented by Cambic Chernozem type (Lăcătușu et al., 2005; Iancu and Buzgar, 2008). The samples were collected from 3 plots cultivated with 3 different grapevine species with a surface area of 1.5 ha. The plots are placed on the hill plateau and the rows are exposed to the South-West. A number of 36 soil samples were taken from 0–40 cm depth according to a regular sampling network (25×25 m) (Fig. 1). The plots selection was made in relation with the possibility of sampling the deep layer within soil profile from an artificial outcrop.

The three soil profiles were sampled from three depths separated as follows: A horizon (~0–40 cm), A/B + B horizons (~40–80 cm) and C horizon (~80–150 cm).

The A horizon shows a dark black-brownish color, passing to dark-brown in

B horizon. The color change to yellow-brownish in C horizon and the texture is like porous-clays. The deep soil layer (C horizon) is lesser affected by both pedogenic processes and anthropogenic impact. Thus, the geochemistry of deep soil layer is considered to reflect the parent material composition (e.g. Sucharova et al., 2012) and can be used as control sample for the assessment of possible contamination.

The sampling was carried out in late October, when the effects of element uptake by the vegetation are suspended and the potentially toxic compounds from annual viticulture practices are still persistent in the upper soil layer.

2.2 Soil analysis

The soil samples were air dried at room temperature, homogenized and ground using porcelain pestle and mortar and then sieved to < 1 mm fraction. The physico-chemical characteristics of soil were carried out according to the standard analytical methods as follows:

- soil pH was measured in a aqueous solution of 1:5 (soil:water) using a WTW Inolab 730 pH-meter, through the potentiometric method;

- soil organic matter (SOM) content was assessed by loss on ignition (LOI) at 550° C for 6 h, according to Wilke (2005);

The chemical analyses of total concentration for major and trace elements in soil plots and profiles were performed by ED-XRF (Energy-Dispersive X-Rays Fluorescence Epsilon 5, PANalytical) spectrometric method. Prior to analysis, the soil and blind powder in a ratio of 5:1 were mechanically mixed in an agate mortar for 20 minutes at 180 rpm. The mixture was hydraulically pressed (20 t/cm²) to acquire the pellets with 9 g in weight. The standar-

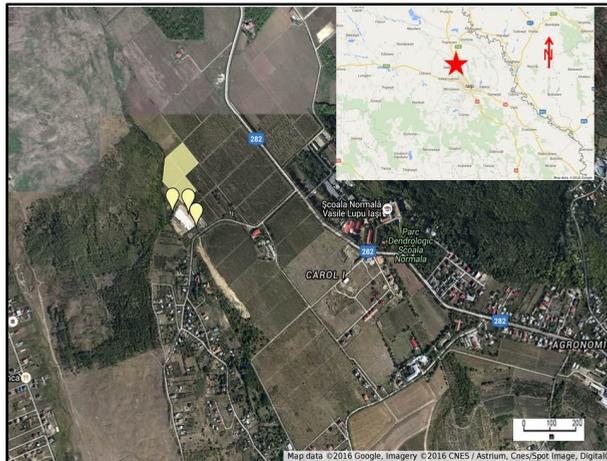


Fig. 1 The sampled plots and profiles location in the Copou vineyard area (www.google.ro/maps).

dization of ED-XRF equipment involved the usage of different geological reference material (SO–1-4: Regosolic clay soil, Podzolic B horizon soil, Calcareous C horizon soil and Chernozemic A horizon soil; STSD–1-4: stream sediment powder; JLk–1: lake sediments, JSd–1-3: stream sediments). The detection limits for each analyzed elements are: $Pb = 2.9 \text{ mg}\cdot\text{kg}^{-1}$, $Ni = 4.65 \text{ mg}\cdot\text{kg}^{-1}$, $Cu = 1.64 \text{ mg}\cdot\text{kg}^{-1}$, $Zn = 2.27 \text{ mg}\cdot\text{kg}^{-1}$, $As = 1.13 \text{ mg}\cdot\text{kg}^{-1}$. The exposure time was 60s, except for As and Cd which need 90 s of detection. The final concentration of each element represents the average of two times measurement.

2.3. Statistical analysis and quantification of contamination

The data interpretation was carried out by descriptive and multivariate statistic methods. The statistic parameters, including average, median, range, skewness, standard deviation and coefficient of variation were performed in order to

identify the distribution and the dispersion of the raw data. The geochemical data more often consist of large number of variables which rarely shows a normal distribution and a low dispersion.

The principal component analysis (PCA) is one of the multivariate statistics exploratory methods widely applied to environmental studies in order to identify natural versus anthropogenic sources of variable (elements) or geochemical behavior of the relevant elements. Original variables are transformed into a much smaller subset of new uncorrelated variables called principal components (PCs) using the eigenanalysis, which maximized the total variance among variables and emphasize the contribution of each variable to the data structure (Bini et al., 2011; Comero et al., 2012). Varimax rotation was applied because orthogonal rotation minimizes the number of variables with a high loading on each component and facilitates the interpretation of results and only principal

components with eigenvalues >1 were retained (Sun et al., 2013). PCA gives optimum results when it is applied to data set without outliers and the distribution get closer to a normal rule (Reimann et al., 2008); its application to heterogeneous data leads to the extraction of wrong information (Reimann et al., 2008; Comero et al., 2012).

Before the use of principal component analysis the outliers from our data set were identified by Hampel's method and replaced by the median values. Then the data were centered and scaled by the mean of Z-score to reduce the effects induced by the differences between data magnitude. Also, the Kaiser–Meyer–Olkin and Bartlett's sphericity tests were applied in order to make sure that the data set is suitable for multivariate statistic interpretation. The KMO and Bartlett's results were 0.614 and 305.414 ($p < 0.05$) respectively, indicating that PCA may be useful for the dimensionality reduction. Moreover, some elements such as Mg, Ni and Cd do not fulfill the statistic criteria to be included in the PCA.

The current literature presents various methods to approach the anthropogenic inputs to the natural variation of soil, sediment, water in order to evaluate the contamination degree. Regarding the soil studies, different geochemical indexes can be applied using standardization to a reference value (e.g. baseline, natural background) or to a reference element (Fe, Ti, Zr, Al) from a deep layer of soil profile from the studied area proximity, considered as conservative or immobile during weathering processes. For these purpose a series of geochemical indexes were calculated in order to point out the human impact on vineyard soil.

Enrichment factor (EF) gives information about loading of a target element from above uncontaminated levels, using standardization to a reference element as Fe, Ti, Zr, Al, calculated with the following equation:

$$EF = \frac{(C_n/C_{ref})_{soil}}{(C_n/C_{ref})_{deep\ layer}}$$

where: C_n is the concentration of the element;

C_{ref} is the concentration of conservative element (our case Ti) in soil samples, respectively the uncontaminated reference deep soil layer.

According to Sutherland (2000) for the interpretation of enrichment factor, five contamination classes are proposed:

- EF > 2 depletion to minimal enrichment;
- EF = 2–5 moderate enrichment;
- EF = 5–20 significant enrichment;
- EF = 20–40 very high enrichment;
- EF < 40 extremely high enrichment.

Generally, a value of EF under 2 reflect the natural variability of the mineralogical composition of samples (Hernández et al., 2003). When the obtained values of EF are higher than 2, the anthropogenic contribution (AC) is obviously and it can be approximated as the percentage from the total content, using the following formula (El Azzi et al., 2013):

$$AC = \frac{C_{n\ sample} - C_{ref\ sample} \times \left(\frac{C_n}{C_{ref}}\right)_{deep\ layer}}{C_{n\ sample}} \times 100$$

The geochemical assessment of soil contamination was also carried out using the contamination factor (single element index) and contamination degree (mul-

multiple element indexes). Contamination factor (CF), proposed by Hakanson (1980), is calculated for single element evaluation using the formula:

$$CF = \frac{C_{n \text{ sample}}}{C_{n \text{ background}}}$$

where: $C_{n \text{ sample}}$ is the element concentration in sample;

$C_{n \text{ background}}$ is the trace element concentration in background. For this study, the deep layer content was used as reference level.

On the base of CF values, several contamination classes are described as follows: $CF < 1$: low contamination; $1 \leq CF < 3$: moderate contamination; $3 \leq CF < 6$: considerable contamination; $CF \geq 6$: very high contamination.

The contamination determined by a single element can be found by the mean of enrichment factor or contamination factor. The cumulated impact of PTE on soil composition is sometime required and can be stated as the sum of contamination factors calculated for all PTE, divided to the studied contaminants. This relation is known as reflecting the soil contamination (Abraham and Parker, 2008) and seven classes were proposed to describe the contamination degree (CD) for the studied area:

$$CD = \frac{\sum_{i=1}^{i=n} CF^i}{n}$$

where: n is the number of analyzed elements;

i is the element;

CF is the contamination factor of the element.

The proposed classes for CD description depending on the obtained value are:

$CD < 1.5$: Non to very low degree of contamination;

$1.5 \leq CD < 2$: Low degree of contamination;

$2 \leq CD < 4$: Moderate degree of contamination;

$4 \leq CD < 8$: High degree of contamination;

$8 \leq CD < 16$: Very high degree of contamination;

$16 \leq CD < 32$: Extremely high degree of contamination;

$CD \geq 32$: Ultra high degree of contamination.

All these geochemical indexes above described were calculated and interpreted in accordance with their hypothetical source (natural, anthropogenic or mixed).

3. Results and discussions

3.1. The physico-chemical proprieties of soil

The soil from vine plots is characterized mainly by neutral to slightly alkaline reaction and moderate SOM content (Tab. 1), properties which fulfill the optimum conditions for vine culture. In the soil upper layer (0–40 cm) of the vine plot, the pH values are controlled by carbonates fraction as their correlation ($r = 0.67$) suggests. The effect of SOM soluble fraction upon pH values seems to be negligible since no correlation has been found between SOM and pH ($r = 0.16$). The soil reaction reflected by pH range can control the availability or immobilization of trace elements. The capacity of organic and inorganic soil particles to retain PTE systematically increases from acid to slightly basic pH, reaching a maximum around neutral values.

Tab. 1 Physico-chemical properties of soils

Soil vineyard plots		min	max	average	median	stdev ¹	skew ²
0–40 cm	pH	6.075	8.604	7.542	7.413	0.615	0.076
	SOM %	5.197	6.857	6.091	6.116	0.421	-0.107
	carbonates %	1.549	2.434	1.907	1.768	0.241	0.839
Soil profiles							
0–40 cm	pH	7.203	8.522	7.805	7.772	*	*
	SOM %	6.000	8.200	7.037	6.893	*	*
	carbonates %	1.720	2.140	1.990	1.980	*	*
40–80 cm	pH	7.586	8.717	8.034	7.928	*	*
	SOM %	2.887	6.400	4.873	5.098	*	*
	carbonates %	1.911	6.823	2.960	2.053	*	*
80–150 cm	pH	7.887	8.996	8.514	8.514	*	*
	SOM %	2.254	3.361	2.784	2.784	*	*
	carbonates %	1.724	7.423	4.766	4.493	*	*

1-standard deviation; 2-Skewness; stdev and skew were not determined in soil because of the low number of samples

Tab. 2 The average concentrations of major oxides (%) in soil profiles from Copou vineyard area

Depths	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	MnO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
1–40 cm	62.15	0.867	12.12	5.691	1.357	0.116	2.548	0.977	2.833	0.203
40–80 cm	63.90	0.907	12.51	6.125	1.478	0.094	2.576	0.431	3.095	0.120
80–150 cm	61.29	0.796	11.34	5.136	1.915	0.082	5.301	0.499	2.638	0.135

3.2. Total concentrations of major oxides

The average concentrations of major oxides in soil from all profiles depths (Tab. 2) denotes low and similar trend of variation for SiO₂, Al₂O₃, Fe₂O₃ and K₂O with a slight accumulation in 40–80 cm layer. The contents of MgO and CaO decrease downward (Tab. 2), but a higher variation is noted for CaO, which attains the maximum concentration in deep layer. The similar trend of variation of CaO and carbonate fraction with depth infers that Ca is mainly associated to carbonates.

The differences between soil major oxides contents from profile upper layers and plots (Tab. 3) are very low suggesting that soil mineral composition is not

significantly changed due to the vineyard practices. The normal distribution of the raw data is observed for the most of major oxides, except for Na₂O, P₂O₅, MgO and CaO with a higher variability induced by the outlier presence.

3.3. Total concentrations of trace elements

The total concentration of trace elements within soil profiles varies in a relative narrow range with depth (Tab. 4). The main trend corresponds to depletion from upper to subjacent layers for Ni, Cu, Zn and As (Fig. 2). The second trend of distribution denotes a low enrichment for Pb and Cr with depth (Fig. 2).

Tab. 3 The statistic parameters of major oxides (%) in soil from Copou vineyard plots

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	MnO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
average	63.46	0.886	11.76	5.027	1.253	0.122	1.517	0.550	2.761	0.185
median	63.42	0.889	11.78	5.025	1.166	0.121	1.367	0.234	2.781	0.177
Stdev ¹	1.196	0.015	0.373	0.074	0.299	0.004	0.443	0.940	0.083	0.052
MAD ²	0.623	0.012	0.216	0.035	0.174	0.003	0.171	0.169	0.047	0.027
CVR ³ (%)	0.982	1.294	1.833	0.697	14.88	2.479	12.47	72.22	1.708	14.97
Skew ⁴	0.094	-0.405	-0.364	0.802	1.401	-0.183	1.887	2.611	-0.269	1.902
S-W ⁵	0.707	0.410	0.418	0.064	0.003	0.340	0	0	0.660	0
min	60.71	0.848	10.85	4.890	0.856	0.113	1.111	0.017	2.580	0.118
max	66.66	0.914	12.59	5.231	2.261	0.128	3.071	3.871	2.928	0.372
outlier no.	-	-	-	1	1	1	3	4	-	2

1-standard deviation; 2-median absolute deviation; 3-robust coefficient of variation; 4-skewness; 5-Shapiro-Wilk normality test.

Tab.4 Statistic parameters of PTE in profiles and vineyard soil of studied area. Concentrations are in mg·kg⁻¹

	Cr	Co	Ni	Cu	Zn	Cd	Pb	As
Soil profiles*								
1–40 cm	60.0	13.08	50.0	28.17	66.3	0.28	24.5	12.25
40–80 cm	61.2	13.44	46.6	24.8	66....	0.32	22.6	11.64
80–150 cm	68.8	10.88	42.4	20.4	50.6	0.19	23.00	10.98
Soil vineyard plots								
average	59.19	13.12	51.83	112	75.08	0.37	30.14	12.83
median	59.0	13.10	52.0	102	74.0	0.35	30.0	12.85
stdev ¹	10.04	0.47	2.36	66.51	5.89	0.15	2.87	0.48
MAD ²	5.50	0.30	1.50	10.00	3.50	0.10	2.00	0.35
CVR ³	9.32	2.29	2.88	9.80	4.73	28.57	6.67	2.72
skew ⁴	0.62	-0.24	-0.37	5.35	1.77	0.23	0.90	-0.08
min	44.00	11.80	46.00	80.00	67.00	0.01	26.00	11.9
max	84.0	14.00	56.00	486.00	98.00	0.71	38.00	13.9
outliers	-	-	-	2	1	-	1	-
NV ⁵	30.00	15.00	20.00	20.00	100.00	1.00	20.00	5.00
AT ⁶	100.00	30.00	75.00	100.00	300.00	3.00	50.00	15.00
IT ⁷	300.00	50.00	150.00	200.00	600.00	5.00	100.00	25.00
GEMAS ⁸	19.5–50.9	9.3–15.9	15–48	11–20.2	62	-	9.85–15.4	6.69–9.31

*only average was calculated. From 1 to 4, the same like in Tab. 3; 5-normal values, 6-alert values, 7-intervention values from RMO MAPP 756/1997; 8-characteristic range of concentrations for agricultural soil from Central-Eastern Europe according to GEMAS project (Albanese et al., 2015).

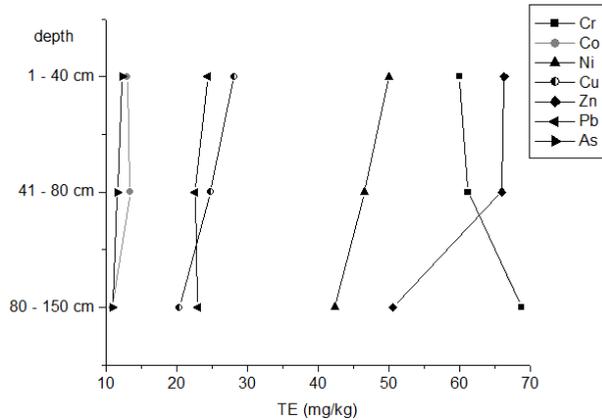


Fig. 2 The PTE distribution along the soil profiles.

The enrichment of upper soil layer (0–40 cm) with trace elements is an usual feature observed when the profile layers are compared (e.g. Alloway, 2013; Kabata-Pendias, 2011). For long period of time, the uncultivated soil trace elements budget can be enhanced by air born particles deposition in the upper soil layer. The retention of trace elements coming from external sources can be supported by the high SOM content and prevailing slight alkaline trend in soil reaction.

Once comparing with the profiles upper layer, the trace elements in plot soil (0–40 cm) generally display the same range of concentration for Cr, Co, Ni and As, being slightly larger for Zn, Cd and Pb. A special attention is drawn for Cu content which increase about 3.5 times in the plot soil. The low variability of PTE concentrations in Copou plot soil is denoted by robust coefficient of variation values ($CVR < 30\%$) (Reimann et al., 2008) which reflect a quite homogenous distribution. The outlier values are isolated and only found for Cu, Zn and Pb (Tab. 4). The standard deviation and skew

of raw data require log-transformation only for Cr, Cu, Zn and Pb in order to improve the data distribution for the further statistic interpretation by principal component analysis.

The concentrations of Cr, Ni, Pb and As are higher than the normal values from the Romanian legislation but not reach the alert threshold (Tab. 4). Moreover, the median values of Cr, Ni, Zn, Pb and As in Copou vineyard soil are slightly higher than their upper limit of concentration range in the agricultural soils from the Eastern Europe according to GEMAS project (Tab. 4) (Albanese et al., 2015). Most of the Cu concentrations are higher than the alert threshold value from the Romanian legislation. Generally, Cu is typically enriched in vineyard soil (Fernández-Calviño et al., 2009; Komárek et al., 2010; Mackie et al., 2012; Ruyters et al., 2013) due to the regular application of Bordeaux mixture in order to fight fungal diseases, especially Downy Mildew. The long term use of Cu fungicide rises the total Cu content in the traditional wine-production areas and values ex-

ceeding $100 \text{ mg}\cdot\text{kg}^{-1}$ (alert threshold) are commonly reported (Mackie et al., 2012; Ruyters et al., 2013; Komárek et al., 2010). In our study, only one of the outlier values ($486 \text{ mg}\cdot\text{kg}^{-1}$) is placed above the intervention threshold (Tab.4). This maximum Cu content can be considered as accidentally overload related to agricultural practices. The Cu retention in vineyard upper soil layer is related to its high affinity for organic matter and Fe-, Mn-hydro-oxides (Komárek et al., 2010). Thus, at high concentration, the toxicity risk is limited and Cu is regarded as contaminant. Furthermore the toxicity risk is also restricted by the depth of root system (Wightwick et al., 2008).

3.4. Quantification of soil contamination

Since the matrix correlation initially applied on data set do not point out any clear relation between PTE and soil physico-chemical properties (pH and SOM), the principal component analysis was used in order to extract hidden multivariate data structure. Principal component analysis has been shown to be very helpful in gaining a better understanding of the main processes (geogenic and pedogenic) and phenomena influencing PTE distribution in soil (Capra et al., 2014). Five principal components with eigenvalues higher than one were extracted (Tab. 5) after the varimax rotation of the initial components, accounting for 73.19 % of the total variance.

The first component (explaining 20 % of variance) is dominated by highly loading of Al, Si and K and also by moderately loading of Na and Fe. These significant loadings of major elements in

the first component denote that their distribution in soil is controlled by the clay fraction and suggest their common origin from parent material. Thus, first PC can be considered as a geogenic component.

The second principal component explains 17.27 % of variance and includes significant loading of Zn, Cu, Mn, Cr and Pb, the most PTE. The main feature of this PC is determined by high loading of SOM. SOM is one of the most important pedogenic components of soil with high capacity of binding both geogenic and anthropogenic PTE. The organic matter is the main sink of PTE soluble forms derived from fertilizers and fungicides compounds regularly used for vine culture. Therefore, the origin of PTE associated with SOM is not easily to be distinguished. The mixed origin is supported for Cu and Zn in studied vineyard showing higher contents than in the deep layer of control samples. The soil reaction promotes the generation of stable PTE-SOM complexes in 6.5–7.5 pH range as well as of soluble PTE-SOM complexes for $\text{pH} > 7.5$ (Komárek et al., 2010; Shaheen et al, 2013; Duplay et al., 2014). The predominant slightly acid and slightly alkaline soil reaction (64 % of samples) of Copou vineyard supports the development of stable complexes of SOM with PTE. The remaining samples characterized by $\text{pH} = 7.5\text{--}8.5$ can be enriched in soluble PTE-SOM complexes increasing their solubility and consequently the toxicity risk.

The moderate loadings of Cr and Mn in the second PC suggest that a low fraction could be added to soil as soluble forms from P- and N-fertilizers are retained by SOM.

Tab. 5 Total variance explained and matrix of principal component analysis for normalized elemental concentrations of vineyard soil in Copou-Iași area. Significant principal component loadings are indicated in bold

Element	Rotated component matrix				
	PC1	PC2	PC3	PC4	PC5
Al	0.868				
Si	0.861				
K	0.703	0.468			
Na	0.675		0.403		
Fe	0.638				0.456
SOM		0.855			
Zn		0.792	0.354		
Cu		0.694			
Cr	-0.329	0.517	0.446		0.367
Pb	0.316	0.409			-0.33
Ca			0.886		
pH			0.870		
P	0.360	0.324	0.477	-0.323	-0.392
As				0.802	
Mn		0.508		0.722	
Ti	0.304			0.690	
Co					0.808
Eigenvalue	3.403	2.936	2.485	2.052	1.227
% variance explained	20.016	17.27	14.677	12.071	9.16
Cumulative % variance	20.016	37.286	51.963	64.034	73.194

The third component explaining 14.67 % of variance includes the high loading of Ca and pH and can explain the buffer capacity of carbonates on soil reaction. This component can also be regarded as a pedogenic one.

The fourth component explaining 12.07 % of variance has high loading for As, Mn and Ti. This inter-relation suggests that Mn- oxy-hydroxides, another soil pedogenic soil component, could be involved in As adsorption.

The fifth component explaining only 9.16 % of variance is not quite relevant because the loadings are weak but it infers the involvement of Fe- oxy-hydroxides in the retention of genogenic Cr content.

The degree of anthropogenic input upon vineyard soil cannot be clearly emphasized by PCA interpretation. Therefore, the geochemical indexes were applied for the assessment of contamination on the base of PTE deep layer reference contents.

The enrichment factor is calculated as a differentiation criteria, because the values higher than 2 can be ascribed to the anthropogenic contamination. The enrichment factors within 2–5 range are predominantly found only for Cu and Cd and denote a moderate anthropogenic input. Except for Cr, the others PTE show low enrichment (Tab. 6) which suggests a low degree of contamination.

Tab.6 The contamination indexes for the Copou vineyard soil

Geochemical indexes		Cr	Co	Ni	Cu	Zn	Cd	Pb	As
EF ¹	average	0.759	1.062	1.077	4.856	1.307	1.747	1.155	1.029
	min	0.552	0.977	0.966	3.516	1.159	0.046	0.990	0.972
	max	1.076	1.141	1.168	20.76	1.688	3.413	1.486	1.087
CF ²	average	0.860	1.206	1.222	5.522	1.484	1.978	1.310	1.169
	min	0.640	1.085	1.085	3.922	1.324	0.053	1.130	1.084
	max	1.221	1.287	1.321	23.82	1.937	3.777	1.652	1.266
AC ³ %	mean	-	6.124	7.70	77.23	23.058	39.60	22.88	4.515
	min	-	0.698	1.474	71.55	13.73	6.210	1.491	0.912
	max	-	12.32	14.38	95.18	40.75	70.70	32.72	7.975

1-Enrichment factor; 2-Contamination factor; 3-Anthropogenic contribution.

The contamination factor also confirm that the Copou vineyard soil attain a moderate to low degree of contamination for Co, Ni, Zn, Cd, Pb and As respectively, while the Cu is the main contaminant of the soil (Tab. 6).

Both geochemical indexes above mentioned suggest that anthropogenic fraction to the total soil PTE content is either negligible or significant. An empirical method (El Azzi et al., 2013) was used in order to assess the contribution (%) of anthropogenic input to the enrichment of soil with PTE. Thus, anthropogenic contribution (AC %) for Cu is very high (Tab. 6), exceeding 70 % from its total concentration in all samples. The next contaminant with a possible high risk of toxicity is represented by Cd. About half of the samples show AC index higher than 50 %, which can be explained by the used of P-fertilizer, as Nanos and Rodríguez Martín (2012) observed. The Zn and Pb total contents also comprise a significant anthropogenic contribution (Tab. 6). Due to the high mobility of Zn in soil (Shaheen et al., 2013) the depletion of the upper layer would be expected. Since

the total Zn concentration in upper layer is higher than in the deep layer, the Zn loss is made up and raised by anthropogenic fraction from fertilizers or fungicides. A low anthropogenic contribution is noted for Co, Ni and As (Tab. 6), while Cr does not seem to be affected.

The geochemical indexes such as enrichment factor and contamination factor describe only a single element index. In order to state the impact of all PTE on soil composition, the contamination degree (Abraham and Parker, 2008) can be used as multiple elements index. The multiple index predominantly take values between 1.5 and 2, denoting a low degree of contamination. Moderate degree of contamination is found only for few samples. The vineyard soil as a whole could be considered slightly contaminated.

4. CONCLUSIONS

The soil from Copou vineyard plots was subject to the geochemical study concerning the PTE distribution, origin and association with soil natural components.

The distribution along soil profiles

shows a narrow range of variation with a slight enrichment in the upper layer for most of the PTE. The distribution of PTE in vineyard plots is quite homogenous as CVRs (%) infers. The concentrations of Cr, Co, Ni and As in vineyard plots are closed to those from the upper profile layers, while for Zn, Cd and Pb are slightly higher. The obvious enrichment is noted for Cu in vineyard plots showing a 3.5 times higher content than in the upper profile layers. The Cu content above both the alert threshold indicated by Romanian legislation and the main range of concentration from agriculture soil from Europe is a usual feature of the vineyard soil.

The principal component analysis denotes the role of the soil pedogenic components on PTE retention in soil. The absence of PTE association with elements forming-minerals suggests that the soil geogenic fraction (found in the first PC) has a limited contribution to the total content of PTE. Consequently, in vineyard soil the organic matter, Mn- and Fe-oxo-hydroxides seem to be involved in the adsorption of PTE derived either from geogenic or anthropogenic sources and thus controlling their mobility in soil. Since the mix origin of PTE is expected for any agricultural soil and being not easily to distinguish from sources using only total content, the geochemical indexes are usually applied in order to extract additional information concerning the anthropogenic contamination and the toxicity risk of high loaded PTE.

The EF and CF results suggest that the natural PTE content in vineyard soil are more or less affected by anthropogenic input. Special attention has to be paid to Cu and Cd, of which concentrations in vineyard soil include the

largest anthropogenic fraction. The higher the fraction received from outer sources, the toxicity risk increases. However, the interactions of SOM with PTE suggested by PCA confine the risk of toxicity as long as the soil physico-chemical properties do not change.

Nowadays, the extending trend of residential district on the vineyard areas placed adjacent to urban space should take into account the risk of toxicity, mainly for Cd since it is known as a carcinogen factor.

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