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TRACE ELEMENTS AND THE ANTHROPIC INFLUENCE ON THEIR DISTRIBUTION IN SOILS FROM APPLE ORCHARDS, FĂLTICENI AND SÂRCA FRUIT-GROWING AREAS (ROMANIA)

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Abstract: For this study, the total contents of some trace-elements (As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) from the soils of two apple orchards located in the fruit-growing areas of Fălticeni (Suceava County) and Sârca (Iaşi County), NE Romania were analysed. The average contents for the two orchard parcels, Fălticeni and Sârca are 18.90 – 23.71 mg/kg Co, 80.92 – 72.91 mg/kg Cr, 58.32 – 40.44 mg/kg Cu, 3.02 – 3.59 % Fe, 903.88 – 887.15 mg/kg Mn, 39.43 – 50.18 mg/kg Ni, 21.24 – 23.28 mg/kg Pb, 73.71 – 84.76 mg/kg Zn and 11.06 – 12.06 mg/kg As. Linear correlations exist between Fe and Mn and the other analysed trace elements. The correlations between Fe, Mn, Co, Ni and As for the soils of the two orchards are similar. Beside this, for the soils in the Fălticeni orchard, positive correlations with Pb and Zn have been identified. As a result of calculating the geochemical background for the 9 elements values exceeding normal threshold given by Romanian Environmental Legislation (OG 756/1997) were recorded for As, Co, Cr, Cu, Mn and Ni. Measurements of pH and %$CaCO_3$ were made and for the Fălticeni orchard the pH suggests that calcareous amendments have to be applied in order to control the soil reaction.

Keywords: trace elements, apple-orchard, soil, pH, geochemical background, calcareous amendments

1. INTRODUCTION

Some trace elements, such as Cu and Zn, have an important role in apple-tree nutrition, while others, such as Pb can cause serious intoxications if accumulated in high concentrations in the plant and/or fruits (Bashkin, 2002).

A great deal of the studies oriented towards the trace elements distribution in soils cultivated with horticultural crops have targeted the impact of potentially-toxic elements, such as As and Pb. As a result of applying pesticides containing As and Pb, the two elements form strong chemical bonds with humic acids and As concentrates mainly on the 0-20 cm depth range and can persist for long periods of time (Newton et al., 2006).

Zn is an important nutrient for apple-trees, as it is present in compounds that participate at the forming of chlorophyll and cellular division (Dart, 2007). Cu is another important trace element when it comes to protecting the tree against pests like apple scab (use of Bordo mix $Ca(OH)_2$ + $CuSO_4$). The Cu content in orchards soils is proportionate to their age (Wenqing et al., 2005).

For the orchards of citric, olive and vineyard associated soils, the average contents are around 60 mg/kg for Zn and 44 mg/kg for Cu (Vavoulidou et al., 2004).

In Romania, for the vineyard area of Huşi, where soils have similar features with those from this study, contents of 84.9 mg/kg Cu, 73.9 mg/kg Zn, 19.9 mg/kg Pb şi 10.5 mg/kg As were recorded (Huzum et al., 2012).

1.1. Study areas

The first studied area belongs to the Research and Production Center for Fruit-Growing from Fălticeni (RPCFG Fălticeni). This is situated on the plateau bearing the same name, a geographical sub-unit of the Suceava Plateau. The RPCFG Fălticeni is located at the intersection of the 47^o 27' N parallel and the 26°17’ E meridian, at an altitude range of 320-400 m. In its immediate vicinity there is the European Road E85 (SCPPF, 1982).

The boundaries of RPCFG Fălticeni also contain the southern versant and the first terrace of the Şomuzul Mare stream, as well as the first terrace of the Moldova River, with slopes between 7 and 42%, sometimes with excess humidity and landslides. The soils of RPCFG Fălticeni are mostly of Haplic Phaeozem type, while on the calcium rich deposits (argillaceous marl type) Rendzinic Phaeozem soil had formed (Costan & Botez, 1962).

The lithic substratum of the RPCFG Fălticeni consists of Volhinian deposits (Fig. 1). For these deposits, 8 levels of calcareous sandstones and oolite limestone exists (Mutihac & Ionesi, 1974). In the middle part of Volhinian-aged strata there are interbedded coal layers, which were extensively studied by Ţibuleac (1998); their thickness does not however exceed 0.5 m.

The fruit-growing area of Sârca is located in the SW of the Jijia hilly plain.

From the Sârca area only Farm no. 6 was studied. This is overlaid on a surface with Haplic and Calcaro-calcic Chernozems (Boronia, 2009).

The Sârca tree-growing area is located within the hydrographic basin of the Bahlui River and is characterised by an accumulation of Bessarabian pellite that correspond to the neritic lithofacies (claystone with *Cryptomactra*). The thickness of these claystone layers is of 320-350 m (Ionesi & Barbu, 1996).

2. MATERIALS AND METHODS

2.1. Sampling and sample preparation

A total of 152 samples were taken (Table 1). Out of those, 109 were taken from the top-stratum (0-20 cm) of the apple-tree rows (R), following a sampling network with 100 m equidistance. Samples were taken also from the 20-40 cm depth range (21 samples) at an equidistance of 300 m.

The distance between the points was slightly reduced for the areas that were close to the road, in order to emphasize the eventual anomalies due to the heavy metal flux from burning hydrocarbons.

Samples were also taken from the space between the apple-tree rows (MR), 0-20 cm depth range (N=22) at equidistance of 300 m.

The sampling was performed with a drill-type sampler; each one sample had weight of about 2 kg. The locations of the sampling points were verified with a GPS ASUS PDA in the WSG84 coordinate system (Fig. 2, Fig. 3).

The samples were manually grinded and then, through sieving, the fraction of less than 1 mm diameter was separated. The laboratory analyses were performed on this fraction alone.

Table 1. The type and number of soil samples collected.

Location	Number of samples	Area (ha)	Topsoil (R)	MR	20-40 cm
Fălticeni	68	40	49	10	9
Sârca	84	50	60	12	12

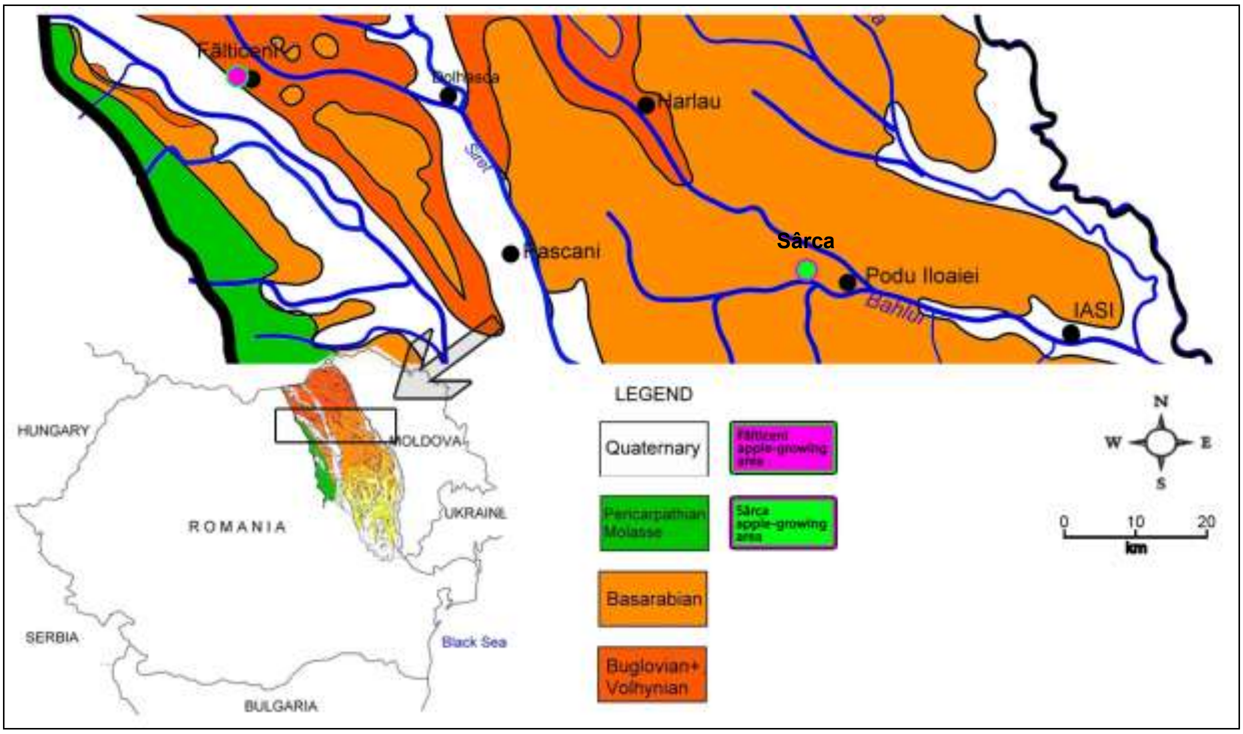

Figure 1. Geological map of the Moldavian Platform, with the location of the studied areas (modified after Ionesi et al., 2005)

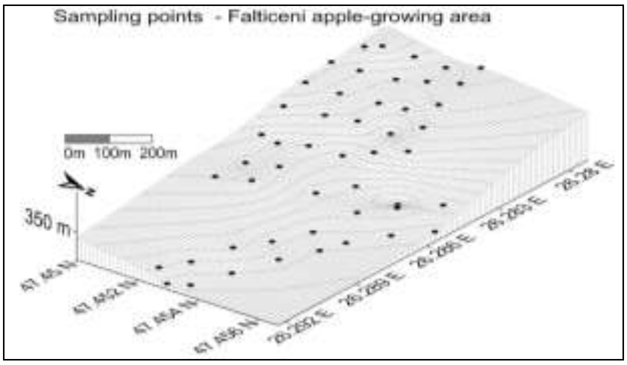

Figure 2. Sampling points from Fălticeni apple-growing area.

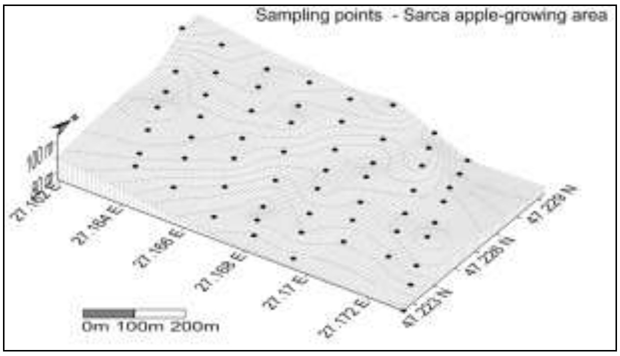

Figure 3. Sampling points from Sârca apple-growing area.

2.2. Trace elements, pH and $CaCO_3$ analysis

The pH analysis was performed through the potentiometric method. For these measurements, a pH-meter model pH-Meter BASIC 20+ and a couple of electrodes: calomel (reference) and pH electrode was used.

In order to measure the %$CaCO_3$, a Bernard Calcimeter was used.

The total contents of trace elements (As, Co, Cu, Cr, Ni, Fe, Pb, and Zn) were determined through energy-dispersive X-ray fluorescence spectroscopy (ED-XRF) at the Geology Department of “Al. I. Cuza” University from Iaşi, using an ED-XRF Epsylon 5 Spectrometer. In order to obtain the powder-pressed pellets for ED-XRF elemental quantification analysis, an amount of soil and synthetic raisin binder, at a ratio of 5:1, was mixed mechanically in an agate ball mill (Fritsch Planetary Mill Pulverisette 5), for 15 minutes, at a speed of 180 rpm. Each powder pressed pellet was obtained using 9 g of soil-raisin mixture at a 20t/cm^2 pressure for 30 seconds. The calibration was performed by using 23 standards: standards provided by geological Survey of Japan (JA-1-3: andesite powder; JB-1-3: basalt powder; JLk-1: lake sediment powder ; JSd-1-3: stream sediment powder; JR-1-2: rhyolite powder; JMs-1-2: marine sediment powder), 8 standards provided by CCRMP-CANMET-MMSL Natural Resources Canada (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) and 1 standard provided by USGS, United States Geological Survey, (RGM-1: rhyolite powder). The exposure time was 60 s, with the exception of As, in which case the exposure time was 90 s. The detection limits for the analysed elements are the following: Co = 1.14 mg/kg, Cr =7.03 mg/kg, Pb = 2.92 mg/kg, Ni = 10.65 mg/kg, Zn = 2.27 mg/kg, As = 1.13 mg/kg.

In order to obtain the statistical parameters, correlation coefficients and graphic representations, the STATISTICA 8, NCSS 2007 and Surfer 9 software were used. The 3D models were constructed from the altitude and positional data collected in the field.

3. RESULTS AND DISCUSSIONS

3.1. Trace elements in soils of the two apple-growing areas

In the Fălticeni Orchard (FO), the content of As vary between 5.54-20.61 mg/kg. The variation interval is smaller for Farm No. 6 at Sârca Orchard (SO), being of 10.65-13.15 mg/kg.

This difference can be due to the topographic features that are more variable in case of RPCFGF. All the analysed samples have As contents that exceed the normal limits accepted by Romanian legislation (5 mg/kg).

The average content for Co at FO is of 18.90 mg/kg and the concentration range is 5.90-28.39 mg/kg. The surface distribution shows that higher contents coincide with topographic micro-depressions, as they are most likely due to the drainage effect.

At SO, the range for Co contents if of 19.13-27.08 mg/kg Co. The average value for the chernozem soil of this parcel is of 23.71 mg/kg and the geochemical background is of 24.84 mg/kg, close to the average value estimated for the Earth’s Crust, of 26.6 mg/kg (Rudnick & Gao, 2003). The normal value for soils (given by OG 756/1997) is exceeded to 79.59% of the FO samples, while at SO all contents are above the normal limit.

At a neutral pH, in case of unpolluted soils, Cr is less mobile and relatively unavailable for the vegetation and this can lead to problems related to the Cr-deficiency (Kabata-Pendias, 2011).

In Fălticeni municipality soils and its surroundings, an average content of 59.1 mg/kg Cr was determined (Prundeanu & Buzgar, 2011), while for the orchards around Fălticeni the average content (using ED-XRF) was estimated at 59.14 mg/kg (Prundeanu et al., 2012). For this study, the Cr varies between 58.93-137.97 mg/kg.

At SO, the minimum value is of 65.53 mg/kg Cr and the maximum is of 91.56 mg/kg. The average content is of 73.91 mg/kg, close to the value determined for FO, of 80.92.mg/kg.

For the orchards with a long history in spraying the trees with fungicides based on Cu, contents between 21.8 mg/kg for a 5 year old orchard and 141 mg/kg for a 45 year old orchard (Zhou et al., 2011) were determined. For the soils of the Fălticeni municipality and surroundings, a content of 36 mg/kg Cu was determined (Prundeanu & Buzgar, 2011), while for the orchards in the area, a content of 44.26 mg/kg was calculated (Prundeanu et al., 2012).

For the samples taken from FO, the Cu content varies between 30.09-100.40 mg/kg, reaching an average of 58.32 mg/kg. The maximum of 100.4 mg/kg is the only case in which the alert threshold is exceeded, while the normal value is exceeded in all cases. The Cu content average value for the 20-40 cm depth range is of 33.52 mg/kg, considerably lower than the upper horizon (58.32 mg/kg). This shows an accumulation of Cu in these soils due to the regular spraying of the trees.

At Sârca, the average content for Cu is slightly lower, of 40.44 mg/kg. The Cu contents range between 30.08-62.20 mg/kg. The contents drop as the depth increases, reaching an average of 33.65 mg/kg for the 20-40 depth range. The slightly reduced difference between the two depth ranges in comparison to the situation at FO can be due to the fact that the parcel of SO has been cultivated more recently than at the FO, thus the anthropic influx of Cu in soil is smaller.

The mobility of Mn in the soil is dependent on the pH and Eh, as it has high mobility in acid soils and a decreased mobility in soils of neutral-alkaline reactions (Lăcătuşu, 2006). For the apple-trees, the Mn needs are relatively high, deficiency signs appearing at under 1 mg/kg active Mn.

Among soil fertilisers with Mn there are $MnSO_4$, MnO_2 and enriched Mn superphosphate (Madjar & Davidescu, 2009). The limits in which the Mn contents vary for the FO are 403-2354 mg/kg. For the soils of SO, Mn contents have a lower variation, in the range of 735.73-937.09 mg/kg. The normal contents are exceeded for 57.14% of FO and 26.66% of SO samples.

The average Ni content is of 39.43 mg/kg, slightly over the average found at apple orchards from the Fălticeni surroundings, with a minimum value of 11.65 mg/kg and a maximum of 53.80 mg/kg. In the SO, the Ni average content is much higher, of 50.08 mg/kg, as the variation range for the chernozem soils here is narrower, having a minimum of 44.71 mg/kg and a maximum of 56.53 mg/kg.

The reduced variations in case of the distribution of trace elements contents can be explained by a more banal topography and a higher homogeneity of soil parameters (pH, %$CaCO_3$) at the SO. All the samples exceed the normal contents for soils.

For the soils of the FO, an average content of 21.24 mg/kg Pb was obtained, higher than the other neighbouring orchards. The content ranges between 13.34-28.01 mg/kg Pb.

The geochemical background was estimated at 24.88 mg/kg Pb. At SO, all of the samples show contents over the normal limit given by OG 756/1997, compared to a 73.47% of the samples at FO.

For the 49 samples collected from the Fălticeni parcel, the variability of Zn contents is relatively high, the range being 45.62 mg/kg – 97.11 mg/kg. The average content is of 73.71 mg/kg, which is close to the value estimated for the Earth’s crust, of 72 mg/kg Zn (Rudnick & Gao, 2003). All the values are below normal limit in soils, while the geochemical background is 86.29 mg/kg.

For the SO, the average Zn content is of 84.76 mg/kg, the minimum value being 72.76 and the maximum 214.98 mg/kg (the most likely source here being a punctual Zn contamination). Besides the maximum content, only one sample exceeds the normal value for soils.

No influence due to adjacent traffic from the two areas could be observed, on any of the 9 studied elements.

3.2. Data analysis

The average contents of elements resulted from FO soil samples show the following distribution (Table 2):

Fe>Mn>Cr>Zn>Cu>Ni>Pb>Co>As

Strong correlations are present between Fe, Mn and the other trace elements (Table 3). This can be the result of trace elements adsorption on Fe and Mn oxides. Another two groups of elements with good linear correlation are Fe, Ni, Co and Ni, Pb and Zn; these correlations are similar with the ones determined in the vineyard area of Huşi (Huzum et al., 2012). A certain negative correlation is present between the percent $CaCO_3$ and Ni and Pb contents.

Table 2. Statistical parameters for the R, 20-40 cm depth range and MR samples for FO.
R – apple-tree rows; MR – middle of the apple-tree rows; 20-40 – 20-40 cm depth range; NV – normal value in soils according to the Romanian legislation; AT – alert threshold for soils with sensitive use.

Statistical parameter	Location	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As
		mg/kg								
Mean	Fălticeni R (n=49)	18.90	80.92	58.32	30226.26	903.88	39.43	21.24	73.71	11.06
G		18.27	79.99	56.41	29688.55	873.41	38.53	20.92	72.82	10.97
Me		19.69	78.86	53.60	31054.14	882.88	41.37	21.92	74.60	11.05
Min		5.90	58.93	30.09	15527.07	410.46	19.54	13.34	45.62	7.61
Max		28.39	125.38	100.40	42804.36	2354.35	52.80	28.01	97.11	15.53
std dev.		4.41	13.03	15.56	5437.33	273.75	7.91	3.53	11.19	1.43
Mean	Fălticeni MR (n=10)	17.45	84.64	58.65	28080.85	813.2	36.93	21.26	69.27	10.2
G		16.6	83.5	55.21	27440.57	772.66	34.85	20.93	67.66	10.11
Me		18.26	83.75	51.15	28535.46	894.52	38.52	22.67	68.96	10.74
Min		6.58	58.5	34.51	15596.59	387.24	15.23	15.42	46.62	6.85
Max		24.35	103.92	88.31	35669.32	1115.24	53.32	26.36	102.41	11.38
std dev.		4.938	14.232	21.328	5772.027	242.311	11.89	3.765	16.106	1.33
Mean	Fălticeni 20-40 (n=9)	19.4	102.58	33.52	30400.52	864.83	39.78	19.76	64.17	10.79
G		18.47	101.33	32.77	29585.69	853.31	37.51	19.36	63.04	10.65
Me		21.28	101.23	35.12	32452.09	851.92	46.83	21	67.89	11.06
Min		8.16	80.68	22.48	16365.93	666.05	20.03	12.22	42.58	7.79
Max		24.66	136.73	44.17	36298.78	1208.18	51.06	24.28	77.63	14.44
std dev.		5.444	17.315	7.211	6633.049	155.33	12.748	3.91	11.868	1.849
NV		15	30	20		900	20	20	100	5
AT		30	100	100		1500	75	50	300	15

G – geometric mean, Me – median, min – minimum, max – maximum, std dev. – standard deviation

Table 3. The correlation coefficients for trace elements and the soil parameters - FO (49 samples).

	pH	$CaCO_3$	Fe	Mn	Ni	Pb	Zn	Co	Cr	Cu	As
pH	1.000										
$CaCO_3$	<u>0.523</u>	1.000									
Fe	0.084	-0.269	1.000								
Mn	0.242	-0.078	**0.740**	1.000							
Ni	-0.138	<u>-0.529</u>	**0.805**	<u>0.344</u>	1.000						
Pb	-0.148	<u>-0.434</u>	**0.650**	<u>0.367</u>	**0.803**	1.000					
Zn	0.040	-0.231	**0.603**	0.270	**0.709**	**0.810**	1.000				
Co	0.039	<u>-0.326</u>	**0.991**	**0.707**	**0.838**	**0.681**	**0.606**	1.000			
Cr	-0.152	-0.246	-0.132	-0.117	-0.047	-0.169	-0.200	-0.116	1.000		
Cu	-0.215	-0.116	0.006	-0.146	0.159	<u>0.358</u>	<u>0.517</u>	0.010	0.049	1.000	
As	-0.016	-0.243	**0.682**	<u>0.530</u>	<u>0.495</u>	<u>0.381</u>	<u>0.315</u>	**0.654**	0.041	-0.012	1.000

Although for the soil samples from the middle of the apple-tree rows (MR) the elements have similar concentrations with the ones sampled from the apple-tree rows (R), it can be observed a general tendency of these trace elements to accumulate on the apple-tree rows, mainly due to the application of fertilizers, fungicides and pesticides. For the 20-40cm depth range we have determined a decrease of the trace elements concentrations comparatively to the topsoil layer. This is not the case for Co and Cr, also the Fe content is higher for the 20-40cm depth interval than in the topsoil.

The correlations coefficients for the three types of soil samples (R, MR and 20-40 cm) are shown in table 4. Most of the trace elements show good positive correlations between the three soil sample types. The ones that don’t confirm this tendency are Cr and Cu. The smaller correlations for Cu between R and MR and 20-40 cm samples suggest the influence of an anthropic input. This leads to Cu accumulation in the soil samples from the apple-tree rows from the use of copper based spraying solutions.

The same statistical parameters were determined for the soil samples collected from the SO (Table 5).

For SO the abundance of trace elements is described by the following decreasing order:

Fe>Mn>Zn>Cr>Ni>Cu>Co>Pb>As

Table 6 shows similar correlations with the ones obtained for the FO. Therefore the Fe, Ni, Co group has strong correlations in respect of their common geochemical behaviour, suggesting a natural source for these elements.

Major negative correlations occur between Mn on one side and As with pH on the other side.

In SO soils Fe and Mn contents show mostly the same correlations as for the FO. This aspect emphasises the importance of the role played by the oxides and hydroxides of Fe and Mn in the trace elements distribution in soils.

As has good positive correlations with Fe, Mn, Ni and Co and negative correlations with pH and percent $CaCO_3$.

From the SO were collected 12 MR soil samples and 12 samples from the 20-40 cm depth range. The trace elements concentrations obtained for these 24 samples are similar to those from the apple-tree rows. The only considerable variation was found for Cu. This shows, same as in the case of the FO, higher contents for R samples compared to MR and 20-40 cm depth range samples (Table 7). Again, this confirms that the copper based solution used in the apple orchards can lead to Cu accumulation in the topsoil.

Table 4. Correlation coefficients for R, 20-40 cm depth range and MR samples.
R – apple-tree rows; MR – middle of the apple-tree rows; 20-40 – 20-40 cm depth range

Fălticeni		Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As
R & MR	n=10	**0.882**	0.162	0.449	**0.888**	**0.864**	**0.891**	**0.910**	**0.616**	**0.931**
R & 20-40	n=9	**0.959**	-0.513	0.476	**0.969**	**0.927**	**0.976**	**0.910**	**0.880**	**0.902**

Table 5. Statistical parameters for the R, 20-40 cm depth range and MR samples for SO.
R – apple-tree rows; MR – middle of the apple-tree rows; 20-40 – 20-40 cm depth range; NV – normal value in soils according to the Romanian legislation; AT – alert threshold for soils with sensitive use.

Statistical parameter	Location	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As
		mg/kg								
Mean	Sârca R (n=60)	23.71	73.91	40.44	35913.75	887.15	50.18	23.28	84.76	12.06
G		23.69	73.65	39.92	35903.96	886.69	50.11	23.26	84.66	12.04
Me		23.77	72.52	38.68	35880.12	890.63	50.42	23.35	85.01	12.05
Min		21.02	65.53	30.08	33991.70	813.18	44.71	20.86	72.76	10.65
Max		27.08	91.56	62.20	39167.39	937.09	56.53	26.39	95.22	13.15
std dev.		1.08	6.46	6.80	850.48	28.91	2.49	1.07	4.16	0.55
Mean	Sârca MR (n=12)	23.83	79.40	36.60	35564.41	875.15	49.97	23.29	82.89	11.92
G		23.77	79.29	36.41	35527.90	874.60	49.84	23.27	82.81	11.90
Me		23.80	80.34	35.88	35949.08	879.03	49.87	23.00	82.31	11.89
Min		19.84	68.82	31.19	32801.79	828.69	44.48	22.13	78.11	11.01
Max		26.48	84.56	42.58	38956.50	913.88	58.36	25.16	88.45	13.86
std dev.		1.784	4.289	3.934	1681.336	32.525	3.837	0.970	3.680	0.813
Mean	Sârca 20-40 (n=12)	23.50	74.83	33.65	35226.37	868.06	50.12	24.85	83.10	11.70
G		23.42	74.63	33.41	35172.25	866.55	49.97	24.52	82.74	11.69
Me		24.28	73.98	32.57	36158.90	859.67	50.61	23.28	81.29	11.79
Min		19.57	65.99	27.91	30983.35	766.73	41.23	21.48	71.30	10.42
Max		25.59	83.94	40.92	36998.18	937.11	55.46	38.67	106.02	12.89
std dev.		1.937	5.636	4.231	1995.506	52.988	3.946	4.713	8.432	0.683
NV		15	30	20		900	20	20	100	5
AT		30	100	100		1500	75	50	300	15

G – geometric mean, Me – median, min – minimum, max – maximum, std dev. – standard deviation

The correlation coefficients of the R and MR samples, as well as R and 20-40cm depth interval samples are positive for all the analysed elements except Cr and Pb in SO. Although Cr and Pb have similar average concentrations in the R, 20-40 cm depth range and MR soil samples the correlation is strongly negative for Cr and not significant for Pb.

For Fe, Mn, Ni, Co and As were determined good correlations in both studied areas, FO and SO. In the soils from FO, beside the correlations of these 5 elements, good correlations with Zn and Pb were shown. The source of Zn and Pb correlations with the other elements only for FO and not also for SO can be explained by the coal-bearing intercalations in the sediments layers.

Although this paper does not intend to present the vertical distribution of elements, because the processes involved have not been studied, a variation of the average contents with depth is noticed for Cu, Mn, Pb, Zn and As in FO and for Cu, Mn, Zn and As for SO. The variation isn't high, except for Cu concentrations.

3.3. Geochemical background and the geoaccumulation index

Although the number of the soil samples is not very high, was possible to calculate the geochemical background for the FO and SO soils. The formula proposed by Reiman & Garrett (2005) was used to determine the geochemical background; the results are shown in table 8. The soils from the FO and SO are of Haplic Phaeozem, respectively Haplic and Calcaro-calcic Chernozems type.

The obtained data show close values for the FO and SO, being in agreement with the similar soil types. For Cu, the value of the geochemical background is not representative due to the high number of anomalous concentrations.

The use of copper based chemicals is the main reasons of the anomalous Cu contents.

Table 6. The correlation coefficients for trace elements and the soil parameters - SO (60 samples)

	pH	$CaCO_3$	Fe	Mn	Ni	Pb	Zn	Co	Cr	Cu	As
pH	1.000										
$CaCO_3$	0.538	1.000									
Fe	-0.520	-0.479	1.000								
Mn	**-0.648**	**-0.699**	0.596	1.000							
Ni	-0.425	-0.344	**0.840**	0.403	1.000						
Pb	0.224	0.511	-0.302	-0.200	-0.189	1.000					
Zn	-0.080	-0.051	0.053	0.095	0.158	0.165	1.000				
Co	-0.483	-0.465	**0.944**	0.559	**0.826**	-0.330	0.060	1.000			
Cr	-0.091	-0.053	0.014	-0.015	0.060	-0.115	-0.086	0.044	1.000		
Cu	-0.092	0.046	0.330	0.217	0.378	0.331	0.138	0.289	0.117	1.000	
As	-0.561	-0.446	**0.744**	**0.638**	0.595	-0.130	0.086	**0.699**	0.036	0.384	1.000

Table 7. Correlation coefficients for R, 20-40 cm depth range and MR samples.
R – apple-tree rows; MR – middle of the apple-tree rows; 20-40 – 20-40 cm depth range

Sârca		Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As
R & MR	n=12	**0.812**	**-0.739**	**0.851**	**0.993**	**0.866**	**0.809**	-0.047	**0.838**	**0.645**
R & 20-40	n=12	**0.887**	-0.562	0.432	**0.963**	**0.946**	**0.644**	-0.221	0.031	0.575

Table 8. The geochemical background for FO and SO soil samples.
Med – median; MAD – absolute standard deviation; GB - geochemical background

Parameter	Location	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As
		mg/kg								
Med	Fălticeni	19.69	78.86	53.60	31054	882.88	41.37	21.92	74.60	11.05
MAD		2.35	6.82	8.88	2448	69.70	4.98	2.14	5.85	0.61
GB		**24.40**	**93.76**	**72.84**	35950	**1022.28**	**51.33**	**26.20**	86.29	**12.27**
Med	Sârca	23.77	72.52	38.68	35880	890.63	50.42	23.35	85.01	12.05
MAD		0.52	4.06	3.17	420	15.49	1.09	0.77	2.32	0.39
GB		**24.84**	**81.39**	**45.66**	36719	**921.60**	**52.61**	**24.88**	89.64	**12.82**

With **bold** font are the GB values over the normal threshold from the Romanian legislation (OG/756-1997).

The geoaccumulation index was determined after the method proposed by Muller in 1969 (Apostoae & Iancu, 2009). The following formula was used (1):

$$(1)\ I_{geo} = \log_2(C_n/KB_n)$$

I_{geo} – the geoaccumulation index; C_n – the concentration of the element *n*; K – correction factor of the geochemical background variation due to different lithological - K=1,5; B_n – the geochemical background of the element n.

The geoaccumulation index was determined for all the studied elements with the exception of Cu, because the value of the geochemical background for copper is not representative.

The geoacumulation index shows values <1 for all the data, according to this the soils from FO and SO are unpolluted.

3.4. pH

The different processes in the soil, for example, the microorganism activity, roots secretions, the presence of carbonates and the humus etc., control the proportion of the H^+ and OH^- (Paulette, 2008).

The pH is often considered to be the most important variable of the soil, which can affect in great measure a wide variety of processes and chemical reactions (Sparcks, 2003).

Within the studied areas there is a high variation of the pH values, the average for FO is 5.47 and 7.38 for SO.

The range of the pH values is 4.58-8.01 for FO, and for SO the range is 6.60-8.20.

In the next table (Table 9) was determined the soil reaction according to the pH_{H2O} (Davidescu & Davidescu, 1999).

Table 9. The soil reaction for the soil samples from FO and SO. FO –Fălticeni orchard; SO – Sârca orchard.

Soil reaction	pH_{H2O}	FO	SO
		pH_{H2O}	pH_{H2O}
		%	
Strongly acid	4.31-5.00	16.3	
Moderately acid	5.01-5.80	44.9	
Weakly acid	5.81-6.40	10.2	
Very weakly acid	6.41-6.80	4.1	6.7
Neutral	6.81-7.20		28.3
Very weakly alkaline	7.21- 7.50	6.1	33.3
Weakly alkaline	7.51- 8.00	18.4	26.7
Moderately alkaline	8.01- 8.40		5.0

For the Fălticeni parcel, a predominantly strong towards moderately acid reaction was noted, as only 24.5% of the samples show pH over 7. The soil reaction has a negative effect on the mobility and availability of nutrient elements in soil. In the SO the situation is different; the predominant reaction is neutral to slightly alkaline, 88.3% of the samples having a pH between 6.8 and 8.

Establishing the need for amendments through qualitative assessment (Madjar & Davidescu, 2009) can be achieved from the pH determined in aqueous suspension.

It is appreciated that in case of the FO, 65.31% of the soil samples suggest an average need for amendments in order to control the low pH values. For the parcel at Sârca there is no necessary intervention regarding the control of soil reaction.

3.5. $CaCO_3$

The carbonates content in the soil samples taken from Fălticeni have an interesting distribution due to some extremely high values in the NE part of the studied parcel, as this is the area with the most reduced altitude. The content of $CaCO_3$ varies in range 0.2% - 28.81%. The average content for the samples considered representative for the FO parcel was estimated at 0.94% $CaCO_3$, 16.33% (8 samples having a content of over 2%). The most likely source for the high carbonate content is a natural one. On the surface of the fruit-growing area of Fălticeni, high contents of Ca as well as the presence of argillaceous marls in the substrata was noted (Costan & Botez, 1962).

At SO, the distribution of the carbonate contents is much more uniform, varying between 0.10% and 5.60%. The average content, determined by removing 3 of the values is of 0.81%, close to the one determined for the Fălticeni parcel.

Notable correlations were determined between the carbonate percentages and Pb (0.51, for 60 samples) and Mn (-0.7 for 60 samples).

4. CONCLUSIONS

The studied areas have shown high correlations between the total content of Fe and Mn and the rest of the analysed elements; the main assumption of this behaviour is the adsorption of the trace elements on Fe and Mn oxides and hydroxides**.** Another two highly correlated associations are Fe, Ni, Co and Ni, Pb, Zn (for the soils from FO).

Depending on the average concentrations, the following contents can be given:

Fe>Mn>Cr>Zn>Cu>Ni>Pb>Co>As – FO

Fe>Mn>Zn>Cr>Ni>Cu>Co>Pb>As – SO

For soils within FO, an accumulation tendency for Ni, As and Zn can be observed for the samples taken from the apple-tree rows (R) in comparison to those taken from between the rows (MR). For SO, the geochemical distribution of elements on the apple-tree rows (R) and between the rows (MR) is similar.

For the 20-40 cm depth range there is a decrease in contents of Cu, Mn, Pb, Zn and As in FO and for Cu, Mn, Zn and As for SO. Cu shows an important depth variation in content due to the use of Cu based solutions which undergone a visible accumulation in the topsoil layer.

The geochemical background exceeds the normal limit given by Romanian legislation for all studied elements, except Zn.

As a result of calculating the geoaccumulation index (for As, Co, Cr, Mn, Ni, Pb, Zn), it can be concluded that the soils from the two studied areas are not affected by pollution.

The average contents exceed the normal value in soils for all studied elements, with the exception of Zn for FO and with the exception of Zn and Mn for SO.

No visible influence of the adjacent traffic on the contents of trace elements in the two areas could be identified.

The soil reaction is neutral to moderately alkaline for the samples at SO and strong to moderately acid for the Fălticeni parcel. For the FO, 65.31% of the samples suggest an average to high need for the application of calcareous amendments in order to control the low pH values.

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