UNIVERSITY “ALEXANDRU IOAN CUZA” FROM IAŞI

FACULTATY OF GEOGRAPHY AND GEOLOGY

Ph.D. thesis summary

GEOCHEMICAL DISTRIBUTION OF SOME ELEMENTS IN THE SOIL-FRUIT SYSTEM FROM THE FRUIT-GROWING AREAS OF FĂLTICENI AND SÂRCA

INTRODUCTION

The studies from the present thesis have followed, mainly, the realisations of the areal distribution of P and K and the trace elements As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the soils and fruits from two apple orchards located in Fălticeni and Sârca fruit-growing areas.

The trace elements distribution from the soil used in horticulture and the fruits produced from this activity are contributing to the estimation of the soil properties and the evaluation of fruit quality.

The soil reaction together with the redox potential is the main factors controlling the mobile phase concentrations of trace elements available for fruit tree nutrition. The obtained results are indicating the necessity to apply calcareous amendments to correct eventual undesired problems generated by the soil acid pH in one of the two studied orchards. The distribution and the mobility of trace elements in soil are influenced by his physical and chemical properties, topography of the apple-orchard and the anthropic input generated by the use of chemical fertilisers and pesticides. One of the studied subjects is the identification of the existence of a trace elements influx in the soil-fruit system due to vehicle traffic from the proximity of the two parcels.

The soil and fruit samples were taken in 2011. The samples preparation, trace elements analysis by ED-XRF, the measurements of pH, carbonates percentage and Eh took place at the Geology Department of „Alexandru Ioan Cuza” University from Iași.

The mobile phase contents in soil and the results for nine trace elements in fruits have been obtained using atomic absorption spectrometry at the Soil-plant Interrelation and Food Quality Laboratory, National Institute of Research and Development from Pedology, Agrochemistry and Environmental Protection.

The trace elements contents in soils are picturing, mainly, their abundance in the geological substratum on which they formed. Their mobility is influenced, amongst others, by the mineralogical composition of the soil. For the qualitative and quantitative description of the soil mineralogy the analysis have been done using scanning electron microscopy coupled with X-ray detectors and X-ray diffractometry.

The interpretation and dissemination of the obtained data was the last step of the study. The preparation of the 2D and 3D maps, interpretation of the trace elements distribution in the orchards areas, the analysis of the trace elements required in the daily diet, like Cu and Zn, or toxic like Pb and Cd from apple varieties, calculation of the geochemical threshold and of the geoaccumulation index are other objectives accomplished in the study.

Chapter I

GEOGRAPHICAL SETTING, GEOLOGY AND SOILS OF THE SUTIED AREAS

I.1. Fălticeni fruit-growing area

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 lithic substratum of the RPCFG Fălticeni consists of Volhinian deposits. The soils of Fălticeni fruit-growing basin are mostly of Haplic Phaeozem type. The area of RPCFG is located in the north-west area of the Fălticeni Plateau; the predominant soil type is Haplic Luvisol with a weakly acid reaction.

I.2. Sârca fruit-growing area

Sârca apple-growing area is located in south-west of Jijia hilly plain. 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*) (Ionesi and Barbu, 1996). From the Sârca area only Farm no. 6 was studied. This is overlaid on a surface with Haplic and Calcaro-calcic Chernozems.

Chapter II

SOIL SAMPLING AND THE ANALYTICAL METHODS

A total of 152 samples were taken. 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 rangeat an equidistance of 300 m.

The sampling network used to sample the fruits was the same with the one used in the soil sampling, with 100 m equidistance. The 109 apple samples were taken from the middle of the tree canopy.

From analytical and economical reasons, from the total of 109 fruit samples only 42 were selected for the chemical analysis of the trace elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn), 21 from each orchard. Including or excluding the samples in the group of the analyzed one has been done taking in consideration the location, concentration of trace elements in soil and the apple variety.

In this study were analyzed a big number of soil and fruit samples in order to determine the trace elements contents, soil parameters and mineralogy.

Chapter III

SOIL MINERALOGY FROM FĂLTICENI SÂRCA FRUIT-GROWING AREAS

In the Fălticeni and Sârca fruit-growing area the geological substratum has an obvious influence on the soil mineralogy. For the Fălticeni parcel the quartz is the main mineral. The high quartz content in the soil of the Fălticeni orchard compared to Sârca orchard is due to the sandy clays and sands on which the soil evolved. On the other side, at Sârca, beside the high content of quartz, illite has an average content of 31.73% in nine soil samples. The high percent of clay minerals from the Sârca orchard is due to the substratum mainly constituted by pelites.

Chapter IV

THE GEOCHEMICAL DISTRIBUTION AND STATISTICAL ANALYSIS OF TRACE ELEMENTS IN SOIL

IV.1. THE GEOCHEMICAL DISTRIBUTION OF TRACE ELEMENTS IN SOIL

In the Fălticeni Orchard (FO), the contents of As vary between 5.54 and 20.61 $mg \cdot kg^{-1}$. The variation interval is smaller for Farm No. 6 at Sârca Orchard (SO), being of 10.65-13.15 $mg \cdot kg^{-1}$. All the analysed samples have As contents that exceed the normal limits accepted by Romanian legislation (5 $mg \cdot kg^{-1}$).

The range of Cd contents for Fălticeni orchard is 0.01 and 0.12 $mg \cdot kg^{-1}$, with an average of 0.06 $mg \cdot kg^{-1}$. In the Sârca fruit-growing basin, the Cd concentrations are similar, with a minimum value of 0.02 $mg \cdot kg^{-1}$ and maximum of 0.16 $mg \cdot kg^{-1}$. All the results for Cd contents are under the maximum allowed content in Romanian legislation.

The average content for Co at FO is of 18.90 $mg \cdot kg^{-1}$ and the variation range is 5.90-28.39 $mg \cdot kg^{-1}$. 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 $mg \cdot kg^{-1}$ Co. The average value for the chernozem soil of this parcel is of 23.71 $mg \cdot kg^{-1}$ and the geochemical background is of 24.84 $mg \cdot kg^{-1}$, close to the average value estimated for the Earth's Crust, of 26.6 $mg \cdot kg^{-1}$ (Rudnick and 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.

For this study, the Cr varies between 58.93-137.97 $mg \cdot kg^{-1}$. At SO, the minimum value is of 65.53 mg/kg Cr and the maximum is of 91.56 $mg \cdot kg^{-1}$. The average content is of 73.91 $mg \cdot kg^{-1}$, close to the value determined for FO, of 80.92 $mg \cdot kg^{-1}$.

For the samples taken from FO, the Cu content varies between 30.09-100.40 $mg \cdot kg^{-1}$, reaching an average of 58.32 $mg \cdot kg^{-1}$. The maximum of 100.4 $mg \cdot kg^{-1}$ 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 $mg \cdot kg^{-1}$, considerably lower than the upper horizon (58.32 $mg \cdot kg^{-1}$). 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 $mg \cdot kg^{-1}$. The Cu contents range between 30.08-62.20 $mg \cdot kg^{-1}$. The contents drop as the depth increases, reaching an average of 33.65 $mg \cdot kg^{-1}$ for the 20-40 depth range.

The limits in which the Mn contents vary for the FO are 403-2354 $mg \cdot kg^{-1}$. For the soils of SO, Mn contents have a lower variation, in the range of 735.73-937.09 $mg \cdot kg^{-1}$. The normal contents are exceeded for 57.14% of FO and 26.66% of SO samples.

The average Ni content is of 39.43 $mg \cdot kg^{-1}$, slightly over the average found at apple orchards from the Fălticeni surroundings, with a minimum value of 11.65 $mg \cdot kg^{-1}$ and a maximum of 53.80 $mg \cdot kg^{-1}$. In the SO, the Ni average content is much higher, of 50.08 $mg \cdot kg^{-1}$, as the variation range for the chernozem soils here is narrower, having a minimum of 44.71 $mg \cdot kg^{-1}$ and a maximum of 56.53 $mg \cdot kg^{-1}$.

For the soils of the FO, an average content of 21.24 $mg \cdot kg^{-1}$ Pb was obtained, higher than the other neighbouring orchards. The content ranges between 13.34-28.01 $mg \cdot kg^{-1}$ Pb.

The geochemical background was estimated at 24.88 $mg \cdot kg^{-1}$ 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 $mg \cdot kg^{-1}$ – 97.11 $mg \cdot kg^{-1}$. The average content is of 73.71 $mg \cdot kg^{-1}$, which is close to the value estimated for the Earth's crust, of 72 $mg \cdot kg^{-1}$ Zn (Rudnick and Gao, 2003). All the values are below normal limit in soils, while the geochemical background is 86.29 $mg \cdot kg^{-1}$.

For the SO, the average Zn content is of 84.76 $mg \cdot kg^{-1}$, the minimum value being 72.76 and the maximum 214.98 $mg \cdot kg^{-1}$ (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.

IV.2. GEOCHEMICAL THRESHOLD AND GEOACCUMULATION INDEX

The geochemical threshold represents the upper limit of the natural geochemical background variation. For the calculation of the geochemical threshold it was used the Median +2MAD (median absolute deviation) formula, this was proposed by Reimann et al. (2005). The values of the geochemical threshold are over the allowed limit for all the studied elements, except Zn and Cd (Prundeanu et al., 2013(a)).

The geoaccumulation index was calculated after the method introduced by Muller in 1969 (fide, Apostoae şi Iancu, 2009). After geoaccumulation index calculation one can conclude that none of the 10 trace elements has an polluting effect on the studied soils.

Chapter V
Soil pH, $CaCO_3$ and Eh

V.1. Soil pH

For the studied areas, the pH values are highly variable, as the average for the Fălticeni parcel is 5.47 and for the Sârca parcel is 7.38. The pH variation interval is 4.58 – 8.01 for the Fălticeni parcel and for the Sârca parcel they fall between 6.60 and 8.20.

V.2. $CaCO_3$

The average content of the representative samples of the Fălticeni parcel was estimated at 0.94% $CaCO_3$, 16.33% (8 samples) of all samples having a $CaCO_3$ content of over 2%. The source of the high carbonate contents is natural. On the surface of the fruit growing area of Fălticeni high contents of Ca and the presence of argillaceous marls in the substratum were reported (Costan şi Botez, 1962).

In the other case, the distribution of the carbonate percentage in the chernozems of Sârca is much more uniform and they vary within the interval 0.10% – 5.60%. The average content is of 0.81%, which is similar to the one obtained for the Fălticeni parcel.

V.3. Eh

For the soils of the Fălticeni parcel, the redox potential is slightly reducing to slightly oxidating and for the Sârca parcel the redox potential is moderately to slightly reducing. For the Fălticeni samples the variation interval is 0.16 V – 0.32 V and for the Sârca samples it is 0.11 V – 0.20 V.

Chapter VI

P AND K DISTRIBUTION IN SOILS OF FĂLTICENI AND SÂRCA FRUIT-GROWING AREAS

The higher contents in the RM samples are the results of applying industrial fertilizers on the apple tree row, directly onto the soil surface and/or leaf fertilizers. In the same way, the different order of the distribution of abundances for the three types of samples from the studied areas can be due to different mobility rates of K an P, conditioned by topographical aspects as well as by physico-chemical parameters.

Chapter VII

THE DISTRIBUTION OF TRACE ELEMENTS IN FRUIT SAMPLES

VII.1. Trace elements distribution in apples

For Cd, the lowest content values have been observed for the *Golden Delicious* apples of Sârca and the *Wagener* from Fălticeni. The maximum allowed microelements content limit is almost twice exceeded for all the other apple varieties from the Fălticeni area and more than twice for the Sârca varieties. The distribution of Cd contents in the harvested fruits from Fălticeni is uniform, having but a slight accumulation in the central area. For the Sârca Orchard, the high Cd contents are concentrated in the central part of the parcel and have a visible increase of contents for the samples taken from the vicinity of the highway. This can indicate a Cd accumulation that is due to the vehicle traffic as well as the dust particles it scatters. Further studies are necessary in order to quantify its influence.

For the orchard parcels of this study, Co contents which vary between 0.027 and 0.476 0,476 $mg \cdot kg^{-1}$ were obtained. If all 42 analysed samples are to be taken into account, the average Co content is of 0.224 $mg \cdot kg^{-1}$.

For Cr, out of the 42 analysed samples, 11 have contents under detection limit (0.005 $mg \cdot kg^{-1}$), 4 of which are originating from the SCPPF and the other 7 from Sârca.

The highest Cr contents are found in the Jonathan variety (SCPPF – 0.096 $mg \cdot kg^{-1}$; Farm no.6 Sârca – 0.101 $mg \cdot kg^{-1}$) and *Idared* (0,093 $mg \cdot kg^{-1}$).

The results of this study places the Cu contents in apples within 0.055- 0.409 $mg \cdot kg^{-1}$, with an average value of 0.221 $mg \cdot kg^{-1}$. The average concentration is under the maximum allowed value in fresh fruits according to the Order 293/2001. The highest content was determined for the *Kaltherer Böhmer* variety, and Pătul variety has the lowest amount of Cu.

For three of the analized apple varieties the average concentrations are over 2 $mg \cdot kg^{-1}$ Fe in the whole fresh fruit. These are *Jonathan* (from the Sârca orchard), *Kaltherer Böhmer* şi *Golden Delicious* (cultivated at the Fălticeni orchard).

Depending on the nine apple varieties studied, Mn concentrations are ranging from 0.328 $mg \cdot kg^{-1}$ (*Starkrimson*) to 0,695 $mg \cdot kg^{-1}$ (*Golden Delicious* cultivated at Sârca orchard) in the fresh fruit.

In the fresh fruit, the average for the 21 samples taken from Fălticeni orchard (FO) is of 0.546 $mg \cdot kg^{-1}$ and for Sârca orchard (FO) of 0,516 $mg \cdot kg^{-1}$. Like in the case of many other trace elements, the studies have shown that Mn is concentrated in the apple peel compared to the fruit flesh. For example, Zachwieja et al. (2002) estimated a ratio of 2,9 between the Mn concentration in the peel compared to fruit flesh.

Regarding the Ni contents in the fresh fruit of the nine apple varieties the maximum content is of 0.257 $mg\cdot kg^{-1}$ Ni for *Golden Delicious* cultivated at Sârca. On the other side, the minimum value is for *Starkrimson* variety, for which the concentration is under the detection limit, 0.04 $mg\cdot kg^{-1}$ Ni. From all 42 analyzed samples, 7 of them have concentrations under the detection limit for Ni. The average content of Ni in fresh apples for all 42 samples is 0.188 $mg\cdot kg^{-1}$.

Regarding Pb, for the all nine apple varieties the variation interval is high, from 0.413 $mg\cdot kg^{-1}$ for *Wagener* and 1.149 $mg\cdot kg^{-1}$ for *Golden Delicious* grown at Sârca. Only two apple varieties have contents of Pb in the limits stated by the national legislation in Order 293/2001, these are *Wagener* and *Kaltherer Böhmer*. The rest of seven apple varieties have average concentrations over the maximum allowed limit.

Zn concentrations in the fresh apple are varying depending on orchard and the apple variety. Thus, the average for FO is of 2.520 $mg\cdot kg^{-1}$ Zn and for the fruit from SO is 2.465 $mg\cdot kg^{-1}$ Zn.

Chapter VIII

MOBILE PHASE CONTENTS OF TRACE ELEMENTS IN SOIL AND FRUIT-SOIL CORRELATIONS

The mobile fractions for the five microelements are highly variable within the two areas. For the Fălticeni fruit growing area, the percentage of mobile phase compared to the total contents in soils are 29.99% Cu, 0.50% Fe, 11.84% Mn, 15.85% Pb, 7.50% Zn, and for the Sârca soils 17.11% Cu, 0.073% Fe, 22.34% Mn, 13.45% Pb, 4.32% Zn.

The influence of the geological substratum which is comprised by sandy clays and sands is confirmed by the high quartz content determined through mineralogical analysis, by the relatively low content in argillaceous minerals and by a soil reaction that is highly to moderately acidic, thus explaining the higher mobile phase contents for Cu, Fe, Zn and Pb that have been observed within the SCPPF area, despite the fact that determinations on granulometric fractions of soil are unavailable. On the other hand, within the Sârca fruit growing area we can consider that the high percentage of argillaceous minerals determined by SEM-EDX leads to a stronger bonding of microelements to soil and thus the bio-available phase is reduced.

The high mobile Mn content (average of 198.54 $mg \cdot kg^{-1}$) from the Sârca soils compared to the average value for the Fălticeni soils (111.83 $mg \cdot kg^{-1}$) cannot be explained through the mobilisation of total Mn in soil. The very high mobile phase content of this element is due to the fact that at Farm no. 6 Sârca there have been treatments with the DITHANE M-45 fungicide, which has among its components Mn and Zn in concentrations as high as 16% for Mn and 2% for Zn.

There were no significant correlations, with the exception of one negative value for the Fe (soil) – Zn (fruit) pair, of -0.48. This thing can suggest an inhibition of the Zn adsorbtion process which is due to the contents of mobile Fe from soil and further research is necessary on this matter. The only element that has a positive correlation for the soil-fruit system is Pb, but the value of the coefficient is low, of 0.35, which doesn’t lead to a conclusive interpretation.

In case of the Sârca fruit growing area there have been no obvious correlations for the soil (mobile fractions) – fruit, with the exception of one single negative correlation between Fe (soil) and Mn (fruit), of -0.49.

Conclusions

The main conclusions that can be drawn from the research undergone are:

1. The mineralogical composition of the soils from the two areas is obviously influenced by the geological substratum on which they have formed. The main mineral is quartz and for the soils of Sârca, a relatively high content of argillaceous material was determined.

2. The geochemical threshold exceeds the normal limit in soils for all studied elements, except Cd and Zn. Still, after calculating the geoaccumulation index it was determined that the soils of the two areas are not affected by pollution.

3. The average contents exceed the normal value in soils for all studied elements, with the exception of Zn and Cd for the Fălticeni parcel and in case of the Sârca parcel the exceptions are Cd, Zn and Mn.

4. For the soils within the fruit growing area of Fălticeni an increased accumulation tendency can be observed for Ni, As, Zn and Cd from the samples taken from the apple tree rows in comparison to the ones taken from the middle of the apple tree rows.

5. For the depth range 20 – 40 cm, from the two fruit growing area, a tendency of decreasing the contents of microelements compared to the topsoil, especially concerning the Cu contents. This element has considerably higher contents in the topsoil taken from the apple tree row than in the 20 – 40 cm depth range. The use of Cu-based fungicides leads to its accumulation in the topsoil.

6. There is no visible influence of adjacent traffic on the microelement content of the soil-fruit system for the two areas.

7. As a function of soil reaction, 65.31% of the soil samples suggest an average to high requirement to apply calcareous amendments in order to control the low pH values of the Fălticeni parcel.

8. In both fruit growing areas, the soil has a very good average supply of

phosphorus.

9. From the point of view of the necessary supply of microelements included in daily duet, the most recommended apple varieties are *Golden Delicious* and *Jonathan*, due to their high Zn and Fe contents. Another important element in diet is Cu; the highest quantity of Cu out of the 9 varieties was identified for *Kaltherer Böhmer*.

10. The maximum allowed contents in fresh fruit are twice exceeded for Pb and Cd. Out of the 9 sampled apple varieties, 7 of them exceed the Pb and Cd maximum allowed contents in fresh fruit. Another element that exceeds the maximum content allowed by Order 293/2001 for 6 samples out of the total of 42 is Zn. However, for every variety the average Zn contents are within normal and legal limits.

11. The mobile phase content in soil follows the distribution tendency of the total contents. The physico-chemical parameters from the two areas together with the treatments (e.g.: the use of fungicide DITHANE M-45) that have been applied in the two orchards directly influence the mobile phase contents from the studied soils.

12. For the studied elements, no correlations between the total contents from soils and from fruit could be established, with the exception of Pb from the Fălticeni parcel, where Pb contents from the fruits had a positive, linear weak correlation (0.35) with the total contents from the soil.

13. Besides the negative correlations between the mobile phase contents of Fe from soils and the contents of Zn (-0.38 SCPPF) and Mn (-0.49 Farm no. 6 Sârca) from fruits, there were no significant correlation coefficients between the mobile phase and the varieties of apple from the two areas.

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