FRAGIPANIZATION PHENOMENON – EFFECTS ON SOILS PEDOGEOCHEMISTRY FROM PROTECTED AREAS (GREENHOUSES AND SOLARIUMS)

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Abstract

In this paper are presented several new aspects related to the effects of fragipanization phenomenon on pedogeochemical processes in particular case of soils from protected areas (greenhouses and solariums). A special attention was paid to dynamic evolution of macro- and micro-elements in conditions of soils from protected areas, affected by fragipanization phenomenon, and to the correlation between these and pedogeochemical segregation and salinization processes. In addition, were highlighted a number of issues relating to the conditions of emergence and dynamics of the frangipane in soils from protected areas. The fragipane represents both a degradation phenomenon and an initiator for soil degradation phenomena. The formation of fragipane horizons is directly correlated with the apparition and development of pedogeochemical segregation, compaction and salinization processes that have strong negative influence on pedological and agrochemical characteristics of soils. The impacts fragipane is highlights, in general, by: (**i**) the discontinuity of water circulation in the soil profile, (**ii**) contrasting physico-chemical conditions between the upper and lower horizons, (**iii**) particular and atypical evolutions of the organic matter dynamics, speciation processes and inter-phase distribution of macro- and micro-elements etc., (**iv**) simultaneously with the formation horizons fragipane (emphasis segregation pedogeochimice) are rapidly degraded the physical-chemical and agrochemical characteristics of soils, with negative effects on their productivity and quality of obtained agricultural products.

Key words: fragipane, pedogeochemical segregation, soils from protected areas, pedogeochemistry

The formation of fragipane and its effects on pedological and agrochemical characteristics of soisl, and the dynamics of pedogenesis processes, are current problems of interest in soil science and agronomy (McDaniel P.A. et al., 2008; Wilson M.A. et al., 2010; Szymański W. et al., 2011; Bulgariu D. et al., 2012). For now, these problems have been able to give only partial solutions, often with particular character subordinated to certain approximations and analogies that are not always in agreement with soils pedogeochemistry, where the fragipane appears (Steinhardt G.C., Franzmeier D.P., 1979; Payton R.W., 1993; Lindbo D.L. et al., 2000; Weisenborn B.N. et al., 2005).

The areas affected by the fragipanization phenomenon, the soils classes that are vulnerable to this phenomenon, physic-geographic areas with high incidence of the fragipanization phenomenon are not well know, the data from literature being, most of time, only as a guide. From our point of view, the frequency of occurrence and spatial extent of the fragipanization phenomenon, and the areas that are affected by this phenomenon are much underrated in the literature. This is because not always a correct diagnosis of fragipane horizons was made (sometimes erroneously the hardpanic horizons) as especially lately the horizons with hardpanic character are wrongly diagnosed as fragipane.

Although it was long time considered a particular phenomenon, a pedological curiosity, recent studies have shown that the fragipanization phenomenon has a relatively high frequency in soil from different classes, in extremely varied physico-geographical and land use conditions. In addition, existing studies have highlighted that fragipane represents both a degradation phenomenon and an initiator for soil degradation phenomena. Formation of fragipane horizons is directly correlated with the occurrence and development of pedogeochemical segregation and salinization processes that have strong negative influences on pedological and agrochemical characteristics of soils from protected areas

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(Filipov F. et al., 2004; 2008; Filipov F., Bulgariu D., 2009; Bulgariu D. et al., 2012). In general, the fragipanization phenomenon in soils of protected areas is characterized by: (**i**) discontinuity of water circulation in the soil profile; (**ii**) contrasting physical-chemical conditions between the upper (above the fragipane horizon) and lower (below the fragipane horizon); (**iii**) atypical developments of pedogenesis processes, chemical and mineralogical equilibriums, macro- and micro-elements and organic matter dynamics; (**iv**) progressive degradation of soils quality (Steinhardt G.C., Franzmeier D.P., 1979; Filipov F. et al., 2004; Weisenborn B.N. et al., 2005; McDaniel P.A. et al., 2008; Filipov F., Bulgariu D., 2009).

In this study are presented several new aspects related to the effects of fragipanization phenomenon on pedogeochemical processes, in particular case of soils from protected areas. A special attention was paid to the evolution chemical-mineralogical equilibriums and to the dynamic of macro- and micro-elements in conditions of soils from protected areas affected by fragipanization phenomenon and to the correlation between these and pedogeochemical segregation and salinization processes. In addition, there were also highlighted a number of issues relating to the conditions of emergence and dynamics of the fragipanization phenomenon in the case of the soils in protected areas.

Table 1

The main locations were carried out the studies

Location	Exploitation way		Highlighted phenomena			
			I	II	III	IV
Iaşi-Copou, „V. Adamachi” farm, USAMV Iaşi	Greenhouse	Intensive / Traditional	+++	+++	+++	++
SCDL Bacău, Bacău County	Greenhouse	Intensive / Ecologic	++	-	-	-
Roman, Neamţ County	Greenhouse	Intensive / Traditional	++	+	+	+
Bârlad, Vaslui County	Greenhouse	Intensive / Traditional	++	+	++	++
Târgul Frumos, Iaşi County	Solariums	Intensive / Traditional	+++	++	++	++
OAT Farm Spătăreşti, Suceava County	Greenhouse	Intensive / Ecologic	+	-	-	-
Târgul Neamţ, Neamţ County	Greenhouse	Intensive / Traditional	++	+	+	++
Dumbrava, Neamţ County	Solarium	Intensive / Traditional	++	+	++	++
Roznov, Neamţ County	Solarium	Intensive / Traditional	++	+	++	++
Sihla, Neamţ County	Greenhouse	Intensive / Ecologic	++	+	++	++

Notations: (I)–Protofragipanization. (II)–Fragipanization. (III)–Pedogeochemical segregation. (IV)–Salinization. Estimating the intensity of manifestation of the phenomena: (+++)–intense; (++)–moderate; (+)–weak; (-)–non-existent.

MATERIAL AND METHOD

Studies were initiated in 2007 (under the grant PN II no. 51045/2007) and aimed soils in protected areas (greenhouses and solariums), used for vegetable production, from the North-East of Romania. Afterwards, the studies have been extended to soils from unprotected areas, with uses and operation way similar to those of greenhouses and solariums. The main locations where the systematic pedological studies were carried out, and where have been evidenced the protofragipanization and / or fragipanization are shown in table 1. Pedologic and pedogeochemical aspects have been presented in several previous studies (Filipov F. et al., 2004; 2008; Filipov F., Bulgariu D., 2009; Bulgariu D. et al., 2012).

The issue of soils from protected areas and fragipanization phenomena have been approached from an interdisciplinary perspective, by unitary integration of pedological, geochemical, mineralogical, physical-chemical, agrochemical data, etc. In this context, the studies were supplemented by pedogeochemical and physical-chemical analyses, theoretical and experimental modelling of the dynamic of pedogenesis processes, specific for these soils. Research strategy, methodology for conducting field studies and pedological and chemical-mineralogical methods of analysis, were presented by the authors, with all the necessary details in a few previous studies (Filipov F. et al., 2008; Filipov F., Bulgariu D., 2009; Bulgariu D. et al., 2009; 2012).

RESULTS AND DISCUSSION

Fragipane horizons are formed in the range 20-50 cm, have a thickness of 23-35 cm and the most frequently textured loamy and sandy-loamy or less fine sandy (figure 1). Are strongly cemented horizons and very low permeability, which imposes severe restrictions on the movement of water and air (figure 4). The structure of fragipane horizons is angular or polyhedral prism, the inside of the pieds although they have a relatively high total porosity, due to the compact packing, there is no continuity between intra-piedals pores and cracks which results in a quasi-isolated from the water percolation.

From texture point of view, characteristic for fragipane horizons is predominant the fine grain size fractions (figures 1-3). Accumulation of fine particle size fractions within these horizons is the result of two synchronous processes: translocation of fine particle size fractions from upper horizons, and the neopedogenesis process that, in conditions of soils from protected areas, are carried out with relatively high speeds (Bulgariu D. et al., 2012).

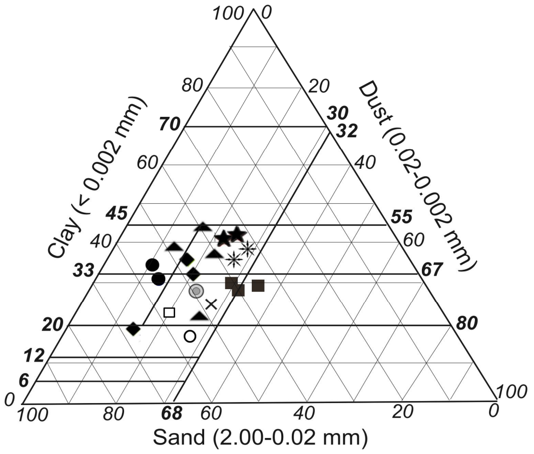

Figure 1. **Classification of protofragipane and fragipane horizons in texture triangular diagram** (according with ICPA Bucureşti). Notations: ★ Copou Iaşi; • SCDL Bacău; ♦ Roman; ■ Bârlad; ▲ Târgu Frumos; ✱ Spătăreşti; ○ Târgul Neamţ; □ Dumbrava; X Sihla; ⦿ Roznov.

In terms of chemical-mineralogical, characteristic for protofragipane and fragipane horizons are: (**i**) relatively high content of clay minerals (with a significant proportion of amorphous varieties), aluminum silicate and silico-alumino-phosphate gels, iron oxides and oxyhydroxides (especially amorphous varieties) and organic compounds (with a high share of fulvic acids - figura 3 and non-humic organic compounds - especially phytic acid); (**ii**) particular occurrence forms of the chemical-mineralogical components: aluminum silicate and the silico-alumino-phosphate gels, are actually solid solutions; organic compounds, iron oxides and oxyhydroxides and clay minerals are "associated" (> 90%) as organic-mineral complexes with specific structure; (**iii**) a low content of carbonates and soluble salts (Bulgariu D. et al., 2008; 2012).

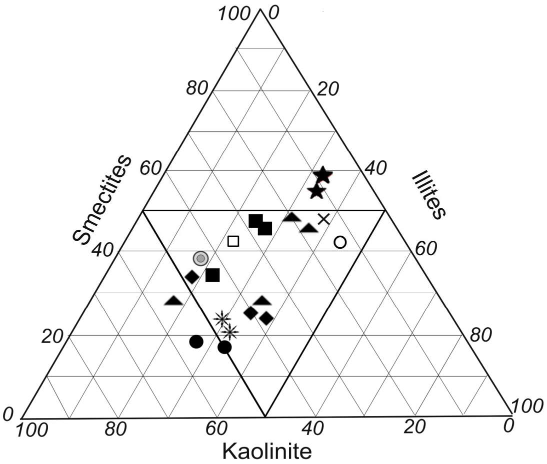

Figure 2. **Distribution of the main clay minerals in fragipane horizons.**. Notations - see figure 1.

From chemical-mineralogical point of view, the formation of fragipane horizons is favoured by: (**i**) predominance of smectites in comparison with illites and kaolinite (figure 2); (**ii**) formation of organic-mineral complexes with amorphous clay core and of aluminosilicate and silico-alumino-phosphate solid solutions; (**iii**) "association" of silico-alumino-phosphate solution with organic-mineral complexes and phytic acids, with the formation of supramolecular complexes (very stable and with flexible structures) (Filipov F. et al., 2008; Bulgariu D. et al., 2008; 2012).

From our point of view, very high impermeability of protofragipane and fragipane horizons is given by the compaction achieved by predominantly "chemical" processes (poly-condensation reactions and complexation reactions) and the accentuated hydrophobisation is printed by mineral-organic supramolecular complexes.

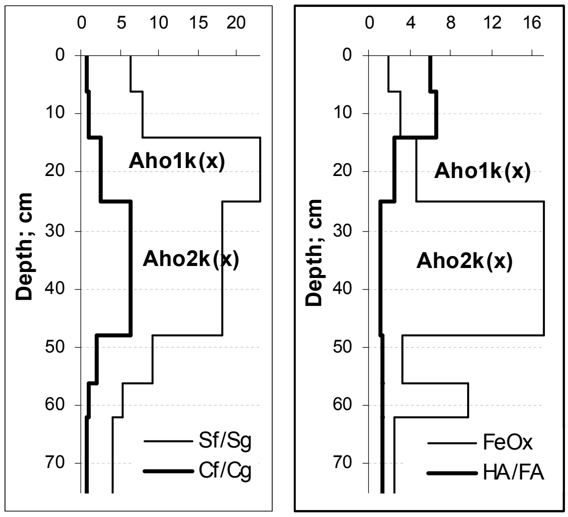

Figure 3. **(a) Variations on profile of the ration between fine and rough fractions of sand** (2.00–0.02 mm) **and clay** (< 0.002 mm); **(b) Variations on profile of of the ratio between amorphous and crystalline froms of iron oxides and oxyhydroxides** (FeOx) **and of the ratio between humic** (HA) **and fulvic** (FA) **acids** (profile IS.1, Copou-Iaşi greenhouse). Aho1k(x)–protofragipane horizon; Aho2k(x)–fragipane horizon. Sf–fine sand (0.20–0.02 mm); Sg–rough sand (2.00-0.20 mm); Cf–fine clay (< 0.001 mm); Cg–rough clay (0.002–0.001 mm).

Fragipane horizons prints developments and physical-chemical properties of soil and differentiated (contrasting) for upper horizons towards to lower horizons - figura 4. This effect, named by as “pedogeochemical segregation”, initiates in soils a series of processes whose combined effect causes major disruption of chemical-mineralogical equilibriums and the dynamics of pedogenesis processes.

In case of Copou-Iaşi greenhouse, the formation of fragipane horizon led to soil profile of three pedogeochemical facieses (figure 4): (**i**) oxic facies, aerobic (in upper horizons) – characterized by weak alkaline conditions, moderate oxidative, salinity, temperature and humidity relatively high, intense biological activity; (**ii**) anoxic facies, anaerobic (in lower horizons) – characterized by weak acid conditions, moderate reductive, moderate salinity, biological activity, humidity and temperature relatively low; (**iii**) suboxic facies – in fragipane and protofragipane horizons Ahok(x) (named by as the pedogeochemical segregation horizons). The individualization degree of these three facieses is directly conditioned by the fragipanization degree.

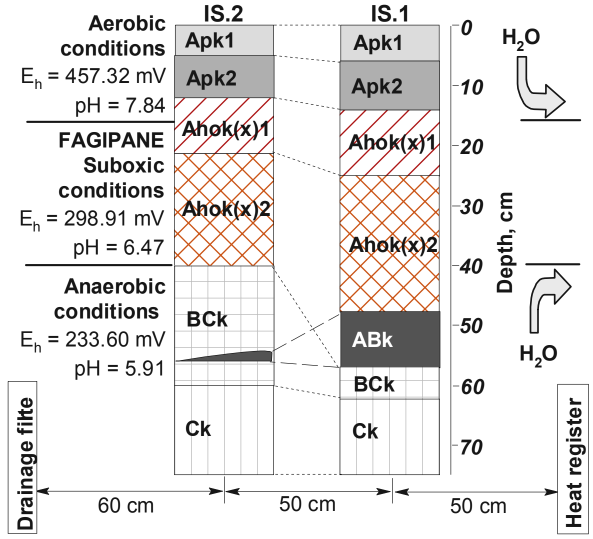

Figure 4. **Representation of toposequences in the anthrosol from Copou-Iaşi greenhouse**. In figure is illustrated the pedostratigraphic correlation of IS.1 and IS.2 profiles from Copou-Iaşi greenhouse and the pedogeochemical segregation induced by frangipane horizon – Aho2k(x).

The effects of fragipanization phenomena (ss. pedogeochemical segregation) is translates, roughly, by: (**i**) the discontinuity of water circulation in the soil profile (figure 4), (**ii**) contrasting physical-chemical conditions between the upper and lower horizons (figures 4-7), (**iii**) particular evolution, atypical, of organic matter dynamics, speciation and interphase distribution processes of macro- and micro-elements, etc.. (figures 5-8), (**iv**) concomitant with the formation of fragipane horizons (with increasing of pedogeochemical segregation) are rapidly degrading the pedological, physical-chemical and agrochemical characteristics of soil, with negative effects on their productivity and quality of obtained agricultural products.

In conditions of soils from protected areas affected by fragipanization phenomenon impose severe restrictions for speciation and distribution processes of macro- and micro-elements (figures 5-7). In Copou-Iaşi greenhouse, in lower horizons the predominant occurrence forms of iron are derived from Fe(II) – figure 5, those of aluminium are dependent by the evolution of $Al(OH)_3$ ↔ $[Al(OH)_2]^+$ equilibrium (figure 6), and those of phosphates are derived from $H_2PO_4^-$ (figure 7).

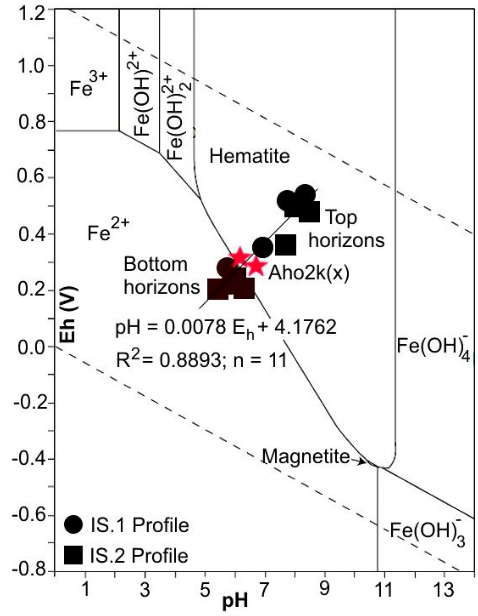

Figure 5. **Influence of frangipane horizon on speciation and distribution of iron in case of antrosol from Copou-Iaşi greenhouse.**

In upper horizons, the predominant occurrence forms of iron are derived from Fe(III), those of aluminium are dependent by the evolution of $Al(OH)_3$ ↔ $[Al(OH)_4]^-$ equilibrium, and those of phosphates are derived from HPO_4^{2-}.

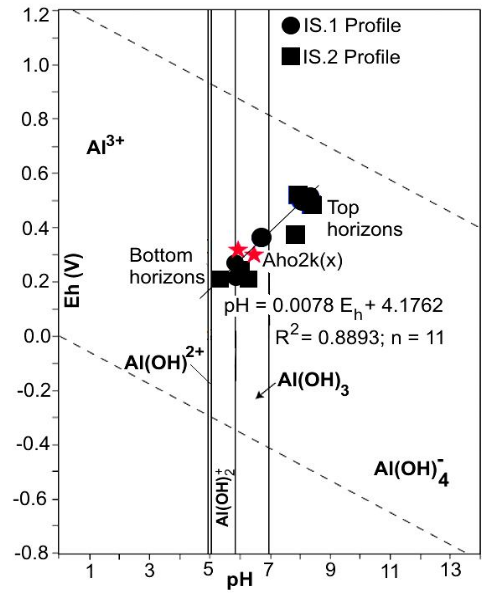

Figure 6. **Influence of frangipane horizon on speciation and distribution of aluminium in case of antrosol from Copou-Iaşi greenhouse**.

In case of microelements, the fragipane horizon restricted the interphases distribution way (on profile and between chemical-mineralogical components of soil), their geochemical mobility and bioavailability. In IS.1 profile from Copou-Iaşi greenhouse, the total contents of copper and zinc have two maximum at the level of fragipane horizon. The concentrations of these two microelements in fragipane horizon are much higher than the average on profile, and that the normal concentration in soils (figura 8), and in case of zinc this exceeded the value of the threshold for sensitive soils.

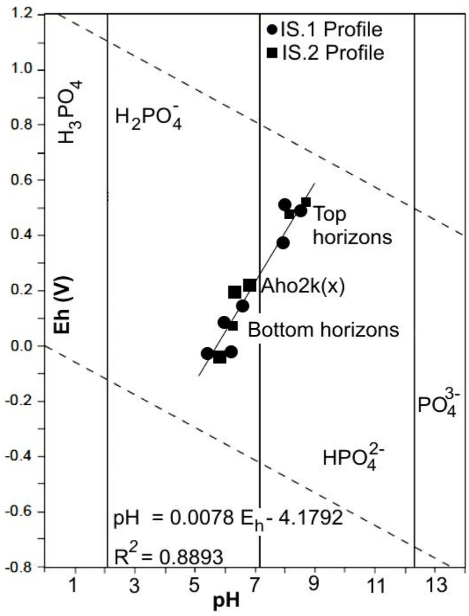

Figure 7. **Influence of frangipane horizon on speciation and distribution of phosphates in case of antrosol from Copou-Iaşi greenhouse**.

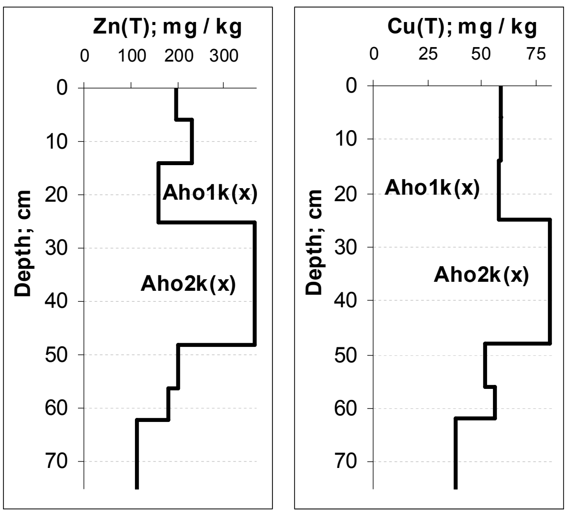

Figure 8. **Variations of total contents of zinc and copper in IS.1 profile from Copou-Iaşi greenhouse.** Details – see table 2.

If we take into account only the total concentrations, then the soils from Copou-Iaşi greenhouse appear to have a very good supply of zinc and copper. In reality, it was found the major deficiencies of zinc and copper (and other microelements) in case of vegetable crops made on these soils. This is due to the accumulation of microelements in the fragipane horizons in forms with reduced pedogeochemical mobility, which significantly limits the bioavailability of microelements. Thus, the zinc concentration in mobile fraction is 66.71 mg / kg in upper horizons and only by 37.39 mg / kg in fragipane horizon, while the zinc concentration in the fraction with moderate mobility is by 26.58 mg / kg in upper horizons and by 53.31 mg / kg in fragipane horizon (table 2). Similarly behaves and other microelements (copper, chrome, etc. – table 2).

Table 2

Zinc and copper concentrations [mg / kg] in extractable fractions from upper horizons, fragipane horizon and lower horizons of IS.1 profile (Copou-Iaşi greenhouse).

Fractions	Upper horizons*	Fragipane horizon*	Lower horizons*
Zinc			
F.1	22.05	4.29	9.70
F.2	40.91	25.75	37.52
F.3	3.75	7.35	5.36
F.4	11.08	24.51	19.25
F.5	6.54	9.76	9.19
F.6	8.96	19.04	11.43
F.7	6.49	9.11	7.31
FMB	66.71	37.39	52.58
FMM	26.58	53.31	39.87
Zn(T) – average on profile			207.14
Zn(T) – average in fragipane horizon			81.49
Zn(T) – normal concentration in soils			100
Zn(T) – alert threshold in sensitive soils			300
Copper			
F.1	19.03	6.53	7.58
F.2	33.19	18.57	35.49
F.3	4.71	6.47	2.65
F.4	13.09	21.70	15.91
F.5	10.61	19.85	11.63
F.6	11.73	17.26	16.23
F.7	7.28	13.08	10.02
FMB	56.93	28.11	45.72
FMM	35.53	58.76	43.77
Cu(T) – average on profile			56.42
Cu(T) – average in fragipane horizon			81.49
Cu(T) – normal concentration in soils			20
Cu(T) – alert threshold in sensitive soils			100

*Average values. Notations: F.1–fraction extractable in water; F.2–easily exchanged fraction (extractable in CH_3-$COONH_4$ 1 M; pH = 7); F.3–fraction sensitive to acidification (extractable in CH_3-COONa 1 M, pH = 5 / CH_3-COOH); F.4–fraction sensitive to complexation (extractable in EDTA 10^{-2} M; CH_3-COONa / CH_3-COOH); F.5–easily reducible fraction (bonded by Fe and / or Mn oxides and oxyhydroxides; extractable in $(NH_4)_2C_2O_4$ / $H_2C_2O_4$); F.6–oxidizable fraction (bonded by organic matter and / or sulphites; extractable in $K_2P_2O_7$ 10^{-1} M); F.7–fix fraction (residual). FMB–mobile and bioavailable fraction (F.1+F.2+F.3). FMM–fraction with medium mobility (F.4+F.5+F.6). Zn(T), Cu(T) – total contents of zinc and copper. Experimental procedure according with Sahuquillo A. et al. (2003).

In conditions of pedogeochemical segregation and salinization processes, even in early stages, there are two dangerous and destructive effects for both chemical-mineralogical equilibriums from soils and for the quality of agricultural product: (**i**) immobilization of iron in low soluble forms, that are inaccessible for plats (figure 5) – which will generate gaps in the supply of soil and plants, both iron and other nutrients; (**ii**) excess mobilization of aluminum in the soil solution as highly toxic forms for plants and biological systems from soil (figure 6) – the mobile forms of aluminium have a high toxicity on plants, comparable with those of Cr(VI).

CONCLUSIONS

The formation of frangipane horizons is favored: the accumulation of fine grain fractions; predominance of smectites towards illites and kaolinite; formation of organic-mineral complexes with amorphous clay core and of aluminosilicate and silico-alumino-phosphate solid solutions; "association" of silico-alumino-phosphate solutions with organic-mineral complexes and phytic acids with the formation of some supramolecular complexes.

Effects of frangipanization phenomenon is characterized by: discontinuity of water circulation in the soil profile, contrasting physical-chemical conditions between the upper and lower horizons, developments atypical of organic matter dynamics, processes of speciation and interphases distribution of macro- and micro-elements etc.; concomitant with the formation of fragipane horizons (emphasis pedogeochemical segregation) is rapidly degrade the pedological, physical-chemical and agrochemical characteristics of soils, with negative effects on their productivity and quality of obtained agricultural products.

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