CONTRIBUTIONS TO THE STUDY OF ORGANIC-MINERAL COMPLEXES FROM HORTIC ANTHROSOLS

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In this paper are presented the preliminary results of studies concerning the composition, structure and stability of organic-mineral complexes from hortic anthrosols. The separation of organic-mineral complexes has been performing by isodynamic magnetic method and by extraction in aqueous Na_2SO_4 –polyethylene glycol two-phase systems. The composition and structure of organic-mineral complexes have been studied by Raman, FT-IR and UV-VIS spectroscopy, optic microscopy, thermal and chemical analysis. In studied horthic antrosol, the content of organic-mineral complexes varied between 20.42-48.36 % [w/w], being evidenced a relative accumulation tendency in Ahok (48.36 %) horizon and in grain size fractions < 0.002 mm (63.62-86.30 %, from total determined organic-mineral complexes), respectively. The maximum weight (29.45-64.56 %) has been observed at grain size fractions < 0.001 mm. The high apparition frequencies and stability have organic-mineral complexes which include in their structures predominantly, the amorphous forms of clay minerals and of iron oxi-hydroxides. In function of clay mineral type from organic-mineral complexes composition, have been observed that the apparition frequency and stability follow the order: smectite > illite >> kaolinite (have been evidenced a special stabilization effect in case of Ca and Mg forms of clay minerals). In function of iron oxi-hydroxides type from organic-mineral complexes composition, has been observed that the apparition frequency and the stability follow the order: $Fe(OH)_3$ (amorphous) > $Fe(OH)_3$ (ferihidrite, amorphous) > γ-$FeO(OH).nH_2O$ (lepidocrocite) > α-$FeO(OH).nH_2O$ (göethite) > α-Fe_2O_3 (hematite). The separated and studied organic-mineral complexes have very complex compositions and structures (generally have 4-5 structure levels), include over 65 % from mineral and organic components of anthrosol and are behaves as supra-molecular assembles very stable and with a high chemical-structural flexibility degree. In function of chemical-mineralogical composition and of their structure, the organic-mineral complexes from studied anthrosol have been classified in four main classes.

Key words: *organic-mineral complexes, hortic anthrosols*

The organic-mineral complexes appear practically in any type of soil, but their composition, stability and weight varied in large limits, in function of pedogenesis conditions and chemical-mineralogical characteristics of soils [1, 6, 8, 11]. Between organic-mineral complexes is an assemble of equilibriums, very sensitive even at relative small variations of physic-chemical conditions from soil, which permit to these to manifest a strong influence on evolution of organic compounds, clay minerals and microelements from hortic anthrosols [9, 10]. Although sometimes are considered meta-stable combinations, the stability of organic-mineral complexes was proved to be relative high. This is probable due to the higher flexibility of their structure to the variation of chemical-mineralogical composition and of physic-chemical conditions from soil [3, 4, 5, 8, 12].

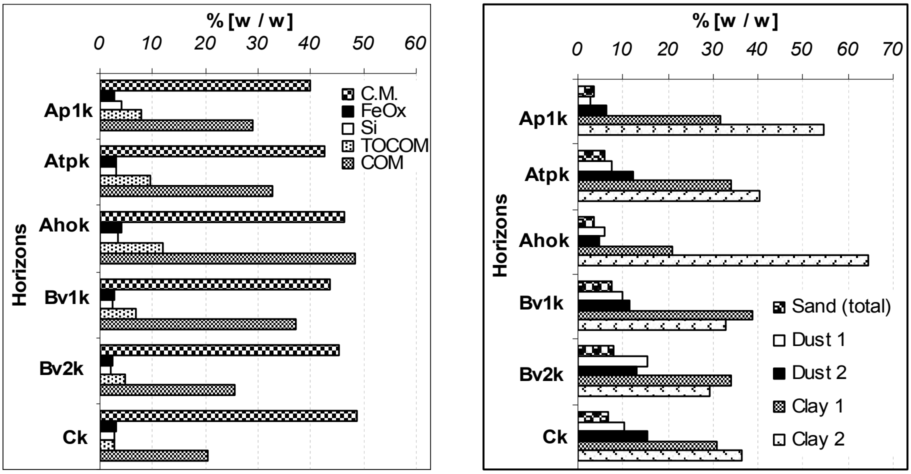
In this paper are presented the results concerning the composition, structure and stability of organic-mineral complexes in function of chemical-mineralogical characteristics of hortic anthrosol from Bacău glasshouses. The non-destructive separation of organic-mineral complexes was performing by isodynamic magnetic method and by extraction in aqueous Na_2SO_4 – polyethylene glycol two-phase systems. The composition and structure of organic-mineral complexes have been studied by Raman, FT-IR and UV-VIS spectrometry, optic microscopy, thermal and chemical analysis. In function of chemical-mineralogical composition and structure, the organic-mineral complexes from studied hortic anthrosol have been classified in four classes. The separated and studied organic-mineral complexes have very complex composition and structures (generally have 4-5 structure levels), include > 65 % from mineral and organic components of anthrosol and behaves as supra-molecular assembles very stable and with a high chemical-structural flexibility degree.

MATERIAL AND METHOD

The studied have been done using samples of hortic anthrosol drawing from Bacău glasshouses perimeter. The samples have been dried in air (14 days), and then have been used for grain-size, mineralogical and physic-chemical analysis. The analyses have been performed on average samples obtained from each grain-size fraction. The experimental strategy follow in this study was in agreement with literature [2, 7], and was presented by as in several previous studies [3, 4, 5]. For the separation of organic-mineral complexes we proceed to the grain-size separation of anthrosol samples, followed by the advanced fractionation (5-8 separation steps) by isodynamic magnetic method. The fractions obtained after magnetic separation have been studied by Raman, FT-IR and UV-VIS spectrometry, optic microscopy, thermal and chemical analysis. On parallel samples, from these fractions, different extractable fractions have been extracted with organic solvents and in aqueous Na_2SO_4 – polyethylene glycol tow-phase systems. These have been chemical analyzed, and by UV-VISA and Raman spectrometry.

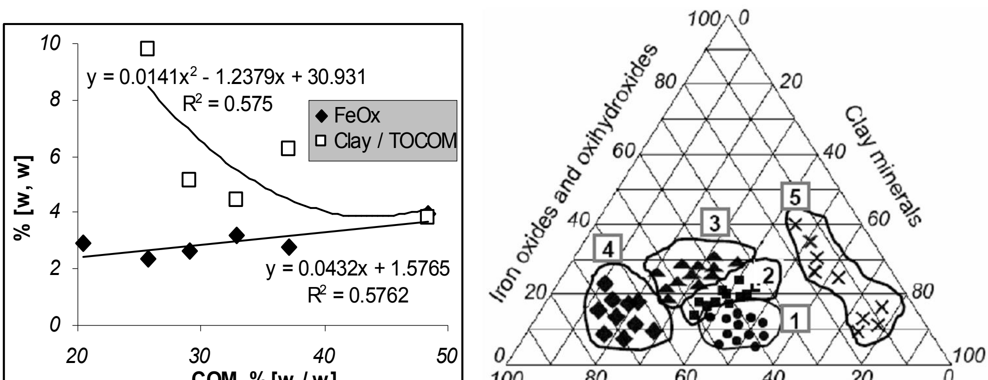
RESULTS AND DISCUSSION

In studied profile, the content of organic-mineral complexes varied between 20.42-48.36 % [w/w] (average: 32.26 %), being evidenced a relative accumulation tendency in Ahok (48.36 %) (*fig. 1 a*) horizon and in grain-size fractions < 0.002 mm (63.62-86.30 %, average: 74.70 % from total of organic-mineral complexes). The maxim weight (29.45-64.56 %, average: 43.05 % from total organic-mineral complexes) has been observed at grain-size fractions < 0.001 mm.



(a) (b)

Figure 1 (**a) Distribution (% from soil samples) of clay minerals (CM), iron oxides and oxi-hydroxides (FeOx), organic compounds (total contents; TOCOM), silica (Si) and organic-mineral complexes (COM) in profile of studied hortic anthrosol. (b) Distribution (% from total content) of organic-mineral complexes on profile and in grain-size fractions: sand (total); 2.0-0.02 mm, dust 1: 0.02-0.01 mm, dust 2: 0.01-0.002 mm, clay 1: 0.002-0.001 mm, clay 2: < 0.001 mm. The data have been obtained for the profile 1 - Bacău glasshouses.**



(a) (b)

Figure 2 **(a) The correlations between the content of organic-mineral complexes (COM), iron oxides and oxi-hydroxides (FeOX). (b) The distribution of organic-mineral complexes from studied hortic anthrosol in function of the content of clay minerals, humus, iron oxides and oxi-hydroxides: organic-mineral complexes with crystalline clay nucleus (1) and amorphous (2), with nucleus of iron oxides and oxi-hydroxides (3), with ionic complex nucleus (4) and without nucleus (5).**

Ours results indicate the existence of some direct correlations between the content and distribution of organic-mineral complexes and the contents of organic matter, clay minerals, iron oxides and oxi-hydroxides and silica (fig. 2). The high apparition frequencies and stability have organic-minerals complexes which include amorphous forms of clay minerals, iron oxides and oxi-hydroxides and silica [1, 3-5, 8, 12].

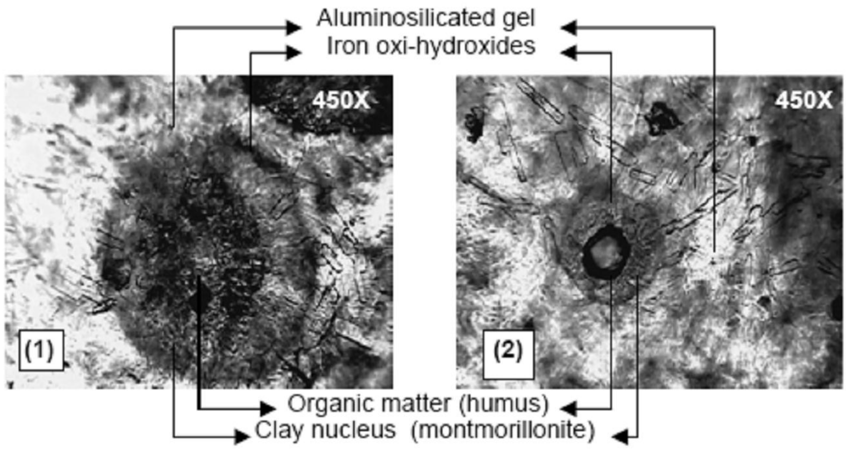


Figure 3 **The organic-minerals complexes with amorphous clay nucleus (1) and crystalline (2) separated from Ahok horizon of studied hortic anthrosol.**

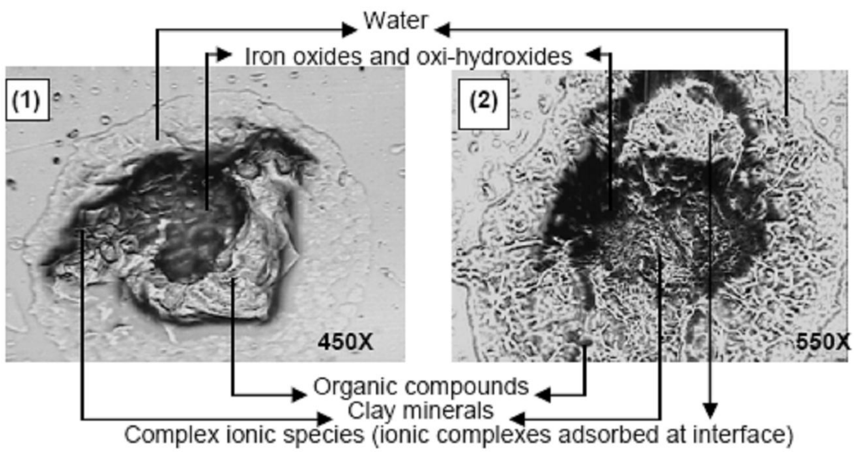


Figure 4 **The organic-mineral complexes with amorphous iron oxides and oxi-hydroxides nucleus (1) and crypto-crystalline (2) separated from Ahok horizon of studied hortic anthrosol**

In function of clay mineral type from the composition of organic-minerals complexes, has been observed that the apparition frequency and stability follow the order: smectite > illite >> kaolinit (have been evidenced a special stabilization effect in case of Ca and Mg forms of clay minerals). In function of iron oxides and oxi-hydroxides type from organic-minerals complexes composition has been observed that the apparition frequency and the stability follow the order: $Fe(OH)_3$ (amorphous) > $Fe(OH)_3$ (ferihidrite, amorphous) > γ-$FeO(OH).nH_2O$ (lepidocrocite) > α-$FeO(OH).nH_2O$ (goethite) > α-Fe_2O_3 (hematite).

From chemical-mineralogical composition point of view, the organic-minerals complexes from studied anthrosol are very different, the components of these varied in large limits, both as type and as weight (*fig. 2 b*). The main components of studied organic-minerals complexes are clay minerals (62.08-78.86 %, average: 70.90 %), organic matter (9.76-22.05 %, average: 16.77), iron oxides and oxi-hydroxides (4.15-7.61 %, average: 6.15 %), aluminosilicates gels (2.63-5.69 %, average: 3.73 %), water, simple and / or complex metal ions (1.27-3.17 %, average: 2.43 %), etc. The weight and the structural role of these components are different from an organic-minerals complex type to other (*fig. 2 b, 3-5*).

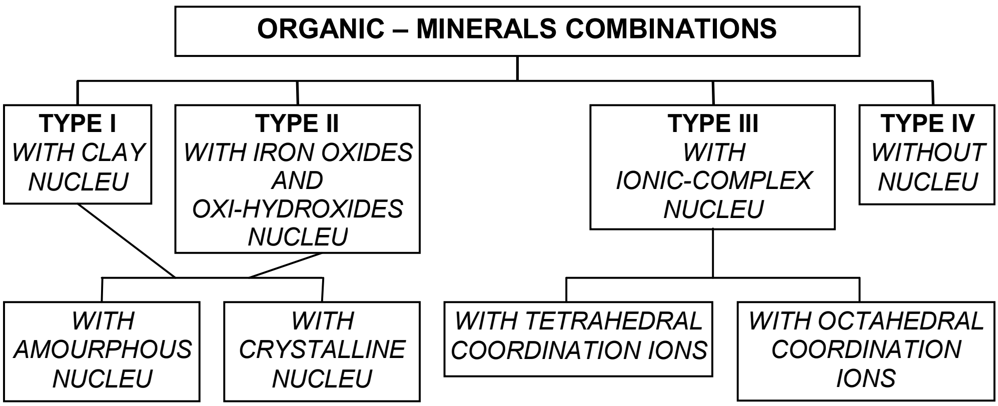


Figure 5 **The classification of organic-minerals complexes separated from studied hortic anthrosol (Bacău glasshouses) in function of chemical-mineralogical composition and structure.**

The microscopic and spectral studies [3-5] have indicated more occurrence forma of organic-minerals complexes in studied anthrosol (*fig. 3, 4*). In our opinion, according with their structure and chemical-mineralogical composition, the organic-minerals complexes from studied hortic anthrosol can be classified in four main classes (fig. 5). Between occurrence forms of organic-mineral complexes is assemble of equilibriums, very sensitive even at relative small variations of extern physic-chemical factors. Thus, the variation of physic-chemical conditions from soil, determined a fast modification of chemical-mineralogical composition and a re-organization of organic-minerals complexes structure, these adopting supra- and / or macro-molecular forms, which ensure the maximum stability in the new conditions. Because such complexes have been observed even in the strong salinized and / or alkalinized horizons of hortic antrosols, shows that these complexes are presented more like supra-molecular assembles, than as colloidal forms or micro- and macro-molecular complexes.

CONCLUSIONS

1. In studied hortic anthrosol, the content of organic-mineral complexes varied between 20.42-48.36 % [w/w] with an accumulation tendency in Ahok horizon (48.36 %) and in grain-size fractions < 0.002 mm (63.62-86.30 %).

2. In function of chemical-mineralogical composition and structure, the organic-minerals complexes from studied hortic anthrosol have been classified in four main categories: (i) with clay nucleus (amorphous or crystalline), (ii) with iron oxides and oxi-hydroxides nucleus (amorphous or crystalline), (iii) with nucleus represented by ionic complex and (iv) without nucleus.

3. The organic-minerals complexes have very complex compositions and structures (generally have 4-5 structural levels), and in studied hortic anthrosol conditions are presented mare like supramolecular assembles, than as colloidal forms or micro- and macro-molecular complexes.

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