Some Physicochemical Aspects of Genesis of Vertic Soils and Vertisols
Quelques aspects physico-chimiques de la génèse de vertisols et de sols vertiques

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Properties of vertisols, widely occurred on all continents, and diversity of pedogenous factors of different regions have been well studied. However, some aspects of their genesis are still obscure that may be connected with the lack of knowledge of physicochemical properties. In earlier studies (1, 2) the attempt of clarifying the peculiarities of formation of vertisols from Russia was undertaken basing on the nature and properties of organomineral fractions. It has been shown that such determinant processes as swelling and shrinking of soil mass tightly correlate with the low content of clay associated organic matter, the predominant component of which is high hydrophilic smectite.

This work is directed to deduce the special features of Ca-Na exchange reactions in vertisols connected with mentioned trait of soil composition and some diagnostic characteristics of these soils.

Soils of two dry steppe regions – Vertisol and Typic Chernozem of Moldova and Vertic soils of gilgai complex of the Central Precaucasus as well as Vertisol and Cinnamonic soils of subarid subtropic region of the South Caucasus (Alasan valley of Georgia) were investigated. Properties of these soils were studied in details by Samoilova et al. (10, 2) and Kovda (3). Some properties of the soils are partly based on the data of mentioned authors and partly on our data (Table 1).

Thermodynamic parameters for Ca→Na exchange were obtained from the experiment with modeling of ion exchange equilibrium. The method is described by Shaimukhametov (5). On the base of solid phase and solution analysis data the normalized exchange isotherms were constructed and the following parameters were calculated: the Gaines-Thomas selectivity coefficient (K_{G-T}), the exchange equilibrium constant (K_{eq}), the standard free energy change (\Delta G^o), the activity coefficients of adsorbed cations (f_{Na}, f_{Ca}), the Gapon selectivity coefficients (K_G).
The values of $\Delta G^\circ$ shown in Table 2 are positive. These data indicate the greater affinity of all samples to Ca than to Na, though the extent of affinity varies significantly in the range from 518 to 4424 J/eq.

Two types of variability of Ca-Na exchange parameters are distinct: spatial and profile. The former is determined by non-uniformity of lithogenous material as well as its
Table 1. Some physical and chemical properties of the soils used

<table>
<thead>
<tr>
<th>Soil</th>
<th>Horizon</th>
<th>Depth, cm</th>
<th>pH (0.01M NaCl)</th>
<th>N₁, %</th>
<th>CEC, meq 100g⁻¹</th>
<th>Exchangeable cations, meq 100 g⁻¹</th>
<th>clay, %</th>
<th>smectite, %</th>
<th>illite, %</th>
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<tbody>
<tr>
<td>Vertisol,7</td>
<td>Ap,ve</td>
<td>10-20</td>
<td>1.23</td>
<td>42.80</td>
<td>37.1, 3.2, 1.3, 1.2</td>
<td>53.5, 43.6, 10.7</td>
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<td></td>
</tr>
<tr>
<td>Cinnamo-nic, 9</td>
<td>A1</td>
<td>3-16</td>
<td>2.04</td>
<td>48.30</td>
<td>41.2, 4.9, 0.9, 1.4</td>
<td>44, 33.9, 9.8</td>
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<tr>
<td>Alazan valley(The South Caucasus)</td>
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<tr>
<td>Chernozem</td>
<td>Ap</td>
<td>0-22</td>
<td>6.65</td>
<td>2.70</td>
<td>37.90</td>
<td>32.5, 2.8, 1.2, 1.4</td>
<td>50</td>
<td>13.3, 28.7</td>
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<td>A</td>
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<td>7.00</td>
<td>2.43</td>
<td>36.00</td>
<td>32.7, 2.11, 0.6, 0.6</td>
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<td>15.2, 26.5</td>
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<td>14</td>
<td>Ave</td>
<td>45-70</td>
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<td>3.64</td>
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<td>49.5, 19.7</td>
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<td></td>
<td>ABca</td>
<td>145-160</td>
<td>7.85</td>
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<td>56.60</td>
<td>35.2, 14.4, 6.0, 1.0</td>
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<td>45.5, 14.3</td>
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<td>Moldova</td>
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<tr>
<td>Chernozem</td>
<td>A</td>
<td>0-22</td>
<td>7.26</td>
<td>1.54</td>
<td>43.43</td>
<td>29.5, 10.9, 2.0, 1.1</td>
<td>52</td>
<td>23.4, 20.8</td>
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<tr>
<td>Typic,18</td>
<td>A</td>
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<td>7.46</td>
<td>2.20</td>
<td>29.30</td>
<td>24.7, 2.8, 1.0, 0.9</td>
<td>35</td>
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The Central Precaucusus, gilgai

<table>
<thead>
<tr>
<th>Chernozem, mound, 87</th>
<th>A11</th>
<th>0-30</th>
<th>7.62</th>
<th>1.54</th>
<th>43.43</th>
<th>29.5, 10.9, 2.0, 1.1</th>
<th>52</th>
<th>23.4, 20.8</th>
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<tr>
<td>Vertisol, microslope, 88</td>
<td>A11</td>
<td>0-30</td>
<td>5.60</td>
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<td>A12</td>
<td>50-90</td>
<td>7.01</td>
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<td>45.65</td>
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<td>21.0, 21.5</td>
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<td>7.26</td>
<td>3.89</td>
<td>34.29</td>
<td>30.8, 2.3, 0.6, 0.6</td>
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<td>Typic, 11</td>
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<td>2.20</td>
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<td>24.7, 2.8, 1.0, 0.9</td>
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<td>2.5, 24.5</td>
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The Central Precaucusus

| Chernozem, Typic, 18 | A   | 0-20 | 7.26 | 3.89 | 34.29 | 30.8, 2.3, 0.6, 0.6 | 35 | 2.5, 24.5 |
| Typic, 11           | A   | 0-20 | 7.46 | 2.20 | 29.30 | 24.7, 2.8, 1.0, 0.9 | 35 | 2.5, 24.5 |
Table 2  Thermodynamic parameters for Ca-Na exchange

<table>
<thead>
<tr>
<th>Soil</th>
<th>Horizon</th>
<th>Depth, cm</th>
<th>$\bar{E}_{eq}$</th>
<th>$K_G$</th>
<th>$\Delta G_0$, $\text{kal eq}^{-1}$</th>
<th>$\Delta G_0$, $\text{J eq}^{-1}$</th>
<th>$C_{eq}$ $\text{smekt}$</th>
<th>$N_{eq}$ $\text{illite}$</th>
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<td>Alazan valley (The South Caucasus)</td>
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<tr>
<td>Vertisol, 7</td>
<td>Ap, ve</td>
<td>10-20</td>
<td>0.70</td>
<td>0.319</td>
<td>195</td>
<td>814</td>
<td>0.03</td>
<td>0.023</td>
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<td>A1</td>
<td>3-16</td>
<td>0.39</td>
<td>0.117</td>
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<td>0.47</td>
<td>0.233</td>
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<td>1740</td>
<td>0.07</td>
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<tr>
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<td>0.202</td>
<td>343</td>
<td>1435</td>
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<td>291</td>
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<td>C</td>
<td>120-160</td>
<td>0.54</td>
<td>0.264</td>
<td>334</td>
<td>1397</td>
<td>0.01</td>
<td>0.007</td>
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<td>0.46</td>
<td>0.191</td>
<td>432</td>
<td>1808</td>
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<tr>
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<td>A13</td>
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<td>0.202</td>
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<td>1717</td>
<td>0.08</td>
<td>0.035</td>
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<td>AC4a-C</td>
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<td>299</td>
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<tr>
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<td>A11</td>
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<td>0.171</td>
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<td>1998</td>
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<tr>
<td>Chernozem</td>
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<td>0-20</td>
<td>0.15</td>
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<td>1057</td>
<td>4424</td>
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<tr>
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<td>11</td>
<td>0-20</td>
<td>0.45</td>
<td>0.192</td>
<td>438</td>
<td>1835</td>
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<tr>
<td>Montmorillonite</td>
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<td>1.70</td>
<td>-294</td>
<td>-1230</td>
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alteration during soil formation. Parent materials of the studied soils could be divided into two groups according to the clay minerals composition. The first group is presented by Quaternary loess-like (soil 10) and eluvial-talus deposits of Maykop clays (s.87-89, 18). The main component of the clay fraction of these rocks is illite and swelling minerals are presented by montmorillonite predominant mixed-layered constituents. The second group includes Sarmat clays (s. 14) and slopewash-talus deposits of volcanic rocks (s. 7, 9). Swelling phase of clay minerals of this group constitutes 70-90 % and is represented by individual minerals of montmorillonite. The isotherms for Ca-Na exchange on the parent rocks of both groups as well as on Wyoming bentonite are shown on Figure 1. They demonstrate regular increase of preference for Ca over Na with diminishing of the montmorillonitic component in clays and, conversely, with the increasing amount of rigid structure minerals (mainly illite). This trend is also in agreement with the values of $\Delta G_0$ (Table 1). The amount of smectitic component in the rocks of the first group is 13-38 % and illite-smectite ratio – 0.35-1.84, whereas for the second group these parameters are 45 % and 0.31, respectively. The $\Delta G_0$ value for the exchange reaction on the first group of rocks is 1250-1540 J/eq, for the second group – 520 J/eq, and for Wyoming bentonite – -1230 J/eq. The Gapon coefficients change with the same regularity in this order 0.006 – 0.012 – 0.017. According to the literature data (9), the increase of $\Delta G_0$ (from 406 to
1680 J/eq) from montmorillonitic Vertisols through Vertic to montmorillonitic-illitic Mollisols of Morocco was revealed from thermodynamic analysis of Ca-Na exchange reactions. Such dependence could be explained with the help of the ion exchange theory. Accordingly to this theory at the constant electrolyte concentration the amount of adsorbed bivalent metal cation depends on the surface charge density of sorbent. The later determines the value of negative potential of the particles surface. It is known that the surface charge density of illite is greater than that of montmorillonite that makes bivalent cation sorb preferably on illite.

Spatial variability of exchange reactions parameters connected with the influence of soil formation processes could be revealed in greater affinity of Vertic soils and Vertisols for Na than corresponding zonal soils within one bioclimatic zone. This feature is more pronounced for the pair of soils of Alasan valley: Cinnamonic (s. 9) and Vertisol (s. 7), developed on genetically uniform rocks, and is less expressed for the soils of Moldova and Central Precaucasus (Table 2). The same dependence is reported for the Morocco soils (9), where $\Delta G^\circ$ of Ca-Na exchange for the upper horizons of Mollisol ranges from 2557 to 3038 J/eq whereas for the same horizon of Inceptisol $\Delta G^\circ$ was equal to 1845 J/eq. In order to clarify the reasons of the different affinity of zonal and Vertic soils to cations the correlation analysis of relationship between the exchange equilibrium constant and factors influencing the Ca-Na exchange (the amount and mineral composition of clay fraction, the amount of organic matter) was used for upper horizons. The results of the ion exchange modeling experiment were interpreted on the basis of a concept about the exchangeable complex as a system of organomineral constituents including organo-clay particles (<1µm) and metal-organic compounds not bound with mineral particles (light fraction with density <2 g cm$^{-3}$). The level of their accumulation, their composition and properties diverse essentially in soils of different origin (8) that influences the exchangeable properties of soils. It has been found (7) that organo-clay particles in Chernosems contribute most (to 90%) to CEC, therefore, their properties should affect direction and the character of exchange reactions in soil. As found earlier (1), one of the main specialties of Vertic soils and Vertisols is lower content of organic matter associated with clay in comparison with zonal soils. It has been proposed to express this feature as a ratio between the content of organic matter and the amount of clay or smectite component as the mineral with the most developed surface (Corg/clay and Corg/smect). For upper horizons correlation between these parameters and $K_{eq}$ of Ca-Na exchange is significant ($r^2 = 0.66$ and 0.81, correspondingly) at level $P= 0.05$. Therefore, the less preference of Vertic soils for Ca over Na in comparison with zonal soils could be explained by the lower content of organic matter associated with clay.

Profile variability of the exchange constants, namely, the increase of the affinity to Ca from parent material to upper horizons, was revealed in numerous works for soils of different genesis (4, 5, 6). So, for the soils formed on the rocks of the first group (see above) $\Delta G^\circ$ changes from 1250-1550 J/eq for AC and C horizons, to 1800-4420 J/eq for A horizons, and for the second group – from 520 to 814-1740 J/eq (Table 2). The same dependence is illustrated at Figure 2. The growth of the affinity to Ca to upper horizons is explained by the increase of surface charge density of soils. The later is considered to be affected by the accumulation of organic matter as these two parameters correlate positively (4). On the other hand, organic matter could affect Ca-Na exchange because
of its high affinity to Ca vs. Na (4, 5). In the profile of Moldova Chernozem (s.10) fluctuations of mineralogical composition of clay are not significant that allows us to notice the impact of organic matter on Ca-Na exchange reactions (Table 1, Fig. 2). However, in studied soils not only the amount of organic matter rises to upper horizons but the content of illite as well (Table 1). This phenomenon could act similarly and it seems difficult to separate the influence of each factor on exchange properties.

It is evident that beside of the influence of clay organic matter the accumulation of light fraction humic substances plays significant role as well. These substances have the extremely high preference for bivalent cations. This is true in our case, because 36% of organic carbon is concentrated in this fraction (2).

Hereby, isotherms and thermodynamic parameters of Ca-Na exchange ($K_{eq}$, $\Delta G^\circ$, $K_G$) demonstrate the preference of all soils for Ca over Na. The values of $\Delta G^\circ$ are minimal in low horizons (520-1540J/eq). Within these layers $\Delta G^\circ$ decreases with the increase of the content of smectitic component in mixed-layered minerals and from the soils with mixed-layered minerals to soils containing individual smectite. Soil formation processes intensify the growth of affinity to Ca ($\Delta G^\circ$ achieves the values of 2180-4420 J/eq). This is connected with illite content increment in clays as well as with the accumulation of organic matter, especially associated with clay.

Vertic soils and Vertisols have lower affinity to Ca because of the peculiarities of their composition, namely, low content of clay organic matter in combination with well developed clay particle surface tied with the domination of smectitic minerals. Analysis of selectivity coefficients dependence on the exchangeable cation content showed that the affinity of soils to Na was the greatest at the small fraction of adsorbed Na charge (<5%). It is in agreement with literature data (5). Minimum of Na affinity was revealed at the fraction of adsorbed Na about 5-15 % (Fig. 2).

The conclusions discussed above appear to be very important for the understanding of the genesis of salt affected Vertic soils and conditions contributing to the soil mass displacement and sleekenside formation. In order to clarify our thoughts we tried to analyze the dependence of the extend of sleekenside development in Vertic profile of gilgai complex upon the properties of clay-organic fraction and parameters of soil solutions (Table 3).

According to the table data and theoretical speculations the most favorable conditions for the processes of swelling and consequent displacement of soil layers are in the middle part of the profile that corresponds to the most intensive development of sleekensides (3). This fact is explained by the sharp descent of humus content in clay fraction and simultaneous increase of smectitic minerals amount, that strengthen the affinity of solid phase to Na. Such conditions are combined with high SAR (≈20), pH and moderate ionic strength of soil solution (0.041-0.158). In upper horizons swelling in prevented by high clay organic matter content along with low smectitic content, low SAR (0.4-1.7) and lower pH of soil solutions. In deeper layers high ionic strength (0.259-0.536) is the main swelling limiting factor.

Table 3. Profile variation of clay fraction properties and parameters of soil solutions of the gilgai complex soils
Properties of Mound Microslope Depression

<table>
<thead>
<tr>
<th>Clay and Soil Solution</th>
<th>Mound</th>
<th>Microlong</th>
<th>Depression</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-20 ìì</td>
<td>70 - 110 ìì</td>
<td>160 - 135 ìì</td>
<td>0-14 ìì</td>
</tr>
</tbody>
</table>

N<sub>total</sub> of clay, g 100 g<sup>-1</sup> of clay
39
50
53
39
47
54
25
38
49

N<sub>total</sub>/Smectite
0.03
0.017
0.008
0.114
0.032
0.008
0.195
0.031
0.014

Soil Solution

| Ionic strength, I** | 0.019 | 0.114 | 0.259 | 0.015 | 0.158 | 0.536 | 0.008 | 0.041 | 0.375 |
| SAR** | 0.4 | 19.1 | 23.2 | 1.7 | 21.4 | 33.6 | 1.3 | 17.5 | 25.7 |
| pH | 7.62 | 8.05 | 8.00 | 5.60 | 7.72 | 7.54 | 5.36 | 7.01 | 7.85 |

* The mineralogical data are from the paper of Kovda et al. (3).
** Ion strength and SAR are estimated with data (3).

In conclusion it can be stated that significant factors affecting the appearance and development of swelling and consequent shrinking and as a result specific structure of vertisols are: 1) low amount of organic matter associated with clay, 2) high content of clay containing a large portion of smectite, 3) consequently, strong affinity to Na, in combination with 4) certain factors of geochemical media: low ionic strength, high SAR and pH of soil solution.

Reference


Key words: clay- organic matter associations, surface properties, cation exchange, clay minerals, swelling, vertisols

Mots clés : associations argile-matière organique, propriétés de surface, capacité d’échange, minéraux argileux, gonflement, vertisols
Fig. 1. Exchangeable isotherms. $E_{\text{Na}}$ and $E'_{\text{Na}}$ are equivalent fractions of Na in an aqueous phase and an exchanger phase, respectively.

Fig. 2. Dependence of Na activity coefficient ($f_{\text{Na}}$) on equivalent fraction of Na ($E'_{\text{Na}}$) for three horizons of Chernozem 10.