Compositional change of solid and liquid phases of soil suspension depending on pH value

S P Zamana¹, T G Fedorovsky¹, N A Golubkina² and A V Sokolov³

¹State University of Land Use Planning, 15, Kazakova str., Moscow, 105064, Russia
²Federal Scientific Center of Vegetable Production, 14, Selectsionnaya str., VNIISSOK, Moscow region, 143072, Russia
³Russian state agrarian correspondence university, 1, Fuchika str., Balashikha, Moscow region, 143907, Russia

E-mail: svetlana.zamana@mail.com

Abstract. The content of mobile forms of chemical elements in soils is affected by many factors including soil pH, grading and humus concentration. The most pronounced influence on elements behavior and their absorption levels by plants is produced by pH, which gives an opportunity to characterize quantitatively the ratio between elements forms in the solution and the equation between liquid, solid and gaseous forms of soil. Thus, the element composition of solid and liquid soil phases depending on pH may become of special interest. The article presents the results of a model experiment to determine the changes occurring in different pH ranges in the solid and liquid phases of aqueous soil suspensions taken from the organogenic horizon of the peat-podzolic soil of the Moscow Region. Potentiometric titration and atomic absorption methods for determination of chemical elements (Ca, Mg, K, Mn, Fe, Al, Si) were used. The element composition of solid and liquid phases of peat-podzolic soil suspension is considered at different pH. The results demonstrate that pH of the soil suspension correlates with element composition changes of both liquid and solid phases, thus indicating soil bioavailability of elements.

1. Introduction

Mobile forms of chemical elements in soils are known to depend on soil pH, grading and humus content. Among the above factors, soil pH influences especially intensively the elements behavior in soils and their accumulation by plants [1-3]. Only at neutral pH (6.5-7.5) most of biogenic elements (N, P, K, S, Ca, Mg, Fe, Mn, B, Cu, Zn, Mo) become bioavailable for plants [4]. Absorption of cations and anions by plant decreases their concentration and activity in soil solution thus decreasing gradually the efficiency of plant nutrition. New ion portions maintaining the activity at the same level enter the solution from the solid phases as a result of dissolution of the sparingly soluble salts present in the solid phases, exchange reactions or aluminosilicate and organic matter destruction. pH value may characterize quantitative ratios between different elements forms in the solution and also characterize conditions of equilibrium of soil solid-liquid-gaseous phases.

Different buffer systems may exist at different soil pH [5]: 1) at pH 3.0 – 4.5 – permanent charge of clay minerals, silicates destruction and formation, organic aluminum complexes; 2) at pH 4.5 – 6.0 – amino groups, carbonates equilibrium, hydroxo complexes of aluminum; 3) at pH 6.0 – 7.5 – hydroxo complexes of aluminum and carbonate equilibrium; 4) at pH 7.5 – 9.0 – hydroxo complexes of aluminum,
phenol hydroxyls, carbonate equilibrium. Ca$^{2+}$, Mg$^{2+}$, K$^+$, Al$^{3+}$ are released during destruction of alumosilicates [6, 7]. In case of soil liquid phase pH, less than 4 significant amounts of Al may be released from the silicate grid.

The following reactions may take place as a result of interaction of organogenic soil horizons with an acid: dissociation of organo-mineral complexes, containing Al, Fe and Mn; protonation of functional groups of specific and nonspecific organic acids; cation exchange reactions; solubilization of strong bases salts and weak organic acids with the appropriate protonation of acid anion. Al, Fe and Mn appear in the solution in case of mobilized ions excess above the capacity of their complex binding by organic compounds.

During the base titration of aqueous suspensions of organogenic soil horizons up to pH 7, carboxyl (COOH) groups of humic (GA) and fulvic acids (FA) can be titrated. At pH>9, deprotonation of GA and FA phenolic and NH$_2$ groups takes place [8]. Additional reactions of iron and aluminum hydroxo complexes with organic ligands may occur. Basic titration of GA and FA is consistent with deprotonation (at pH 3-7) of the first of the most acidic carboxyl groups and at pH > 8 – phenolic and NH$_2$ groups. Carboxyl groups are titrated in a large pH range (from 3 to 7), but COOH groups with pKa from 4 to 5 predominate. At high pH levels, several aluminum organic compounds are destructed, which results in a conversion of Al(OH)$_4$ and Al(OH)$_3$ ions into a solution.

Taking into account a great influence of soil pH on chemical elements absorption by plants, studies on the element composition of solid and liquid soil phases are of great importance.

The work presents the results of element composition changes of solid and liquid phases of aqueous soil suspensions depending on pH.

2. Materials and methods

We carried out a model experiment to determine changes occurring in different pH ranges in the solid and liquid phases of aqueous soil suspensions from the organic horizon of the peat-podzolic soil of the Moscow Region.

3 g of soil were diluted with water at a ratio of 1:25; pH equilibrium values were measured and continuous titration with the base was achieved up to pH 5, pH 6, pH 7, pH 8, pH 9, pH 10 and also with an acid up to pH 4 and pH 3.

The applied method of potentiometric titration consists in registering (using a pH meter) changes in the pH values of the soil suspension or extraction from the soil when a certain amount of acid or base is added to the system [9, 10].

The resulting solution was centrifuged during 10 minutes at 4000 r/min, then the liquid phase was separated from the solid one. The solid phase was dried and used for the determination of: 1) Ca, Mg, K, Mn, Fe, Si, Al in NH$_4$Cl extracts using the AAS method; 2) organic carbon was determined via calculating mass losses during calcination. The same parameters were determined in the liquid phase using AAS, and Turin method was used for determination of water-soluble organic carbon (Cp).

3. Results and discussion

Results of Ca, Mg, K, Fe, Al and Si determination in liquid phase of the organogenic peat-podzol soil horizon suspension in different pH ranges (3-4; 4-4.2; 4.2-5; 5-6; 6-7; 7-8; 8-9; 9-10) are presented in Table 1.

The calcium content at the initial pH value reached 8.0 mM-eq/kg; the lowest value (0.9 mM-eq/kg) was detected at pH 5-6, and the highest (22.2 mM-eq/kg) – at pH 8-9. At pH 5-7, calcium was transported to the soil absorbing complex. Due to the increase of the cation exchange capacity at higher levels of pH, increase in the soluble Ca content at pH 8-9 is caused by dissolving the Ca-containing organic matter that may explain the highest increase in the Ca concentration and organic matter at pH 8-9. Decrease of the Ca level at pH 9-10 (up to 12.9 mM-eq/kg) is associated with a decrease of the soluble organic matter (C$_{p}$= 6.7 g/kg).
The lowest concentration of soluble Mg was manifested at the initial pH equal to 4.2 (2.0 mM-eq/kg); the highest (5.3 mM-eq/kg) – in the pH range of 8-9, which correlate, to a certain extent, with change in the organic matter content at different pH values.

**Table 1.** The composition of the liquid phase of an aqueous suspension of peat-podzolic soil (mM-eq/kg).

| Indicators | Content of | chemical | elements at different values of pH ranges |
|------------|------------|----------|-----------------------------------------|
|            | 3-4 | 4-4.2 | initial pH | 4.2-5 | 5-6 | 6-7 | 7-8 | 8-9 | 9-10 |
| Ca         | 14.5 | 10.3 | 8.0 | 5.8 | 0.9 | 4.5 | 8.7 | 22.2 | 12.9 |
| Mg         | 4.8  | 3.0  | 2.0 | 2.4 | 2.8 | 2.6 | 2.9 | 5.3  | 5.0  |
| K          | 4.6  | 3.1  | 3.0 | 22.8 | 36.8 | 40.8 | 54.8 | 94.8 | 114.8 |
| Mn         | 1.2  | 0.4  | 0.3 | 0   | 0   | 0   | 0   | 0    | 0    |
| Fe         | 0.5  | 0.4  | 0.4 | 0.9 | 1.1 | 1.5 | 2.8 | 4.2  | 7.0  |
| Al         | 6.9  | 5.5  | 5.6 | 6.0 | 5.6 | 4.0 | 6.8 | 11.2 | 18.8 |
| Si         | 1.8  | 1.4  | 1.5 | 2.0 | 2.8 | 4.4 | 4.7 | 7.7  | 11.1 |
| C<sub>p</sub> | 0.8  | 0.9  | 1.1 | 4.3 | 5.5 | 5.8 | 6.3 | 9.6  | 6.7  |
| g/kg       |       |       |     |     |     |     |     |      |      |

The lowest concentration of soluble K was shown at the initial pH level of 4.2 (3.0 mM-eq/kg). With the increase of pH from 4.2 to 10, the potassium content in the solution increased dramatically, parallel to the organic matter increase, reaching 114.8 mM-eq/kg at pH 9-10. Potassium goes into solution in higher quantities than those of Ca and Mg, which is connected with greater solubility of its derivatives.

The iron concentration at pH 4.2 reaches 0.4 mM-eq/kg. By adding alkali, its concentration increased up to 7.0 mM-eq/kg at pH 9-10 due to dissolution of Fe-organic complexes.

The aluminum content in the solution at the initial pH value was equal to 5.6 mM-eq/kg. pH increase caused the elevation of the Al level up to 6.0 mM-eq/kg at pH 4.2-5, and then a decrease at pH 5.6-5 (5.6 mM-eq/kg) and pH 6-7 (4.0 mM-eq/kg). At pH 8-10 its concentration again increased (18.8 mM-eq/kg). The observed changes of soluble Al with pH increase may be connected with the fact that at lower pH there is a partial displacement of the exchangeable aluminum in the solution; at pH 5-6 and pH 6-7 Al precipitates in a form of hydroxide, and at the higher pH hydroxide dissolution is observed with the formation of aluminate ions.

The silicon concentration in a solution at initial pH was equal to 1.5 mM-eq/kg. Increase of pH resulted in a gradual Si level increase up to 11.1 mM-eq/kg at pH 9-10 due to dissolution of organic residues.

Decrease of pH from the initial value to 3 resulted in significant increase of all the above elements in the solution: Ca – up to 14.5 mM-eq/kg, Mg – to 4.8 mM-eq/kg, K– up to 4.6 mM-eq/kg, Fe – up to 0.5 mM-eq/kg, Al – up to 6.9 mM-eq/kg, Si – up to 1.8 mM-eq/kg.

The soluble organic carbon content in a liquid phase of the water suspension investigated at initial pH was equal to 1.1 g/kg. During titration from initial pH to 5 and from 5 to 6 pH, a noticeable increase of the soluble organic carbon content occurred up to 4.3 and 5.5 g/kg, accordingly. At pH 6-7 and 7-8, the soluble organic carbon content changed insignificantly reaching 5.8 and 6.3 g/kg, respectively, and at pH 8-9 the value again increased significantly up to 9.6 g/kg. Increase of the soluble organic carbon content at lower pH is achieved due to predominantly nonspecific organic acids; while at higher pH – by participation of specific humus compounds. During a dissolution of the organic matter as a result of alkali supplementation, a hydrogen bonds destruction in a specific organic matter takes place. The phenomenon may be enhanced with the pH increase.

The content of chemical elements in the solid phase of the organogenic peat-podzol soil horizon suspension investigated is presented in Table 2.

The exchangeable Ca content at initial pH was 98 mM-eq/kg. pH increase up to 9-10 caused its decrease up to 58 mM-eq/kg. The exchangeable Mg content at initial pH was 25 mM-eq/kg, and...
elevation of pH resulted in its increase differing for various pH ranges, reaching 27 mM-eq/kg at pH 7-8. Alkali titration was accompanied by similar to Ca changes in the Mg content, i.e. at pH 4.2-5 and pH 7-8 it increases, while at pH 5-7 and pH 8-10 - decreases. The phenomenon may be connected with the facts that during titration with alkali a simultaneous displacement of Mg and Ca from the soil absorbing complex takes place with the appropriate solubilization of Ca, Mg containing organic compounds, and the mobility increase of solid phase Ca and Mg.

Table 2. The composition of the solid phase of an aqueous suspension of peat-podzolic soil (mM-eq/kg).

| Indicators | Content of chemical elements at different values of pH |
|------------|-----------------------------------------------------|
|            | 3-4  | 4-4.2 | initial pH | 4.2-5 | 5-6 | 6-7 | 7-8 | 8-9 | 9-10 |
| Ca         | 73   | 86    | 98    | 96   | 93  | 87  | 89  | 74  | 58  |
| Mg         | 19.5 | 23.9  | 25    | 26.7 | 26.3| 25.1| 27.0| 26.5| 25.3|
| K          | 3.7  | 3.8   | 5.0   | 20.3 | 26.1| 36.9| 38.5| 68.5| 96.1|
| Mn         | 1.3  | 1.5   | 1.9   | 3.1  | 3.1 | 2.7 | 2.8 | 3.0 | 2.5 |
| Fe         | 0.5  | 1.7   | 2.9   | 9.0  | 3.0 | 3.0 | 3.3 | 3.1 | 2.0 |
| Ceq        | 88.1 | 88.0  | 88.6  | 89.1 | 88.6| 92.7| 91.0| 88.7| 89.1|

The content of exchangeable potassium in the solid phase at initial pH was 5.0 mM-eq/kg and the value increased significantly at higher pH up to 20.3 mM-eq/kg (pH 4.2-5) and up to 96.1 mM-eq/kg (at pH 9-10), which may be connected with the increase of its mobility.

Exchangeable Mn at pH=4.2 was equal to 1.9 mM-eq/kg; at pH 4.2-5 the value increased to 3.1 mM-eq/kg, while at pH 6-10 it was equal to 2.5-3.0 mM-eq/kg. Exchangeable Fe at initial pH was 2.9 mM-eq/kg. Alkali treatment from initial pH to 5 caused the value increased due to the increase of mobility of complexes with organic ligands of lower acidity. At pH 5-7 the value decreased up to 3.0 mM-eq/kg; at pH 7-8 and pH 8-9 it increased a little and became lower 2.0 mM-eq/kg at pH 9-10.

Acidification up to pH 3 resulted in a decrease of all exchangeable cations: Ca – up to 73 mM-eq/kg, Mg – to 19.5 mM-eq/kg, K – to 3.7 mM-eq/kg, Mn – to 1.3 mM-eq/kg, Fe – to 0.5 mM-eq/kg.

4. Conclusion
The model experiment with the organogenic horizon of peat-podzol soil allows revealing that pH of the soil suspension affects changes in the element composition of both liquid and solid phases, thus influencing the chemical elements bioavailability of soil for plants. Acidification of the organogenic horizon up to pH 3 increases the Ca, Mg, K, Mn, Fe, Al, Si content in the liquid phase from 0.2 mM-eq/kg (Fe) up to 6.7 mM-eq/kg (Ca). The pH increase up to pH 10 results in Ca, Mg and Al increase at a certain pH range and the decrease at other pH ranges, while the concentration of K, Fe and Si increases in all pH ranges.

The carbon content of the soluble organic matter in the solid phase of water suspension during pH elevation from 4.2 to 10 increases from 1.1 to 6.7 g/kg, while during acidification from pH 4.2 to pH 3 the value decreases from 1.1 g/kg to 0.8 g/kg.

References
[1] Yagodin B A 1985 Agrochemistry [in Russian – Agrochimiya] 11 117-127
[2] Barber C A 1988 Biological availability of nutrients in the soil. Mechanistic approach (Moscow: Agropromizdat)
[3] Kabata-Pendias A and Pendias X 1989 Trace Elements in Soils and Plants (Moscow: Mir)
[4] Thompson L M and Throw F P 1982 Soils and their fertility (Moscow: Kolos)
[5] Filepp D and Radley M 1989 Soil Science 12 48-59
[6] Dronova T I 2000 Soil Science 5 61-65
[7] Tolpesta I I and Sokolova T A 2013 Soil Science 9 81-90
[8] Gugenberger et al 1989 *Science of the Total Environment* **81-82** 447-457
[9] Sokolova T A, Pakhomov A P and Terekhin V G 1993 *Soil Science* **7** 97-106
[10] Feodorovsky T G, Ladonin D V and Sokolova T A 2005 *Vestnik of MSU. Soil Sci. Series* **1** 22-28