A thermodynamic study of microelement influence on the nitrogen and oxygen activity in soil

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Abstract. Microelement influence on the activity of the most important biogenic elements (oxygen and nitrogen) have been studied through modelling of physical and chemical processes. The obtained results lead to the conclusion that sandy soils do not influence chemical potentials of oxygen and nitrogen due to the silicon dioxide inertness. Clay soils increase oxygen activity and reduce nitrogen activity; at the same time, the influence is smoothed by the process of poorly soluble gibbsite mineral formation as a result of increased aluminium oxide content in the soils. The oxygen chemical activity increases in the presence of copper(II) ions in sandy soils. Iron(II) ions have a negative impact on the oxygen chemical activity; however, they in-crease the nitrogen activity in sandy and clay soils. The oxidation state of a microelement included in micronutrient fertilizers substantially influences the biogenic element activity. Iron(III) ions used as a component of micronutrient fertilizers have an advantage over iron(II) ions, as they increase the nitrogen activity to a greater extent.

1. Introduction

We previously studied the influence of mixed mineral fertilizer compositions [1, 2] and soil chemical composition [3, 4] on the activity of the most important biogenic elements (oxygen and nitrogen) in respective thermodynamic systems through the modelling of physical and chemical processes. In this regard, we studied nitrogen-containing, phosphorus-containing and potassium-containing fertilizers, as well as limestone and slaked lime. The study results have shown that the calcium-containing fertilizers (limestone and slaked lime) are optimal in terms of influence on nitrogen and oxygen activity.

It is known that micronutrient fertilizers contain ionized chemical elements required to biosynthesize the physiologically important substances participating in plant metabolism. Microelements, including manganese, copper, boron, zinc, cobalt, molybdenum and iron, have a substantial impact on growth and development of plants [5].

The objective of this paper is to study the influence of a number of microelements on the nitrogen and oxygen activity, which are the most important participants of plant metabolic processes.

2. Subjects and Methods

The study method is thermodynamic modelling through the Selector software [6, 7]. The method is widely applied for studying equilibrium (as well as partial equilibrium) and non-equilibrium processes, including in soil [8].

Thermodynamic values required for the modelling are found in reference publications [9-12].
Systems studied: microelement compound – component, which characterizes soil – water – air. Thus, the calculations included the independent component (nitrogen and oxygen) characteristics with consideration of all the above phases.

The following soil varieties were modelled:

- clay soils with aluminium oxide (Al2O3) as a basic component, which is a part of clay minerals, such as kaolinite, montmorillonite and illite;
- sandy soils with silicon dioxide (SiO2) as a basic component.

We modelled the clay and sandy soils containing 1 mol of the compound corresponding to the micronutrient fertilizer composition: manganese (II) sulphate, zinc sulphate, copper (II) sulphate and iron(II) sulphate. The chemical activity of the independent components (nitrogen and oxygen) was estimated on the grounds of their chemical potential values: the lower chemical potential of an independent component is, the higher its chemical activity becomes.

3. Results and Discussion

Before studying the influence of the microelements, we estimated the oxygen and nitrogen activity in clay and sandy soils depending on the component, which characterizes each soil type: aluminium oxide or silicon dioxide respectively. The obtained results are shown in figures 1, 2.

![Figure 1. Oxygen chemical potential at an increasing aluminium oxide content (in clay soil) and silicon dioxide (in sandy soil) in thermodynamic systems.](image)

The curves shown in figures 1, 2 confirm the sandy soil inertness, which is associated with the low chemical activity of silicon dioxide. Increased silicon dioxide content in the system does not have a substantial influence on the oxygen (figure 1) and nitrogen (figure 2) activity. Therefore, the influence can be made by introducing additional components to the soil.

Another dependence is observed for clay soils. An increased aluminium oxide content in the soil results in the increased oxygen activity (figure 1) and reduced nitrogen activity (figure 2). At that, the respective curves for both nitrogen and oxygen reach a plateau when aluminium oxide content is 1 mol. It means that a further increase in the aluminium oxide content does not influence the system.
characteristics. This is associated with gibbsite mineral (Al(OH)₃) formation in the system. Further calculations were made for the systems with 1 mol aluminium oxide and silicon dioxide.

![Figure 2. Nitrogen chemical potential at an increasing aluminium oxide content (in clay soil) and silicon dioxide (in sandy soil) in thermodynamic systems.](image)

We shall point out that the oxygen activity is initially higher in clay soils (and increases along with an increase in the aluminium oxide content), while the nitrogen activity is initially higher in sandy soils, and in clay soils, it gets even lower with an increase in the aluminium oxide content.

The microelement content in soils influences the oxygen and nitrogen activity in different ways.

![Figure 3. Influence of the microelements on the oxygen chemical potential in thermodynamic systems.](image)
Zero (0) mark in the Figures corresponds to the modelled soils containing no microelements.

![Graph showing the influence of microelements on nitrogen chemical potential in thermodynamic systems.](image)

**Figure 4.** Influence of the microelements on the nitrogen chemical potential in thermodynamic systems.

First of all, it is important to note that, as compared to sandy soils, in clay soils, the oxygen activity is higher while the nitrogen activity is lower with no regard to the microelement contents.

The oxygen activity (figure 3) in sandy soils slightly increases in the presence of copper(II) ions, while iron(II) ions drastically reduce this parameter both for clay and sandy soils. Such an effect is more articulate for clay soils. The oxygen activity increases in clay soils in the presence of copper(II).

The nitrogen activity (figure 4) increases sharply in the systems containing iron(II) ions both in clay and sandy soils. Other microelements do not have substantial influence on the nitrogen activity in clay soils; as for sandy soils, we can observe negative influence of copper(II) to a greater extent, and manganese(II) to a smaller extent.

It was found that the activity of biogenic elements depends not only on the nature of a microelement, but on its oxidation state. Figures 5 and 6 show the influence of iron(II) and iron(III) on the oxygen and nitrogen activity in sandy soils.

As follows from the curves in figure 5, iron ions generally reduce the oxygen activity in sandy (and clay) soils, as it was noted above. At the same time, Iron(III) ions have a greater negative impact on oxygen activity, as compared to iron(II) ions.

On the contrary, the nitrogen activity increases in the presence of the iron ions, regardless of their oxidation state, which is consistent with the above data. At the same time (figure 6), the positive influence of the iron(III) ions significantly exceeds the influence of the iron(II) ions.

Therefore, the iron(III) ions used as a component of micronutrient fertilizers have an advantage over the iron(II) ions, as they increase the nitrogen activity to a greater extent.
Figure 5. Influence of iron(II) ions and iron(III) ions on the oxygen activity in sandy soils.

Figure 6. Influence of iron(II) ions and iron(III) ions on the oxygen activity in sandy soils.

4. Conclusion
Sandy and clay soils influence the oxygen and nitrogen activity in different ways. Sandy soils do not influence the chemical potentials of oxygen and nitrogen due to the silicon dioxide inertness. Clay soils increase the oxygen activity and reduce the nitrogen activity; at the same time, the influence is smoothed
by the process of poorly soluble gibbsite mineral formation as a result of increased aluminium oxide content in the soils.

In sandy soils, the oxygen chemical activity increases in the presence of copper(II) ions. Iron(II) ions have a negative impact on the oxygen chemical activity both in clay and sandy soils.

Iron(II) ions increase the nitrogen activity in sandy and clay soils. Copper(II) ions and manganese(II) ions decrease the nitrogen chemical activity in sandy soils.

The oxidation state of a microelement included in micronutrient fertilizers substantially influences the activity of biogenic elements. Iron(III) ions used as a component of micronutrient fertilizers have an advantage over iron(II) ions, as they increase the nitrogen activity to a greater extent.

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