EDITORIAL GUEST

NATURAL AND ANTHROPOGENIC CAUSES AND EFFECTS OF SOIL ACIDIFICATION

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Abstract. The paper presents the main topics discussed during the symposium on 'Natural and Anthropogenic Causes and Effects of Soil Acidification'.

Keywords: soil acidification, natural and anthropogenetic causes

INTRODUCTION

The Poland-wide symposium on the subject of 'Natural and Anthropogenic Causes and Effects of Soil Acidification' was carried out in Lublin from the 21st to 22nd of September 1993. The organizers were: Soil Science and Agricultural Chemistry Committee (Polish Academy of Sciences), University of Agriculture in Lublin, Institute of Agrophysics (Polish Academy of Sciences) and the Polish Soil Science Society, Lublin Division, who acted as the main organizer.

The Organizing Committee of the symposium asked outstanding and well-known Polish specialists of soil science, soil fertilization, environment protection, soil chemistry and plant breeding, especially on the toxic effect of strong soil acidification and, connected with it, high concentration of mobile - biologically active forms of aluminium and manganese in soil - to have lectures on the causes, effects and methods of counteracting the acidification of soil. Over 70 abstracts of the original research pertaining to various aspects of soil acidification came to the Organizer's address. All the lectures and abstracts were published in Polish in the Symposium proceedings.

Only the lectures were presented during the plenary sessions of the symposium, the remaining works were discussed in the form of posters and then published in English. The majority of papers is published in this volume and some also in the Polish Journal of Soil Science [1-3].

The author of the present paper acting as the President of the Organizing Committee was entitled by the Organizers to write the Editorial Guest.

In this article I tried to make the synopsis of the subjects discussed in: programmatic lectures, plenary discussion and posters, abstracts and results presented in posters as well as my own publications and research related to soil acidification.

NATURAL CAUSES OF ACIDIFICATION

The majority of Polish soils as well as many countries of Europe, Asia and North America, where humidic climate occurs, are of acid reaction.

In Poland, such soils came into being mainly on post-glacial rocks which, in majority of cases, were of acid character. Intensive periglacial phenomena connected with the effect of running water caused not only the segregation of
soil material but also its elution. Although in the conditions of those times intensive chemical weathering did not occur, because of low temperatures and the lack of directly and indirectly influencing biological factor, the disintegration of carbonates and the elimination of alkaline components could occur. The appearance of plant cover, initially characteristic of tundra (birch-trees, willows, which comparatively quickly were forced out by pine-trees) intensified the processes of decalcification. This process was accompanied by organic substance, moor, which was formed from the litter of coniferous forest with the contribution of fungi. Acid solutions of not only fulvic acids but also of phenols and polyphenols accelerated the decomposition of some primary minerals as well as of rare clay minerals. The products of the decomposition of these compounds in the conditions of strong humidity were transported into the depth of soil and the genetic soil horizons characteristic of podzolic soil came into being.

Among the natural factors of soil acidification, the direct and indirect effect of CO₂ is important. It penetrates soil from the atmosphere but it also comes into being in soil as the result of root respiration as well as the mineralization of organic matter. It increases the solubility of CaCO₃ and leaching of bases into the soil profile. Especially intensive elution of alkaline cations Ca²⁺, Mg²⁺ and K⁺ occurs in bare soils, which is proved by lysimetric studies and the chemical composition of draining waters. The place of the eluted alkaline cations is initially taken by H⁺ and then by, in case of advanced chemical degradation, also Al³⁺ and Mn²⁺.

It should be also stressed that in the conditions of limiting the oxygen inflow into soil from atmosphere, either by the increase of humidity, or because of compaction, the utilisation of chemically bounded oxygen in the form of nitrates, manganese oxides, iron oxides or sulphates by microorganisms for the oxidation of organic matter begins. In all these stages of reduction, the consumption of H⁺ protons occurs, as the results of which the neutralization of acidity procedes. And reversely, the processes of oxidation occurring in the aerobic conditions lead to the increase in acidification.

All the natural processes occurring in soil and contributing to the acidification are usually so intensive that they lead to degradation. The real chemical degradation of soil occurs when the natural factors are combined with anthropopressure. The majority of the symposium participants were of the opinion that the influence of man might have had decisive influence on the shaping of soil reaction in Poland only in the second half of the twentieth century.

FERTILIZATION AS A SOIL ACIDIFYING FACTOR

The decisive role in the acidification of soil plays the application of mineral fertilizers especially nitrogen ones and potassium ones (tough slightly less) in the majority of soils agriculturally utilized. The application of nitrogen in the form of ammonium NH₄⁺, or urea CO(NH₂)₂ which undergoing hydrolysis in soil transforms also into ammonium form which causes the acidification of soil solution both through biological oxidation or nitrification and through its uptake by the root system. Applying the fertilization with nitrogen in the amount of 70 kg N ha⁻¹ - it is the average dose of nitrogen applied in Poland in the years 1975-89 in the form of ammonium sulphate (NH₄)₂SO₄ - we cause the increase in the amount of protons in soil by 7700 mol H⁺/ha, in the form of ammonium nitrate NH₄NO₃ and urea CO(NH₂)₂ by about 2500 mol H⁺/ha.

The effect of potassium salts on the condition of soil acidification undergoes not so much direct concentration of H⁺ protons, although this cannot be excluded, but mainly the displacement of Al³⁺ ions from the sorptive complex to the soil solution. The activation of exchangeable acidity and the revealing of acid effect of aluminium ions procedes as the result of this because aluminium chloride, which comes into being, is hydrolysed and strong hydrochloric acid appears which increases the acidification and multiplies the toxicity of aluminium for plants.
Much valuable and credible information pertaining to the effect of mineral fertilization on the condition of soil acidification are supplied by long-term static pot experiments. In the experimental field in Skierniewice after 70 years of applying mineral fertilizers without liming and organic fertilization, the pH of podzolic soil decreased from 5.3 in the control object '0' to 3.5 in NPK objects and 3.3 in PN objects, such a strong acidification caused mainly by ammonium sulphate, but also by ammonium nitrate (pH decreased to 4.2) causes such a far-reaching considerable soil degradation that practically no plant growth is observed there. One of the main primary causes was surely the acidification. It also caused secondary effects leading to the deterioration of physical, chemical and biological properties, including the increased elution of bases from soil and the decomposition of aluminosilicates and the appearing of toxic amounts of active aluminium and manganese forms, which, according to many symposium participants, are the main cause of chemical degradation caused by strong acidification. A permanent fertilization experiment in Łyczyn, on podzolic soil formed from loamy sand laying on boulder clay, showed that the fertilization with nitrogen alone caused the decrease in barley yield down to none already after 11 years, rape after 16 years, rye after 25 years and potatoes after 26 years. Liming and the application of farm manure on these soils eliminated the negative effect of exclusively mineral fertilization, and especially the fertilization with nitrogen.

**INDUSTRIAL POLLUTION AS A SOIL ACIDIFYING FACTOR**

Great role in the acidification of soil is played also by the anthropogenic causes of industrial origin. Acid and acid-forming substances emitting into the atmosphere by industrial objects, motorization, household fire-places and burning litter dominate among them. These substances are first of all SO\(_2\) and NO\(_x\) emitted in large amounts (according to statistical Yearbook in 1992 - 2.035 mln tons of SO\(_2\) and about 650 thousand tons of NO\(_x\)), but also CO\(_2\), H\(_2\)S, CS\(_2\), HF, Cl\(_2\) and aerosols of H\(_2\)SO\(_4\). It should be mentioned also that GUS (the Main Office of Statistics) data take into consideration only these amounts of gas pollution, which are emitted from very large emitters. The emissions from very small, local heating plant, household fire-places and mechanical vehicles are not considered there. Moreover, it should be stressed that nowadays about 350 thousand tons of SO\(_2\) more falls onto the territory of Poland than the amount of country's emission due to transborder translocation. These pollution fall on soils and plants in gas form (dry deposition) or in the form of acid rainfalls. In both forms they cause unfavourable changes in soil and plants, and in extreme cases they may lead to the total degradation of plant-soil cover. Also solid and liquid falls getting onto the surface of soil are of local significance in the acidification of soil. Pyrite strippings from coal desulphurisation and native sulphur sprayed around the mine and from untight transportation means, acid phosphogypsum and many other wastes belong to them. They often constitute the most radical, local factor of acid soil degradation and the destruction of plant cover. It is most often assumed that nowadays a year total SO\(_2\) deposit on the territory of Poland in wet and dry form amounts 3.0-3.5 mln ton. At the assumption of even distribution it gives from about 96 to 130 kg of SO\(_2\)/ha which is equal to from 147 to almost 200 kg H\(_2\)SO\(_4\)/ha. It should be stressed here that the emission in the form of acid falls prevails over the dry deposit. What is more, other acid-forming air pollutions should be mentioned here, including mainly nitrogen oxides which constitute about 1/3 of acid-forming share in the acid falls.

The differentiation of acid-forming air pollution deposit is very distinct on Polish soils. Its intensity significantly diminishes from the most acidified areas of southern and south-eastern Poland to its north-eastern end, considered 'green lungs of the country'. It is estimated that Suwałki (NE Poland) receives about 45 kg of H\(_2\)SO\(_4\)/ha/year, while sulphur
deposit in the towns of Katowice agglomeration amounts from 200 to 770 kg H₂SO₄/ha/year. Assuming the average deposit of SO₂ as the one equal to 150 kg of H₂SO₄/ha/year it is possible to assume that it is the source of 3061 mol H⁺/ha/year. If this value is increased by about 30% (acid-forming effect of NOₓ and others) the anthropogenic industrial causes of the acidification of soil in Poland should be estimated on the level of 4000 mol H⁺/ha/year. Comparing them with the acidifying effect of the average doses of nitrogen fertilizers it is possible to conclude that in central, northern and eastern Poland on the soils intensively utilised for agriculture, mineral fertilization is the main cause of anthropogenic acidification of soil. Only in the areas considered the areas of ecologic disaster, the acid-forming air pollution of industrial origin are the more intensive factors of soil acidification than fertilization.

**SOIL RESISTANCE TO ACIDIFICATION**

Soils differ significantly with their ability of absorbing proton without the change of pH. This ability is called the resistance to acidification or buffer capacity. It depends on the amount and quality of buffering substances contained in soil and from the reaction products. The range of pH, at which subsequent buffering systems are activated is changeable (Table 1). In our climate conditions the following factors are very significant in forming the resistance to acidification:

- carbonates, mainly CaCO₃, buffering within the range of 6.2-8.6 pH,
- silicates, within the whole scale of the pH of our soils,
- exchangeable cations, within the pH range 4.2-5.0,
- buffering by aluminium beneath pH 4.2 and additionally by iron below pH 3.8.

**PLANT RESPONSE TO SOIL ACIDIFICATION**

The negative effect of low soil reaction on the plant growth is directly connected with:

1. The increase in the concentration of hydrogen ions. This factor is important only in the conditions of very low pH<3.0 and that is why it is not taken into consideration in the cultivated soils.
2. The increase in the concentration of exchangeable, mobile aluminium ions. This factor has the decisive effect in soils with pH<4.5 and in case of soils poor in organic matter, available

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**Table 1. Buffering systems and their pH ranges in soil**

<table>
<thead>
<tr>
<th>Buffering substances</th>
<th>pH ranges</th>
<th>Main products lowering sorptive capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buffering range by CaCO₃</td>
<td>8.6 &gt; pH &gt; 6.2</td>
<td>Ca (HCO₃)₂ in solution (Ca and alkalinity leaching)</td>
</tr>
<tr>
<td>Buffering range by silicates</td>
<td>Full pH scale (dominating buffering reaction in calcium-free soils; pH &lt; 5)</td>
<td>Clay minerals (increase in sorptive capacity)</td>
</tr>
<tr>
<td>Buffering range by exchangeable cations</td>
<td>5 &gt; pH &gt; 4.2</td>
<td>Non-exchangeable n Al (OH)₃⁺ in solution (blocking of stable charge, CEC reduction)</td>
</tr>
<tr>
<td>Oxides - Mn</td>
<td></td>
<td>Mn²⁺ - exchangeable (base saturation reduction)</td>
</tr>
<tr>
<td>Clay minerals</td>
<td></td>
<td>Al³⁺ - exchangeable (base saturation reduction) sulphate hydroxy-Al (accumulation of acid in case of H₂SO₄ addition)</td>
</tr>
<tr>
<td>Inter-layer Al</td>
<td></td>
<td>Al³⁺ in solution (Al translocation, reduction of stable charge)</td>
</tr>
<tr>
<td>n[Al (OH)₃]²⁺</td>
<td></td>
<td>H⁺ + exchangeable Fe organic-ferric complexes (translocation of iron)</td>
</tr>
<tr>
<td>Buffering range by Al hydroxy-Al sulphates</td>
<td>4.2 &gt; pH</td>
<td>Exchangeable H⁺ + Fe (translocation of iron, destruction of clay minerals)</td>
</tr>
<tr>
<td>Buffering range by Aluminium/iron</td>
<td>3.8 &gt; pH</td>
<td></td>
</tr>
<tr>
<td>Buffering range by Fe Fe(OH)₂</td>
<td>3.2 &gt; pH</td>
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</table>
phosphorus and exchangeable forms of Ca\(^{2+}\) and Mg\(^{2+}\) even in the conditions of pH<5.5.

3. The increase in the concentration of active reduced forms of Mn\(^{2+}\). It is especially important in case of pH<5.5 of mineral soils with heavy granulometric composition in which the reduction processes may be prevailing (too wet soils and compact soils fertilized with large doses of organic fertilizers).

Indirect unfavourable effect of low reaction on plants is connected with the increased elution and, in consequence, with the decrease in the exchangeable cations content, especially Ca\(^{2+}\) and Mg\(^{2+}\) in the sorptive complex and soil solution, as well as with the inhibition of their uptake by plants because of the antagonistic effect of aluminium and manganese ions. The occurrence of mobile aluminium, iron and manganese forms in soil solution also causes the decrease in the available for plants forms of phosphorus and molybdenum.

The weak growth of plants, low yielding, deterioration of biological value of feed and food on acid soils and in extreme cases the complete falling out of plants on acid soils is most frequently connected with the toxic effect of aluminium.

SYMPTOMS OF ALUMINIUM TOXICITY ON PLANTS

The symptoms of the toxic effect of aluminium ions observed on plants are not specific. In the above-ground parts we usually deal with the symptoms of magnesium, calcium, phosphorus or molybdenum deficiency in plants (cauliflower) especially sensitive to the lack of this microelement in the substrate. In case of the occurrence of toxic amounts of aluminium in the subsoil, which happens even after liming, the Al toxicity shows within the above-ground parts with the symptoms of drought.

Aluminium ions influence the roots directly from the soil solution, the inhibition of elongating growth, strong thickness occurs and the amount of lateral roots and hairs reduced. After the longer effect of aluminium stress the growing points get brown and the roots die. The roots of mature plants are usually more resistant to aluminium than the roots of young plants.

Natural, wild growing populations on acid soils generated ecotypes tolerating aluminium. The aluminium stress constitutes such a strong selective pressure that the ecotypes appear only in few generations. Some species, however, seem to be completely deprived of genes conditioning tolerance and in such cases the generation of forms more resistant to Al is possible only by the introduction of genetic material from other species. The research which have been carried out for many years proved that in the cultivated plants genetic variability exists in the respect of the reaction to aluminium both among the species and varieties or genotypes within the cultivated species. The existence of such a variability constitutes the basis for the selection aiming at the increase of the plant's tolerance to aluminium. It demands the knowledge of the inheritance of this property and getting to know biological and biochemical mechanisms conditioning this tolerance.

There are many hypotheses, more or less empirically confirmed illustrating the mechanisms of plant tolerance to the toxic concentration of Al\(^{3+}\) in soil. They can be divided into two basic groups: extracellular and intracellular ones.

Extracellular mechanisms are first of all:
- immobilization of Al\(^{3+}\) within cell-walls,
- selective transmissivity of plasmodesm for aluminium,
- the formation of pH barrier in rhizosphere,
- the effusion of Al outside.

The lack of low effectivity of extracellular mechanisms influence are induced by such intracellular mechanisms as:
- the chelating of aluminium in cytoplasm,
- the accumulation of Al in an insoluble form in vacuole,
- the generation of proteins binding aluminium,
- the formation of enzymatic systems resistant to aluminium,
- the increase in the activity of enzymes compensating their inactivation by Al.
Big differences in the tolerance of plants to the toxic effect of $Al^{3+}$ within the same species give the possibilities of breeding the varieties of plants adjusted to growing in acid soils. It seems that this direction of plant breeding is justified and has good prospects. The rise of the level of toxicity boundary of aluminium for plants in connection with the regular liming will allow the enlarging the acreage of the cultivation of plants sensitive to Al - barley and wheat, as well as of their yield­ing. This tendency direction in breeding should be developed also because, even liming does not distinctly change the reaction and does not eliminate the occurrence of mobile Al in deeper layers of soil, from which the plants uptake water and nutrients, especially during drought.

The nutrition of plants in the acid soils is paid a lot of attention to, however, hitherto existing research concentrate mainly on the disturbed uptake of phosphorus and calcium. The complex approach to the state of plant supply with other macro- and microelements is not much taken into consideration. The approach to this problem through the prism of ion balance as the mutual relations between cations and anions and the separation between the very cations and anions in plants should become the main point of interest of the specialists of, not only soil fertility, fertilizing and physiology, but also specialists dealing with the biological quality of feed and food.

Magnesium deficiency should be payed a lot of attention, too. It most often occurs in the conditions of acid soils and the very supplying plants with Mg without the elimination of its uptake blocking, which is the occurrence of mobile aluminium, does not help much.

It is also presumed that in acid soils, at comparatively low concentration of $Al^{3+}$, the plants increase the uptake of potassium which, reversely to aluminium, keeps the cellular plasm in the proper hydratation state.

These conradictory processes of the intensified potassium uptake and the limited accumulation of calcium, phosphorus and magnesium may be the cause of the decrease in the biological quality of yield of the cultivated plants. Apart from the complex approach to ion balance state in plants, the relation $K:(Ca+Mg)$ is an important index considered the main 'grass tetany', especially for graminiferous fodder crop.

During the symposium a lot of attention was payed to the revealing of heavy metals toxicity in dependence on soil reaction. It was stressed that maintaining neutral reaction of soil may at least protect the plants against the excessive accumulation of metals. It is especially important in the areas where soils are polluted with industrial dust containing large amounts of toxic heavy metals.

**FINAL REMARKS**

The reaction of soil determines so many processes taking place in the whole soil profile in the system: soil solution - living organism and within plant organisms, as well as animals dwelling in soil, that it is impossible to discuss them all in this paper. I have just mentioned the most important, according to my opinion, problems presented during the symposium by the participants representing various fields of agricultural and natural science. Other problems, also interesting, but slightly more distant from the main stream, pertained mainly to:

- the effect of acidification and alkalization of soil on the water circulation in the conditions of anthropopressure,
- plant species composition of the habitat with various levels of acidification,
- the increased occurrence of diseases in the cultivated plants depending on the soil reaction.

**CONCLUSIONS**

The symposium chose the Conclusion Board which, on the basis of the plenary discussion and the proposals directly put forward by the participants, made the synthesis of the problems and presented it in the from of the following conclusions:

1. The Lublin scientific centre should continue the organization of symposia devoted to the question of soil acidification. It was proposed to organize the following one in 3 or 4
years and to devote it to the problem of the effect of soil reaction on the revealing of metal toxicity.

2. Among the problems connected with soil acidification a special place should be found for the questions of:
   - manganese and aluminium toxicity, and in case of polluted soils also other heavy metal toxicity,
   - the state of ion balance and plant nutrition (especially K, Mg, Ca, and P),
   - the significance of organic matter in the formation of soil resistance to the acidification and the decrease in aluminium toxicity,
   - the change of directions and the intensification of microbiological processes in dependence on soil reaction,
   - genetic progress pertaining to breeding the cultivated plants with an increased tolerance to aluminium.

3. Analysing the effect of the pollution of industrial origin on the acidification of soil, apart from often discussed SO2 and NOx, the direct and indirect role of carbon dioxide emitted by the industry.

4. In soils intensively utilized in agriculture the nitrogen fertilization, and partly the potassium one, constituted the main acidification factor. Only in the areas considered the areas of ecologic disaster, the air pollution of industrial origin acidifies soil stronger than fertilization.

5. Liming, often with magnesium lime constitutes one of the basic elements of acidified soil reclamation, because it contributes not only to the detoxication of harmful metals but it also improves the structure and numerous physical, physicochemical, chemical and biological properties of soil. That is why the collapse of the production, distribution and application of lime fertilizers should not be allowed. It is vastly the question of influencing the awareness of decision makers and people responsible for the national economy.

REFERENCES