THE ATMOSPHERICALLY POLLUTION AND THE SOIL ACIDIFICATION

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Abstract: *The soil acidity is a feature that limits the growth of the plants and the harvest all over the world. There are different ranges of acidity following the pH range: medium acid between 5.6 and 6.0, heavily acid between 5.1 and 5.5, very acid between 4.5 and 5.0 and extremely acid under 4.5 . The chemical reaction of the soil is directly involved in the mobility and accessibility of the elements that are necessary in nutrition and also of the toxic elements for plants and microorganisms. The solubility of the chemicals is directly influenced by the pH. Some of the compounds from the soil are harmful for the plants when the concentration in the solution of the soil exceeds some limits. This effect is increasing with the value of the acidity. The most incriminated ions are* H^+, Al^{3+} *and* Mn^{2+}, *especially when the pH value is bellow 4.*

Keywords: *soils acidification, permanent charges, pH-depending charges.*

Introduction

The main consequence of the soils acidification is the decrease of his basicity and the substitution of the basicity cations from the adsorptive complex with those of the acidity cations. From this complex physicochemical process occur the characteristics, especially negative, of the acid soils with consequences on the growth of the plants and soil's microorganisms.

The acid reaction has mainly a negative effect upon the crops. This is done due to the leaching of the basic cations leading to a depletion of the nutrients. At the same time both aluminium and manganese reaches toxic levels for the plants and requires adjustments for the crops.

Materials and methods

Types of acidity of the soil

As stated before the hydrogen ions responsible for the acidity of the soil are formed by the negative bond of the clay particles and from the iron and aluminium hydroxides. They release the hydrogen ions from all the soils having a lower pH than their iso-electric point. The carboxylic and phenolic groups of the humic acids, different types of organic or inorganic acids that are soluble in the soil's solution and - in certain conditions - the water itself can turn into hydrogen sources.

The German school for soil science has classified the acidity following the place occupied by the ions of H^+ and OH^-, as follow:

a) *the actual acidity (active* or *effective)* determinate by the concentration of the hydrogen ions in the de soil solution, and

b) *the potential or reserve acidity* determined by the un-dissociated H^+ ions that are adsorbed in the clay-humic complex. The sum of these two forms of acidity is known as the *total acidity of the soil* (Kim A. T., 1992).

The actual acidity determines directly the plant' growth and is a consequence of the potential acidity following the cations exchange when part of the hydrogen cations contained in the soil solution are neutralized. It can be calorimetrically or potentiometrically determined and is measured in pH units.

According to the actual outlooks, the negative load of the colloids that are compensated by the basic cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and by the acid cations (H^+, Al^{3+}) are of two types: a) *permanent charges* and b) *pH-depending charges*.

The permanent negative charges are derived from the isomorphic substitutions from the clay's minerals, from the oxygen ions located at the exterior of the clay particles and, finally, from the carboxylic functional groups of the humic substances with a higher dissociation constant value. These charges remain unmodified, no matter the pH value of the soil solution.

The pH-depending charges are derived from the dissociation of –COOH and phenyl –OH groups from the humic substances having a low dissociation constant value (dissociate only at high pH values), and from the dissociations of the H^+ ions from the –OH groups situated on the external sides of the clay particles which increasingly dissociate starting at a pH of 5.6 to 11 and, finally, from other substances, some with amphoteric features (humico – ferric – aluminum complexes) that release hydrogen ions when exposed to a higher pH than their iso-electrical point.

When the soils are very acide and have vermiculite and di- and trioctahedral minerals, the negative charges of the colloid particles are partially blocked by retaining the ions of Fe and Al hydroxides. These hydroxides reduce the cations exchange rate of these minerals. If the value of the soil pH increases, the ions of Fe and Al hydroxides precipitate as $Fe(OH)_3$ and $Al(OH)_3$. The negative charges of these particles are released and can retain various cations among them H^+ or Al^{3+}[7]. The permanent charge reflects the cations exchange capability (T) of the soil.

The notion of "*permanent charge*" was introduced in the soil science by Schofield in 1949. He noticed that the T value of the soil in the inferior horizons of a Rothamsted soil profile remained constant if the pH of the soil's treatment solutions varied between 2.5 and 5, but the T value increased if the pH value of the treatment solution varied between 5 and 7.

The Al^{3+} ions and those of aluminum polymers can generate H^+ when they are in soluble forms in the soil solution or in adsorption state. There is a direct relation between the hydrolysis of these ions and the soil acidity. This feature can be illustrated by the reactions of Al^{3+} and aluminium hydroxides:

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+;$$
$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^{2+} + H^+;$$
$$Al(OH)_2^{+} + H_2O \rightarrow Al(OH)_3^{o} + H^+;$$
$$Al(OH)_3^{o} + H_2O \rightarrow Al(OH)_4^{-} + H^+.$$

Al the above mentioned hydroxides and some others of them can be noticed in the soil solution following the pH values, from the first reaction to the last one along with the pH values from 3 to 10.

As soon as a calcareous amendment is applied to an acid soil, all the H^+ ions are neutralized, followed by the neutralization of the aluminium polymer hydrolysis products. The insoluble precipitate of $Al(OH)_3$ is named gibsite and it is created at pH greater than 6.5 when it turns insoluble.

The Al^{3+} ions can behave either as a base or acid accordingly to the pH of soil solution. These can be illustrated by the following chemical reactions after Havlin:

a) **as base:**

$Al(OH)_3 + H^+ ==== Al(OH)_2^+ + H_2O;$
$Al(OH)_2^+ + H^+ ==== Al(OH)^{2+} + H^+;$
$Al(OH)^{2+} + H^+ ==== Al^{3+} + H_2O;$
$Al(OH)_3 + 3\ H^+ === Al^{3+} + 3\ H_2O.$

b) **as acid:**

$Al^{3+} + OH^- ==== Al(OH)^{2+},$
$Al(OH)^{2+} + OH^- ==== Al(OH)_2^+;$
$Al(OH)_2^+ + OH^- ==== Al(OH)_3;$

c) **as anion:**

$Al(OH)_3 + OH^- ==== Al(OH)_4^-.$

As a consequence of the hydrolysis of the aluminium hydroxides can result in polymers having two or four electric positive charges and releasing of H^+ ions in the solution. The polymers have positive charges and don't take part to the ion exchange but they change the negative permanent charge of the soil.

The Fe hydroxides also form polymers that behave similar with the Al hydroxides but they have a smaller impact in the changing of the soil's reaction.

Very important in the process of soil's acidification are the industrial pollution with acid-generating gases (NO_x, SO_2, HF, HCl, etc.). All those gases released in the atmosphere are driven by the air flow far from the generating sources and carried by the rain to the soil.

From the reaction between the N and S oxides with the water results acid rains. Part of the acid rains is naturally neutralized by the atmospheric NH_3 or by the cations contained in the fine dust. If the acid rain reaches the earth it changes the pH of the soil towards acid.

The acid rain replaces gradually the Na^+, K^+ Ca^{2+} and Mg^{2+} ions from the colloids particles with H^+ and Al^{3+} ions. It takes years or decades of acid rain to change the pH. As a consequence of soil acidification the mobility of Al^{3+}, Fe^{2+} and Mn^{2+} is altered and the crops and soil microorganisms suffer.

As an example, around the fertilizers and synthetic fibers plants from Piatra Neamț, the pH of the soils reached values of 3.8-4.0 and due to this the flora and the crops were damaged around the plants [8].

Results and discussion

Man induced acidification

Soil acidification can be induced by particles of aluminum silicates, oxides of Fe and Al or by different acids and salts formed in the soil solution as a result of man induced pollution. These salts are mainly N-based fertilizers that release HNO_3 or H_2SO_4. The fertilizers are currently used in agriculture and some of them can seriously alter the soil's fertility. Anhydrous ammonia, ammonium nitrate, urea, ammonium sulphate and even the mono- and di-ammonium phosphate can alter the soil pH [5], [8].

Simple or concentrate super phosphate containing calcium monophosphate can also trigger a strong acidifying reaction of the soil solution because of the hydrolysis of the calcium monophosphate that release phosphorous acid:

$$Ca(H_2PO_4).H_2O + H_2O \rightarrow CaHPO_4.2H_2O + H_3PO_4$$

Calcium diphosphate stays put where the grain of fertilizer reaches the soil but the phosphorous acid migrates around the grain changing the soil. It affects the oxides of Fe and Al and the cations in the soil solution or the adsorbed ones. First the simple phosphates of Al, Fe, Ca, Mg, K and NH_4^+ are formed in colloids forms. Latter these turns into complexes phosphates like taranakites, which are heavy soluble.

Lindsay and Stephenson, 1959, (cited by [2]), discovered that in the beginning the diffusion of H_3PO_4 from the grains of fertilizer determine a very low pH, around 1.5. In a second phase the pH rapidly shifts towards neutral due to the reaction between H_3PO_4 and the minerals around the grain of fertilizer.

Pyrites particles (FeS_2) that contaminate the soil naturally or because of man's activity can generate sulphuric acid and ferrous hydroxide leading to soil acidification.

Following the alteration of some minerals or decomposition of the manure some salts having an acid reaction can be found. The cations of these salts can replace changeable Al^{3+} from the acid soil and reduce the acidity. The capacity to replace Al^{3+} is determined by the valence of the ions resulted from decomposition of the vegetal fertilizer or of the amendments such as $CaCO_3$.

CO_2 can come from the air contained by the soil, from the atmosphere or from activity of the living beings. CO_2 can combine with the water and forms H_2CO_3. While reacting with soils containing $CaCO_3$ it can induce their basicity decreasing. With acid soils it doesn't change much the chemic reaction because while at pH below 6.35, the ionization of H_2CO_3 is low [6].

Conclusions

The decrease of the basicity and alteration of the reaction of the soil is a natural process. The rain has naturally an acid reaction (pH 5.7-6.0). The higher is the amount of rain, the stronger is the alteration and the basicity decrease of the minerals in the rocks.

There is a direct link between the fertilizers containing nitrogen and soil acidification. It all depends on the composition of the fertilizers. If the fertilizer has a basic cation like Ca or K, the acidifying action is diminished.

In order to correct the acidity of the soil it is necessary to apply amendments. They interact with the soil changing the proportion and the degree of saturation of the adsorptive complex with Ca and other basic cations raising the pH towards the optimum level.

Almost all the crops require an optimum pH of 6.5-7. The amount of amendments used must move the pH towards the optimum range of a specific crop. When the acidity of the soil is raising and the pH is under 5.8 the nutrition of the plants is altered. When pH is between 5 and 4 the growth in plants is poor. When pH is under 4 most of the plants cannot survive.

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