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IMPACTUL ACIDIFIERII ASUPRA MOBILITĂȚII ALUMINIULUI DIN SOLURILE PLANTAȚIILOR DE AFIN FERTILIZATE CU COMPOST OBȚINUT DIN NĂMOL ORĂȘENESC

IMPACT OF ACIDIFICATION ON ALUMINUM IN THE SOILS OF HIGHBUSH BLUEBERRY PLANTATIONS FERTILIZED WITH COMPOST OBTAINED FROM URBAN SLUDGE

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Abstract

Different fertilization systems cause changes in the content of mobile forms of Al (aluminum) in the soil, due to changes in pH. The toxicity Al is one of the major limitations that inhibits the growth and development of plants in acidic soils. In acidic soils (pH <5.0), phytotoxic aluminum (Al^{3+}) rapidly inhibits root growth and subsequently affects the absorption of water and nutrients by plants. Stationary fertilization experiments with wastewater sludge compost treatments to blueberry plants were evaluated. In the spring of 2020, an experiment with increasing doses of compost of 0, 20, 40, 60, 80 t /ha in vegetation pots, under soil water controlled conditions, was organized. Three years after compost fertilization, a 4.2 pH level (strong acid) was experimentally induced in the soil of all vegetation vessels planted with blueberries. The content of phytotoxic forms of aluminum increased with increasing dose of compost, compared to unfertilized control. At the induction of the soil pH of 4.2, in the variant fertilized with the maximum dose of compost (80 t/ha) the mobile and phytotoxic content of Al increased 30 times compared to the same experimental variant from the pre-acidification conditions. In the same time, under the newly created conditions, the mobile phosphorus content in the soil decreased dramatically. In the compost maximum fertilization dose, the mobile phosphorus content from the soil was significantly lower than the unfertilized control.

Cuvinte cheie: fitotoxicitate, fosfor mobil, deficiente nutritionale.
Key words: phytotoxicity, mobile phosphorus, nutritional deficiency.

1. Introduction

Acidic soils are characterized by nutrient deficiency and the presence of toxic metals such as manganese (Mn), iron (Fe) and aluminum (Al), represent the main limiting factor for plant growth (Bojórquez-Quintal et al., 2017). Aluminum in the soil enters the composition of aluminosilicates (feldspars, kaolinite) and other insoluble forms, which are harmless to plants at neutral pH values (Bruner and Sperisen, 2013, Kopittke et al, 2015). In acidic soils (water pH < 5.0) aluminum is solubilized, thus becoming available to plants in the form of Al^{3+} and $Al(OH)^{2+}$ (Foy et al., 1978, Kinraide, 1997, Yamamoto, 2002). Acidic soils comprise approximately 50% of the world's arable land (Kochian, 2015). Aluminum toxicity to plants includes two categories of responses: (1) short-term responses that can be observed within minutes to an hour after exposure to Al, and (2) long-term responses that require hours or days to occur (Simoes, 2012, Kochian, 2004, Kopittke, 2015). However, the effects of Al toxicity on plant growth depend on Al concentration, plant species, genotypes, plant age and growth conditions (Bojórquez-Quintal et al., 2017). Soil structure also influences the Al solubilization process. Indeed, the aggregation of clay particles prevents protons from reaching their adsorption sites, which decreases the rate of Al release (Furrer et al., 1991).

Most of the $A1^{3+}$ ions in the soil solution comes from exchangeable Al that is bound to specific soil surfaces by electrostatic forces (Pineros et al., 2002). Between layers of silicate minerals, Al is present as hydrolyzed polymers and is immutable, but can react to changes in pH (Ritchie, 1995).

The availability of Al^{3+} in the soil solution depends not only by the dissolution of minerals or exchanges with inorganic surfaces (Exley, 2003), but also by the content of soil organic substances (Zhang et al., 2010). The reactions of Al with soil organic matter have been studied by several authors (Stevenson and Vance, 1989; Huang et al., 1995; Ritchie, 1995). These studies showed that Al can react with soluble or insoluble organic substances. The active fraction of organic compounds, with high molecular weight (>1000), is represented by humic substances whose insoluble form represents 25 to 67% of the total organic matter in the soil (Stevenson and Vance, 1989). This form that specifically adsorbs Al contains carboxyl groups (ionizable in pH acids) that represent the total cation exchange capacity (CEC) of the organic matter (Zhang et al., 2010). It also exhibits phenolic hydroxyl groups that dissociate at basic pH (Ritchie, 1995). In addition, Tipping and Woof (1990) showed that the release of Al from insoluble humic substances is slower in the presence of high calcium concentrations. The soluble form of organic matter includes humic acids, low molecular weight fulvic acids and (low molecular weight) organic molecules such as citrate (Ritchie, 1995). These compounds can form complexes with Al and thus play the role of soil detoxification.

According to Noble et al. (1988), Al chemistry in solution is closely related to pH. In solution, the monomeric species $A1^{3+}$ predominates under acidic conditions, while at higher pH, the monomeric species Al $(OH)^{2+}$ and A1 $(OH)_2^{+}$ are the major forms. At a pH close to neutrality, gibbsite is formed, which represents a solid phase. The $Al(OH)_4$ form dominates under basic conditions (Delhaize and Ryan, 1995). At the plant level, Al toxicity relates only to some of its soluble forms, while others have only low or no toxicity (Fageria et al., 1988).

Symptoms of Al toxicity are not easy to identify. In general, young seedlings are more prone to Al toxicity than older plants. It is generally known that plants grown in acidic soils due to Al solubility at low pH have reduced root systems and show a variety of nutrient deficiency symptoms with a consequent decrease in plant yield. The translocation of Al to the upper parts of the plant is very slow and has a very low concentration (0.2 mg Al g^{-1} dry matter) except for Al hyper accumulating plants such as tea (30 mg Al g^{-1} dry matter in old leaves) . Aluminum toxicity inhibits root growth by preventing cell division and elongation even with short exposure to Al. Roots damaged by aluminum become stubby and often acquire a brown coloration. Thin roots and fine branching are reduced and the root system often has a "coralloid" appearance. At the tip of the root, cracks can be easily seen in the epidermis. Cortex cells show uneven and radial expansion, which results in root thickening and mechanical stress on the epidermis (Ciamporova, 2002). Foliar symptoms resemble those of phosphorus (P) deficiency, i.e. small, dark green leaves and late maturity, purple discoloration of leaves and leaf veins, yellowing and death of leaf tips. In some cases, Al toxicity appears as an induced calcium (Ca) deficiency or reduced Ca transport problem, i.e. curling or rolling of young leaves and collapse of growing points or petioles.

Hyper accumulating plants show high metal concentrations in their aboveground tissues relative to external concentrations in the soil. There are some plants that have the ability to hyper accumulate Al (more than 1,000 ppm) in dry leaf tissue without any toxic effect in the system. Such plants are known as Al hyper accumulating plants. Al hyper accumulators mainly belong to families such as *Anisophylleaceae*, *Hydrangeaceae*, *Melastomataceae*, *Memecylaceae*, *Rubiaceae*, *Theaceae*, *Symplocaceae* and *Vochysiaceae*.

Aluminum has the following effects on plants: aluminum decreases the amount of roots a plant produces and also reduces the function of the roots that are produced. This means that the plants are not able to absorb as much water or as many nutrients as they need. Aluminum prevents the absorption of phosphorus, calcium, magnesium and sulfur in plants.

2. Material and methods

2.1. Study Area

The present study was carried out at the Research Institute for Fruit Growing Pitesti, Romania (44°51′ 30” N, 24° 52” E), in an experiment located in vegetation pots planted with blueberries, 'Simultan' cultivar. The soil used to make up the nutrient mixture in the vegetation pots was a loam one with a loamy-sandy texture, with a low natural fertility.

In order to study the effect of compost applied as a fertilizer, an experiment was designed with a single factor (five experimental variants with four replicates) - doses of compost obtained from urban sludge with the following gradations:

V1 = compost, 0 t/ha (unfertilized control)
V2 = compost, 20 t/ha
V3 = compost, 40 t/ha
V4 = compost, 60 t/ha
V5 = compost, 80 t/ha

The five experimental variants were randomly placed in four replicates.

From the agrochemical point of view, the soil is part of the acid class, with a low-very low content of humus in the arable horizon, very low of nitrogen and alow content of phosphorus and potassium.

2.2. The objective of the research

In the experiment organized in pots of vegetation, planted with blueberries and fertilized with compost obtained from urban sludge in doses of 0, 20, 40, 60, 80 t/ha, a strongly acidic pH was induced in the soil (pH=4.2). Acidification of the soil was done by dripping a solution of nitric acid, for one week, in June. After this period, soil and plant material samples were collected and chemical analyzes were performed to determine the elements of acidity (pH and mobile aluminum) and fertility (nitrogen, phosphorus, potassium, carbon, respectively humus) from the soil and the foliar diagnosis was carried out, for all experimental variants. The aluminum content of the plant material and the blueberry fruits were also determined. The results of the chemical analyzes were compared with the set of results of the chemical analyzes performed over a period of three years, prior to soil acidification.

The purpose of creating these new conditions in the soil was to highlight the mobile aluminum ions concentration, since the chemical analysis of the soil carried out before acidification did not detect amounts greater than 25 ppm of mobile aluminum in all variants, although very large amounts of aluminum are introduced in the soil when fertilizing with compost (compost contributes with an intake of 24,000 mg/kg of total Al.

2.3. Soil Sampling and Laboratory Analysis

The compost applied in the experimental variants was obtained through the controlled aerobic fermentation of the urban sludge from Mioveni. Regarding the dry matter (d.m.), the content of the compost is 1.52% N of d.m., 1.38% P-P_2O_5 of d.m., 0,675% K-K_2O of d.m., organic carbon 21.5% of d.m. In terms of heavy metal content, this compost is within the maximum limits accepted in EU countries (EC 889/2008), values that do not exceed the maximum limits allowed for sludge that can be applied on agricultural land, namely: 10 mg/kg Cd, 50 mg/kg Co, 500 mg/kg Cr, 500 mg/kg Cu, 1200 mg/kg Mn, 100 mg/kg Ni, 300 mg/kg Pb and 2000 mg/kg Zn (Dumitru, 1990). However, there are very high aluminum content (Al=24,048.30 mg/kg), often with phytotoxic effects and which could cause environmental problems, especially for acid soils.

Before applying the compost, the soil chemical properties were analyzed using the followingmethods described by Florea et al. (1987): total nitrogen by Kjeldahl method (Kjeldahl, 1883); extractable phosphorus (P-AL) by Egnér - Riem Domingo method (Egnér et al., 1960), by which the phosphates are extracted from the soil sample with a solution of acetate - ammonium lactate at pH=5.75, and determined colorimetric phosphate anion extracted as molybdenum blue (Egnér et al., 1960); exchangeable potassium (K-AL) by Egnér - Riem Domingo method by which the hydrogen and ammonium ions of the extraction solution replace by exchange the exchangeable potassium ions in the soil sample which are thus passed into the solution (Egnér et al., 1960). Potassium dosing in the solution thus obtained is done by flame emission photometry-organic carbon - wet oxidation method followed by titrimetric dosing by Walkley - Black, (Gogoasa modification) and humus (deduced by calculation from organic carbon); soil pH, soil: water ratio=1:2.5 by the potentiometric method; mobile aluminum by the Sokolov method (Sokolov, 1939); sum of exchangeable bases and hydrolytic acidity (Kappen method), base saturation degree being determined by calculation, depending on the sum of bases.

2.4. Vegetable material Sampling and Laboratory Analysis

In June month, leaf samples were collected from which the level of supply of plants with nutrient macro elements (nitrogen, phosphorus and potassium -total forms) was determined by the following methods: total nitrogen - Kjeldahl method (Kjeldahl, 1883); total phosphorus - colorimetric method (Egnér et al.,1960); total potassium - the method of dosing by flame emission photometry (Egnér et al, 1960); aluminum content - with EDTA titrimetric method use and black eriochrome.

Fruit samples were also collected and determinations of aluminum content were performed - with EDTA titrimetric method use and black eriochrome.

2.5. Statistical Analyses

Statistical analyze was performed with an IBM SPSS (SPSS 14) software. The results of chemical analyzes performed on soil, plant, fruit samples, collected from the experimental variants, were processed using the variance analysis method and the multiple comparison method.

3. Results and discussions

3.1. Correlations between the agrochemical indicators analyzed after the compost application to 'Simultan' blueberry cv.

During the 3 years of experimentation, the pH of the nutrient mixture (soil+peat) in the vegetation pots really revealed an alkalization of the mixture (in the range of 6-7 was the pH value), under the influence of the administration of increasing doses of compost (compost pH=7.04). An unfavorable influence on the pH of the soil solution in the pots was also induced by the irrigation water, whose pH was 7.67, throughout the blueberry vegetation period.

The phenomenon of phosphorus degradation in the soil is highlighted by the significant negative correlation obtained between the dose of compost and phosphorus in the soil. In addition, the distinctly significant positive correlation between the dose of compost and mobile aluminum explains the depreciation of the level of mobile phosphorus in the soil that is blocked in compounds hardly soluble with aluminum, although the chemical analysis does not detect concentrations of mobile aluminum higher than 25 ppm.

A significant positive correlation observed between humus content and soil aluminum (Fig. 1) could explain the binding of aluminum to the organic component as described in the literature (Zhang et al., 2010).

3.2. Influence of pH on soil aluminum mobilization

After soil acidification at pH 4.2, mobile aluminum concentrations in the soil recorded values exceeding 800 ppm in some repetitions of the variant fertilized with the maximum dose of compost, 80 t/ha (Fig. 2), simultaneously with a drastic decrease in phosphorus mobile to lower levels than in the unfertilized control (Fig. 4 and Fig. 5). The chemical analysis of the soil showed values of the mobile aluminum content 30 times higher at the maximum dose of compost, compared to the same variant before acidification (Fig. 8). This explains the blocking of phosphorus from the soil by the aluminum contained in the compost, in increasing amounts, with the increase in the doses of compost. At pH> 5.5, although large amounts of mobile aluminum are not detectable in the soil fertilized with compost, this can be mobilized at any time when the soil pH decreases (Fig. 3), causing serious phytotoxic effects. The phenomenon is well known in specialized literature. The symptoms of toxicity due to aluminum in the soil manifested in the leaves as a phosphorus deficiency, namely the red-violet coloring of the leaves (Fig. 9).

After 7 days, during which the plants were maintained at pH 4.2, the aluminum concentrations in the leaves recorded levels of 648 mg/kg and 390 mg/kg in the fruit, in all variants fertilized with compost. Aluminum was not detected in the unfertilized control.

The toxicity of aluminum in the soil is a limiting factor for the growth of plants grown in acid soils (Foy, 1973, 1974, 1984, 1992, 1996, Foy et al., 1978, 1993). Aluminum toxicity could be observed in the root system especially in the tips of the roots and in the lateral roots which thicken and turn brown (Kinraide, 1988, Roy, 1988). Even if the root system has many lateral roots, they lack fine ramifications (Foy, 1978, Philip Barlow, 2014). Symptoms of aluminum toxicity on the roots of blueberry plants grown in vegetation pots and fertilized with compost were observed after the plants were uprooted (Fig. 10).

4. Conclusions

Free aluminum strongly immobilizes soluble phosphate and makes soil phosphorus almost useless as a nutrient when suboptimal absorption of phosphorus in plants occurs.

Ideally, aluminum KCl extract should be less than 20 ppm to have healthy plant root growth.

At a neutral or slightly acidic pH, mobile aluminum in the soil cannot be detected by chemical analysis, but once the soil pH drops to strongly acidic, very large amounts of aluminum become soluble and mobile in the soil solution.

High concentrations of aluminum (over 800 ppm Al) come from the administered compost. Soil acidification has shown that it is mobile in soil and produces phytotoxic effects.

At these concentrations in the soil, blueberry plants absorbed aluminum in the leaf (648 ppm) but also in the fruit (390 ppm), above the maximum allowed limit, which is 1 mg/kg aluminum in fruit according to FAO (2011).

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Tables and Figures

		Al mobil (mg/kg sol)	Humus (%)	P-P2O5 (mg/kg sol)
Al mobil (mg/kg sol)	Pearson Correlation	1	0,514(*)	-0,109
	Sig. (2-tailed)		0,050	0,698
	N	15	15	15
Humus (%)	Pearson Correlation	0,514(*)	1	-0,302
	Sig. (2-tailed)	0,050		0,275
	N	15	15	15
P-P2O5 (mg/kg sol)	Pearson Correlation	-0,109	-0,302	1
	Sig. (2-tailed)	0,698	0,275	
	N	15	15	15

* Correlation is significant at the 0.05 level (2-tailed).

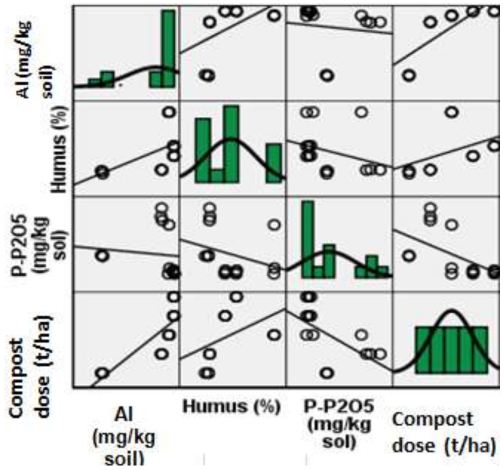

Fig. 1. Correlations between the elements analyzed and the doses of compost applied

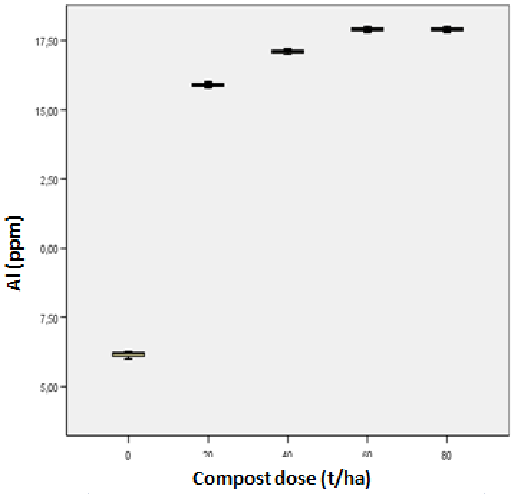

Fig. 2. The influence of compost fertilization on mobile aluminum content in the soil, three years after fertilization (before acidification with HNO_3)

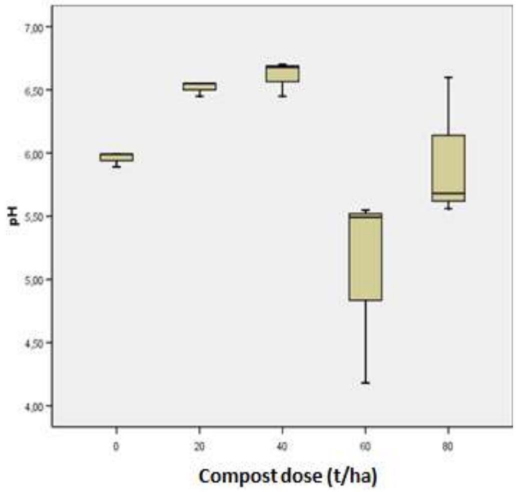

Fig. 3. The influence of compost fertilization on soil reaction, three years after fertilization (before acidification with HNO_3)

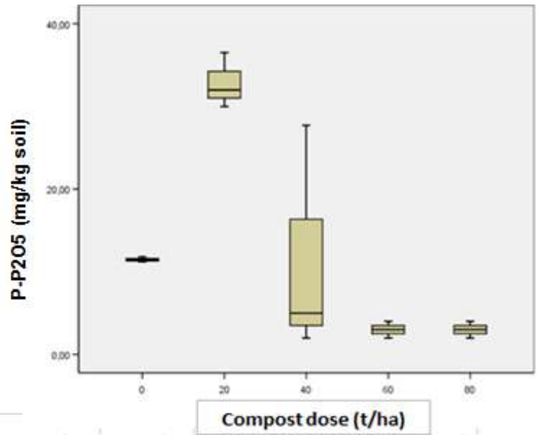

Fig. 4. The influence of compost fertilization on mobile phosphorus content of the soil (before acidification with HNO_3)

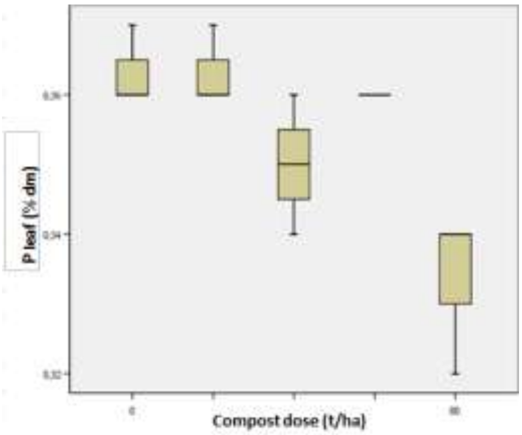

Fig. 5. Influence of compost fertilization on leaf phosphorus content (before acidification with HNO_3)

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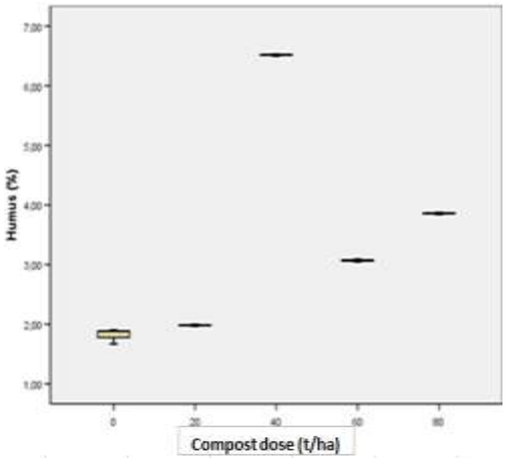

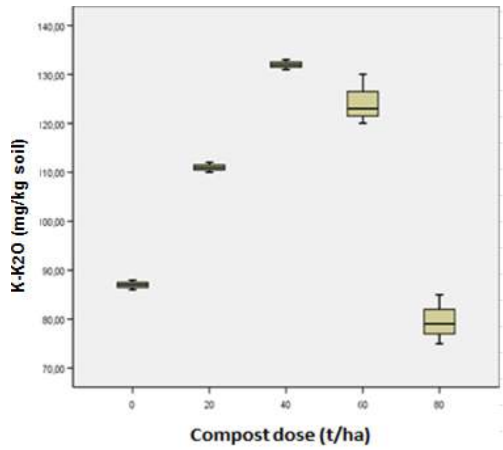

Fig. 6 The influence of compost fertilization on soil humus content three years after fertilization (before acidification with HNO_3)	Fig. 7. The influence of compost fertilization on soil potassium content after three years of fertilization (before acidification with HNO_3)

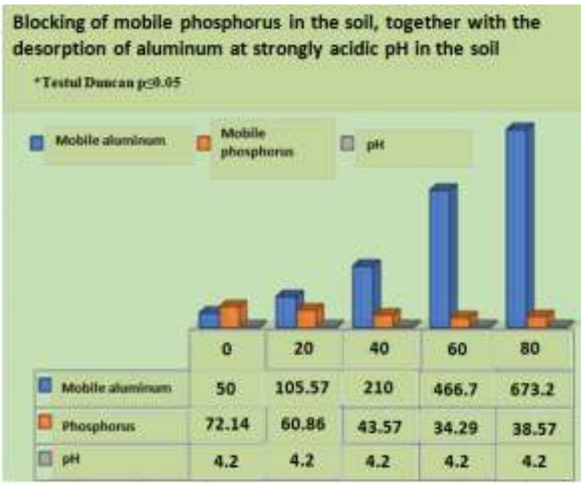

Fig. 8. The influence of soil acidification on mobile aluminum desorption

Fig. 9. Symptoms of aluminum toxicity observed on blueberry leaves
a) at the dose of 40 t/ha compost (June)b) *Gardening-abc.com*

Fig. 10. Symptoms of aluminum toxicity observed on the roots of blueberry plants under the influence of fertilization with urban sludge compost