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Mung bean response during immobilization of exchangeable aluminum in acidic soil

Short Communication

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Abstract: A soil incubation and shot-term plant growth experiment was conducted to study the effect of ferruginous mineral application on exchangeable Al immobilization. The mineral containing mainly siderite was mixed at various rates with A-horizon soil and incubated at 80% humidity for 45 days. Following the incubation, a short-term plant growth test was carried out using *mung beans*. The ferruginous mineral application into tested soil resulted in a reduction of the exchangeable aluminum concentration and soil acidity. An increase in root growth and stalk length, as well as a general improvement of plant condition was observed in the case of ferruginous mineral application. This observation was confirmed by chemical analysis of roots and stalks. The greatest amount of essential elements: calcium and magnesium and the lowest amount of aluminum were determined in green part of *mung beans* sown in the soil with addition of 2% ferruginous mineral.

Keywords: *Al phytotoxicity • Al immobilization • Soil acidity • Siderite*

1. Introduction

Aluminum toxicity is a major limiting factor of plants' growth and forest production in many parts of the world [1,2]. Aluminum is a basic mineral component. Soil aluminum content depends on a parent rock and soil type [3]. Soil aluminum is mainly found in the form of primary minerals and aluminosilicates [4,5]. The series of reactions in the process of weathering lead to the formation of aluminosilicates enriched in aluminum by the gradual leaching of cations: Na, Ca, K, Mg, with simultaneous formation of amorphous silica [6]. The release of aluminum from the crystal structures in the environment proceeds slowly, however, this process accelerates under acidic conditions. The soil acidification is mainly caused by acidic oxides (CO_2, SO_2 and NO_x) present in the air as the products of industrial combustion of carbon, oil products and natural gas. These oxides adsorbed on the surface of dust particles or dissolved in the water are introduced into the soil. Alkaline minerals and humus initially neutralize acid rain, however, the prolonged exposure to acid rains leads ultimately to strong soil acidification. The following values of the soil pH collected in the Silesian Beskids (southern Poland) were measured: pH_{H2O} – 3.35 and pH_{KCl} – 2.57 [7]. Highly acidic conditions significantly increase the solubility of aluminosilicates and cause a release of various aluminum ions into the soil solution. The hydrated ion $[Al(H_2O)_6]^{3+}$, as well as hydrocomplexes $Al(H_2O)_4(OH)_2^{+}$, $Al(H_2O)_5(OH)^{2+}$ and polynuclear species $Al_p(OH)_q^{(3p-q)}$ (1≤p≤24:1≤q≤60)$^{+}$ are recognized as very toxic to plants and aquatic organisms [6,8].

Phytotoxicity of aluminum is well recognized [2,9,10]. The exchangeable aluminum alters mitosis, which leads to the inhibition of root's growth and ramification, hence results in root's stunting and breakability [1]. As a result, root apices become swollen and damaged, the root is more susceptible to injuries, whilst the water and essential elements (*e.g.* Ca, Mg, P) uptake is restricted. Toxic level of aluminum ions lowers chlorophyll's concentration and reduces electron flow, thus limits the process of photosynthesis [10] which manifests in stunted, chlorotic and curled along the margin foliage and collapse of growing points or petioles. This leads to a weakening of plants, impairs immunity to disease and adverse weather conditions, or even causes wilting [2,9].

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Plants have developed a broad variety of aluminum resistance mechanisms. Aluminum tolerance varies among plant species and a place of their cultivation and may be genetically determined [4]. There are two main mechanism of Al tolerance: external and internal. The external mechanisms depends on the pH change in rhizosphere, selective aluminum blocking on the root surface due to Al binding by the substances secreted by the roots (citric acid, phosphorous, polysaccharide derivatives), Al immobilization by the components of cell wall or changes in plasmalemma [1,2,4,9,10].

The internal mechanism depends on the change of Al containing cell metabolism: toxic ions are bounded by chelating substances, neutralized in vacuoles or the change of enzyme activity may occur [1,2,4,9,10].

A very common method to the change of soil acidity and aluminum toxicity reduction is liming [11-13]. The application of limestone, dolomite or gypsum is appropriate for agriculture soils. Its usage in the large area of forests and mountains is limited by some technical problems. Another way for aluminum detoxification is the use of organic manure: tree leaves and plant or grass straw which are widely used as green manure [1,14] and pig, cattle, rabbit or goat feces which are used as animal manure [15,16]. An application of industrial by-products (*e.g*. phosphogypsum, red gypsum or sugar foam) is also worth mentioning [17].

The aim of this study was to examine the *mung bean* response to the application of ferruginous mineral (containing mainly siderite) in the process of exchangeable aluminum immobilization in acidic soil. The *mung bean* was selected for this study due to its high Al sensitivity and short growth time. The applied waste is a byproduct from the iron ore's landfill located in the northern part of the Silesian providence, approximately 15 km west of the city of Częstochowa (southern Poland). The beneficial effect on soil acidity and exchangeable aluminum content was noticed in our preliminary experiments.

2. Experimental procedure

2.1. Waste mineral sampling and analysis

Solid lumps of waste mineral, with a diameter of 2 to 15 cm, were collected from iron ore's landfill, located in the northern part of the Silesian providence (southern Poland). The mineral was air dried, initially crumbled and then ground in ball mill and passed through a 0.2 mm sieve. Microwave digestion in the mixture of concentrated $HCl+HNO_3+HF$ (6:2:1.5, v/v) followed by ICP-AES analysis was performed to determine the total concentration of metals. Fluoride concentration was determined by spectrophotometric method [18]. Mineral, which was additionally grounded (mesh size <0.125 mm) and dried at 40°C for 5 hours, was also analyzed by the powder diffractometer XRD 3003 TT (Seifert) with scintillation detector.

2.2. Soil sampling and analysis

Soil sample, from the horizon A_1, was collected in June 2010 in spruce forest in Wisła District, southern Poland (49°38′03.66″ N, 18°50′46.90″ E; 560 m above the sea level). Soil, following the removal of stones and needles, was divided to three portions. The ferruginous mineral was added into two of them in the amount of 5 and 20 g per kg of soil (accounted for dry mass) respectively and mixed thoroughly. The probe of soil without treatment was used as a control sample. The control samples as well as soils with mineral addition were incubated for 45 days maintaining soil approximately 80% moisture. Subsequently, the samples were used for *mung beans*' cultivation. Additionally, the samples of incubated soils were air-dried, grounded using an agate mortar and passed through a 0.2 mm sieve. Accurately weighed 0.5 g of soils were initially incinerated in a muffle furnace at 450 - 500°C for 5 hours and subsequently transferred into PTFE vessels and microwave digested using the mixture of concentrated acids ($HCl+HNO_3+HF$, 6:2:1.5, v:v). Total contents of metals (aluminum and iron) were determined using ICP-AES. Soil pH was determined potentiometrically in 1 M KCl (1 : 2.5 g/v) (pH_{KCl}) and in deionized water (1 : 2.5 g/v) (pH_{H2O}) according to the procedure described by Ostrowska *et al.* [19]. The content of exchangeable aluminum was determined by titration with NaOH after soil extraction with 1 M KCl (1:2.5 g/v), adjusted to the desired pH from 5.8 to 6.0 [19]. The quality of the analysis was controlled using the certified reference material NCS DC 85105. The total content of carbon (C_{tot}) and nitrogen (N_{tot}) was determined using Perkin Elmer 2400 analyzer. The content of organic matter (OM) was analyzed according to the procedure described by Ostrowska *et al*. [19]. Each determination was carried out in at least three replications.

2.3. Short term plant growth test

Following the incubation, each sample (control, 5 g kg^{-1} addition, 20 g kg^{-1} addition) was divided into 6 plastic pots. Nine seeds of *mung bean* were sown in each pot (contained approximately 100 g dry mass soil). After the germination, the seedlings were grown for 12 days. Plant growth was documented photographically. After this time the plants were harvested and roots were separated from green part. Shoots and roots were washed with deionized water, dried at 80°C for 24 hours, and the dry matter was measured. Plant materials were ground and microwave digested in HNO_3, and the selected elements were determined using ICP-AES.

The short-term plant growth test was repeated in similar conditions after three months using the soil samples (control and with addition) from the previous experiments.

3. Result and discussion

The X-ray structural study indicates that the main compound of used mineral is siderite, however, the presence of structure like $CaFeF_5$ and CaF_2 was also noticed. Chemical analysis showed the presence of iron (38%), fluoride (0.57 g kg^{-1}) and basic cations, such as Ca^{2+} (21.4 g kg^{-1}), Mg^{2+} (20.1 g kg^{-1}) and K^+ (2.69 g kg^{-1}). The mineral contained also manganese (4.5 g kg^{-1}) and phosphorus (1.35 g kg^{-1}) in amounts typical for the soils. The heavy metal content did not exceed polish national standards [20] as well as European standards for agriculture soil [21] therefore, the waste mineral can be considered as harmless to the environment.

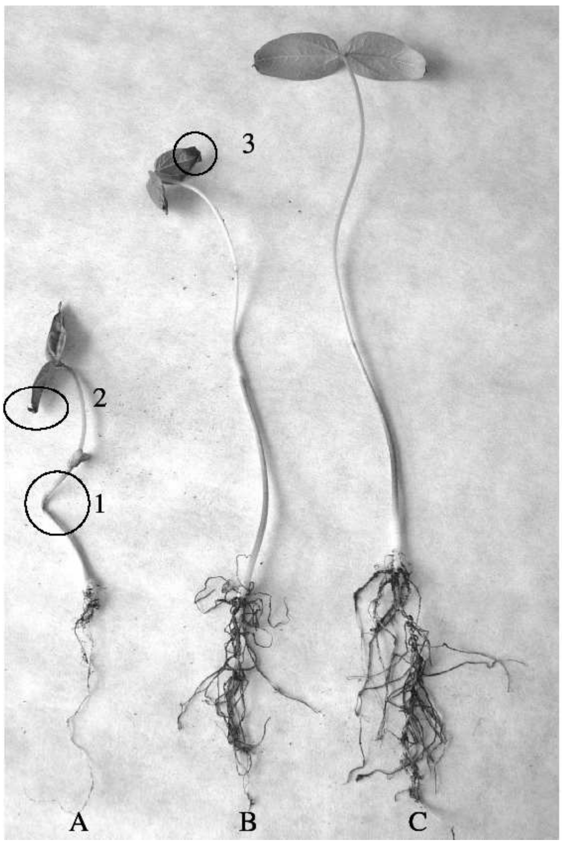

Figure 1. The *mung bean* cultivated in control soil (A), soil with 0.5% mineral addition (B) and 2% mineral addition (C)

Results presented in Table 1 proved waste mineral addition to increase soil pH and decrease the amount of exchangeable aluminum.

These results were reflected in the condition of cultivated plants. The fastest growth in plants grown in the soil with addition of 2% ferruginous mineral has been observed from the seed germination.

This trend has continued until the end of the experiment. Several days after germination, serious stalks weakening and bending (Fig. 1 A1) and leaves curling (Fig. 1 A2) and withering of most beans growing in control soil were observed. These symptoms were observed also in some plants grown in soil with 0.5% mineral addition (Fig. 1 B3). Significant difference occurred in stem length, the shortest (mean 9.14 cm) was observed in plants growing in soil without mineral addition and significantly longer in the bean growing on soils with mineral addition, mean 13.3 cm and 17.6 cm, for 0.5% and 2% mineral additive, respectively.

The comparison of plants cultivated in soils with and without additive revealed that the root development has decreased in the following order: beans grown in soil with 2% addition of mineral > beans grown in soil with 0.5% addition of mineral > beans grown in control soil (Fig. 1). The root system in the control sample was stunted with abundant, short and brittle laterals. All these observations are in good agreement with previously reported in the literature as the symptoms of aluminum phytotoxicity [2,9].

The beneficial effect of the mineral on soil properties and plants' growth was verified by repeating the experiment on the reused soils from previous experiment. The same observation in plants' condition was made: a significant difference in bean growth was noticed between the control and treated soils.

The beans growth-based assumptions were confirmed by the determination of selected elements in the stalks of cultivated plants (Table 2).

The smallest uptake of aluminum and the largest uptake of the desired calcium and magnesium ions occurred in plants grown in soil with 2% addition of the mineral. There were no significant differences in the content of iron and phosphorus in the tested stalks.

An interpretation of the selected elements content in the roots is problematic and can be misleading and is mainly related to the soil residues remaining on the root surface. The soil particles have strong adhesion to the fragile roots and capillaries, which make them difficult to remove. It was mainly observed in very well developed lateral roots of beans, grown in soil with the mineral addition (20 g kg^{-1}). Similar challenges were also reported by Poschenrieder *et al*. [9]. Thus the results of the analysis can not clearly recognize whether

Table 1. Basic properties of soils (control (0) and after ferruginous mineral (FM) treatment).

FM treatment g kg^{-1}	pH_{H2O}	pH_{KCl}	$Al_{exch,}$ mg kg^{-1}	OM, %	Al_{tot}, g kg^{-1}	Fe_{tot}, g kg^{-1}	C_{tot}/N_{tot}
0	3.48±0.07	2.78±0.06	327±49	46.5±1.0	11.9±0.4	19.3±0.3	25.0
5	3.76±0.01	2.99±0.02	278±25	43.2±0.4	11.1±1.3	21.3±0.3	24.5
20	3.89±0.03	3.24±0.02	226±32	44.8±0.3	12.5±4.4	28.8±0.7	25.1

Table 2. Total content of selected elements in different parts of plants grown in soils: control (0) and with ferruginous mineral (FM) addition (5) and (20); mean value ± confidence interval; confidence level p = 95%, number of determinations n ≥ 3.

Part of plant/ FM treatment g kg^{-1}	Al_{tot}, mg kg^{-1}	Ca_{tot}, mg kg^{-1}	Mg_{tot}, mg kg^{-1}	Fe_{tot}, mg kg^{-1}	P_{tot}, mg kg^{-1}
Stalk /0	758±73	1191±276	1847±184	180±33	5804±65
Stalk /5	667±47	2037±177	2998±637	169±9	6688±57
Stalk /20	443±72	3503±919	3335±853	189±50	5957±94
Root/ 0	2386±238	1789±91	800±15	1414±397	4296±107
Root /5	2773±475	1926±241	941±23	1764±110	4124±118
Root /20	3949±547	2309±457	1590±31	3409±369	4230±137

the elements were contained in the tissue of roots or adsorbed on their surface. However, the results of the calcium and magnesium determination are consistent with expectations and confirm their higher uptake by plants grown in the soil with the addition of waste mineral. The higher content of aluminum in the plant roots can be explained as a result of plant defense mechanisms involving the immobilization of Al ions in the root, or as previously mentioned adsorption or adhesion of soil particles, which can be a source of these ions. The results showing a decrease in exchangeable aluminum content in soil with 2% mineral addition (Table 1) suggest that second hypothesis (Al-rich soil particles adsorption) could be taken as more possible.

The plant roots iron content in the samples grown in soil with additive was at least twice as high as the iron content in the control sample.

4. Conclusions

Presented results proved the ferruginous mineral to be an effective additive in exchangeable aluminum immobilization. The decrease in soil acidity was also observed. These positive effects were verified by observation of the *mung bean* growth. Plants cultivated in soil with 2% mineral addition were in general good condition, whereas the plants cultivated in the control soil suffered from leaves curling, withering and bending of stalks. The repeated experiments prove the effect of mineral addition to be long term stable and persistent after first *mung bean* cultivation.

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