

Bauxite Residue Safety Disposal and Possibilities to further Utilisation. II. Maize Plants Growth on the Acidic Soils (Pilot and Demonstration Stage)

**Gheorghe Dobra¹, Sorin Iliev¹, Lucian Cotet¹, Vicol Alistarh¹, Alina Boiangiu¹, Radu
Lacatusu², Nicolae Ionescu³ and Laurentiu Filipescu⁴**

1. Vimetco Alum SA Tulcea, Romania

2. ARD, Station of Albota-Pitesti, Arges County, Romania

3. INCD-ICPA Bucharest, Romania

4. University Politehnica Bucharest, Romania.

Corresponding author: aboianiu@alum.ro

Abstract

A new approach of bauxite residue use in agriculture concerns remediation of the acidic soil by deep reshaping of the land surface layer, in order to change its agro-chemical properties and to achieve a reasonable degree of fertility. This target was reached by using three soil properties control adjuvant: the bauxite residue for better pH and soil properties control, the organic fertilizer as a source of organic carbon and the Nitrogen (N), Phosphorus (P) and Potassium (K) or NPK mineral fertilizers as a source of the main macro and micronutrients. In an experiment carried out at glass house scale on maize plants, it was proved the above adjuvant promoted intensive vegetative growth in maize plants (waist, green mass and dried mass), as well as the high productions in cobs and grains. Also, samples of the harvested green mass, cobs and grains contain macronutrients, micronutrients and heavy metals in normally limits of concentration, usually found in maize. These results backed up all the reasons to resume the experiments at a pilot scale in natural conditions, on a well-known soil as a natural acidic soil. The research program has included the best choice of experimental factors, a meaningful analytical and measurement program, and the maize crop parameters measurements covering all the maize plants morphometric data at both flowering and maturity stages. Also, the macronutrients, micronutrients, heavy metals and lanthanides content were carefully investigated in soil, plants and grains. All the soil and crop parameters measurements, carried out in the larger experimental field set up, are in good agreement with the glass house experimental data. Accordingly, these new collected data confirmed, as a main contribution, the soil pH control in both high vegetative growth and raises in crop yield, as well as in the crop quality. This first stage of experiment on maize (2018) will continue with a second stage on wheat (2019) and third stage on lucerne (2020).

Keywords: bauxite residue, agro-chemistry, acid soil, remediation, maize crop.

1. Introduction

In our previous works [1, 2] it was demonstrated that bauxite residue, obtained as a by-product in alumina manufacturing technology, has some remarkable ecological properties: no radioactivity, low concentration level of the heavy metals and lanthanides, acceptable alkalinity, after natural drying and carbonation, and compatible particle size distribution with most of the agricultural soils. Also, several types of artificial soils with bauxite residue and other available residuals content, enriched with organic and mineral fertilizers, have been formulated for achieving a reasonable degree of fertility. These soils were tested with encouraging results on the growth of several common natural floras species and on crop plants [3-6]. This new approach of bauxite residue use in agriculture concerns the acid soils remediation by deep reshaping the land surface layer, in order to change the agro-chemical properties of this kind of soils and achieving a reasonable degree of fertility. This target was reached by using three soil properties control adjuvant: the bauxite residue for better pH and soil properties control, the organic fertilizers as

source of organic carbon and NPK mineral fertilizers as source of the main macro and micronutrients. In a glass house scale experiment on maize plants, set up for the optimal dosages of the above adjuvant, it was proved the new reshaped soils really gained some higher fertility than the initial acid soil. Actually, the adjuvant promoted an intensive vegetative growth in maize plants (waist, green mass and dried mass), as well as the high productions in cobs and grains. Also, the samples of harvested green mass, cobs and grains contain the macronutrients, micronutrients and heavy metals in normally limits of concentration, found usually in maize. Under these conditions, Alum SA Tulcea decided to resume experiments at the pilot scale in natural conditions on a well-known soil recognized for its grade as acidic soil.

Our previous study on maize growth on amended acidic soils in glass house showed there is no crops growth, if the soil is not neutralized previously with an adjuvant like bauxite residue. Accordingly, the experimental program was intended to collect reliable data about the soil neutralization effects on soil itself, as well as on the crop growth of maize in terms of quantity and quality, under a meaningful organic and mineral fertilization.

The selected location for carrying out the experiments was the Agricultural Research and Development Station of Albota - Pitesti, Arges County, recognized for its works on the acid soils remediation. The entire research program was supervised by National Research and Development Institute for Soil Science, Agrochemistry and Environment ICPA Bucharest.

2. Experimental Part

For characterization of the experimental materials, the samples from soil and adjuvant were collected as follows: a) soil from the 0-20 cm horizons of all control variants; b) bauxite residue dried and partially carbonated material delivered by Alum SA Tulcea; and c) Organic Bio Enne Co-Actyl complex fertilizer and mineral NPK fertilizer. Physical and chemical properties of these experimental materials were measured by specific standardized methods, described in our previous works [1-5] and in the recent literature. [7].

2.1. Albota's Albic Luvisoil

The analytical data from Table 1 shows that reaction of the Albota's albic luvisoil in the 0 - 20 cm horizon is moderately acidic ($pH_{H_2O} = 5.30$). This soil has a low humus content (2.45 %), a small-medium content of N_{TOTAL} (0.143 %), a high supply of mobile P_{AL} (39 mg/kg), a low mobile K_{AL} supply (83 mg/kg) and a good supply of mobile sulfur S-SO₄ (23 mg/kg).

Table 1. Soil pH and and macronutrients content in the Albota albic luvisoil.

Soil Samples	Horizon	Depth, cm	pH, units	Humus, %	N_{TOTAL} , %	P_{AL} , mg/kg	K_{AL} , mg/kg	S-SO ₄ , mg/kg
Albota 1	Ao	0-20	5,14	2,44	0,158	38	89	23
Albota 2	Ao	0-20	5,21	2,50	0,138	41	80	24
Albota 3	Ao	0-20	5,29	2,41	0,132	39	80	23

* N_{TOTAL} -Nitrogen; P_{AL} -Phosphorus mobility; K_{AL} -Potassium mobility, S-SO₄-Sulphur mobility

Depending on the alkaline cations sum (SB), the Albota's albic soil (0 - 20 cm) falls into the low content class of alkaline cations (14.54 meq/100 g soil). The hydrolytic acidity (A_H) placed this soil into class of the strong hydrolytic soils (8.1 meq/100g sol). Hence, the analyzed soil has a high total cationic exchange capacity ($T_{8.3}$) (22.5 meq/100g soil) and its saturation in bases is oligomeric (64 %) (Table 2). The distribution of the exchangeable cations (given both in meq/100g soil and in percent, %, from total T exchange capacity in the Table 3 and Table 4) shows the presence of Ca 46.3 %, Mg 11.2 %, Na 0.2 %, K 1.1 %, and H 41.2 %. These values are

usual for such a type of soils. Unusually, is the presence of aluminum ions in a small quantity (1.29 meq. /100 g soil). Concerning the content of metallic microelements, mobile and total forms (Table 5 and Table 6) are found to be in normal content ranges.

Table 2. Alkali cations sum, hydrolytic acidity and saturation in alkali cations of the soil.

Soil Samples	Horizon	Alkaline cations (SB), meq/100 g	Hydrolytic acidity (A _H), meq/100g	Cationic exchange capacity (T=SB+A _H), meq/100 g	Alkaline saturation (V _{AH}), % from T
Albota 1	Ao	0-20	14,67	8,53	23,19
Albota 2	Ao	0-20	14,15	8,00	22,15
Albota 3	Ao	0-20	14,46	7,69	22,15

The average content, in total forms of metallic microelements (heavy metals in mg/kg) is as follows: 51.0 (Zn), 14.3 (Cu), 26.44 (Fe), 834.0 (Mn), 16.6 (Pb), 25.1 (Cr), 10.6 (Co) and 25.6 (Ni).

Table 3. Exchangeable cations from horizon A₀ of the Albota's albic luvisoil (g/100 g).

Soil samples	Horizon	Depth, cm	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SB	SH	T=SB+SH
Albota 1	Ao	0-20	10,61	2,54	0,05	0,28	13,48	9,77	23,25
Albota 2	Ao	0-20	10,21	2,50	0,04	0,22	12,96	9,15	22,11
Albota 3	Ao	0-20	10,41	2,52	0,06	0,22	13,20	8,91	22,12

*SB-alkaline cations; SH-hydrogen cation; T=SB+SH-total cationic exchange capacity

Table 4. Exchangeable cations from horizon A₀ of the Albota's albic luvisoil (% from T).

Soil Samples	Horizon	Depth, cm	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SH	V _{AH}	Al _{schimbabil} , g/100g
Albota 1	Ao	0-20	45,6	10,9	0,2	1,2	42,0	58,0	1,21
Albota 2	Ao	0-20	46,2	11,3	0,2	1,0	41,4	58,6	1,05
Albota 3	Ao	0-20	47,1	11,4	0,3	1,0	40,3	59,7	1,16

*SH-hydrogen cation; V_{AH} - Alkaline saturation

Table 5. Microelements content as mobile forms in the Albota's albic luvisoil.

Soil Samples	Horizon	Depth, cm	Zn, mg/kg	Cu, mg/kg	Fe, mg/kg	Mn, mg/kg
Albota 1	Ao	0-20	1,6	3,0	145,1	52,6
Albota 2	Ao	0-20	1,3	2,7	134,7	47,4
Albota 3	Ao	0-20	1,5	2,7	131,8	51,1

Table 6. Microelements content (total heavy metals) in Albota's albic luvisoils (mg / kg).

Soil Samples	Horizon	Depth,cm	Zn	Cu	Fe	Mn	Pb	Cr	Co	Ni
Albota 1	Ao	0-20	51	14,5	26.046	816	16.3	24,7	7.5	25,4
Albota 2	Ao	0-20	51	14,6	26.803	815	17.1	25,9	12.4	26,1
Albota 3	Ao	0-20	49	13,8	26.477	871	16.3	24,7	11.9	25,2

With regard to the soil particle size distribution analysis, there is a higher content of clay below 2 microns (35.5 %) followed by the presence of dust with the particle diameter between 0.002 and 0.02 mm in amount of 34.5 %, the fine sand, with a particle diameter between 0.02 and 0.2 mm, in amount of 24.7 %. and finally the coarse sand, particle diameter of 0.2 to 2 mm, accounting for 5.2 %. This particle size distribution symbolizes the clay - clayey texture class of soil. Therefore, the

Albota's albic luvisol in the surface horizon (0 - 20 cm) has a moderately acidic reaction, low humus and total nitrogen content, a high supply of Pmobile but small in Kmobile. Accordingly this soil is an oligomezobasic soil with a low content of alkali cations, but high exchangeable hydrogen and hydrolytic acidity. The mobile and total contents of trace elements (heavy metals) are within normal limits.

2.2. Bauxite Residue

The bauxite residue composition and its particular properties identified as main remediant adjuvant in acid soil rehabilitation has been presented in the first part of this paper.

2.3. Organic Bio EnneCo-Actyl Complex Fertilizer and Mineral NPK Fertilizer

The organic Bio EnneCo-Actyl complex fertilizer is a very active organic fertilizer, used as a source of organic carbon in soils. It contains 12 % organic nitrogen, 23 % sulfur in SO₃ form, and in its composition the C/N ratio is 3. Organic nitrogen content is provided from the previously hydrolyzed animal proteins, giving to the final pelletized fertilizer an excellent transformation speed, close to that of urea. The reason for selection this product was based on its agronomic specificities and contributions, which are: increasing the mineralization process rate and root growth, increasing the process of humification, stimulation of photosynthesis and preventing the abiotic stresses, stimulation of both nitrogen and sulfur absorption and their conversion in roots, biotransformation of atmospheric nitrogen into ammonium.

As mineral complex NPK fertilizer there was chosen a common NPK grade, formulated with urea instead of ammonium nitrate.

2.4. Experimental Program

Experimental program covered all the stages of experiments with plants versus dose of bauxite residue on the albic luvisol from Agricultural Research and Development Station of Albota - Pitesti, Arges County.

The factors in the above experiments were:

- a) Bauxite residue variable doses (t/ha): 0, 10, 20, 40 and 60;
- b) Dose of the mineral fertilizer (kg/ha active NPK), one fixed dose: N120 P60 K40/ha;
- c) Dose of the organic Bio EnneCo-Actyl complex fertilizer(t/ha), one fixed dose: 25 t/ha;
- d) Plots size (square meters): 50 mp (10x5);
- e) Repetitions: 3;
- f) Arrangement of variants: Latin square (Figure 1);
- g) Non-irrigation;
- h) Bauxite residue application in all the variants: 24.04.2018;
- i) Fertilizers application: 24.04.2018;
- j) Maize experimental variety: Hybride DKC 4590;
- k) Sowing date: 26.04.2018;
- l) Crop rotation: 3 year crop rotation, Maize - 2018, Wheat - 2019, Lucerne – 2020.



Figure 1. Field plot layout and experimental design.

Table 7. Experimental variants.

Variants	Bauxite residue,t/ha	NPK-urea, kg s.a./ha	Organic Bio EnneCo-Actyl, t/ha
V1	0	0	0
V2	10	0	0
V3	10	N ₁₂₀ P ₆₀ K ₄₀	0
V4	10	N ₁₂₀ P ₆₀ K ₄₀	25
V5	20	0	0
V6	20	N ₁₂₀ P ₆₀ K ₄₀	0
V7	20	N ₁₂₀ P ₆₀ K ₄₀	25
V8	40	0	0
V9	40	N ₁₂₀ P ₆₀ K ₄₀	0
V10	40	N ₁₂₀ P ₆₀ K ₄₀	25
V11	60	0	0
V12	60	N ₁₂₀ P ₆₀ K ₄₀	0
V13	60	N ₁₂₀ P ₆₀ K ₄₀	25

V1. Control; V2–V4. BR 10 t/ha; V5-V7. BR 20 t/ha; V8-V10. BR 40 t/ha; V11-V13 60 t/ha

Total number of variants:

13 x 50 x 3 = 1950 m² + 550 m² for protection of the experiment = 2500 m². The experimental variants are presented in the Table 7.

Analytical management of the experimental program encompassed the following type of analyses: and determinations:

- Analysis of the soil upon set-up of the experiment (pH, humus, N_{TOTAL}, N-NO₃, P_{AL}, K_{AL}, SB, A_h, Al_{MOBILE}, V_H (saturation degree), mobile micronutrients and heavy metals (Fe, Mn, Cu, Zn, Pb, Cd, Cr, Ni, Co);
- Analysis of soil collected in the silk phenophase (pH, humus, N_{TOTAL}, N-NO₃, P_{AL}, K_{AL}, SB, A_h, V_H (saturation degree), Al_{MOBILE}, mobile micronutrients and heavy metals (Fe, Mn, Cu, Zn, Pb, Cd, Cr, Ni, Co);
- Analysis of macro- and micro-nutrients content of the leaves under main maize plant ear;
- Analysis macro- and micro-nutrients content in maize grains;
- Analysis of bauxite residue (pH, C_{ORG}, N_{TOTAL}, P_{AL}, K_{AL}, Fe, Mn, Cu, Zn);
- Measurements of the morphometric parameters of maize plants over the full vegetative season;
- Measurements of the harvested maize crop production.

Statistical analysis of the collected data was done by variance analysis, the Duncan test.

All experiments in open field was carried out according to the Agricultural Research and Development Station of Albota - Pitesti, Arges County standards and methodology. All the chemical analysis program was carried out according to the National Research and Development Institute for Soil Science, Agrochemistry and Environment – ICPA Bucharest standards and methodology.

3. Results

3.1. Climatic Data during Season 2018

The climatic conditions of the pre-blooming and blooming period were very good, rich in rain, which favored the intense growth of plants. To this was added the high temperatures throughout the maize plants development period. Figure 2 shows the recorded temperature and rainfall values from April to September (maize growing season). Thus, the flowering of maize plants took place on 20.07.2018, when panicle appeared at the top of the stem, and after two days appeared the silk.

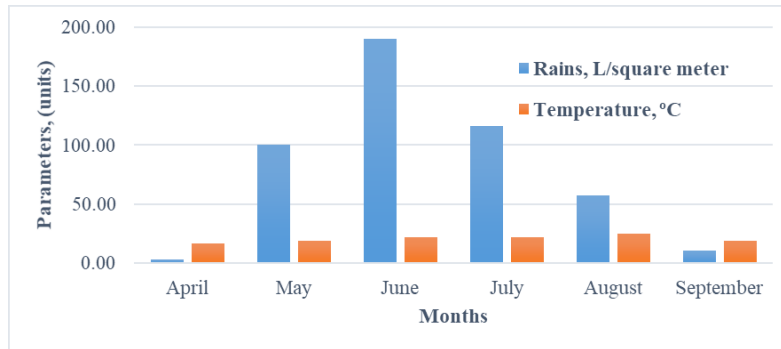


Figure 2. Rainfalls and temperature during the maize full vegetative season 2018.

3.2. Growth of the Maize Plants during Flowering and Maturation Stages

Under the above good development conditions, the maize plants have reached waists ranging from 2.20 m to 2.41 m, with an overall average of 2.28 m. But these data could not statistically differentiated on the basis of a dependence between variants composition and the expected effects of treatments with different fertilizing formulas (Figure 3).

On the contrary, there were recorded statistically significant data concerning the dependence between variants composition and maize green mass weight in kg/plant. Thus, when applying formulas with higher content of bauxite residue, the increases of 43-64 % in green mass are real and repeatable in the flowerig stage.

As can be seen in the Figure 3, during maize maturation stage, the vegetative growth rate was very low. Nevertheless, the plants height reached a maximum of 2.69 m, the general average being 2.48 m, 20 cm greater than the height recorded in the blooming phenophase. So far, the plants mass increased between 593 and 846 g, with an arithmetic mean of 691 g, i.e. only 12 g more than in the blooming period. Also, the differences between both waist and vegetative mass growth of the plants in all applied variants are statistically relevant during the maturation phenophase.

Stage of deposition of the reserve substances in maize grains (maturation) covers a quite large interval of about 3 weeks. In the case of the maize DKC 4590 hybrid, this period ran from 26.07.2018 to 12.08.2018. At the end of this stage grains humidity approaches to 25-30 %. At about 25 % humidity, the black layer forms where the grain attaches to the cob, and the maize reached technical maturity, a sign that harvesting can begin.

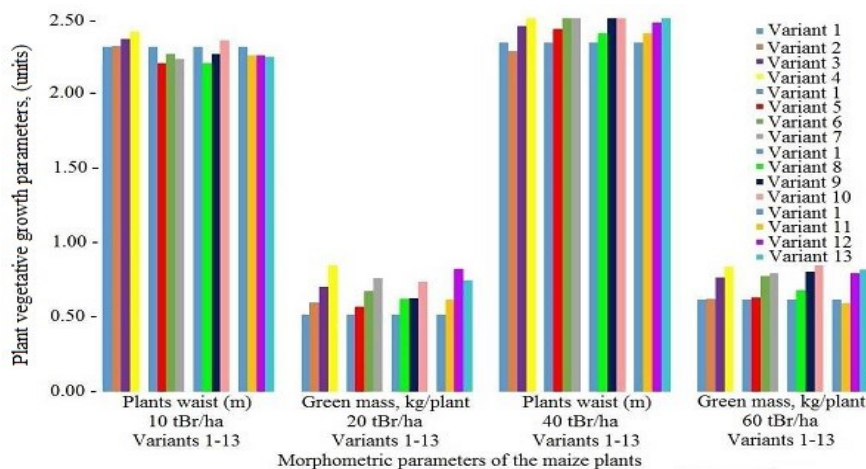


Figure 3. Morphometric parameters of the maize plants during full vegetative season 2019.

3.3. Growth Production in Maize Grains

As vegetative growth was highly differentiated in all the variants as a function of the applied soil treatments, it is expected that the grains production in maize crop will be also, differentiated by significant data. All the collected data were presented in Figure 4. The maize grains production was obviously increasing from variant 2 till variant 13. Roughly, the maize production growth rises from 11.4 to 16.8 t/ha, with an average yield of 14.4 t/ha Figure 4. In the terms of percentage, the yield growth due to application of research programs is ranging in 11.4 – 41.0 %, and all the data have statistical significance. It should mentioned that in variants with increasing doses of bauxite residue associated with mineral and organic fertilizers, on some of maize stems there were formed two cobs on the same plant, averaging 12.1 t/ha, compared to the untreated, unfertilized control of 11.9 t/ha. Therefore, bauxite residue treatments associated with mineral fertilization or with mineral and organic fertilization have also, recorded significant increases in the production of maize grains. Figure 4 give some more information about how each of the three adjuvant contributed to increase in the maize crop production. Bauxite residue does not promote itself any kind of plant growth. By neutralizing the acidic soil, some small increases in the maize crop production might be possible by mobilization some natural resources of the soil at higher pH values. At a dose of 10 tBR/ha, the soil resources are too poor to sustain the growth and consequently, the grains production drops from 11.9 t/ha (control value) to 11.4 t/ha. Further dose, 20 tBR/ha, equilibrated the soil acidity and significant growth in grains production was recorded (from control 11.9 t/ha to 13.1 t/ha, Figure 4). Next doses 40 and 60 tBR/ha are enough to push the soil pH to some alkaline values and grains production dropped larger under the former values, till 12.6 t/ha and respectively, till 11.3 t/ha. Mineral fertilization with N120 P60 K40 urea formulation brought in the most of increases in maize crop production. As Figure 4 shows, the grains production was stepping up proportionally with the dosage of bauxite residue and reached reliable values of 15.5 -17.0 t/ha at a constant dose of NPK fertilizer (120 kg/ha N, 60 kg/ha P and 40 kg/ha) and at variable dosage of bauxite residue, 20-60 tBR/ha. Organic fertilization did not sustain the maize yield growth only in a small extent (Figure 4). From this point of view, it seems the best results were obtained in variant 10, when 40 tBR/ha ware applied. Actually, the contribution of organic Bio Enne Co-Actyl complex fertilizer lays rather in increasing the organic carbon content in soil and less in providing a high yield of maize. Organic fertilization did not sustain the maize yield growth only in a small extent (Figure 4). From this point of view, it seems the best results were obtained in variant 10, when 40 tBR/ha ware applied.

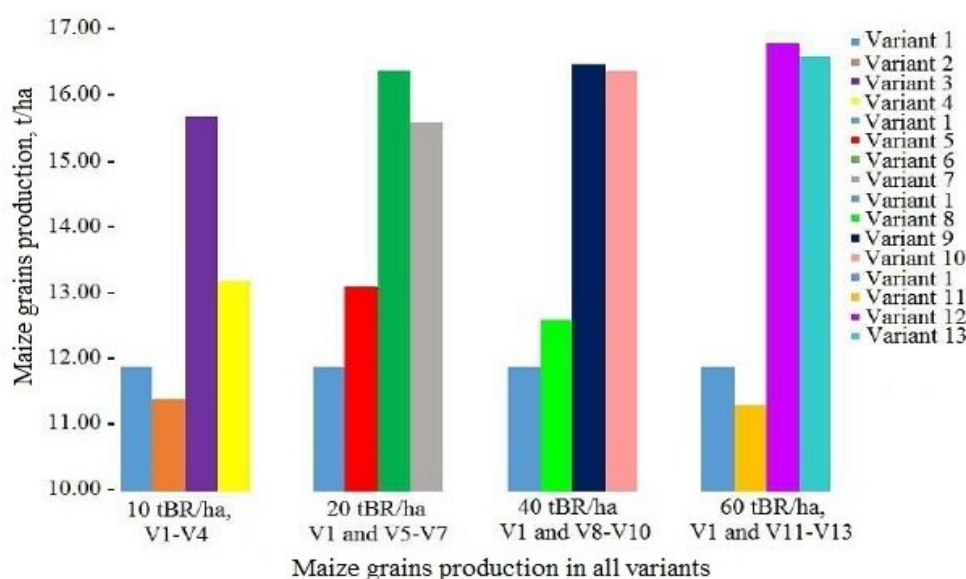


Figure 4. Maize grains production.

3.4. Albota's Albic Luvisoil Composition and Agrochemical Properties after Flowering

As expected, there are changes in the composition and in the soil agrochemical properties. Some are statistically relevant, some are not. Due to the short time contact between soil and the bauxite residue (BR application was made shortly time before seeding), the real changes will be seen in the second step of crop rotation (wheat crop), which is on the experimental field during 2019 year. So far, the pH of soil, horizon 0-20 cm, in all the variants was fluctuating from 5.13 in the untreated and unfertilized control up to 6.59 in the variants treated at 60 tBR/ha under mineral fertilization (the only one with statistical relevance Figure 5). In other variants, the pH recorded values were above the control variant with roughly 0.60 pH units, but they had not statistical significance. Thus, the entire experiment was carried out on a slightly acid soil.

The humus content of albic luvisoil in all the experimental variants was fluctuating between 2.19 and 2.56 % (Figure 5), with an average value of 2.38 %, and a standard deviation of 0.11 %. Although there were some collected data with statistical relevance against control variant, it could not be specified which applied treatments would have had any influence on the soil humus content. However, in the variants that received organic fertilization, the humus content increased by 0.10 % (with no statistical significance). On the whole, the soil has low humus content yet.

The variation range of the total nitrogen content (N_{TOT}) in the upper horizon of soil is placed between 0.17 and 0.135 %, with an average value of 0.125 %, meaning a quite a small content. A slight increase in total nitrogen (N_{TOT}), statistically significant, was brought in soil by the maximum bauxite residue dose, applied without fertilizers. In the same variant there was found a 0.37% increase in organic matter, but these above details have no relevance for the entire experiment (Figure 5).

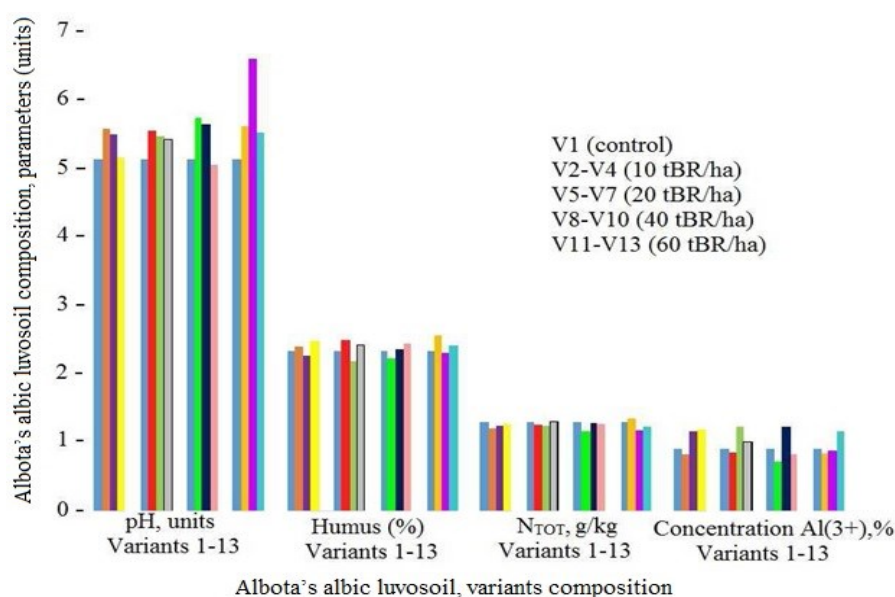


Figure 5. Albota's albic luvisoil composition.

The nitric nitrogen content in Albota's albic luvisoil is normal for this type of soil and for the level of fertilization applied (Figure 6). Although there was a difference of 37 mg/kg between the nitric nitrogen ($N-NO_3$) level in the richest variant and in the poorest variant in this component, no statistical relevant differences were recorded between the control variant and any of the other variants. Nevertheless, it should be noted that in the variants which were fertilized only with mineral fertilizers at high doses of bauxite residue (40 and 60 t/ha), there were recorded the highest concentrations of nitric nitrogen (variants 9 and 12) (Figure 6).

The mobile phosphorus (P_{AL}) content (soluble in the ammonium lactate-acetate, AL) is placed in a relatively narrow interval, ranging from 18 to 45 mg/kg, and averaging 27 mg/kg. At this medium level in soils the mobile phosphorus content is considered satisfactorily for a good crop fertilization. The top value of this parameter was 45 mg/kg in variant 12 (Figure 6).

The mobile potassium (K_{AL}) content (soluble in the same reagent as mobile phosphorus) recorded low value, ranging from 58 to 81 mg/kg, with an average value of 68 mg/Kg, meaning an unsatisfactory supply for crops. Similar to the phosphorus, the highest content values of mobile potassium are found in the variants under mixed mineral and organic fertilization. The differences between the variants are not statistically relevant (Figure 6).

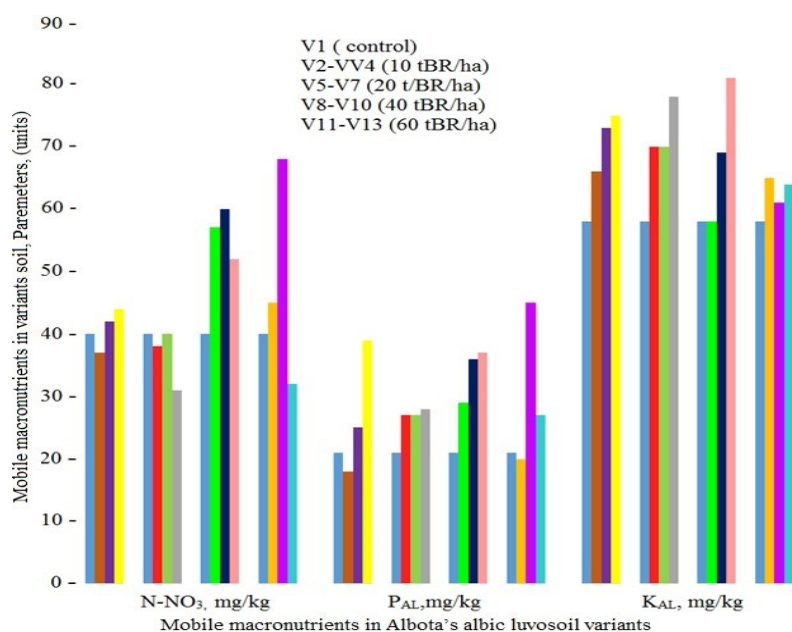


Figure 6. Macronutrients mobility in soil (0-20 cm) during maize flowering.

Therefore, the albic luvisol at the end of the maize blooming phenophase was weakly acidic, has low concentrations in humus, total nitrogen, and mobile potassium and phosphorus. Due to its composition the bauxite residue raises the ionic exchange capacity of the Albota's albic luvisoil. Indicators of the ionic exchange properties in soils are: the sum of the exchangeable bases-SB, the hydrolytic acidity- A_H , the total cationic exchange capacity T and the degree of saturation in bases- V_H). All of these parameters measured under experimental program conditions are presented in the Figure 7. According to the experimental data, there were recorded statistically significant positive differences in the variants where the soil was treated with the maximum bauxite residue doses (40 and 60 t/ha). Therefore, it could be concluded that the bauxite residue improves with no doubts the cationic exchange capacity of the Albota's acidic soil.

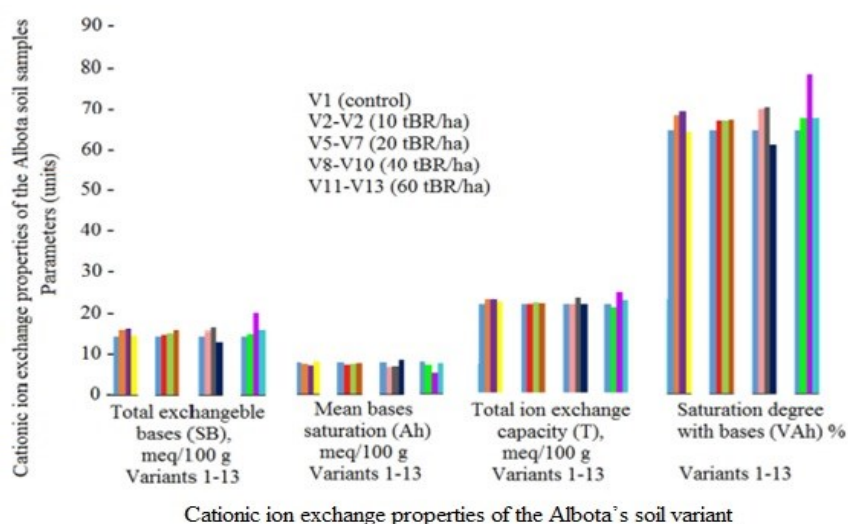


Figure 7. Cationic ion exchange properties of the Albota soil samples from horizon 0-20 cm layer during the maize plant flowering.

3.5. Macro, Mezzo and Micro Nutrients cu, in Leafs under the Main Maize Ear

The nitrogen content of the maize leaves, harvested under the main plant ears at the maize blooming phase end, fluctuated between 2.22 and 3.22 %, with an average value of 2.87 % (Figure 8). It is clear that the highest content of nitrogen is was found in the fertilized variants, which have been receiving bauxite residue doses for soil neutralization. The average nitrogen content of these variants was 3.17 %. Comparing these figures with the normal nitrogen content (ranging between 3.0 -3.5 %) we find that only the fertilized variants have delivered to plants the normal required nitrogen amounts.

Although the phosphorus content in the leaves falls within the normal concentrations range (the concentration range 0.25-0.28 %, with an average value of 0.27 %), there were found no statistical relevant differences between all the variants (Figure 8).

Also, the same statistical irrelevant differences were found in the case of potassium (K) content in leaves. Moreover, in the case of potassium, the content in leaves is below the minimum value (1.7 %) of the normal concentrations range. Actually, the potassium concentrations were fluctuating between 1.0 and 1.68 %, averaging 1.49 % (Figure 8). The low potassium content of the leaves has to be related to its reduced concentrations in soil, as was mentioned above. Neither of the concentrations of other two mezzo nutrients, calcium (Ca) and magnesium (Mg), were not significantly influenced by the applied experimental treatments. However, unlike potassium, these concentrations lay within the normal ranges. Thus, the calcium content ranged between 0.39 and 0.63 %, with an average value of 0.53 %, and the magnesium concentrations have fluctuated between 0.24 and 0.34 %, with an average value of 0.29 %. Moreover, the concentrations of these two mezzonutrients are rising, as far as the bauxite residue doses are increased. But, this assumption is statistically valid only for the variants under mineral and organic fertilization (Figure 8).

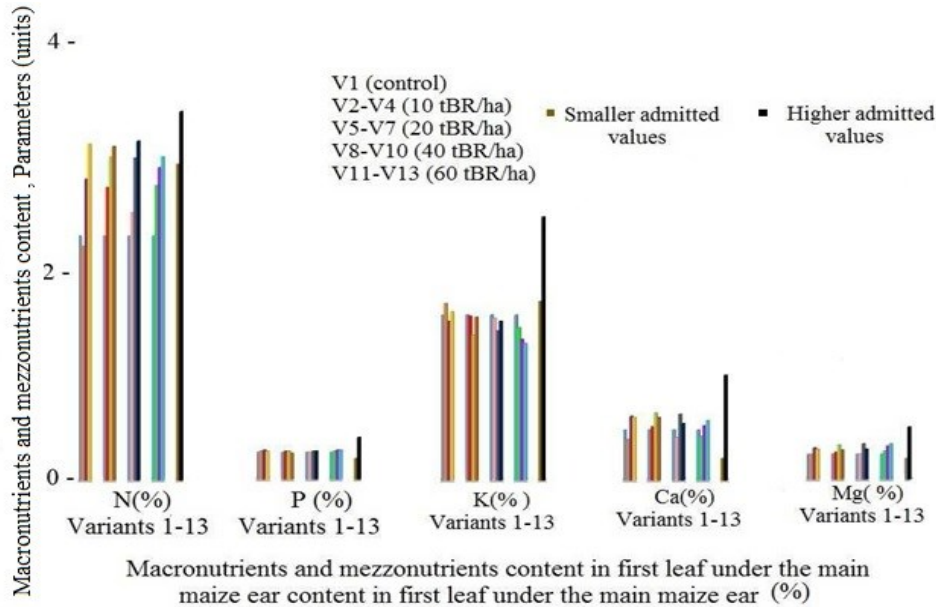


Figure 8. Macro- and mezzo nutrients content in first leaf under the main corn ear.

The concentrations of the four micronutrients (Cu, Fe, Mn and Zn) in leaves under the main maize ear are presented in the Figure 9. Copper (Cu) concentrations in the maize leaves are placed in the first half of the normal ranges, which is extended over 5.83 and 8.80 mg/kg interval, with the mean value of 7.80 mg/kg. The differences in copper concentrations, between the control variant and the rest of variants are statistically relevant. Iron (Fe) concentrations range is bounded by 112 and 208 mg/Kg-, averaging 117 mg/Kg. All the values from Figure 9 are close to the maximum limit, and all the data are statistically relevant, excepting one without statistical significance. Manganese (Mn) is the only micronutrient, whose values exceed the normal concentrations range in maize leaves (26-150 mg/Kg). Actually, its concentrations range from 160 to 262 mg/Kg, with an average of 220 mg/Kg. Thus, the average value (220 mg/kg) is with 70 mg/kg higher than maximum limit in normal ranges of variation of manganese concentrations in maize leaves. The phenomenon is due to the residual acidity in soil after the bauxite residue treatments. Also, the higher manganese concentration in leaves might be brought by bauxite residue itself. This hypothesis is sustained by the statistical significance of the data concerning the differences between the manganese concentration in leaves in the variants where high doses of bauxite residue were applied (20; 40 and 60 t/ha) and the manganese concentration in the control variant.

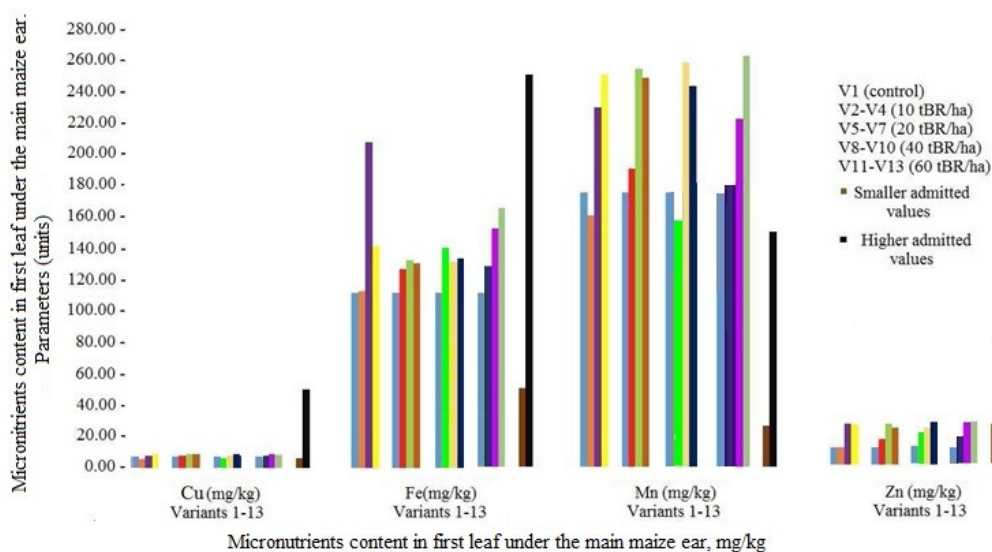


Figure 9. Micronutrients content in first leaf under the main corn ear.

Finally, the zinc concentrations in the maize leaves were ranging from 10.7 to 26.6 mg/kg, with an average value of 21.2 mg/kg. Thus, the concentrations of zinc (Zn) in maize leaves lay in some lower ranges than normal value recorded for this micronutrient. In addition, the differences between the above zinc concentrations in the control variant and zinc concentrations in other variants, where acidic soil was treated with larger doses of bauxite residue (40 and 60 t/ha) under mineral and organic fertilization, have statistical relevance.

Therefore, it could be concluded that the application of bauxite residue to the Albota's albic luvisol in association with mineral fertilization or with mineral and organic fertilization has contributed to a balanced nutrition of maize with macro, mezzo and microelements.

3.6. Macronutrients and Mezzo Nutrients in the Maize Grains

All data collected in the experiment about macronutrients and mezzo nutrients concentrations in the maize grains are given in the Figure 10. Maize grains have accumulated small amounts of nitrogen, consistently below normal. Thus, the concentrations in nitrogen are ranging from 0.86 % to 1.20 %, with a total average of 0.91 %, i.e. this is 1 % below the normal concentration. Higher values in nitrogen concentrations were recorded for variants treated with higher doses of bauxite residue (40 and 60 t/ha) under mineral fertilization.

At a low nitrogen content, there was normally to expect the crude protein content would be lower than are normally found in the maize grown under ideal conditions of vegetation. Experimental data showed that crude protein content in maize grains fluctuated between 5.38 % and 7.50 %, averaging 6.22 %. Hence, the average value was 38 % lower than the normal protein content. This drop in protein average percentage in grains is a result of the nitrogen accumulation in leaves at the lower limit of the normal ranges (Figure 8), as well as the nitrogen low content of the grains (Figure 10).

Although the phosphorus in leaves was found at normal levels, (Figure 8), the phosphorus in maize grains did not accumulate enough to reach the normal concentrations. In fact, phosphorus content in maize grains lays in the values interval of 0.11 % and 0.20 %, with an average content of 0.16 %. This average content was 36 % less than the usually recorded concentrations in most favorable conditions, but the differences between variants have no statistical relevance (Figure 10).

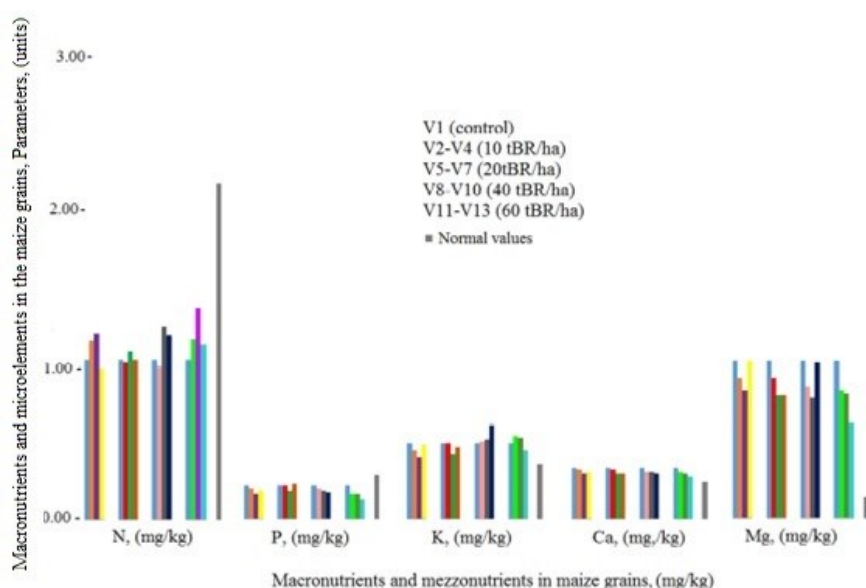


Figure 10. Macronutrients and microelements in the maize grains.

Even if in soil and in the maize leaves the content of potassium was found below the normal limits, the maize grains were accumulating potassium above the normal limits. Thus, the average content (0.42 %) is 35 % higher than the content considered normal in the most favorable conditions (0.31 %). With one exception, there were no statistically relevant differences between experimental variants (Figure 10).

In the case of calcium, there were recorded concentrations 28 % higher than the usual values recorded in common maize crops (0.21 %). Unexpectedly, the highest statistically relevant, concentrations were recorded at the control variant and at the lowest dose of bauxite residue in soil (10 t/ha), unfertilized variant. It seems that in Albota's acidic soil, neutralized or non-neutralized by bauxite residue, calcium absorption process in maize grains undergoes an inhibition effect (Figure 10).

A similar phenomenon was noticed in the case of magnesium, where the highest concentrations in the maize grains were recorded even in the control variant and or in the lowest doses of applied bauxite residue. Consequently, the highest magnesium concentration in the maize grains averaged 6 times higher than the normal concentration. Actually, magnesium concentration is ranging between 0.54 % and 0.90 %, with an average value of 0.76 %. Other way, it is possible to accept that unusual accumulation of potassium and magnesium in maize grains is due to their ion high mobility in the treated and untreated experimental soil (Figure 10).

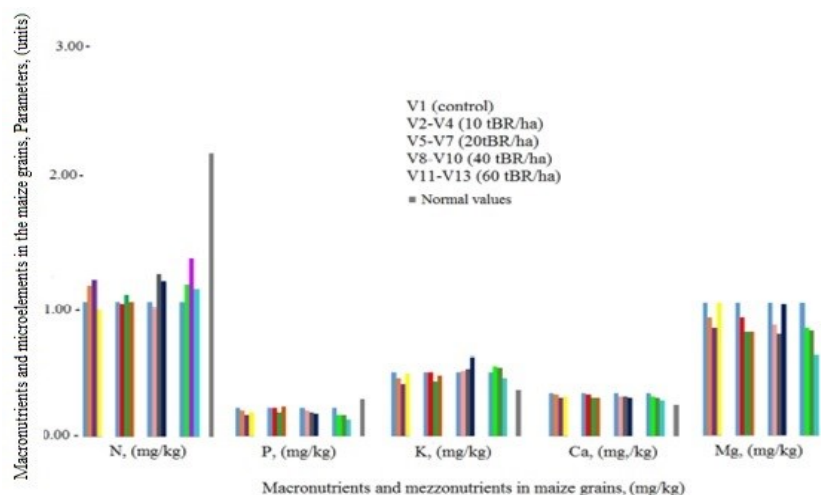


Figure 11. Macronutrients and microelements in the maize grains.

3.7. Micronutrients in the Maize Grains

The micronutrients concentrations in the maize grains are of little importance for the conclusions of this experiment. Only if, some specific interests are requiring to know the concentration and behavior of the over toxic elements, or large unusual rises in concentration of other usual elements in the soil composition, which have been transferred from soil in the maize grains, might be of particular interest.

For the purpose of this study, the level of concentrations and the distribution of micronutrients in soil, in plant stem, and in leaves and grains, might contribute to the validation of most experimental collected data.

For better knowledge, the copper content in maize grains lays in the values interval from 0.83 mg/kg to 1.57 mg/kg, with an average content of 1.10 mg/kg, the range of variation in iron content of maize grains is extending from 7.67 mg/kg to 22.67 mg/kg, with an average value of 14.54 mg/kg. The manganese concentrations in maize grains are bounded into the interval from 2.23 mg/kg to 4.10 mg/kg, with the overall average value 3.12 mg/kg. The zinc concentrations in maize grains are covering the interval from 6.90 mg/kg to 20.47 mg/kg, with an average value of 14.82 mg/kg. All the data are shown in the Figure 11. For copper, iron and zinc, all the experimental values concerning micronutrients accumulation in grains are smaller than usual values. For manganese, all the experimental values concerning micronutrients accumulation in grains are bigger than usual values.

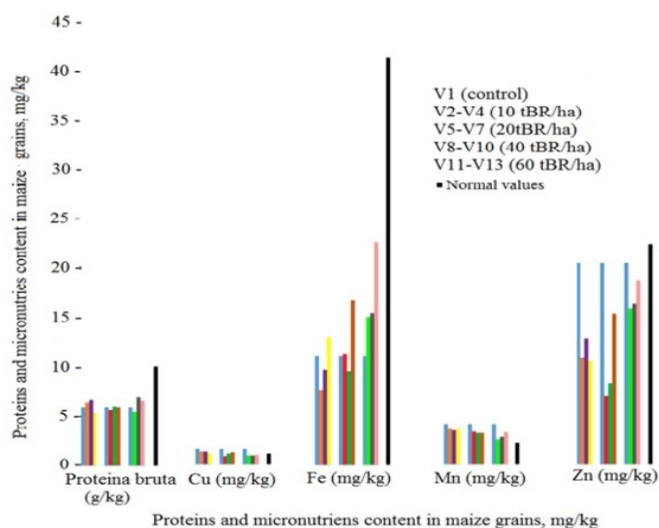


Figure 12. Proteins and micronutrients content in the maize grains.

There are differences of micronutrient concentrations in the variants containing different doses of bauxite residue, but few of them have statistical relevance. Excepting manganese, in all of other variants the micronutrients are accumulating in soil.

4. Conclusions

This paper describes a complete open field experiment designed to demonstrate the ability of bauxite residues to remediate an acidic soil and to provide to this soil enough fertility to sustain crops growth, by an appropriate fertilization plans. The experiment was preceded by another successful experiment carried out on maize crop, at glass house scale by National Research and Development Institute for Soil Science, Agrochemistry and Environment – ICPA Bucharest, using the Albota's albic luvisoil, The experimental set up, analytic program, technical measurements and specific assistance come from Agricultural Research and Development Station of Albota - Pitesti, Arges County, Romania.

The bauxite residues, identified as main remediant adjuvant in acid soil rehabilitation, have been fully analyzed in our previous papers, collecting data about its chemical composition and agrochemical properties. The Albota's albic Luvisoil was fully analyzed in this paper and the collected data concerns about its chemical composition (macro, mezzo and micronutrients content, humus, total nitrogen,) the physical properties (pH and particle size distribution) and the agrochemical properties (alkali cations sum, hydrolytic acidity and saturation in alkali cations of the soil, exchangeable cations, mobile macronutrients as PAL, KAL S-SO₄ and microelements as total and as mobile forms), All the analysis were carried out before experiment and after the flowering of maize plants, in order to demonstrate the remediated effect of the bauxite residue on soil. Organic Bio Enne Co-Actyl complex fertilizer and mineral NPK fertilizer formulated with urea instead of ammonium nitrate are common fertilizers grades described in the technical literature.

Experimental program covered all the stages of experiments with plants versus dose on the Albota's albic luvisoil. The main details of this program are: Maize variety: Hybrid DKC 4590; Bauxite residue variable doses (t/ha): 0, 10, 20, 40 and 60; Mineral fertilizer dose (kg/ha active NPK), one fixed dose: N120 P60 K40/ha; c) Bio Enne Co-Actyl complex fertilizer (t/ha), one fixed dose: 25t/ha. Experimental data concerns: vegetative growth in maize plants waist and green mass in 2 stages, flowering and maturity, maize crop production, macro- and mezzo- and

micronutrients content in first leaf under the main maize ear, Macro- and mezzo- and content in maize grains, proteins and micronutrients content in the maize grains.

Vegetative growth: The increases of 43-64 % in green mass are real and repeatable in the flowering stages. It is reasonable to consider the dose of about 40 t/ha as optimal at least for maize plants growth in height and weight.

Maize grains production: The maize grain production was obviously increasing from variant 2 till variant 13. Roughly, the maize production growth rises from 11.4 to 16.8 t/ha, with an average yield of 14.4 t/ha, independently of fertilization formulas. In the terms of percentage, the yield growth due to application of research programs is ranging in 11.4 – 41.0 %, and all the data have statistical significance.

Macronutrients, mezzo nutrients and micronutrients in leaves under the main maize ear: It could be concluded that the application of bauxite residue to the Albota's albic luvisol in association with mineral fertilization or with mineral and organic fertilization has contributed to a balanced nutrition of maize with all the classes of nutrients. Macronutrients and mezzo nutrients in grains status: There are unusual accumulation of potassium and magnesium in maize grains due to their ion high mobility in the treated and untreated experimental soil. Micronutrients in in grains status: There are differences of micronutrient concentrations in variants containing different doses of bauxite residue, but few of them have statistical relevance. Concentration variations are lower than usual known value

Proteins in grains status: Experimental data showed that crude protein content in maize grains lays between 5.38 % and 7.50 %, averaging 6.22 %. The average value was 38 % lower than the normal protein content in maize.

5. References

1. Gheorghe Dobra et al., Bauxite residue safety disposal and possibilities to further utilization. Part 1. Acid soils remediation, *Journal of Siberian Federal University. Chemistry* 2017 10(1) 6-21.
2. Gheorghe Dobra et al., Bauxite residue safety disposal and friendly environmental processing permanent care at Vimetco Alum SA Tulcea, *Bauxite Residue Valorization and Best Practices Conference, Leuven, 2015*.
3. Gheorghe Dobra et al., Full analysis of Sierra Leone bauxite and possibilities of bauxite residue filtration, *Journal of Siberian Federal University. Eng. technol.*, 2016, 9(5), 643-656.
4. Radu Lacatusu et al., Plant growth suitable nutritive red mud composite materials from the Romanian dry landfilled red mud. I. Red mud chemical and agrochemical characterization, *Rev. Chim (Bucharest)*, 2014, 65 (9), 1008-1014.
5. Gheorghe Dobra et al., Plant growth suitable nutritive red mud composite materials from the Romanian dry landfilled red mud. II. Formulation nutritive composite materials and plant growth tests at laboratory and glasshouse scale., *Rev. Chim (Bucharest)*, 2014, 65 (11), 1294-1305.
6. Radu Lacatusu et al., *Chimia globala a solului. Tera Noastra*, Iasi, 2017.
7. Radu Lacatusu et al., Growth of some pasture plants on a composite nutritive layer with red mud, *Research Journal of Agricultural Science*, 2015, 47(3), 69-78.
8. Radu Lacatusu et al., The effect of acid rock from Călimani mountains on making up a nutritive support for plants, based on red mud, *Soil Forming Factors and Processes from the Temperate Zone* 2013, 12 (2), 1-7.
9. Radu Lacatusu et al., Growth of some pasture plants on a composite nutritive layer with red mud, *Research Journal of Agricultural Science*, 2015, 47(3), 69-78.