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THE ADSORPTION CHARACTER OF PERLITE, INFLUENCE ON NITROGEN DYNAMICS IN SOIL

SUMMARY

In this research the sorption of the cations NH_4^+, Al^{3+}, Fe^{2+}, Mn^{2+}, and Mg^{2+} in powdered perlite and its mixture with soil was monitored. Of all observed cations in perlite by the first minutes of laboratory experiments, which is very fast, the ammonia sorption cations reacted fastest. The dynamics of nitrate and ammonia nitrogen in the soil after application of perlite in different quantities were observed. Reduced ammonia content was apparent in variants with perlite one (1) month of application. Three (3) months later, distributed ammonium content increased in variants with perlite from 24% to 59%, compared with the control variant due to the gradual release of ammonium perlite lattice. Six (6) months after the application, statistically significant differences were found not only between the control variant and variants with perlite, but also between the individual variants with different perlite doses (n = 13.2; P = 0.003 according to Kruskal-Wallis test). The process of nitrification in the soil was strong because of the applied perlite. The content of nitrate nitrogen in the soil is reduced by 66% to 78% compared to control variation in the fall time; therefore, the amount of nitrate leaching from soil horizons groundwater is minimal. In summary, perlite can be considered to be a slow release nitrogen fertilizer. This research concluded that the perlite can find application in the production of mineral fertilizers that is gradually giving the necessary cations.

Key words: Ammonium, nitrate, soil nitrogen dynamics, perlite.

INTRODUCTION

Perlite is a 100% natural siliceous volcanic glass mineral, which traps crystalline water into its mass. Perlite expands when rapidly heated in temperatures of 700°C–1100°C (Dogan and Alkan, 2004). The heating causes entrapped water molecules in the rock to turn to steam and expand the particles.

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Controlled rise of temperature forms a white mass of minuscule glass bubbles. Perlite melts and expands in an extremely porous surface and increasing its volume up to 4-20 times of its original volume (Ennis, 2011). It is very porous, has a strong capillary action and can hold 3–4 times its weight in water. (Bures *et al*. 1997a). This microstructure gives the material a set of favourable properties such as excellent insulation properties, low density and high porosity (Sengul *et al*., 2011; Kramar and Bindiganavile 2013; Polat *et al*., 2015; Markoska *et al*., 2018). We recorded a number of advantages of perlite over other substrates like stability, properties such as: ultra-lightweight, excellent water retention up to four times its weight, advanced drainage and aeration, pH natural and asbestos free, chemically inert, sterile, free of weeds and permanent, serves as an insulator to reduce extreme soil temperature fluctuations, reduces concentrations of salt and also promotes the long term effect of fertilizers (Raviv, M., and Lieth, J, H, 2008; Asher B.,T *et al*., 2008). Moreover, it is commonly used in the food industry, filter product, growing of seed, regulating of the soil in agriculture, and in so many other industrial applications (Alihosseini *et al*., 2010).

Perlite has very good physical characteristics. The physical properties of container-growing substrates, particularly air space, container capacity, and bulk density, have a significant impact on plant growth, and knowledge of these properties is essential in properly managing nursery irrigation and fertilization programs (Yeager *et al*., 2000; Markoska *et al*., 2018). Because of their extremely high sorptive capacity, which depends on the dominant mineral, perlite can be used in different fields, which include agriculture.

Perlite is used in agriculture as a fungicide, herbicide, or plant nutrient carrier. This is feasible simply because of the high sorptive capacity of this rock. When nutrients are introduced into the soil in this way, their consumption rate is reduced, so there is no further need for redundant delivery of raw materials and consequently fewer nutrients (mostly nitrogen, which causes eutrophication of water sources) are leached into ground and surface waters Markoska, 2019; Markoska *et al*., 2018). The atmospheric complex can be divided into two groups: basic cations or more simply bases (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and acid cations H^+ and Al^{3+}). Different ions have different energy of adsorption, and they are attracted from the colloidal system by different forces.

Perlite has a high content of total or total adsorption capacity with an average value of 173.32 cmol (+)kg^{-1}. The influence of capacity in perlite is probably due to the mineral composition, resulting from the surface reactions that occur during treatment with acid solution, the part that participates in substitution adsorption. (Markoska, 2019).

The authors Dogan and Alkan (2004) in their study proved that during the thermal treatments of perlite there is a structural transition from amorphous to crystalline, accompanied by increased cation exchange capacity from 20-30 to 35-50 cmol (+) kg^{-1}, as a result of increased specific surface area from 1.2 to 2.3 m^2/g.

Figure 1. Powdered and Raw Perlite (Photo: Markoska, 2020)

MATERIAL AND METHODS

The experimental part served to determine the influence of perlite on nitrogen adsorption and its dynamics in soil. The experimental part was divided into two parts: field part and laboratory part. The used perlite originates from Cerava Poliana, Mariovo Gradesnica, Republic of North Macedonia, and was applied in expanded (commercial) form.

The analysis of the chemical composition of the examined mineral raw material is shown in (Tables 1 and 2). A similar chemical composition is determined in researches of many authors: Herskovitch *et al*. (1995); Uemura *et al*. (1999); Jing, Fang, Liu, & Liu (2011). In the Table 1 we presented chemical composition of perlite.

Table 1. Chemical composition of perlite

Oxides	**Mass percent [%]**
SiO_2	75.47
Al_2O_3	12.77
Fe_2O_3	0.94
CaO	0.61
MgO	0.10
Na_2O	3.04
K_2O	4.51
TiO_2	0.20
Loss of mass	2.36
Total	100

Based on the results obtained from the examinations of the chemical composition of the perlite raw material, it can be concluded that the content of SiO_2 in relation to the other oxides is dominant and is 75.47%. The loss of combustion is the adsorbed water in the material, which is 2.36%. Raw perlite has a low percentage of Fe_2O_3 (0.94%).

The presence of non-ferrous metal oxides is very small. From the results obtained by analysis of trace elements in the raw material perlite, it can be concluded that it also contains low concentrations of As, Cd, Cr, Pb, Mn, Ni, Cu, Cr, B. The trace element can be defined as an element that is represented in the rock in concentrations less than 0.1wt % which is less than 1,000 ppm. Determining the chemical composition is essential because it provides an opportunity to assess the source of the elements present in the raw material itself.

Instrumented Chemical Analyses - ICPA apertures instrument is used to determine the chemical composition of raw perlite. As a consequence of the results of laboratory experiments, the effect of perlite on the dynamics of mineral nitrogen in soil with a depth of 0.0–0.3 m was verified in field experiments.

Selected chemical soil properties were determined using the obligatory methods for soil analysis (Mitrikeski *et al*., 2013).

There were 4 variants of the experiment:

Q, control variant without any fertilization;
Perlite 1, 500 kg of perlite type per hectare;
Perlite 2, 800 kg of perlite type per hectare and
Perlite 3, 1000 kg of perlite per hectare.

All variants were carried out 4 times. The area of the experimental field was 50 m^2 (10 x 5m). The experimental crop was medium-ripening white tomato (*Solanum melogena*) grown with the usual agricultural techniques. Seedlings were planted on 15 April and harvested on 31 August 2019. Average soil samples were taken and analysed for pH, nitrogen (ammonia and nitrate), and the contents of available phosphorus, potassium, magnesium, before the experiment was set up and after its completion on each site. In addition, once a month, soil samples from a depth of 0.0–0.3 m were taken from each site in order to monitor the dynamics of ammonia and nitrate nitrogen in the soil. The statistical processing assumed that the perlite dose influenced both ammonium and nitrate content in the soil. The Kruskal–Wallis test was chosen for verification of this hypothesis. In the case of rejection of the null hypothesis, the non-parametric Mann–Whitney test was used.

RESULTS AND DISCUSSION

The exchangeable perlite cations Ca^{2+}, Mg^{2+}, K^+, and Na^+ are already present in natural deposits. These cations can be exchanged by NH_4^+ and other metal cations, depending on the pH value of the solution and their concentrations.

The time-dependent development of NH_4^+ sorption from solution in perlite is shown in Figure 2, where the curve reflects the time dependence of the sorption of the initial NH_4^+ concentration.

The development of the sorption indicates a very rapid response and, in the first minute, a sorption of more than 90% of the maximum potential ammonia concentration in perlite on an infinite timescale can be observed. During the next period from 2 min up to several hours, the concentration of NH_4^+ does not change significantly and is almost constant.

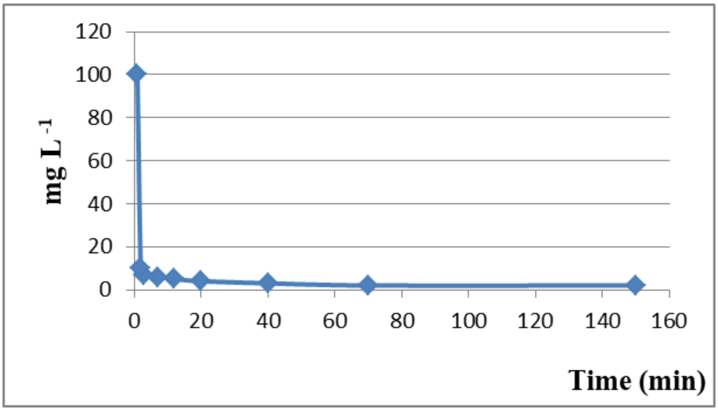

Figure 2. Sorption rate of ammonia cations (NH_4^+) on powdered perlite (0.1 kg L^{-1}, fraction under 45 pm).

Figure 3 presents the rate of sorption of the other observed cations. Similar to the sorption rate of the ammonia cations, the iron cation sorption (Fe^{2+}) was very fast.

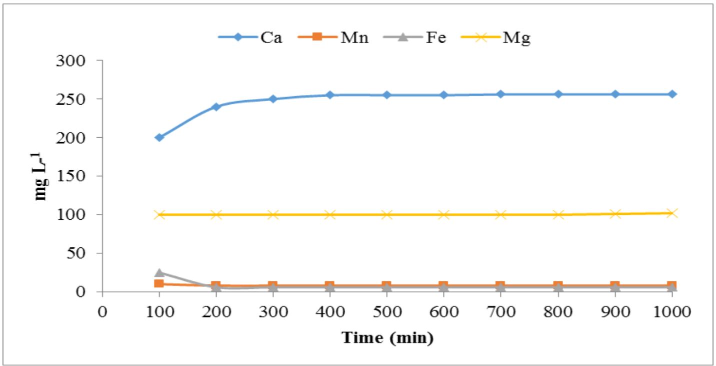

Figure 3. Sorption rate of selected cations Mg^{2+}, Fe^{2+}, Mn^{2+}, and Ca^{2+} on powdered perlite (0.1 kg L^{-1}, fraction 45 μm)

A significant decrease in Fe^{2+} concentration could also be caused by Fe^{2+} oxidation to Fe^{3+}, and it is coagulated at filtration. Manganese (Mn^{2+}) sorption was also fast in the first minute, but as manganese has less sorption selectivity than perlite, no significant reduction in concentration occurs, only approximately 40%. The calcium (Ca^{2+}) concentration in solution did not have a tendency to increase by time. The concentration of Mg^{2+} was initially slightly decreased and then increased slightly later. On the basis of experiments in which the time dependence of NH_4^+, Fe^{2+}, Mn^{2+}, Ca^{2+}, and Mg^{2+} sorption in the perlite powder was measured, it can be concluded that the sorption of the cations is extraordinarily fast.

This is illustrated by the fact that in the first minute sorption in perlite reached more than 90% of the maximum possible concentration of equilibrium, which would stabilise in infinite time. It can be assumed, however, that this processes depend on the sizes of the perlite particles, so when they increase, the stabilisation of sorption equilibrium, and especially that of NH_4^+, will be slower. The stabilisation of ionic exchange balance in several minutes or hours can be considered as fast because the perlite will be in the soil for several years after its application. This knowledge can be applied to liquid nitrogen-based plant nutrition on the basis that perlite applied to the soil would prevent the escape of redundant ammonium ions, as these would be bound to perlite in moist soil very quickly and would be gradually released into the soil solution.

The observed cation solution was verified by a field experiment based on Vertisols (FAO Classification, 2006); (WRB Classification, 2016) which the basic chemical properties are shown in Table 2 (nutrient analyses according to the Mehlich method, organic carbon according to the Tjurin method).

Table 2. Physics-mechanical and chemical soil parameters and clay content in the soil Vertisol.

Depth in m	pH in KCl	pH in H_2O	N-NO_3 [mg kg^{-1}]	N-NH_4^+ [mg kg^{-1}]	N an	N_{total}	P	K	Mg	Silt + Clay < 0.02 [mm]
0-0.3	7.1	7.9	31.3	23.8	55.1	1743	88.0	381.0	136.0	65.50
0.3-0.6	7.1	8.0	21.6	24.8	46.4	1417	59.0	264.0	143.0	60.30

In Figure 4, the dynamics of NH_4^+ in the soil is presented. It can be seen that after 1 month of perlite application to the soil, the Vertisols topsoil contained 14 % to 20 % more ammonia nitrogen (91.5 mg kg^{-1} of soil) in the control variant compared with the experimental variants (76.2 – 80.0 mg kg^{-1} of soil).

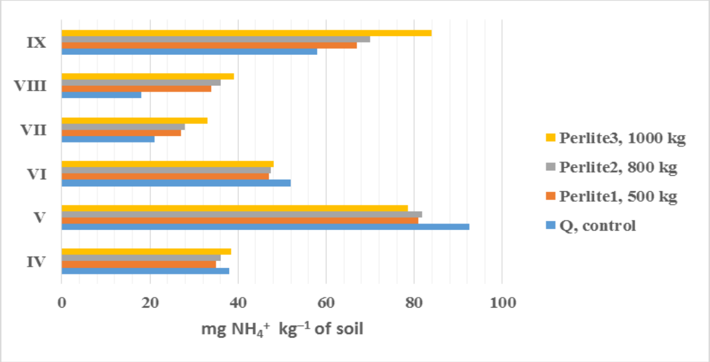

Figure 4. Dynamics of ammonia nitrogen in the soil horizon 0.0–0.3 m after the application of different amounts of perlite

There was a change in this subsequent period; the content of ammonia nitrogen in the topsoil in the variants with applied perlite increased and after 3 months reached 24 % to 59% higher values (depending on the amount of perlite) than the control variant. At the end of the field experiment (5 months after the application of perlite), the experimental variants reached 66.5–84.9 mg, and the control variant reached only 53.2 mg per kilogram of soil.

From the calculated values of the Mann–Whitney test, we can conclude that statistically significant differences in mean NH_4^+ concentrations in the soil were confirmed not only between the control variant and the observed ones, but between all observed variants, as well (Table 3).

Statistical analysis of the results according to the Kruskal–Wallis test confirmed the significant differences between the mean values of all observed variants (H =13.2 with P = 0.003). The Mann–Whitney test results are given in Table 3. After the perlite application, the nitrate nitrogen content also changed during the observed period (Figure 5). All variants kept the spring maximum in April (23.3–26.5 mg kg^{-1} of soil) and the summer minimum in June and July (1.3–4.8 mg kg^{-1} of soil). At the time of crop harvest (in August) there was an apparent increase in nitrate nitrogen (10 mg kg^{-1} of soil) in the control variant, which corresponded to the so-called autumn maximum. This was not confirmed in the variants with perlite because the nitrification process of ammonia nitrogen, owing to the presence of perlite in the soil, becomes slower.

Table 3. The main statistical parameters from the last measurement at the end of the field experiment (ammonia nitrogen).

	Control variant	500 kg perlite ha^{-1}	800 kg perlite ha^{-1}	1000 kg perlite ha^{-1}
Minimum	52.50	65.30	67.40	84.10
Maximum	54.10	66.90	69.50	85.40
Median	53.20	66.90	69.25	85.05
Arithmetic mean	53.25	66.50	69.10	84.90
Standard deviation	0.633	0.700	0.383	0.472

Table 4. Mann–Whitney test results of the observed variants (regarding ammonium nitrogen).

	500 kg perlite ha^{-1}	800 kg perlite ha^{-1}	1000 kg perlite ha^{-1}
Control variant	0.000^{+} (0.03)	0.000^{+}(0.03)	0.000^{+} (0.03)
600 kg perlite ha^{-1}		0.000^{+}(0.03)	0.000^{+} (0.03)
900 kg perlite ha^{-1}			0.000^{+} (0.03)

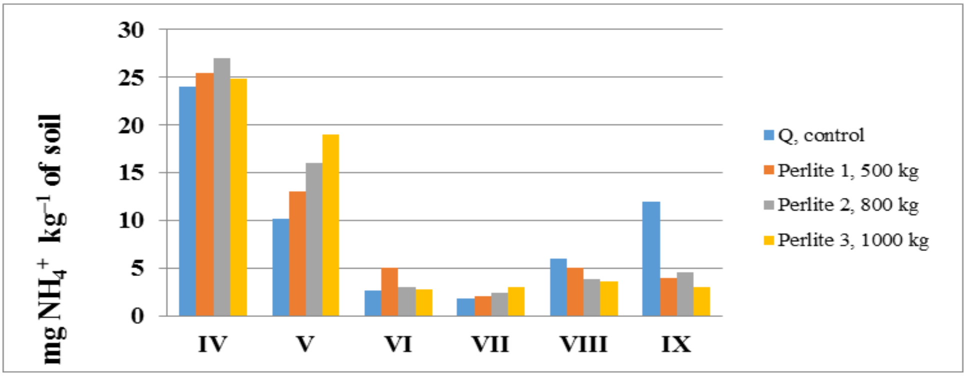

Figure 5. Dynamics of nitrate nitrogen in the soil horizon 0.0–0.3 m after the application of different amounts of perlite

From this perspective, the application of perlite holds back the chemical change of ammonium cations into nitrate anions, thereby decreasing the amount of nitrate leaching into the groundwater. In this way, it is possible to significantly reduce nitrogen loss, which reaches, according to several authors, 25%–35% of the total amount of applied nitrogen in mineral fertilizers.

In our case, the content of nitrate nitrogen in the soil in the experimental variants was 66% to 78% lower in comparison with the control variant. Statistical analysis of the results according to the Kruskal–Wallis test confirmedthe significant differences between the mean values of all observed variants (H =12.7 with P =0.003). The Mann–Whitney test results are given in Table 5.

Table 5. Mann–Whitney test results of the observed variants (regarding nitrate nitrogen).

	500 kg perlite ha^{-1}	800 kg perlite ha^{-1}	1000 kg perlite ha^{-1}
Control variant	0.000^{+} (0.03)	0.000 (0.03)	0.000^{+} (0.03)
500 kg perlite ha^{-1}		1.500^{-} (0.6)	0.000^{+} (0.03)
800 kg perlite ha^{-1}			0.000^{+} (0.03)

Stabilization of the exchange equilibrium was reached in only a few hours. Our results showed a reduction of ammonia nitrogen content in the soil a short time after perlite application. This reduction of the contents in the experimental variants can probably be attributed to fixation of ammonium ions by specific areas in the perlite crystal lattice, because they bind to the perlite with the greatest intensity of all cations (Markoska, 2019).

During the 5 months of the experiment, we found higher contents of ammonia nitrogen in the variants with perlite, which means ammonia nitrogen is gradually released from perlite and more is available for cultivated plants. Application of 2 t of perlite in heavy soils increased the hydrolysable nitrogen content twice, and when they used 4 and 6 t of perlite, it increased by 4 and 5 times, respectively.

The fact that perlite can relatively strongly fix the ammonia nitrogen leads to the reduction of nitrogen leaching. This is confirmed not only by our results, but also by researchers in many countries who have had positive results with perlite application decreasing nitrogen loss due to leaching (Işıldar, 1999; Gholamhoseini *et al*., 2009; Ippolito *et al*., 2011). Perlite is also used to remove nitrates from water (Mazeikiene *et al*. 2010). In their experiments there was an observed decrease of the N-NO_3^- in the soil only to the level of 41%–48% after the perlite application compared with the nitrate nitrogen content in the control variant. Whereas at the beginning of the experiment statistically significant differences were confirmed only between the control variant and observed variants, in the last month of the experiment they were also confirmed between all observed variants. This was confirmed by a Kruskal Wallistest with a relatively high level of significance (H =12.7 and P = 0.003). Regarding the obtained results, it is possible to conclude that sorption of cations NH_4^+, Fe^{2+}, Mn^{2+}, Ca^{2+}, and Mg^{2+} in perlite with a grain size of less than 45 μm takes place very quickly. More than 90% of the maximum possible concentration of those cations is sorbed in the first few minutes.

CONCLUSIONS

The dynamics of ammonia nitrogen in the soil during the 5 months of evaluation endorse perlite as slow-releasing nitrogen fertiliser. It has a significant effect in the prevention of nitrogen loss from soil. Short time after perlite application, the nitrogen content in the evaluated soil decreased as a result of NH_4^+ fixation by perlite, the increase was probably caused by the gradual release of nitrogen from the perlite crystal lattice. Therefore, the perlite works in the soil as a sort of slow-releasing nitrogen fertilizer with NH_4^+ ions and indirectly limits the intensity of nitrification in the soil. Thus provided a sufficient amount of nitrogen throughout the vegetation period for cultivated plants. On the other hand, the presence of perlite in the soil in habits the process of nitrification to a certain extent, so that the nitrate leaching into deeper soil horizons is not so intensive. Perlite application to soil favorably affects the environment by preventing the leakage of mineral nutrients (especially nitrogen) in to groundwater and increasing the efficiency of nutrients occurring in soil, and it does not negatively affect the quality of the cultivated products. It is fair to say that natural perlite plays a positive role in plant nutrition.

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