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Use of Pyrophyllite as Soil Conditioner in Lettuce Production

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ABSTRACT

In recent years, there has been an increasing interest in the possibility of the use of aluminosilicate minerals in order to maintain and improve soil productivity. The unique ion-exchange and adsorption properties of pyrophyllite minerals indicate the possibility of its application in agriculture as soil conditioner. The aim of this study was to evaluate whether the application of pyrophyllite could reduce the use of mineral fertilizers in lettuce production without adverse effects on its yield and quality. The experiment was carried out from November 2018 to April 2019 inside a polyethylene covered greenhouse in Gornji Moranjci, Bosnia and Herzegovina. The following quality parameters were analysed using standard methods: ascorbic acid content, total phenolic content, total antioxidant capacity and content of potentially toxic heavy metals (Cr, Pb, Ni, Cu, Zn and Mn) in lettuce. The results of this study showed that the substitution of fertilizers with pyrophyllite in amount of 25% and 50% of recommended fertilizer rate under experimental conditions increase lettuce yield and total antioxidant capacity compared to the control treatment, i.e. 100% recommended fertilizer rate. The results of this study also support the hypothesis that pyrophyllite could be used as remediation material in polluted soils by heavy metals. However, further investigation is necessary to confirm these hypotheses across different soil ecosystems.

INTRODUCTION

Applying fertilizer in agricultural production has shown a steady increase in recent decades, resulting in the gradual soil degradation. The numerous other processes, such as nutrient depletion, leaching and pollution of soils by hazardous substances from industry have also contributed to the soil degradation (Lal 2015). Although the soil degradation is a worldwide phenomenon, it is fact that is in most developing countries the phenomenon is being hastened by land use mismanagement. Better use of soil resources through optimizing fertilization, increasing biodiversity and improving soil quality has therefore been considered as a priority for achieving sustainable agriculture (Gomiero 2016).

In recent years, there is an increasing interest for using of natural aluminosilicates in order to maintain and improve soil productivity. Clay minerals, e.g. zeolite and bentonite are known to have ability to increase soil capacity to hold available forms of nutrients (Ghazavi 2015, Jakkula & Wani 2018). Contrary to zeolite and bentonite, pyrophyllite application in agriculture is not substantially present due to its lower availability and insufficient knowledge of its potential use in agriculture.

Pyrophyllite is a dioctahedral 2:1 clay mineral with the chemical formula $Al_2Si_4O_{10}(OH)_2$. It resembles closely with talc and the only difference between them is that talc contains Mg^{2+} instead Al^{3+} in octahedral positions. The elementary sheet of pyrophyllite is composed by aluminium-oxygen/hydroxyl octahedra between two layers of silicon-oxygen tetrahedra. The basal surfaces of this elementary sheet do not contain hydroxyl groups, which explains the hydrophobicity of pyrophyllite (Drits et al. 2012).

Resemblance to the structure with talc and some other clay minerals indicate that pyrophyllite application in soil could also be effective in increasing soil's ability to hold nutrients and thus reducing leaching. The fact that pyrophyllite is used in the agriculture industry as a carrier for fertilizers and pesticides supports this hypothesis.

The present study was conducted to evaluate whether the application of pyrophyllite can reduce the use of mineral fertilizers in lettuce production without adverse effects on its yield and quality. If that is possible, the additional aim of this study was to determine the optimal ratio between fertilizer and pyrophyllite in order to achieve this purpose. Lettuce was selected as the subject of this study, primarily because the production of this vegetable is consistently increasing in this country and therefore any effort to improve lettuce production is of great interest for both the producer and the consumer.

MATERIALS AND METHODS

Aluminosilicate minerals (pyrophyllite): The pyrophyllite materials used in this study were obtained by grinding and sieving pyrophyllite ore from deposits in Parsovići-Konjic, Bosnia and Herzegovina and characterized by following properties: alkaline, hydrophobic material, very soft and white to grey in colour. The hardness on the Mohs' scale is 1.5 and cation exchange capacity (CEC) ranges between 50 and 70 meq/100g. Median total SiO_2, Al_2O_3, K, Ca, Mg, Cu, Ni, Zn, Co, Mn, Pb and Cr contents were 67.55%, 19.10%, 0.3%, 6.65%, 0.14%, 1.40 mg/kg, 2.74 mg/kg, 25.68 mg/kg, 0.4 mg/kg, 93.14 mg/kg, 7.97 mg/kg and 0.76 mg/kg, respectively. The above-mentioned results of pyrophyllite chemical analysis were obtained at Faculty of Agriculture and Food Sciences University of Sarajevo.

Lettuce (*Lactuca sativa* L. var. *shangore*): This lettuce is one of the favourite butterhead lettuce varieties in Bosnia for producers as well as consumers. It is cultivated from late autumn to spring in greenhouses and its vegetation period ranges from 45 to 50 days after planting in a heated greenhouse. This lettuce is adaptable to most soil types, it has green leaves and form tight and heavy heads, more than 0.3 kg. It grows fast and keeps the leaves out upright.

Study area: The experiment was carried out from November 2018 to April 2019 inside a polyethylene covered greenhouse in Gornji Moranjci, Srebrenik Municipality, Bosnia and Herzegovina (44°41′N, 18°26′E and altitude 275 m). The length, width, eaves height and ridge height of the experimental greenhouse were 50 m, 8 m, 2.2 m and 3.7 m, respectively. Humidity regulation in greenhouse was achieved by opening of two side roll-up vents while the row cover was used to protect the lettuce against frosts. The climate in studied area is classified as Cfb by Köppen and Geiger climate classification (Rubel & Kottek 2010). The annual mean air temperature is 11.1°C and precipitation 856 mm with significant rainfall even in the dry months. The soil of the experimental site is classified as Dystric Cambisol, according to FAO Soil Classification (FAO 2014). This type of soil is characterized by an ochric (Aoh horizon) or umbric (Aum horizon), which lies directly above the cambic horizon (B)v horizon, acidic reaction, base saturation less than 50%, low to moderate water storage capacity and a medium nutrient storage capacity.

Soil pH in KCl, organic matter, available phosphorus (P_2O_5) and potassium (K_2O) contents in the 0-30 cm studied soil layer before lettuce planting were 5.1, 3.83%, 15.1 mg/100g and 31.3 mg/100g, respectively. Median total Cr, Pb, Ni, Cu and Zn contents were 128.48 mg/kg, 17.68 mg/kg, 104.55 mg/kg, 15.76 mg/kg and 36.95 mg/kg, respectively. In accordance with results of soil chemical analysis and nutrient needs of lettuce, the following fertilization recommendation was given: 300 kg/ha NPK 7:20:30 (nitrogen-phosphorus-potassium) as part of the basic fertilization and if necessary 100 kg/ha KAN (calcium ammonium nitrate) as part of fertilization during vegetation (recommended fertilizer rate was recalculated based on plot area).

Experimental design and treatments: The experimental area in greenhouse was divided into twenty-one equal plots. Each plot had an area of 5 m^2. The experiment was laid out in randomized complete block design with seven treatments in three replications. Experiment treatments (T) were as follows:

T1 - recommended fertilizer rate (RFR) without pyrophyllite (PP), i.e. control treatment (150 g NPK 7:20:30 at each plot)

T2 - 25% of RFR was replaced with PP particle size 3 mm (112.5 g NPK 7:20:30 + 37.5 g PP)

T3 - 25% of RFR was replaced with PP particle size 0.1 mm (112.5 g NPK 7:20:30 + 37.5 g PP)

T4 - 50% of RFR was replaced with PP particle size 3 mm (75 g NPK 7:20:30 + 75 g PP)

T5 - 50% of RFR was replaced with PP particle size 0.1 mm (75 g NPK 7:20:30 + 75 g PP)

T6 - 75% of RFR was replaced with PP particle size 3 mm (37.5 g NPK 7:20:30 + 112.5 g PP)

T7 - 75% of RFR was replaced with PP particle size 0.1 mm (37.5 g NPK 7:20:30 + 112.5 g PP)

Fertilizers and pyrophyllite material in the all experimental plots were applied two weeks before planting lettuce (7 December 2019). No other fertilizers were added during the lettuce vegetation. All other agrotechnical measures needed for optimum lettuce growth (pest control measures, irrigation) were performed identically on all experimental plots until the time of lettuce technological maturity.

Analysis of lettuce yield and quality: All lettuce plants in the experiment area were harvested at the same time (31 March 2019). Average yield was determined as the average fresh harvest weight per m^2.

Lettuce nutritional quality was analysed by detecting the following parameters: ascorbic acid content, total phenolic content, total antioxidant capacity and content of potentially toxic heavy metals (Cr, Pb, Ni, Cu, Zn and Mn). Ascorbic acid (AA) was estimated by 2,6-dichlorophenolindophenol titration method (AOAC 2006). Lettuce extract for estimation of total phenolics, total flavonoids and total antioxidant capacity was prepared by macerating of lettuce powder (1 g) in 30% ethanol for 6 hours. Thereafter, the extract was filtered. Total phenolic content (TPC) was estimated by the Folin-Ciocalteu method (Ough & Amerine 1988) and total antioxidant capacity (TAC) by ferric reducing antioxidant power (FRAP) assay (Benzie & Strain 1996).

Extraction of heavy metals from lettuce powder was performed using HNO_3-H_2SO_4 solution (Lisjak et al. 2009) as follows: 1 g of lettuce powder was placed into 100 mL round bottom flask and then 10 mL 65% HNO_3 and 4 mL 95-98% H_2SO_4 were added. The reaction mixture in flask was covered with a watch glass, allowed to stand for few hours and then heated gently on a hot plate for 30 min. Thereafter, the flask with reaction mixture was allowed to cool to room temperature, filtered through quantitative filter paper into 50 mL flask and diluted to the mark with distilled water. The content of Cr, Pb, Ni, Cu, Zn and Mn in obtained extract was determined by atomic absorption spectrophotometry on AA-7000 Shimadzu, according to method ISO 11047 (ISO 1998). Standard solutions of the examined heavy metals were prepared by appropriate dilution of stock standards (Merck) with deionized water.

Statistic data processing: All the experimental measurements were made in triplicate and the results were expressed as mean ± standard deviation. Analysis of variance (ANOVA) was performed using Microsoft Excel 2013 software program, and the significant differences between the variants were determined using Least Significant Differences test at 0.05 level of probability ($P \leq 0.05$).

RESULTS

The results of the analysis of yield and some quality parameters of lettuce depending on the experimental treatment are given in Table 1.

As presented in Table 1, the partial replacement of fertilizer by pyrophyllite did not negatively affect the yield and quality compared to the control treatment. Moreover, the yield and examined lettuce quality parameters were mainly higher in the treatment where the pyrophyllite was applied as a replacement for a part of the fertilizer. The highest yield was obtained in treatment 2 and 3 where pyrophyllite was applied as a replacement for 25% of recommended fertilizer rate. The data in Table 1 also indicate that all treatments with pyrophyllite increase the antioxidant capacity of lettuce, especially where pyrophyllite (particle size 0.1 mm) was applied as a replacement for 75% of recommended fertilizer rate.

Heavy metal contents (Zn, Cu, Mn, Ni, Cr, Pb) in the plant samples depending on the experimental treatment are presented in Table 2. Presented data have shown that the content of Zn, Cu, Ni, Cr and Pb in lettuce was below the maximum permissible value of heavy metals in food crops reported by FAO/WHO (2001). Accordingly, the maximum permissible value for Zn, Cu, Ni and Cr is 100 mg/kg, 40 mg/kg, 4 mg/kg and 2.3 mg/kg on dry weight basis, respectively. Upper limits of Pb in edible products is regulated by EU Legislation (2011). Accordingly, Pb threshold limit for lettuce is 3.6 mg/g on dry mass basis.

DISCUSSION

The results of this study showed that the substitution of fertilizers with pyrophyllite in amount of 25% and 50% of recommended fertilizer rate increase lettuce yield compared to the yield achieved in the control treatment, i.e. 100% NPK recommended rate. Only the treatments where the pyrophyllite was applied as a replacement for 75% of recommended fertilizer rate did not show a positive effect on lettuce yield. The above-mentioned results indicate that pyrophyllite may increase soil's ability to hold and slow release of nutrients, thus preventing fertilizer leaching. Consistently, the inclusion of the pyrophyllite in fertilizer management can play a significant role in food crops production as a soil conditioner for improving fertilizer efficiency.

Mukherjee (2013) noted that the increase in crop yield due to the pyrophyllite addition in soil is result of its ability to release the tightly bound phosphates already existing in the soil making them available for plants. At the same time, pyrophyllite contains certain amounts of potassium, calcium, magnesium and iron, contributing significantly to the plant growth and development.

The results of this study also showed that treatments with pyrophyllite, to a greater or lesser extent, increase the content of phenolics and antioxidant capacity of lettuce, especially where pyrophyllite (particle size 0.1 mm) was applied as a replacement for 75% of recommended fertilizer rate. We assume that the lettuce in treatments where pyrophyllite was applied as a partial replacement for fertilizer had a lower amount of available nutrients in the soil resulting in its temporary stress, and consequently in higher synthesis of phenolics and other antioxidants. Relationship between treatment with pyrophyllite and ascorbic acid content in lettuce in the present study was not observed.

Table 1: Yield, ascorbic acid content (AA), total phenolic content (TPC) and total antioxidant capacity (TAC) in lettuce.

Treatment^1	Yield (kg/m^2)	AA (mg/100 g)	TPC (mg/100 g)	TAC µmol Fe^{2+}/100 g
T$_1$	7.00 ± 1.47^{d}	12.88 ± 8.31	6.13 ± 13.61^{d}	109.47 ± 76.93^{c}
T$_2$	9.57 ± 1.28^{ab}	15.97 ± 8.31	18.46 ± 29.13^{bc}	188.84 ± 195.69^{bc}
T$_3$	9.74 ± 0.50^{a}	12.28 ± 4.75	30.56 ± 8.84^{ab}	263.78 ± 241.65^{ab}
T$_4$	9.08 ± 1.31^{abc}	15.89 ± 8.31	8.05 ± 5.85^{d}	157.77 ± 103.25^{bc}
T$_5$	7.46 ± 1.65^{d}	14.58 ± 4.26	9.93 ± 3.63^{d}	182.50 ± 50.35^{bc}
T$_6$	6.82 ± 2.62^{d}	12.20 ± 7.32	8.24 ± 4.49^{d}	145.07 ± 154.71^{bc}
T$_7$	6.86 ± 0.14^{d}	13.88 ± 8.31	39.00 ± 17.77^{a}	365.80 ± 166.83^{a}
LSD$_{0.05}$	1.34	-	13.52	125.57

* Means denoted by the same letter indicate no significant difference ($P \leq 0.05$)

[1] Experimental treatment: T$_1$ - recommended fertilizer rate (RFR) without pyrophyllite (PP), i.e. control treatment; T$_2$ - 25% of RFR was replaced with PP (3 mm); T$_3$ - 25% of RFR was replaced with PP (0.1 mm); T$_4$ - 50% of RFR was replaced with PP (3 mm); T$_5$ - 50% of RFR was replaced with PP (0.1 mm); T$_6$ - 75% of RFR was replaced with PP (3 mm); T$_7$ - 75% of RFR was replaced with PP (0.1 mm)

Table 2: Heavy metal contents in lettuce (mg/kg dry mass).

Treatment^1	Zn	Cu	Ni	Cr	Pb
T$_1$	74.2 ± 14.2^{abcd}	3.71 ± 0.7^{a}	1.88 ± 0.6	2.0 ± 1.2	3.28 ± 1.4^{a}
T$_2$	78.4 ± 9.1^{a}	3.39 ± 0.9^{abc}	1.39 ± 0.8	1.9 ± 1.1	3.23 ± 2.8^{ab}
T$_3$	58.0 ± 13.2^{e}	3.69 ± 0.9^{ab}	1.22 ± 0.4	2.5 ± 1.5	2.55 ± 0.2^{abc}
T$_4$	76.6 ± 11.4^{abc}	3.32 ± 1.2^{abcd}	1.51 ± 0.2	1.9 ± 0.4	2.0 ± 0.9^{abcd}
T$_5$	77.8 ± 11.5^{ab}	3.3 ± 0.5^{abcde}	1.69 ± 0.6	1.2 ± 0.4	2.0 ± 1.9^{abcde}
T$_6$	51.3 ± 12.1^{ef}	2.7 ± 0.7^{cdef}	1.12 ± 0.2	2.2 ± 0.8	0.77 ± 1.2^{def}
T$_7$	42.4 ± 15.2^{f}	2.2 ± 1.3^{f}	1.41 ± 1.3	1.6 ± 0.3	0.46 ± 0.1^{f}
LSD$_{0.05}$	11.81	0.91	-	-	1.34

* Means denoted by the same letter indicate no significant difference ($P \leq 0.05$)

[1] Experimental treatment: T$_1$ - recommended fertilizer rate (RFR) without pyrophyllite (PP), i.e. control treatment; T$_2$ - 25% of RFR was replaced with PP (3 mm); T$_3$ - 25% of RFR was replaced with PP (0.1 mm); T$_4$ - 50% of RFR was replaced with PP (3 mm); T$_5$ - 50% of RFR was replaced with PP (0.1 mm); T$_6$ - 75% of RFR was replaced with PP (3 mm); T$_7$ - 75% of RFR was replaced with PP (0.1 mm)

Another important effect of pyrophyllite is related to the removal of toxic heavy metals from soil (Prasad & Saxena 2008) and results of the present study support this hypothesis. Namely, the content of all examined heavy metals in lettuce in treatments with pyrophyllite was lower compared to the content of heavy metals in lettuce obtained in the control treatment. These differences between treatments were not only significant for the content of Cr and Ni in lettuce. We assume that the reason for that was the high content of Cr and Ni in the studied soil and therefore the amount of applied pyrophyllite was not adequate to significantly reduce mobility of Cr and Ni in the soil and thus their availability to plants. Namely, the average content of Ni and Cr in studied soil was 104.55 mg/kg and 128.48 mg/kg, respectively. These values greatly exceeded the limit value prescribed by legislation in Bosnia and Herzegovina (Official Gazette of FBIH 2009) or by legislation in some European countries (Pérez et al. 2002). Accordingly, the maximum permissible value for Ni and Cr in soil is 40 mg/kg and 100 mg/kg, respectively.

Many scientists agree that the ability of clay minerals to decrease the mobility of heavy metals in soils is the result of adsorption of heavy metals in their interlayers or on its surface areas (Ijagbemi et al. 2009, Khan & Singh 2010, Ararem et al. 2011, Demirkiran et al. 2016) but this adsorption mechanism is still not fully understood. Some clay minerals that have high cation exchange capacity, i.e. montmorillonite and bentonite in principle achieve this effect through ion exchange reaction (Önal 2007, Wigger & Loon 2017). The cation exchange capacity for pyrophyllite is lower, but not its efficiency in removing heavy metals from the soil, and results of many studies confirm this hypothesis (Scheidegger et al. 1996, Caporale & Vioalante 2016, Uddin 2017). Bergaya et al. (2006) reported that pyrophyllite has ability to easily disperse in water due to weak van der Waals bounds, resulting in less clumping. This dispersing property allows higher exposure area for pyrophyllite in soil and therefore more heavy metals or other pollutants could potentially be absorbed and thus neutralized. Furthermore, pyrophyllite contributes to the increase of soil pH, resulting in lower mobility and thus the availability of heavy metals for plant.

In general, the results of this study indicate that the application of pyrophyllite under experimental conditions can reduce the use of mineral fertilizers in lettuce production without adverse effects on its yield and quality, especially where the pyrophyllite is applied in the amount of 25% of recommended fertilizer rate. The results of this study also support the hypothesis that pyrophyllite could be used as the resort to help clean up the soils from the damage caused by heavy metal pollution.

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