MINERAL COMPOSITION OF POTTED CABBAGE (*BRASSICA OLERACEA* VAR. *CAPITATA* L.) GROWN IN ZEOLITE AMENDED SANDY SOIL

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Sindesi, O.A., Lewu, M.N., Ncube, B., Mulidzi, R. and Lewu, F. (2021). Mineral composition of potted cabbage (*Brassica oleracea* var. *capitata* L.) grown in zeolite amended sandy soil. *Agriculture (Pol'nohospodárstvo)*, 67(3), 103 – 112.

Vegetables are essential components in human diets because they are rich in vitamins, minerals, and dietary fibre. There is a growing interest in human nutrition enhancement through vegetable consumption to reduce micro mineral deficiencies, especially in households with low buying power. A greenhouse pot experiment was conducted to evaluate the effect of zeolite amendment on the mineral composition of cabbage (*Brassica oleracea* var. *capitata* L.), in relation to the soil chemical status. The experiment was carried out over two growing seasons (winter/spring) of 2018 and 2019. The treatments were in the ratios of 0:10, 1:9, 2:8, 3:7 zeolite to sandy soil, on a weight-to-weight basis. Zeolite improved soil chemical status ($p < 0.05$), except for soil iron (Fe) and phosphorus (P) contents. There was also a general improvement of macro minerals in cabbage with increased zeolite application, especially in the second season. Zeolite did not improve the micronutrients of the vegetable. This indicates that cabbage planted under zeolite amended soils provides no additional contribution to the fight against micronutrient deficiencies. However, zeolite showed potential for soil conditioning in soil macronutrients and soil pH.

Key words: cabbage, zeolite, soil conditioner, soil amendment, soil fertility

Fruits and vegetables are essential in human diets due to their nutritional value arising from high mineral, vitamin, and dietary fibre content (Cvetković *et al.* 2019). Diets high in fruits and vegetables have been associated with reduced risks of numerous chronic diseases, including cancer and cardiovascular diseases, and maintaining healthy body weight. Nutrient content and total nutritional benefits of fruits and vegetables depend on the crop cultivar, agricultural production practices, and ripening stage

(Cvetković *et al.* 2019). There is an interest in the nutritional enhancement of highly utilised vegetables, especially, using them to reduce micro mineral deficiencies in humans (Mzoughi *et al.* 2019).

Micro mineral deficiency is a widespread public health problem. It is the result of the low bioactivity of trace minerals, particularly iron (Fe) in the daily diet (Tulchinsky 2010). Micro mineral deficiencies have been combated by increasing dietary plant varieties in diets (Mzoughi *et al.* 2019). However, in

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poor households, buying power is limited to a few products at a time (Headey & Martin 2016).

Increasing the nutritional contents of vegetables with agricultural practices is one of the ways of improving the micronutrient contents in food crops (Bernacchia *et al.* 2016). This can be through the manipulation of factors governing soil nutrient availability. Soil pH is part of the main factors that govern the solubility and bioavailability of soil elements leading to the accumulation of nutrients in plants (Clemente *et al.* 2005). Other factors include soil physical, chemical, and biological properties, as they condition plant growth and survival in soil (Bernacchia *et al.* 2016).

Amendments such as zeolite have shown the potential to mitigate soil acidity and improve soil physiological and chemical properties (de Campos Bernardi *et al.* 2013; Ramesh *et al.* 2015). Zeolites are aluminosilicate minerals (Gül *et al.* 2005), that are alkaline, porous structured, with a high cation exchange capacity (CEC), and great affinity for ammonium (NH_4^+) cations (He *et al.* 2002; Ahmed *et al.* 2008). Zeolite applicability to agriculture has been linked to its (i) high cation exchange; (ii) high water-holding capacity and (iii) high absorption capacity (de Campos Bernardi *et al.* 2013). In heavy metal contaminated soils, zeolite has been shown to reduce their bioavailability due to their negative charge (Garau *et al.* 2007). Heavy metals are not easily biodegradable and persist in soils for long periods (Garau *et al.* 2007; Ramesh & Reddy 2011) and their competitiveness in soils may account for the unavailability of some of the essential plant micronutrients. Zeolite accelerates the soil natural reactions which reduce mobility and bioavailability of heavy metals to plants (Madejón *et al.* 2006).

The impact of zeolite on plant growth, yield, and crop mineral composition has been investigated in other studies (Gül *et al.* 2005; Ahmed *et al.* 2008; Eshghi *et al.* 2010; Ramesh & Reddy 2011; Zbahce *et al.* 2015; Ramesh *et al.* 2015; Hazrati *et al.* 2017). However, zeolite use for crop production has not received much interest, especially in South Africa. There is limited information on the impact of zeolite on the mineral composition of vegetables such as cabbage (*Brassica oleracea* var. *capitata* L.), which is a major part of the South African diet (Afolayan & Jimoh 2009; Bvenura & Afolayan 2015). This

study aimed to evaluate the effect of zeolite on the mineral composition of cabbage, in relation to soil chemical status.

MATERIAL AND METHODS

Experimental site and treatment details

A greenhouse pot experiment was conducted at the Agricultural Research Council (ARC) Infruitec-Nietvoorbij, Stellenbosch, South Africa (33.914476° S and 18.861322° E). Six-week-old cabbage (cv. Copenhagen) seedlings were transplanted into potted zeolite amended sandy soil and studied over two growing seasons (winter/spring, 2018 and 2019). The treatments were: 0% zeolite + 100% sandy soil, 10% zeolite + 90% sandy soil, 20% zeolite + 80% sandy soil and 30% zeolite + 70% sandy soil (i.e. ratios of 0:10, 1:9, 2:8, 3:7 zeolite to sandy soil) on a weight by weight basis. Treatments were replicated 6 times and arranged in a randomized complete block design. The total weight of soil or soil and zeolite per pot was 12 kg. Urea (46% N) and single-super phosphate (20% P) was applied to all pots at a rate of 1.17 and 3 g/pot respectively, while potassium chloride (50% K) was applied at 1.92 g/pot before transplanting. Additionally, a urea side-dress of 1.11 g/pot was applied in split applications at 3 and 6 weeks after transplanting (WAT). Seedlings were planted at one seedling per pot into 30 cm diameter and depth plastic pots. Soil water content was regularly monitored gravimetrically and through the weighing of pots. Irrigation water was maintained above 50% field capacity (FC) throughout the study.

Weeds were manually removed while insect pests were controlled with Makhro Cyper® (active ingredient: cypermethrin, 200 g/L), using 1 mL in 10 L of water in the first growing season. In the second growing season, Avi Gard Mercaptothion® (active ingredient Organophosphate 500 g/L) was used to control pests at a rate of 15 mL of chemical to 10 L of water. The pesticide had to be changed because the pests appeared to develop immunity against the first pesticide.

Harvesting and sample processing

Harvesting was done 126 days after transplant-

ing (DAT), by cutting the stem close to the head. The head was then chopped into small pieces and oven-dried at 70°C in a forced-air oven till constant weight. Dry samples were separately milled using the Polymix PX-MFC, 90D miller manufactured by Kinemanetika AG, Switzerland. The milled samples were placed in well labelled airtight containers and later stored in the refrigerator before mineral analysis.

Plant tissue analysis

To determine the mineral element composition, the plant samples were dry-ashed in a muffle furnace at 500°C for 6 hr and extracted using hydrochloric acid for total acid digestion in the determination of phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), manganese (Mn), iron (Fe), copper (Cu) and zinc (Zn).

Soil chemical analysis

Standard baseline soil chemical analysis was carried out before the application of treatments and again at harvest (for both seasons) using the standard procedures of the Non-affiliated Soil Analysis Work Committee (1990). Total available P, K, and soil pH were determined using ICP-OES Bray II, Tetraphenylboron, and Potassium Chloride (KCl) methods respectively. Soil exchangeable Ca, Mg, and Na were extracted using 1.0 N ammonium acetate while Fe, Cu, Mn, and Zn were determined by the EDTA (ethylene diamine tetraacetic acid) titration method. All reagents used for chemical analysis were of analytical grade.

Statistical analysis

Data were subjected to analysis of variance (ANOVA) using SAS (version 9.4, SAS Institute Inc., Cary, NC, USA, 2000). ANOVA was done per season, using SAS statistical software. Results of both seasons were also combined and investigated in one overall ANOVA after testing for season homogeneity of variance using Levene's test. The Shapiro-Wilk test was performed to test for deviation from normality. Fisher's least significant difference was calculated at the 5% level to compare treatment means. A probability level of 5% was considered significant for all tests.

RESULTS AND DISCUSSION

Table 1 presents the soil baseline chemical properties at the commencement of the study while the composition and characteristics of zeolite used as a soil amendment in this study are presented in Table 2.

Cabbage macro mineral contents in relation to soil nutrient availability and zeolite application

The macronutrient contents of the cabbage head evaluated in this study are presented in Figure 1. In the second season of the study, the level of P in cabbage heads generally increased ($p < 0.05$) with the increase in soil zeolite application, unlike in the first growing season where there was no significant difference. Cabbage P contents in the first season were consistent with the findings of (Pasković *et al.* 2013) where there was no significant difference in P with zeolite application. However, the second season's results followed the trend also observed by (Zheng *et al.* 2019) on rice grown under zeolite application.

In relation to soil P (Figure 2), P contents in the soil did not follow the trend observed in cabbage P. In both seasons, soil P significantly decreased ($p < 0.05$) with the increase in zeolite application (Figure 2). Soil P in this study was in contrast with

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Soil baseline chemical properties

Soil parameter	Value
pH _(KCl)	5.4
[mg/kg]	
Phosphorus (P)	47.0
Potassium (K)	47.0
Iron (Fe)	362.0
Zinc (Zn)	6.2
Manganese (Mn)	24.2
Copper (Cu)	0.4
Exchangeable cations [cmol/kg]	
Calcium (Ca)	5.83
Magnesium (Mg)	0.39
Sodium (Na)	0.11

KCl – pH measured in potassium chloride solution.

the findings of previous studies (Ozbahce *et al.* 2015, 2018; Zheng *et al.* 2019) who all found soil P to increase with increased zeolite application. Soil P is hypothetically made available by the application of zeolite, as reactive products such as Ca^{2+} and H_2PO_4^- move into zeolites exchangeable sites thereby allowing for more P rock dissolution, making P to be readily available for plant assimilation (Nur Aainaa *et al.* 2018; Zheng *et al.* 2019). Soil P can be stored in the soil by adsorption, organic matter, soil solution, microbial biomass, etc. Soil P in the first season decreased even while there was no increase in cabbage P uptake, unlike in the second season

where cabbage P increased thereby decreasing soil P content after plant uptake.

In both growing seasons, cabbage grown on zeolite amended soil had higher levels of K and Na ($p < 0.05$) (Figure 1). The observed increase in K content in the cabbage head was in line with previous research findings (Gül *et al.* 2005), which found that zeolite as a soil conditioner was able to increase the content of both N and K in the plant tissue of crisp-head lettuce. The effect of zeolite on cabbage K content was however contradictory to other findings (Pasković *et al.* 2013) that found no significant difference in K of chicory cultivated under different

Figure 1. Cabbage macro mineral response to zeolite application (a–e). Bars with the same letters show no significance at $p < 0.05$. Note: P – phosphorus; K – potassium; Ca – calcium; Mg – magnesium; Na – sodium.

levels of zeolite. However, soil K and Na increased with an increase in zeolite application in both seasons (Figure 2). The increase may be attributed to the 2.3% Na₂O and 1.7% K₂O in the zeolite composition (Table 2). Additionally, the soil K increase can also be associated with zeolites affinity towards K⁺ cations (de Campos Bernardi *et al.* 2013; Ozbahce *et al.* 2018).

On the other hand, cabbage Ca and Mg content showed interchanging trends within the two seasons (Figure 1). In the first growing season, the amount of mineral Ca in the cabbage head reduced ($p < 0.05$) with the application of zeolite. However, in the second season, there was no significant difference in Ca levels on both zeolite amended sandy soils and the control ($p > 0.05$), which is probably due to the residual effect of zeolite. Cabbage Mg content was also not affected ($p > 0.05$) in both growing seasons except for the observed drop that was recorded in

the non-amended sandy soil in the second season ($p < 0.05$). Soil exchangeable Ca and Mg generally increased ($p < 0.05$) with zeolite application (Figure 2). Nevertheless, there was less Mg in the soil in all treatments at the end of the second season compared to the Mg levels at the end of the first season. The increase in the exchangeable Ca and Mg (Figure 3) with the increase in zeolite application may be due to zeolite cation exchange capacity (CEC) and improved soil pH (Ramesh & Reddy 2011).

The cabbage Ca, Mg, and K contents in this study were similar to previous findings (Pasković *et al.* 2013), although their results showed a non-significant increase (Mg and K) in chicory leaves with a decrease in Ca as a result of zeolite application. In another study (Gül *et al.* 2005) the contents of Ca and Mg were relatively low in crisp-head lettuce that was cultivated under zeolite than those cultivated under perlite. The results of this study were also similar to others where there were no significant differences in Ca and Mg contents in beans grown using different zeolite levels (Ozbahce *et al.* 2018). This was attributed to high soil pH and excessive soil P. The Ca²⁺ cations moved to zeolite exchangeable sites which allowed more P availability while Ca became limited to plants (Nur Aainaa *et al.* 2018; Ozbahce *et al.* 2015; Zheng *et al.* 2019) and low solubility and mobility in soils, especially under water stress. Available soil P and plant P uptake could be improved through the application of zeolite. However, little is known about the impact of zeolite on P uptake in rice under water stress. A two-year lysimetric experiment using a split-split plot design investigated the effects of zeolite (0 or 15 t/ha). Cabbage Ca contents generally decreased in the first season while soil exchangeable Ca increased. High levels of Ca in soils have been proven to reduce the absorption of Mg and K in soils (Pasković *et al.* 2013), which was observed for K in this study. The increasing availability of these nutrients (Ca, Mg and K) in soil aligns with the increase in zeolite application in this study. These findings are in line with those obtained by other studies (Ozbahce *et al.* 2015; Ramesh & Reddy 2011) who established that the application of zeolite to soil increased the availability of Ca, Mg, and K.

T a b l e 2
Zeolite characteristics

Physical properties	Description
Colour	White to grey
Appearance	Granules
pH (30 g in 60 mL water)	8
Cation exchange capacity [mg/kg]	16
Water adsorption (on sinter plate)	400%
Chemical property	Typical [%]
Silicon dioxide (SiO ₂)	64.3
Aluminium oxide (Al ₂ O ₃)	12.7
Titanium dioxide (TiO ₂)	0.1
Magnesium oxide (MgO)	1.3
Sodium oxide (Na ₂ O)	2.3
Iron (III) oxide (Fe ₂ O ₃)	1.3
Calcium oxide (CaO)	1.2
Potassium oxide (K ₂ O)	1.7
Loss on ignition	8.4
Mineralogy	Approximate
Clinoptilolite [%]	>90
Quartz [%]	<5

The response of soil trace elements and pH to zeolite application

Zeolite has been reported to have the ability to increase soil pH, similar to agricultural lime (Ramesh *et al.* 2015; Tsadilas *et al.* 1997). The baseline soil pH of 5.4 (Table 1) was near vegetable critical acidic values. However, the soil pH increased significantly ($p < 0.05$) with the application of zeolite (Figure 3). This pH increase could be attributed to the alkaline nature, high CEC, and the negative charges of zeolite, which permit cation sorption (Nur Aainaa *et al.* 2018). This demonstrated the liming effect of zeolite in soils (Polat *et al.* 2004; Ramesh & Reddy 2011). Zeolite has also been shown to adsorb heavy metals into its cavities and channels and further block their

reception to plants by making the metal ions insoluble (de Campos Bernardi *et al.* 2013; Omar *et al.* 2011; Ramesh & Reddy 2011; Reháková *et al.* 2004). Much of this has been attributed to the CEC of zeolite which exchanges plant nutrients and sorb soil heavy metals while slowly releasing the nutrient (Ramesh & Reddy 2011), in addition to the alkalinity of zeolite which increases soil pH. The adsorption of metals in soil is generally directly proportional to soil pH, which also governs metal uptake by plants (Rieuwerts *et al.* 1998; Kukier *et al.* 2004; Fornes *et al.* 2009).

The soil micro minerals in this study responded differently to zeolite application between treatments and seasons (Figure 4). Soil Zn and Cu of the second

Figure 2. Effect of zeolite on soil macronutrients (a–e). Overlapping error bars show no significance at $p < 0.05$. Note: see Figure 1.

Figure 3. Effect of zeolite on soil pH. Overlapping error bars show no significance at $p < 0.05$. Note: KCl – see Table 1.

season, and Fe in both seasons generally decreased with zeolite application, whereas soil Zn and Cu (first season) and Mn (both seasons) increased even though the soil pH increased with zeolite. This was similar to findings of an earlier study (Tsadilas *et al.* 1997) which found that zeolite increased the sorption of the heavy metal Cd on soils and as a result, it became insoluble and unavailable for plant assimilation. However, the increase in soil Mn in both seasons and Zn (second season) was similar to previous findings (Ozbahce *et al.* 2018), where soil Zn and Mn increases were linked to the presence in the zeolite used as a soil amendment. However, this was not

the case for Fe. The applied zeolite contained Fe, but soil Fe was lower at the end of both growing seasons.

Micro mineral contents in cabbage head in response to zeolite application

All the micro minerals content of cabbage heads evaluated in this study were found to be at higher levels in the non-amended treatments, especially in the second season (Figure 5). Fe and Cu showed no significant difference ($p > 0.05$) in the first season among treatments while micro mineral Zn tended to decrease with increased zeolite application for both seasons. Similar to some previous studies (Reháková *et al.* 2004), zeolite resulted in a significant decrease in microelements in the cabbage plant tissues, except for Mn in the first growing season which had the highest content (30.83 mg/kg) in the 30% zeolite treatment.

Fe and Zn are essential micronutrients required for human growth and health. There is a widespread problem of these nutrient deficiencies among populations (Tulchinsky 2010; Kondaiah *et al.* 2019) but can be alleviated by supplementation and food fortification. Cross-sectional studies in humans showed positive association of serum zinc levels with hemoglobin and markers of iron status. Dietary restriction

Figure 4. Effect of zeolite on soil trace minerals (a–d). Overlapping error bars show no significance at $p < 0.05$.

of zinc or intestinal specific conditional knock out of ZIP4 (SLC39A4). Alleviation of these deficiencies is mostly through increased plant intake, so such plants with enhanced Fe and Zn contents are of high importance (Mzoughi *et al.* 2019). In previous studies (Jacobs 2011), increased zeolite application to the soil decreased Zn and Fe accumulation on *Hieracium aurantium* and *Rumex acetosella*. The results in the study were similar, as the highest concentrations of Fe and Zn were found in the non-amended treatments. Iron availability is dictated by the soil redox potential and soil pH, Fe is readily oxidised at high pH and is predominantly in the form of ferric oxides (Morrissey & Guerinot 2009). The accumulation of Fe on the cabbage grown under zeolite amended soil followed this trend and decreased with increased zeolite application which had increased soil pH. Zinc accumulation on the cabbage head was also highest on the non-amended treatment. Zinc assimilation by plants depends on the content and form of Zn, it further depends on the genetic characteristics of plants and soil chemical characteristics (Murtic *et al.* 2017). The accumulation of the micromineral in cabbage in relation to soil pH proved that heavy metals generally have low solubility at higher pH as they are normally present in their hydroxide forms

(Singh *et al.* 2016). In this study, zeolite application did not enhance micromineral accumulation in the cabbage heads. However, the potential environmental availability of heavy metals from contaminated soils may be controlled by soil amendments using exogenous zeolite.

CONCLUSIONS

Zeolite generally improved the soil chemical status of macrominerals and soil pH. The baseline soil pH of 5.4 was near the vegetable requirement for critical acidic values for growth. The soil pH increased significantly after the application of zeolite. However, there was a decrease in phosphorus. The cabbage content of macro minerals was similar under both the zeolite amended and non-amended treatments, except for sodium and potassium. Zeolite did not improve the micro mineral content of cabbage. Soil Fe and Mn also decreased compared to non-amended soils. Soil Zn and Cu of the second season, and Fe in both seasons generally decreased with an increase in zeolite application, whereas soil Zn and Cu (first season) and Mn (both seasons) increased even though the soil pH increased with ze-

Figure 5. Cabbage microminerals in response to zeolite application. Bars with the same letters show no significance at $p < 0.05$.

olite. This study showed that crops cultivated under zeolite can have some nutrient benefits for macro minerals. However, micromineral enhancement was not observed in this study. Further studies should explore the use of zeolite in combination with other nutrient sources that supply micronutrients.

Acknowledgement: The authors thank the National Research Foundation (NRF) [Grant number: 114405] of South Africa for financial support towards this research. Any opinion, findings and conclusions, or recommendations expressed in this article are those of the author(s), and that the NRF accepts no liability whatsoever in this regard.

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Received: April 22, 2021

Accepted: June 16, 2021