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Clinoptilolite Zeolite on Tropical Peat Soils Nutrient, Growth, Fruit Quality, and Yield of *Carica papaya* L. cv. Sekaki

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Received: 21 August 2020; Accepted: 1 September 2020; Published: 3 September 2020

Abstract: Papaya cultivation on nutrient deficient acidic peat soils causes poor growth, yield, and fruit quality of this crop. Alkalinity and the high affinity of clinoptilolite zeolite (CZ) for macronutrients could improve pH, nutrient availability, and papaya productivity on peat soils. A one-year field experiment was conducted to determine the effects of CZ on: (i) soil ammonium, nitrate, P, and K, and (ii) growth, yield, and fruit quality of papaya grown on a peat soil. Treatments evaluated were: (i) different amounts of CZ (25%, 50%, 70%, and 100% of the existing recommended rate of CZ) + NPK fertilizer, and (ii) NPK fertilizer alone. The peat soils with CZ improved pH, ammonium, nitrate, P, and K availability because of the sorption of these nutrients within the structured framework of the CZ. Co-applying CZ (70% to 100%) and NPK fertilizers improved the NPK contents in papaya leaves and the growth, yield, and fruit quality of papaya because of the significant availability of ammonium, nitrate, P, and K in the peat soil for their optimum uptake by the papaya plants. Ability of CZ to buffer the soil pH reduced the need for liming. It is possible to use CZ to improve papaya productivity because CZ can regulate nutrient availability.

Keywords: natural zeolite; nitrogen; organic soil; papaya; potassium; phosphorus

1. Introduction

In Southeast Asia, tropical peatlands cover approximately 27.1 million hectares [1], out of which 2.6 million hectares are located in Malaysia [2,3]. The peat soils in Malaysia constitute approximately 8% of the total land area of this country [4]. The peat soil is categorized as a marginal soil (Class 4) with severe limitations for crop cultivation because it requires careful agronomic management [5,6]. Tropical peat soil is formed through the accumulation of undecomposed and partially decomposed woody plant materials under waterlogged conditions [3,7]. Generally, tropical peat soil is an organic soil having a minimum of 50% to 65% organic matter but less than 35% mineral content, with a thickness of 40 to 50 cm within the first 100 cm of the soil surface [8–10].

In Malaysia, besides forestry, agriculture is the main economic activity on peatlands. At present, approximately 1.08 million hectares or 40.2% of peatland in the country have been developed for oil palm, pineapple, sago, rubber, coconut, and mixed horticulture [11–13]. However, only premium or cash crop commodities, particularly oil palm and pineapple, are largely cultivated on peat soils [4]. Fruit crops are planted on peat soils under mixed cropping systems. Fruit crops such as papaya, pineapple, banana, coconut, ciku, rambutan, and durian cultivate on peat soils, accounts for 16% of the total fruit agriculture area in Malaysia [4]. Agronomic challenges, particularly nutrient deficiency, high acidity, irreversible drying, low bearing capacity, and waterlogging conditions, are the main problems encountered by farmers in managing peat soils in Malaysia [4,14].

Papaya (*Carica papaya* L.) is one of the fruit crops which is extensively grown in the tropics and sub-tropics, not only because of the ease of its cultivation, but the cultivation of papaya on peat soils is economically rewarding or lucrative [15–18]. The papaya tree is a semi-woody and short-lived perennial herb that belongs to the family *Caricaceae* [19]. Although papayas can be grown on different soils and climatic conditions [17], papaya cultivation on peat soils remains a constraint to farmers because of nutrient deficiency, regular flooding, and poor root anchorage in peat soils [20–22]. These agronomic challenges need to be addressed to ensure productive papaya production. Papayas are also fast-growing plants that continuously produce fruits throughout the year, and because of this they require high regular nutrients supply [23].

Nitrogen, P, and K are required in sufficient quantities because these nutrients affect the physiology of papayas [24]. For example, optimum amounts of N and P are required during the early growth of papayas (from transplanting to pre-fruiting stages) to ensure optimum growth of foliage, trunks, and roots [25]. However, K level is increased at the fruiting stage of papaya plants because K is essential for improving their fruit quality, namely fruit sweetness and pulp thickness [26]. Conversely, P supply is reduced at the fruiting stage because unbalanced or excessive use of P decreases papaya fruit size [25]. The recommended fertilization rates for papayas at the early growth and fruiting stages are 15:15:15 ($N:P_2O_5:K_2O$) and 12:12:17:2 ($N:P_2O_5:K_2O:MgO$), respectively [25]. Thus, ensuring N, P, and K availability in tropical peat soils, in particular where the loss of these nutrients through leaching is high, it is essential to ensure optimum papaya growth and productivity through balanced use of fertilizers.

Nitrogen content is high in tropical peat soils, but it is mostly in organic forms [20,27]. Moreover, availability of inorganic N is low because of the slow N mineralization and acidity of peat soils [4,20,28]. Application of nitrogen-based fertilizers to peat soils has not been successful because of the high C/N ratio of peat soils. This results in N immobilization because soil microbes use inorganic N from N fertilizers for decomposition of organic matter before being utilized by plants [29]. Peat soils have low capacity to adsorb or absorb P because of their low clay contents and absence of iron and aluminium ions to form insoluble phosphate compounds [21,30]. Excessive fertilizer application leads to P leaching, particularly in high rainfall areas because of the low P retention capacity of peat soils [14].

Potassium is low in peat soils because humic compounds of these soils do not form coordination bonds with K ions [21] because the hydrogen ions are tightly bonded to the functional groups in humic compounds. Thus, they lack ion exchange properties [14]. The low clay content and mineral matter in peat soils contribute to low K fixation in peat soils, particularly those in the tropics [31]. Moreover, K is highly mobile and prone to leaching because a significant amount of available K is present in the soil solution [14,20].

Although papaya requires regular nutrient supply, it is not recommended to apply high amounts of N, P, and K fertilizers to build up N, P, and K ions in peat soils, including those in the tropics, because during high rainfall these plant nutrients will be leached. Therefore, there is a need for efficient synchronization of fertilization programmes and optimum uptake of nutrients by papaya plants for their growth and development on peat soils. With this approach, the polluting effects of the unbalanced and excessive use of fertilizers on the environmental quality could be avoided. Furthermore, to improve the nutrient holding capacity of peat soils, the temporary nutrient retention properties of zeolites such as clinoptilolite zeolite could be exploited in the fertilization regimes of papaya cultivation on peat soils.

Clinoptilolite zeolite is a naturally occurring hydrated zeolite mineral that is used in agriculture for different purposes [32]. Various studies have demonstrated the ability of CZ to improve soil physical and chemical properties on marginal soils, particularly acidic, sandy, and clayey soils [33–38]. These improvements include soil acidity, water holding capacity, nutrient retention, uptake and use efficiency of nitrogen, phosphorus, and potassium. It is reported that amending soils with CZ increased crop yields for barley, maize, rice, potatoes, wheat, strawberry, and sunflowers [32,39–43]. The effectiveness of CZ in improving soil and crop productivity can be attributed to its structure, which is formed from silica and alumina tetrahedral units with interconnected pores linked by shared oxygen atoms. This unique structure of CZ provides large internal microporous surface area for nutrient sorption (adsorption and desorption) via cation exchange [44–46] and nutrient entrapment in the cavities of CZ [37]. These characteristics of CZ enable it to sorb nutrients [47]. Although there are no regulations on the utilization of CZ as a soil amendment by the Department of Agriculture Malaysia, amending CZ with inorganic fertilizers on acid soils significantly minimized ammonia loss from urea, reduced nutrient leaching, improved soil chemical properties, nutrient uptake and use efficiency, and increased yields of lowland rice (cv. MR219) and maize (*Zea mays* L.) cultivation in Malaysia [48–51]. Moreover, the application of CZ effectively mitigated P fixation in acid soils besides reducing the need for chemical fertilizers, namely Egypt Rock Phosphate in maize cultivation [38,52,53]. Although the effectiveness of CZ in improving nutrient uptake and use efficiency of rice and maize cultivated on mineral acid soils is well documented [43,48,52–54], there is a dearth of information on amending organic soils, such as peat soils, with CZ to improve the response of papaya plants to N, P, and K fertilizers on drained tropical peat soils.

Eksotika, Sekaki, Subang, and Solo are among the popular papaya varieties which are cultivated in Malaysia [55]. Sekaki is mostly cultivated for domestic consumption because of its larger fruit size, but it is also an important cultivar for export [16,56]. Papaya production in Malaysia was estimated at 88,480 metric tons in 2018 on a total area of 3267 hectares [11]. The export value for this production is approximately US $23.4 to 28 million annually [19], suggesting the contribution of the papaya industry to the economy of Malaysia especially the livelihood of papaya growers cannot be overlooked. Thus, there is a need to improve the fertility of peat soils on which this cash crop is grown.

To this end, the first objective of this study was to determine the effects of CZ on exchangeable ammonium, available nitrate, available P, and exchangeable K availability in a peat soil which is cultivated with papaya. The second objective of the study was to determine the effects of CZ on papaya leaf N, P, and K contents, growth, fresh fruit yield, and quality of papaya fruits. In this present study, we hypothesized that CZ will increase exchangeable ammonium, available nitrate, available P, and exchangeable K in peat soils to ensure their optimum uptake and use efficiency. This hypothesis is based on the assumption that CZ's unique structure and high cation exchange capacity will enable timely sorption and desorption of nutrients, particularly N, P, and K ions. Additionally, the CZ is expected to increase papaya fresh yield and fruit quality through improved N, P, and K uptake. This assumption is also based on the fact that being alkaline, the CZ will improve N, P, and K availability through amelioration of the peat soil's acidity. To test the afore-stated hypotheses, a field study was carried out to determine if co-application of CZ and NPK compound fertilizer could improve soil exchangeable ammonium, available nitrate, available P, exchangeable K availability, the recovery of these nutrients, yield, and fruit quality of Sekaki cultivation on a sapric peat soil. Information obtained from this study could provide an understanding on fertilizer nutrients' management in papaya cultivation on tropical peat soils.

2. Materials and Methods

2.1. Experimental Site Description and Peat Soil Characteristics

The field experiment was conducted from April 2018 to February 2019 at the Malaysian Agricultural Research and Development Institute (MARDI) Research Station, Saratok, Sarawak, Malaysia (1°55′30.9′′ N 111°14′15.1′′ E). The mean relative humidity of the research station ranges from 59.7% to 60.1% and the mean temperature ranges from 22.8 to 32.5 °C. The research station receives an annual rainfall of 3676 mm with a distinct dry period between April and August (106 to 290 mm), and intense wet period which starts from October to February (317 to 556 mm).

The peat soil at the research station is classified as well decomposed sapric peat (Von Post Scale; H7 to H9). The soil is dark brown to almost dark with a significant amount of amorphous materials (indistinguishable plant structure). The thickness of the peat soil at the research station ranges from 0.5 to 3 m.

The experimental area (0.25 hectares) was an abandoned area which was planted with vegetables (brinjal, okra, chili, and spinach) under rain shelter from 2003 to 2005. Thereafter, the area was left to fallow until we embarked on our present study. Land clearing was carried out using a hydraulic excavator in March 2018. At the experimental site, the water table fluctuated between 30 to 41 cm. Peat soil sampling was carried out systematically in 16 points located over a 10 m × 10 m grid, and peat soil samples were collected at depths of 0 to 10 cm and 20 to 40 cm. Afterwards, the soil samples were analysed for bulk density, moisture, pH, cation exchange capacity (CEC), total organic carbon, total nitrogen, ammonium-nitrogen, nitrate-nitrogen, available phosphorus, and exchangeable potassium. Bulk density was determined using the core method [57]. Soil moisture was determined using the method of Lim [57], whereas soil pH was measured based on a 1:5 soil to water suspension [58]. Soil CEC was determined using the method of Harada and Inoko [59]. Total organic carbon was determined using the Walkley and Black method [60], whereas total nitrogen was determined using the Kjeldahl method [61]. Soil exchangeable ammonium-nitrate and available nitrate-nitrogen were determined using the steam distillation method [62]. Soil available P and exchangeable K were determined using the method of Olsen and Sommers [63] and Knudsen et al. [64], respectively.

The physical and chemical characteristics of the peat soil used for this experiment are presented in Table 1. The low bulk density of the peat soil relates to the decomposition and compaction of sapric materials upon drainage and peat cultivation. The high-water table at the experimental site relatively explains the high moisture of the peat soil. The peat soil is acidic, whereas the high CEC of the soil is attributed to the nature of its organic matter and stages of decomposition in peat soils. Exchange of ions in peat soils is generally associated with the carboxyl and phenolic radicals of humic substances and hemicelluloses [14]. The high organic carbon but low total nitrogen content of the soil relates to the botanical origin of the sapric peat soil, suggesting that minimal nitrogen is mineralized unless a substantial amount of nitrogen fertilizers is utilized. In general, available P and exchangeable K of the peat soils are low, whereas ammonium-nitrogen and nitrate-nitrogen contents are typical of a drained cultivated peat soil.

Table 1. Selected physical and chemical properties of a peat soil at different depths at the Malaysian Agricultural Research and Development Institute (MARDI) Peat Research Station, Saratok, Sarawak, Malaysia.

Soil Properties	Mean Value Obtained per Soil Depth	
	0 to 20 cm	20 to 40 cm
Bulk density (g cm^{-3})	0.13 (±0.003)	0.12 (±0.004)
Moisture (%)	83.7 (±0.65)	87.9 (±0.42)
pH	3.4 (±0.02)	3.5 (±0.05)
Cation exchange capacity ($cmol_{(+)}$ kg^{-1})	148.4 (±3.76)	141.6 (±2.39)
Total organic carbon (%)	41.2 (±0.35)	40.5 (±1.06)
Total nitrogen (%)	1.41 (±0.003)	1.12 (±0.007)
Ammonium-nitrogen (mg kg^{-1})	142.5 (±3.05)	98.3 (±2.58)
Nitrate-nitrogen (mg kg^{-1})	76.3 (±1.47)	87.9 (±2.53)
Available phosphorus (mg kg^{-1})	32.6 (±0.75)	39.7 (±0.58)
Exchangeable potassium (mg kg^{-1})	29.4 (±0.53)	35.8 (±0.79)

Values in parentheses represent standard error of the mean.

2.2. Characterization of Clinoptilolite Zeolite

The natural zeolite used in this present study was CZ because of its cation exchange capacity, abundance, and low cost. The CZ was in powder form (greyish-white), was commercially available and originated from Indonesia. pH of the CZ was measured in a ratio of 1:2 CZ to water [65] and its CEC was determined using the cesium chloride method [66]. The functional groups of the CZ were determined using Fourier Transform Infrared (FTIR) analysis (Nicolet 6700, Thermo Electron Corporation, Madison, WI, USA). Morphological and elemental characteristics of the CZ were determined using Ultra High-Resolution Scanning Electron Microscope (FESEM) with Energy Dispersive X-Ray (EDX) (Nova NanoSEM 230, Fei Company, Hillsboro, OR, USA), whereas surface area of the CZ was determined using a surface area analyser (ASAP 2460, Micromeritics Instrument Corp, Norcross, GA, USA).

2.3. Plant Material and Papaya Cultivation on Peat Soils

Papaya cv. Sekaki, which is propagated by seeds, was used in this study because it is one of the most commonly cultivated varieties in Malaysia. The papaya seeds were procured from a commercial source (Green Eagle Seeds, Puchong, Malaysia) and soaked for 24 h before they were sown in plastic seedling trays containing peat moss. At 18 days of germination, the seedlings were transplanted into polyethylene bags (24 cm × 33 cm) which were filled with peat moss, sand, and chicken dung (2:1:1 *v*/*v*). Afterwards, the transplanted papaya plants were grown in a greenhouse for two months. Thereafter, the seedlings were transported to the field at the research station on 24 April 2018. At this stage, the papaya plants' growth was uniform (approximately 35 to 40 cm in height and 10 to 12 mm in stem diameter). The seedlings were transplanted into planting holes measuring 30 cm × 30 cm × 30 cm at a spacing of 2.5 m × 2.5 m. Each hole was filled with 200 g triple superphosphate (containing 42% P_2O_5). When necessary, the papaya plants were manually irrigated and managed by following standard agronomic practices [25,67].

2.4. Experimental Design and Treatments

The experimental design which was used in this study was a randomized complete block design with three blocks. The field experiment had five treatments, and details of the treatments evaluated are summarized in Table 2. Each of the five treatments within a block had four papaya plants. The treatments consisted of different amounts of CZ. The amounts of the CZ used were calculated based on the fertilizer requirement of papaya cultivation on peat soils [25]. The compound fertilizers used in this study were $N:P_2O_5:K_2O$ and $N:P_2O_5:K_2O:MgO$ in ratios of 15:15:15 and 12:12:17:2, respectively. The fertilization programmes for $N:P_2O_5:K_2O$ were monthly for the first three months after planting, whereas $N:P_2O_5:K_2O:MgO$ was applied from the fourth to the tenth months after planting. The CZ and NPK fertilizers were thoroughly mixed based on the information in Table 2 (treatments T1 to T5). The mixture, consisting of CZ and NPK fertilizers (T1 to T5), was applied circularly onto the soil (approximately 20 cm) from the collar of the papaya plants below the canopy of the plants to ensure they were not injured.

Table 2. Clinoptilolite zeolite and nitrogen, phosphorus, and potassium application rates.

Fertilization Treatments		Application Rate		
		1st and 2nd Month after Planting	3rd Month after Planting	4th to 10th Month after Planting
T1	100% CZ + NPK	50 g CZ + 50 g NPK 15:15:15	100 g CZ + 100 g NPK 15:15:15	200 g CZ + 200 NPKMgO 12:12:17:2
T2	70% CZ + NPK	35 g CZ + 50 g NPK 15:15:15	70 g CZ + 100 g NPK 15:15:15	140 g CZ + 200 g NPKMgO 12:12:17:2
T3	50% CZ + NPK	25 g CZ + 50 g NPK 15:15:15	50 g CZ + 100 g NPK 15:15:15	100 g CZ + 200 g NPKMgO 12:12:17:2
T4	25% CZ + NPK	12.5 g CZ + 50 g NPK 15:15:15	25 g CZ + 100 g NPK 15:15:15	50 g CZ + 200 g NPKMgO 12:12:17:2
T5	Control: NPK only	50 g NPK 15:15:15	100 g NPK 15:15:15	200 g NPKMgO 12:12:17:2

Note: CZ—clinoptilolite zeolite.

2.5. Soil Sampling and Nutrients Determination

Peat soil samples were taken 30 days after fertilization during flowering (three months after planting), fruiting (four months after planting), and at harvest (six months after planting). This method of sampling was used to determine the effects of the CZ on soil pH, ammonium, nitrate, P, and K availability in the peat soil throughout the growth and development phases of the papaya plants. For each treatment, the peat soil sampling was carried out systematically at a distance of 30 cm from the collar of the papaya plants. The peat samples were taken at depths of 0 to 20 cm and 20 to 40 cm from each plant, giving a total of forty soil samples per block. Soil pH was measured based on a ratio of 1:5 soil to water suspension [58]. Soil exchangeable ammonium and available nitrate were determined using the steam distillation method [62], whereas available P and exchangeable K were determined using the method of Olsen and Sommers [63] and Knudsen et al. [64], respectively.

2.6. Crop Data Collection Procedures and Nutrient Analysis

The nutrient contents of the papaya plants were determined at the flowering stage (three months after planting). For this, leaf samples were collected from the bottom fourth or fifth leaf, including midrib from each plant for each treatment, giving a total of twenty leaf samples per block. The papaya plant tissues were oven-dried at 60 °C, ground, and analysed for total N, P, and K. Total N was determined using the micro Kjeldahl method [68], whereas the dry ashing method was used to extract P and K from the papaya plant tissues [69]. The extracts were analysed for P using the blue development method [70], whereas K was analysed using inductively coupled plasma optical emission spectrometry (ICP-OES Optima 7300DV, PerkinElmer, Waltham, MA, USA).

Vegetative growth variables, namely height and stem girth, were recorded at the flowering (three months after planting) and harvesting (six months after planting) stages. Papaya plant height was measured (m) from the base of the stem to the axil of the youngest leaf, whereas stem girth was measured (cm) at 10 cm from the surface of the soil using a measuring tape. Data on the number of days taken to first flowering and fruit harvest were recorded.

Papaya fruit harvest was carried out from October 2018 to February 2019. The fruits were harvested weekly when they were one-quarter to one-half ripe. Number of fruits per plant and fruit yield were recorded. Number of fruits per plant was counted from the base to the tip of the papaya plants at 30-day intervals by visual counting, whereas fruit yield was calculated based on mean fruit weight and plant density. Fruit quality characteristics such as fresh fruit weight, fruit length, fruit diameter, and total soluble solids (TSS) were also determined using standard procedures. The papaya fresh fruit weight was determined using a digital weighing balance (EK-15KL, A&D Company, Toshima-ku, Tokyo, Japan) whereas fruit length and fruit diameter were measured using a Vernier calliper (CD-18″C, Mitutoyo Corporation, Kanagawa, Japan). The papaya fruit length was determined from the longitudinal section of the fruit and was measured from the base of the calyx to the tips of the fruit. Fruit diameter was measured at the broadest part of the papaya fruit from the equator. Total soluble solids of the papaya fruits were determined using a handheld refractometer (Atago PAL-1, Spectrum Technologies Inc, Aurora, IL, USA).

2.7. Statistical Analysis

Treatment effects were detected using analysis of variance (ANOVA), whereas means of the treatments were compared using Tukey's test at $p \leq 0.05$. The statistical software used for this analysis was Statistical Analysis System (SAS) Version 9.1.

3. Results

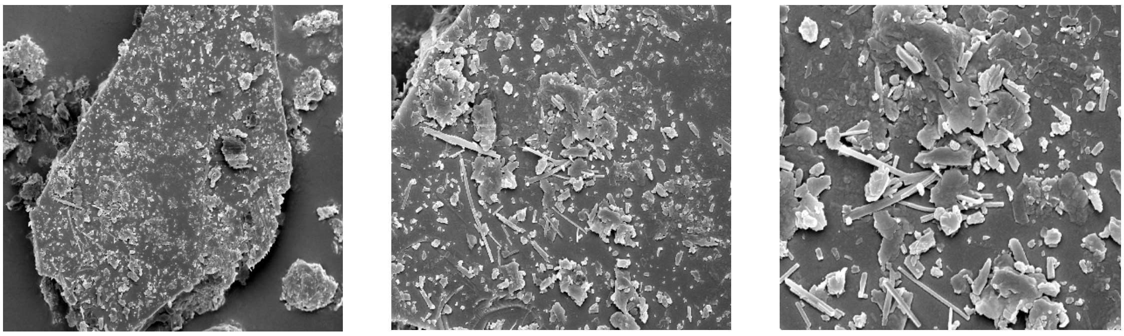
3.1. Characteristics of Clinoptilolite Zeolite

The pH, CEC, chemical composition, functional groups, and surface area of the CZ are presented in Table 3. The high pH of the CZ suggests this mineral was alkaline. The high CEC of the CZ indicates its nutrients holding capacity. From the EDX results, the CZ consisted of silicone dioxide, aluminium oxide, iron oxide, magnesium oxide, potassium oxide, calcium oxide, and sodium oxide. The main functional groups of the clinoptilolite zeolite were hydroxyl stretching vibration, alkene, and C-O radicals. The surface area of the CZ was 23.19 m^2 g^{-1} and this surface area is consistent with those reported in the literature for natural zeolites [71–73]. The surface morphology of the CZ is presented in Figure 1. From the scanning electron microscopy (SEM) micrographs, the CZ was crystalline with irregular rod-shaped particles.

Table 3. Selected chemical and physical properties of clinoptilolite zeolite.

Properties	Values
pH	8.77 (±0.03)
Cation exchange capacity ($cmol_{(+)}$ kg^{-1})	103.8 (±0.21)
Chemical composition (weight %)	SiO_2: 78.08 Al_2O_3: 7.03 Fe_2O_3: 10.70 K_2O: 1.29 CaO: 1.27 MgO: 1.10 Na_2O: 0.53
Functional groups (cm^{-1})	OH: 3696.17 C=C: 1634.66 C-O: 992.85
Surface area (m^2 g^{-1})	23.19

Values in parentheses represent standard error of the mean.

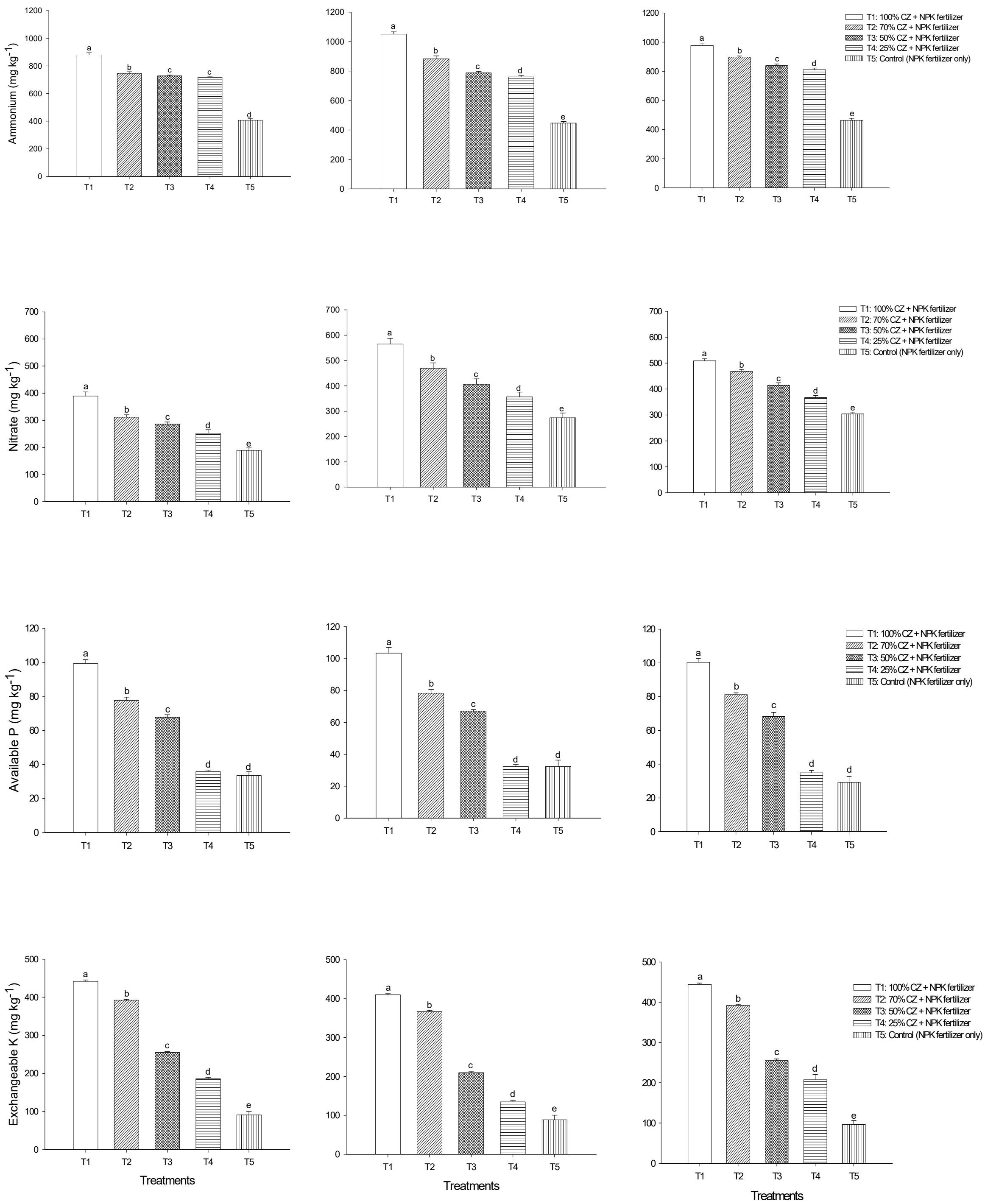


(**a**) (**b**) (**c**)

Figure 1. Scanning electron micrographs of clinoptilolite zeolite at (**a**) 10 µm; (**b**) 4 µm; and (**c**) 2 µm.

3.2. Ammonium, Nitrate, Phosphorus, and Potassium in Tropical Peat Soils Cultivated with Papaya

Soil exchangeable ammonium, available nitrate, available P, and exchangeable K availability at the flowering, fruiting, and harvesting stages of the papaya plants are presented in Figure 2. Compared with the control (T5), the treatments with CZ (T1 to T4) showed higher exchangeable ammonium, available nitrate, available P, and exchangeable K. However, an exception to this finding was the less effectiveness of T4 in retaining available P compared with control, which was the treatment without CZ (T5). T1 showed the highest concentrations of ammonium, nitrate, P, and K in the peat soils compared with other treatments (Figure 2).



(**a**) Flowering stage (**b**) Fruiting stage (**c**) Harvesting stage

Figure 2. Exchangeable ammonium, available nitrate, available phosphorus, and exchangeable potassium in a peat soil treated with different amounts of CZ and NPK fertilizer throughout papaya plant growth stages: (**a**) flowering stage; (**b**) fruiting stage; and (**c**) harvesting stage. Error bar represents standard error of the mean. Means with different letters indicate significant difference between treatments by Tukey's test at $p \leq 0.05$. CZ: clinoptilolite zeolite; T1: 100% CZ + NPK fertilizer; T2: 70% CZ + NPK fertilizer; T3: 50% CZ + NPK fertilizer; T4: 25% CZ + NPK fertilizer; T5: Control (NPK fertilizer only).

Unlike available P, the mean soil exchangeable ammonium, available nitrate, and exchangeable K from all treatments including control (T1 to T5) were higher at 20 to 40 cm than at 0 to 20 cm (Table 4) and this finding was consistent in all the growth stages of the papaya plants. During the growth phases of the papaya plants, the treatments with CZ (T1 to T4) significantly improved soil pH compared with the chemical fertilizer without CZ (T5) (Table 5).

Table 4. Mean exchangeable ammonium, available nitrate, available phosphorus, and exchangeable potassium over all treatments (T1 to T5 and control) in a peat soil at different soil depths and growth stages of papaya plants treated with different amounts of CZ and NPK fertilizer.

Growth Stages	Soil Depth (cm)	Exchangeable Ammonium (mg kg^{-1})	Available Nitrate (mg kg^{-1})	Available Phosphorus (mg kg^{-1})	Exchangeable Potassium (mg kg^{-1})
Flowering	0 to 20	683.91 ^{b} ± 36.71	262.12 ^{b} ± 16.78	61.51 ^{a} ± 7.08	268.19 ^{b} ± 36.04
	20 to 40	707.93 ^{a} ± 46.62	309.00 ^{a} ± 18.74	64.04 ^{a} ± 6.52	278.24 ^{a} ± 33.27
Fruiting	0 to 20	765.53 ^{b} ± 47.49	368.60 ^{b} ± 25.50	61.46 ^{a} ± 8.12	237.93 ^{b} ± 35.47
	20 to 40	805.97 ^{a} ± 58.26	459.53 ^{a} ± 27.49	63.88 ^{a} ± 6.82	245.68 ^{a} ± 32.35
Harvesting	0 to 20	783.06 ^{b} ± 41.22	395.89 ^{b} ± 19.10	60.93 ^{b} ± 7.97	270.41 ^{b} ± 36.04
	20 to 40	811.70 ^{a} ± 53.00	429.26 ^{a} ± 19.69	64.63 ^{a} ± 6.71	287.53 ^{a} ± 31.56

Values (mean ± standard error) with different letters within the same column are significantly different by Tukey's test at $p \leq 0.05$.

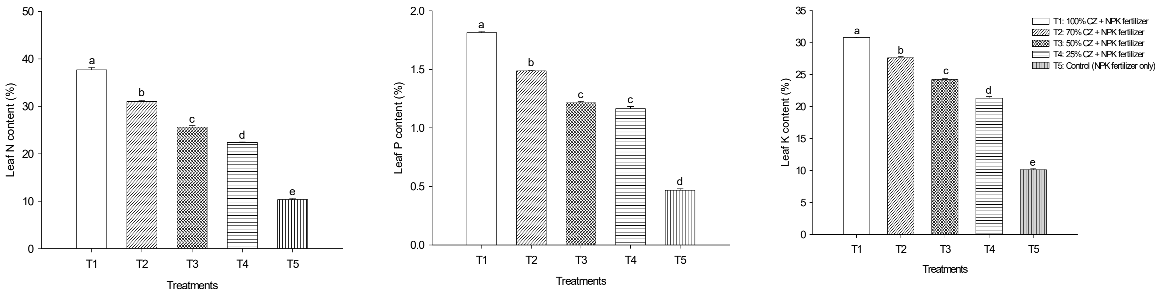
Table 5. pH of peat soils cultivated with papaya at flowering, fruiting, and fruit harvest stages.

Treatments	Growth Stages		
	Flowering	Fruiting	Harvesting
T1	6.21 ^{a} ± 0.03	6.26 ^{ab} ± 0.04	6.39 ^{a} ± 0.07
T2	6.12 ^{b} ± 0.02	6.32 ^{a} ± 0.03	6.27 ^{b} ± 0.05
T3	6.19 ^{ab} ± 0.02	6.18 ^{b} ± 0.03	6.20 ^{c} ± 0.03
T4	5.90 ^{c} ± 0.02	5.77 ^{c} ± 0.02	5.65 ^{d} ± 0.02
T5	4.56 ^{d} ± 0.04	4.46 ^{d} ± 0.07	4.27 ^{e} ± 0.01

Values (mean ± standard error) with different letters within the same column are significantly different by Tukey's test at $p \leq 0.05$.

3.3. Growth, Fruit Quality, and Yield of Carica papaya cv. Sekaki

During flowering of the papaya plants, the treatments with clinoptilolite zeolite (T1 to T4) significantly improved leaf N, P, and K concentrations compared with chemical fertilizer only (T5) (Figure 3). Moreover, during the flowering and harvesting stages (Table 6), the heights and stem girths of the papaya plants with CZ (T1 to T4) significantly increased compared with the treatment without CZ (T5). Among the treatments with CZ, T1 caused the highest improvement in leaf N, P, and K concentrations, height, and stem girth during the growth phases of the papaya plants (Figure 3 and Table 6). Days for first flowering after planting of the papaya plants and days for the first harvest of the papaya fruits were significantly reduced with the use of CZ (Table 6). Treatment one (T1) which had the highest amount of the CZ and showed the shortest days for the first flowering of the papaya plants and fruit harvest, but the opposite was true for the treatment without CZ (T5).



(**a**) (**b**) (**c**)

Figure 3. Leaf nitrogen (**a**); phosphorus (**b**); and potassium (**c**) contents during flowering of papaya cv. Sekaki cultivation on a tropical peat soil treated with different amounts of CZ and NPK fertilizer. Error bar represents standard error of the mean. Means with different letters indicate significant difference between treatments by Tukey's test at $p \leq 0.05$. CZ: clinoptilolite zeolite; T1: 100% CZ + NPK fertilizer; T2: 70% CZ + NPK fertilizer; T3: 50% CZ + NPK fertilizer; T4: 25% CZ + NPK fertilizer; T5: Control (NPK fertilizer only).

Table 6. Vegetative growth of papaya cv. Sekaki cultivation on tropical peat soil treated with different amounts of CZ and NPK fertilizer.

Treatments	Plant Height (m)		Stem Girth (cm)		Days Taken to 1st Flowering	Days Taken to 1st Harvest
	Flowering Stage	Harvesting Stage	Flowering Stage	Harvesting Stage		
T1	0.95 ^{a} ± 0.008	1.74 ^{a} ± 0.008	12.73 ^{a} ± 0.044	35.32 ^{a} ± 0.367	66.92 ^{d} ± 0.22	161.58 ^{e} ± 0.22
T2	0.89 ^{b} ± 0.015	1.66 ^{b} ± 0.008	11.61 ^{b} ± 0.079	32.12 ^{b} ± 0.085	69.08 ^{cd} ± 0.55	167.67 ^{d} ± 0.08
T3	0.89 ^{b} ± 0.014	1.65 ^{b} ± 0.008	11.44 ^{b} ± 0.036	31.77 ^{b} ± 0.073	70.58 ^{c} ± 0.22	173.00 ^{c} ± 0.38
T4	0.87 ^{b} ± 0.005	1.65 ^{b} ± 0.010	10.93 ^{b} ± 0.300	30.33 ^{c} ± 0.036	75.75 ^{b} ± 0.66	177.58 ^{b} ± 0.30
T5	0.77 ^{c} ± 0.003	1.55 ^{c} ± 0.007	8.53 ^{c} ± 0.150	26.75 ^{d} ± 0.101	83.08 ^{a} ± 0.94	184.58 ^{a} ± 0.22

Values (mean ± standard error) with different letters within the same column are significantly different by Tukey's test at $p \leq 0.05$.

Fruit quality and fruit yield characteristics of papaya cv. Sekaki with CZ and NPK fertilizers are presented in Table 7. In terms of fruit quality, T1 to T4 significantly improved fruit weight as well as the fruit sweetness (TSS content) compared with T5. In addition, the treatments with CZ (T1 to T4) significantly increased number of fruits per papaya plant, fruit yield per papaya plant, and total papaya fruit yield per plot compared with the treatment without CZ (T5) (Table 7). With the exception of T3 and T4, the other treatments with the CZ (T1 and T2) significantly increased the papaya fruit length and fruit diameter.

Table 7. Fruit quality and yield of papaya cv. Sekaki cultivated on a tropical peat soil treated with different amounts of CZ and NPK fertilizer.

Treatments	Fruit Quality		Fruit Yield				
	Fruit Weight (kg)	Fruit Sweetness (TSS: °Brix)	Number of Fruits Per Plant	Fruit Length (cm)	Fruit Diameter (cm)	Fruit Yield Per Plant (kg)	Total Fruit Yield Per Plot (kg)
T1	2.60 ^{a} ± 0.04	12.08 ^{a} ± 0.05	30.67 ^{a} ± 0.22	25.79 ^{a} ± 0.69	13.73 ^{a} ± 0.28	79.88 ^{a} ± 1.63	319.50 ^{a} ± 6.54
T2	2.48 ^{b} ± 0.03	11.75 ^{b} ± 0.07	28.25 ^{b} ± 0.14	25.24 ^{a} ± 0.54	13.70 ^{a} ± 0.24	70.07 ^{b} ± 1.05	280.27 ^{b} ± 4.21
T3	2.22 ^{c} ± 0.02	11.69 ^{b} ± 0.10	25.92 ^{c} ± 0.08	24.69 ^{a} ± 0.54	12.89 ^{ab} ± 0.13	57.64 ^{c} ± 0.53	230.57 ^{c} ± 2.11
T4	2.22 ^{c} ± 0.01	11.62 ^{b} ± 0.02	23.58 ^{d} ± 0.44	23.94 ^{ab} ± 0.60	12.72 ^{b} ± 0.11	52.31 ^{d} ± 1.21	209.22 ^{d} ± 4.86
T5	1.04 ^{d} ± 0.03	9.61 ^{c} ± 0.05	14.50 ^{e} ± 0.90	21.21 ^{b} ± 0.70	12.09 ^{b} ± 0.03	15.09 ^{e} ± 0.54	60.36 ^{e} ± 2.18

Values (mean ± standard error) with different letters within the same column are significantly different by Tukey's test at $p \leq 0.05$. TSS: Total Soluble Solid (°Brix—pure sucrose content).

4. Discussion

4.1. Ammonium, Nitrate, Phosphorus, and Potassium in a Tropical Peat Soil Cultivated with Papaya

During the growth phases of the papaya plants, the higher concentrations of soil exchangeable ammonium and K for the treatments with CZ (T1 to T4) could be attributed to the adsorption and absorption of these ions onto and within the lattices of the CZ [35,36]. This is because the structure of CZ is made up of hydrated aluminosilicates with interconnected pores and voids linked by shared oxygen atoms which provided large internal microporous areas for ion adsorption and cation exchange [44–46,74]. This allows CZ to selectively control the types of ions to be retained or passed through its surface [35,36]. This was possible because the high CEC, which is caused by the high negative charges of the CZ, enabled, for example, sorption of the ammonium and K ions. Moreover, the CZ has a high affinity for ammonium and K ions [39]. Furthermore, the higher concentration of ammonium in the peat soil with the CZ is consistent with the increase in the soil pH, particularly at the growth phases of the papaya plants (Table 5) because mineralization of organic N to ammonium increases with increasing soil pH [27,65].

The higher soil available nitrate in the plots with CZ compared with the plots without the CZ was because of the ability of this mineral to absorb negatively charged anions such as nitrate and phosphate [65]. The buffering capacity of the CZ increased the peat soil pH to facilitate nitrification [37,65]. Apart from the ability of the CZ to absorb P ions, the effectiveness of T1 to T3 in retaining P ions is also related to the ability of the CZ to serve as a "cation bridge" by providing negative surface charges for the adsorption of iron or aluminium in peat soils [21]. This enables disintegration/dissolution of the humic metal chelation bond between iron or aluminium and organic matter in peat soils to free these metals and form a coordination bond with P.

Among the treatments with CZ, T1 was more effective in causing higher retention of exchangeable ammonium, available nitrate, available P, and exchangeable K in the peat soils because of the higher amount (100%) of the CZ in this treatment. The higher amount of the CZ increased the nutrients' concentrations because of the increased number of negatively charged surfaces for adsorption or ion exchange or nutrient absorption. Conversely, the nutrient adsorption or absorption capacity decreased with the decreasing amount of CZ, and this explains the less effectiveness of T4 in retaining available P in the peat soils during the growth phases of the papaya plants under this treatment. The lower amount of the CZ (25%) provided insufficient number of negatively charged surfaces [75] for the adsorption of, for example, iron or aluminium in the peat soil to form a coordination bond between these metals and P.

During the growth phases of the papaya plants, the significantly higher retention of ammonium, nitrate, P, and K in the peat soils could also be associated with the increase in the soil pH (Table 5) because the adsorption capacity of the CZ had been reported to be positively correlated with pH level [76]. As the surface of the CZ becomes more negatively charged with increasing soil pH, this process increases the affinity of CZ for nutrient exchange or adsorption [77]. The ability of CZ to buffer soil pH could reduce the need for liming peat soils with the conventional liming materials such as calcium carbonates, quick lime, among others whose liming effects are temporary besides them being expensive liming agents.

On the contrary, the low soil pH with the use of NPK fertilizers only (T5) explains the lower exchangeable ammonium and available nitrate concentrations in the peat soil with this treatment. The acidic condition of the peat soil might have restricted or retarded mineralization of organic N to ammonium and nitrification of ammonium to nitrate [27,65]. Unlike ammonium and nitrate, the lower available P in the T5 plots could be attributed to the absence of clay and iron or aluminium in peat soils. For example, P sorption is restricted by the absence of iron or aluminium because iron or aluminium exists in a non-extractable form and they are strongly chelated by the humic matter in peat soils. This causes inorganic P to be mobile and get easily leached, particularly during high rainfalls [14,78]. The low K content in the T5 plots was because of the functional groups, such as carboxyl, hydroxyl, and phenols, among others of the humic substances in peat soils that do not form coordination bonds with K ions [21]. Moreover, K ions in peat soils are prone to leaching because of the absence of mineral matter and low clay content [18].

The higher contents of the exchangeable ammonium, available nitrate, available P, and exchangeable K at 20 to 40 cm (Table 4) relate to the high preferential flow of peat soil water. This enables rapid transport of water and mobilization of nutrients [27]. It was possible that some of the macronutrients which were leached from 0–20 cm of the peat soil were adsorbed or absorbed by the CZ at 20 to 40 cm [38].

4.2. Growth, Fruit Quality, and Yield of Carica papaya cv. Sekaki

The increase in leaf N, P, and K contents during the flowering phase of the papaya plants relates to the retention of soil ammonium, nitrate, P, and K within the lattices of CZ. The temporary retention of ammonium, nitrate, P, and K ions resulted in the timely availability of these nutrients for optimum use by the papaya plants, particularly during the early vegetative stage (Figure 2) of the papaya plants. This observation is also consistent with the nutrient contents in the papaya leaves, growth variables, fruit yield, and fruit quality, which were presented in the results section. For example, the increase in the P concentration in the papaya leaves with the application of different amounts of CZ gives credence to the ability of this mineral to absorb or regulate the availability of anions such as phosphate in peat soils. The timely release of P by the CZ through diffusion led to P uptake by the papaya roots [38,53,79]. Likewise, the increase in the papaya plant height, stem girth, fruit number, fruit weight, and fruit TSS with the treatments with CZ (T1 to T4) was because of the sufficient availability of ammonium, nitrate, P, and K in the peat soil [35,36,65,80,81]. This also explains the shortest days for the first flowering of the papaya plants and fruit harvest with the use of CZ.

The pure sucrose (TSS) contents expressed in °Brix of the papaya fruits with the different amounts of CZ which ranged between 11.62 and 12.08 exceeded the 11.5 °Brix limit required by the international market [26,82]. The range also exceeded the 10 °Brix range reported for papaya cv. Sekaki [82], but the range was within the 9 to 12 °Brix limit for raw papaya required for use as a food product [83]. Although the treatments with the different amounts of the CZ improved the papaya fruit quality and fruit yield, the less effectiveness of the relatively lower amounts of the CZ in T3 and T4 in increasing fruit diameter and fruit length was unexpected. The reason for this observation is unclear, but this anomaly could be attributed to the lower amount of CZ used (25% to 50%). The amounts were not sufficient to increase the negatively charged surfaces of the soil for the adsorption or absorptions of nutrients by the peat soil.

In this present study, the use of NPK fertilizers only (T5) could not significantly improve the growth, fruit yield, and fruit quality of the papaya plants, not only because of the acidity of the peat soil and lower availability of ammonium, nitrate, P, and K in the peat soil, but also due to the leaching of these nutrients. On the contrary, among the CZ treatments, the effectiveness of T1 and T2 in improving papaya growth variables, fruit yield, and fruit quality was because of the higher amounts of the CZ (70% to 100%) in these treatments. The higher amounts of the CZ increased the negatively charged surfaces in the peat soil for temporary adsorption/absorption of macronutrients in peat soils. Furthermore, the temporary adsorption/absorption of ammonium, nitrate, P, and K ions within the lattices of CZ enables these ions to leach out as water moves through the soil and is taken up in small amounts by papaya plants. The effectiveness of T1 and T2 in improving the papaya fruit quality and yield is consistent with the higher retention of ammonium, nitrate, P, and K in the peat soils with CZ compared with other treatments including control (Figure 2). Sekaki is a medium-sized papaya fruit weighing between 1.5 to 2 kg/fruit. The higher fresh fruit weight of T1 to T4 (ranging between 2.2 to 2.6 kg/fruit) indicates good fresh fruit yield compared with control. Generally, papaya planted on peat soils bears fruit after 8 to 10 months with yields approximately 30 tonnes per hectare for the first year of production [84]. In comparison, amending peat soils with CZ is able to produce an average of 62.4 tonnes of fresh papaya fruit yield per hectare within six months after planting. This research has demonstrated that it is possible to use CZ in papaya cultivation on tropical peat soils to improve papaya productivity through the regulation of the timely availability of nutrients in the soil.

5. Conclusions

Amending N, P, and K fertilizers with CZ increases ammonium, nitrate, P, and K availability in papaya cultivation on a tropical peat soil because this mineral is able to synchronize the availability of N, P, and K ions with the uptake of these macronutrients by papaya plants. This approach also improves papaya plant growth, fruit yield, and fruit quality. The buffering capacity of CZ also causes increases in peat soil pH or reduces peat soil acidity, thus serving as a potential liming material for production agriculture on tropical peat soils. Relatively higher amount of CZ (70% to 100%) in conjunction with NPK fertilizers promises to be more effective in improving the productivity of tropical peat soils and papaya. The outcomes of this study have demonstrated that it is possible to use CZ in papaya cultivation on tropical peat soils to improve papaya productivity through the regulation of the timely availability of nutrients in peat soils. The findings in the study suggest that monthly fertilization using compound NPK fertilizers in conjunction with 70% to 100% CZ is promising and could be adopted by local farmers to improve soil acidity, macronutrients availability, fresh fruit yield, and fruit quality of papaya grown on peat soils. However, further studies are needed on nutrient leaching and enhancement on the rate of CZ in conjunction with compound NPK fertilizers as a value-add product to improve the effectiveness of CZ as a potential amendment for sustainable cultivation of tropical peat soils. In addition, results from one cycle of papaya cultivation may not be conclusive enough to confirm the findings obtained from the study. Further field trials are being investigated in our on-going field experiments to verify the results of this present study because climatic factors such as temperature and rainfall distribution between planting cycles may affect the outcome of the study.

Author Contributions: Conceptualization, L.N.L.K.C.; methodology, L.N.L.K.C. and O.H.A.; validation, L.N.L.K.C. and O.H.A.; formal analysis, L.N.L.K.C.; investigation, L.N.L.K.C. and S.S.; resources, L.N.L.K.C., O.H.A. and S.A.A.T.; data curation, L.N.L.K.C.; writing—original draft preparation, L.N.L.K.C.; writing—review and editing, L.N.L.K.C. and O.H.A.; visualization, L.N.L.K.C. and S.A.A.T.; supervision, L.N.L.K.C. and M.Z.A.G.; project administration, L.N.L.K.C. and S.A.A.T.; funding acquisition, M.Z.A.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Government of Malaysia under the 11th Malaysia Plan Development Project through Malaysia Agricultural Research and Development Institute, grant number P-RS402C.

Acknowledgments: The authors would like to extend their special thanks and appreciation to Universiti Putra Malaysia Bintulu Campus Sarawak, Malaysia for the collaborative research.

Conflicts of Interest: The authors declare no conflict of interest.

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