Impact of natural zeolite in agriculture with special reference to field crops

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Abstract
Farming with natural rocks and minerals is an age-old practice for food production since stone ages. The intensive production practices associated with imbalanced fertilizer management practices has led to declining quality and or quantity of the soil resource base and climate change. To feed the growing population, soil degradation is the key issue which needs urgent attention. In this context, farming with zeolite has drawn attention. Zeolites are natural rocks and gained a momentum in the recent past due to its large number of physico-chemical properties. They can be used both as carriers of nutrients and as a medium to free nutrients (Sangeetha et al., 2016).

Combined application of clinoptilolite zeolite, organic and inorganic fertilizers leads to saving of inorganic fertilizers resulted in improving the growth, increasing the dry matter production, yield and N, P and K uptake in Zea mays L. and also conserve agro-ecosystem for sustainable crop production (Ahmed, 2010). The effect of zeolite and its combination with chemical fertilizer and organic fertilizers (Sugarcane filter cake) increase sugarcane yield as compared to without fertilization (Cairo et al., 2017). Amending urea with rice straw compost and clinoptilolite zeolite improved nitrogen use efficiency because of temporary adsorption and desorption of ammonium on the exchange sites of compost and clinoptilolite zeolite and yield of Zea mays L. (Omar et al., 2018). Combined use of 80 kg / ha N as urea + 50 kg / ha composted manure + 21% zeolite result highest CEC (meq/100gm soil), facilitated highest leave nitrogen concentration (%) and quantity and quality sunflower dry matter yield (kg / ha), but the impact of their application was greater in the second year than in the first year (Gholamhoseini et al., 2012). Integration of 10 t zeolite / ha with either alternate wetting and drying (AWD) or complete flooding (CF) management reduced NH3 volatilization without increasing N leaching and increased rice grain yield and water productivity, with an increased economic benefit of $126 – 195 / ha, as compared to CF without zeolite (Sun et al., 2019). Although considerable research has been advanced, further research needs to carry out for their efficient utilization in farming.

Keywords: Natural zeolite, clinoptilolite, NH4+-enriched zeolite, sugarcane filter cake

Introduction
To feed the world growing population, effort has been made to expand crop and animal production, more and more attention is being paid to various mineral materials as soil amendments and as dietary supplements in animal husbandry. The relationship between the agricultural and geological sciences is not new and crop production depends on the existence and maintenance of fertile soil and other soil constituents. Recently, one group of minerals has emerged as having considerable potential in a wide variety of agricultural processes. This group of minerals is the zeolite group which having unique ion-exchange, dehydration-rehydration, and ad-sorption properties and contributing significantly many years of agricultural technology. Most of the initial research works on the use of zeolites in agriculture took place in the 1960s in Japan to control the moisture content and to increase the pH of acidic volcanic soils. In addition of small amounts of the Zeolites such as clinoptilolite and mordenite to the normal protein diet of pigs, chickens, and ruminants gave noticeable increases in the body weight and general “health” of the animals. The use of zeolites in rations also appeared to reduce odor and associated pollution problems and to provide a means of regulating the viscosity and nitrogen retentivity of animal manure. These same zeolites were also found to increase the ammonium content of rice paddy soils when added with normal fertilizers. The growing awareness of such phenomena and of the availability of inexpensive natural zeolites in the Western United States and in geologically similar parts of the world has
aroused considerable commercial interest. Zeolites are fast becoming the subject of serious investigation in dozens of agricultural laboratories. In this context, farming with natural zeolites has assumed to be of great significance (Rhodes, 2010).

Natural zeolite minerals in India were reported in amygdaloidal vesicles in the Deccan lava flows. Since the 1970s, the state of Maharashtra has provided zeolites that have come out of the enormous lava flows called the Deccan Traps were reported way back in the 18th century itself, regarding their formation and distribution in the lava flows. These minerals do not occur everywhere in the Western Deccan Traps, but are restricted to certain localities around Mumbai (Bombay), Vadodara (Baroda), Pune (Poona), and Nasik. Heulandites (most popular Zeolites of the world) zone was found in the highlands of plateau in the region around Pune (Maharashtra), which is the top-most region up to the highest point Kalsubai. In this region, around 30% of the rock is occupied by Zeolites (Phadke, 1984). In addition to Maharashtra, zeolite occurs as filling in the amygdulid cavities in deccan trapbasalts of Gujarat, Madhya Pradesh and Karnataka too (Ramesh et al., 2015) [13]. Swedish mineralogist, Alex Fredrik Cronstedt first identified zeolites as a mineral long back in 1756, when he collected some crystals from a copper mine in Sweden. Zeolites mean ‘boiling stones’ in Greek, because of their ability to froth when heated to about 200°C. Thereafter, zeolites were considered as a mineral found in volcanic rocks for a period of 200 years. Their commercial production and use started in the 1960s. Zeolites are composed of pores and corner sharing aluminosilicate (AlO₄ and SiO₄) tetrahedrons, joined into three dimensional frameworks. The pore structure is characterized by cages approximately 12 Å in diameter, which are interconnected by channels about 8 Å in diameter, composed of rings of 12 linked tetrahedrons. The pores are interconnected and form long wide channels of varying size depending on the mineral. These channels allow the easy movement of the resident ions and molecules into and out of the structure. Zeolites have large vacant spaces or cages within and resemble honeycomb or cage like structures. The presence of aluminium results in a negative charge, which is balanced by positively charged cations. The general empirical formula is MₓₙO₄Alₓ₋ₙSiₓO₄yH₂O. Where M represents any alkali or alkaline earth cation, n the valence of the cation, x varies between 2 and 10, and y varies between 2 and 7, with structural cations comprising Si, Al and Fe³⁺ and exchangeable cations K, Na and Ca (Sheppard and Mumpton, 1981) [11]. Hemingway and Robie,1984). Tetrahedral AlO₄³⁻ and SiO₄²⁻ bound by oxygen atoms to form tectosilicates called Zeolites.

The mineral has a three-dimensional crystal lattice, with loosely bound cations, capable of hydrating and dehydrating without altering the crystal structure. Other useful chemical and physical properties include: high void volume (~ 50%), low density (2.1-2.2 g/cm³), excellent molecular sieve properties and high cation exchange capacity (CEC) of 150-250 cmol /kg, cation selectivity, specifically for cations like ammonium, potassium, cesium, etc.

Impact of Natural Zeolites in agriculture have been studied by the different experts in worldwide, where some of the research findings are discussed with special reference to field crops.

Impact of Zeolite along with organic and inorganic matter

The increase in plant height is the result from increased soil fertility and available plant nutrient elements in soil. Composted rice husk has proved its potential in growth promotion and improvement in biochemical parameters of plants. The addition of chemical fertilizer and compost affect different natural processes in the soil where compost enhances the organic matter percentage of soil. Increase in soil pH increases the availability of soil nutrients for the plants. In an experiment’s treatment combination 3.70 g urea + 2.50 g TSP + 1.90 g MOP + 192 g Clinoptilolite Zeolite + 385 g Compost has showed higher plant height as compared to the other treatment combination, similarly the no of leaves also increases in maize plant with interaction of clinoptilolite Zeolites alongwith organic and inorganic matter. Likewise cob weight (6.6 t/ha) and grain/cob (709) has been found higher in the treatment. This might be due to combination of organic fertilizer + zeolite and reduced rate of inorganic fertilizers to boost yield as well as to maintain and improve soil health. This will enhance growth, yield, quality, nutrient uptake of maize and also conserve agro-ecosystem for sustainable crop production. Treatments with zeolite showed the best N, P and K (2.18, 1.17 and 2.13 g/plant) uptake in plant tissues because of less leaching of these nutrients. Zeolites help to retain nutrients in root zone and, therefore, improving the long term soil quality by enhancing nutrient absorption (Ahmed, 2010) [11]. José Luise et al., 2017 [6] reported that application of manure compost along with zeolite was simultaneously applied at a dose of 90 t ha⁻¹ (3%) (MCZ) in Barley crop the soil alkaline phosphatase activity (APA) showed significant differences between the treatment involving amendment with compost and that involving compost supplemented with zeolite. Cellobiohydrolylase activity (CBH) was found significantly higher in treatments manure compost at a dose of 38 t/ha (MC) and MCZ than in conventional mineral fertilization using an NPK complex (8-24-8) which was added to the soil at the recommended dose (0.35 t/ ha) (MF) and zeolite supplemented with Leonardite at a dose of 75 t/ha (ZL) respectively. Similar values of urease activity (URA) were measured in MC, MCZ, and MF during the barley cultivation, being significantly higher than that of ZL. However, the grain yield (with moisture content of 13%) was significantly higher in treatment ZL, in comparison to MC and MF, and this parameter was not significantly different in the MC, MCZ, and MF treatments.

A field study was carried out by Latifa Omar et al., 2018 [7] on amending chemical fertilizers with rice straw compost and clinoptilolite zeolite and their effects on nitrogen use efficiency and fresh cob yield of Zea mays L. with following treatments combination viz., Soil only (control) (T₁), 7.40 g urea + 5 g TSP + 3.80 g MOP (T₂), 7.40 g urea + 5 g TSP + 3.80 g MOP + 192 g clinoptilolite zeolite (T₃), 5.55 g urea +...
3.75 g TSP + 2.85 g MOP + 385 g compost + 192 g clinoptilolite zeolite (T1) and 3.70 g urea + 2.50 g TSP + 1.90 g MOP + 577 g compost + 192 g clinoptilolite zeolite (T2). At 72 days after planting, T2, T3, and T4 significantly increased the ratio of Zea mays L. cob yield to the amount of applied N than T1 (first planting cycle). In the second planting cycle, T2 and T3 increased cob yield of Zea mays L. It must be emphasized that, the chemical fertilizers in T2 are 50% less than that of the standard recommendation (T1). In the first and second planting cycles, the grain yields of Zea mays L. in T2, T3, and T4 higher than T1. Higher retention of soil N, exchangeable NH₄⁺, and the corresponding increase in N concentration and N uptake in the aboveground biomass are responsible for the significantly higher cob yield of Zea mays L. in the plots with chemical fertilizers, rice straw compost, and clinoptilolite zeolite than in the plot with chemical fertilizers only. The rice straw compost increased cob yield of Zea mays L. because of the temporary retention of NH₄⁺ and timely release of NH₄⁺. Higher number of grains per cob and cob yield of Zea mays L. were obtained in T2, T3, and T4 because the rice straw compost and clinoptilolite zeolite of these treatments improved nutrients availability.

Majid Gholamhoseini et al., 2012 [9] reported that Zeolite-amended cattle manure effects on sunflower yield, seed quality, water use efficiency and nutrient leaching on sandy loam soil during the 2008 and 2009. In both years, the application of manure + zeolite considerably increased DMY, but the effect was stronger in 2009. In 2008, there was no significant DMY difference between the different zeolite treatments, but in 2009, DMY was significantly higher for 80 kg/ha N as urea + 50 kg/ha composted manure +21% (w/w) zeolite than for 80 kg/ha N as urea + 50 kg/ha composted manure +14% (w/w) zeolite and 80 kg/ha N as urea + 50 kg/ha composted manure +7% (w/w) zeolite. Many researchers have reported that manure application has positive effects on the physicochemical properties of soil and improves crop yields (Bhattacharyya et al., 2008; Basso and Ritchie, 2005; Herenica et al., 2007). Additionally, it seems that adding zeolite to fresh manure prevents the N loss from the soil due to absorption and subsequent release of the N by the zeolite. In this way, composted manure can act as a slow-release fertilizer to supply N to the crop gradually. A direct relationship between N supply and crop dry matter has been reported by Hermanson et al. (2000) [8]. Thus, it is to be expected that integrated treatments with zeolite (especially treatment 80 kg/ha N as urea + 50 kg/ha composted manure +21% (w/w) zeolite and 80 kg/ha N as urea + 50 kg/ha composted manure +14% (w/w) zeolite) will increase crop dry matter yield.

Impact of Zeolite along with inorganic matter
Mehrab et al., 2018 [10] reported that application of 1g / kg NH₄⁺-zeolite (NH₄⁺-enriched zeolite) + 60 kg / ha urea fertilizer in wheat cultivation, the yield of wheat and N in shoot found higher in sandy loam textures soil as compared to the clay soil. Nitrogen uptake by plants in soils treated with Z₄ (only N fertilizer) and Z₄ (NH₄⁺-enriched zeolite) was significantly higher than those of Z₂ (raw zeolite), because an amount of N was absorbed by the raw zeolites and was unavailable for plants, thus reducing the percentage of N uptake in the growing plants. Application of materials with properties of zeolite probably causes a slow and controlled N release. Although these properties reduce the plant nitrogen uptake, they can prevent the loss of nitrogen from soil. Pedro Cairo et al., 2017 [11] reported that treatment Zeolite 7.5 t ha⁻¹ + Sugarcane Filter Cake (SFC) 22.5 t ha⁻¹ showed the best result in Sugarcane production, organic matter, water-stable aggregates and degree of soil aggregation in vertisols in Cuba. The soil water regime by comparing the control treatment with the soil treated with Z 7.5 t ha⁻¹ + SFC 22.5 t ha⁻¹, when sampling moisture is carried up from a meter deep after 25 mm of rainfall. In control treatment, water accumulated on the surface, remaining much drier in depth, due to the limited speed of water infiltration. However, treatment of soil with zeolite guarantees the uptake of rainwater in depth, due to the structural changes, which is synonymous with a better use of rainwater and subsequent supply of assimilable water to plants. In the natural soils, all the detained superfluous water is lost by evaporation surface area which may be decisive in cane yield. The results show that the effect of the zeolite and its combination with organic fertilizer not only has its influence on the topsoil but also in depth.

CH. Ravalı, 2019 reported that application of different levels of zeolite and nitrogen on grain yield and nutrient uptake of maize grown in red soil, the grain yield of maize ranged from 14.86 to 46.80 g pot⁻¹. The grain yield of maize was significantly improved by application of different combinations of nitrogen and zeolite levels. Among all the treatments, N₂₀₀ Z₅ (Nitrogen @ 200 kg ha⁻¹Zeolite @ 7.5 t ha⁻¹) resulted in higher grain yield (46.80 g pot⁻¹) which is on par with N₂₀₀ Z₅ (Nitrogen @ 200 kg ha⁻¹ + Zeolite @ 5 t ha⁻¹) where the grain yield recorded was 45.35 g pot⁻¹. The lowest grain yield was observed in control (14.86 g pot⁻¹). Among the three nitrogen levels, N₂₀₀ produced significantly higher grain yield (42.79 g pot⁻¹ mean value) compared to other levels of nitrogen. Among four zeolite levels, Z₅ produced higher grain yield (36.62 g pot⁻¹) which is significantly superior over other zeolite levels and control (14.86 g pot⁻¹). At harvest, the highest increase in grain (425.83 mg pot⁻¹) and stover (278.45 mg pot⁻¹) was observed in Z₅ N₂₀₀, which was significantly superior over all other treatments and the lowest N uptake was found in control (26.91 mg pot⁻¹). The increase in P uptake in maize at different stages with the addition of zeolite may be due to increase in the P content in the plant tissues and dry matter production. These results were in accordance with the findings of Ahmed et al., (2010) [11]. There was a significant influence of both zeolite and nitrogen levels in increasing the K uptake at 60, 90 DAS and at harvest, due to less leaching of potassium. This is because when zeolites are mixed with soil, they help to retain nutrients from the applied fertilizers in the root zone. These results were in line with the findings of Rabai et al., (2013).

Lilia Bikkina, et al., 2019 reported that complex treatments with activated zeolite stimulated elongation of elevated potato stems by 0.05-0.15 m, and separate treatments by 0.05-0.10 m to the mineral fertilizers N:80-P:80-K:90. Potato harvesting was carried out on 80 days after spraying. The ultrafine zeolite use contributed to obtaining the greatest yield increases. Treatment of seed tubers caused an increase in potato yield by 7.3%, non root by 4.3%, complex treatment by 12.8% to the mineral fertilizers N:80-P:80-K:90. A significant reserve of potato yield was noted during complex treatment, compared with separate treatments, the tubers yield increased by 5.1 and 8.2% respectively.
Impact of Zeolite, inorganic matter and irrigation management

Aynur Ozbahce et al., 2014 reported that application of Zeolite doses (Z1:0; Z2:30, Z3:60, Z4:90, and Z5:120 t ha\(^{-1}\)) in main plot and irrigation levels (I20c: 0.50, I5c: 0.75, and I100c:1.00) in subplots in Common bean seeds (Phaseolus vulgaris L., cv. Akman-98) along with 50 kg N, 40 kg P, 50 kg K, 30 kg Fe, and 30 kg Zn per hectare, which lead to highest yields (4777 and 4114 kg ha\(^{-1}\), respectively) were obtained from the Z2I100 treatments in 2011–2012. Z3I100 (4690 and 3599 kg ha\(^{-1}\)) and Z4I100 (4297 and 3733 kg ha\(^{-1}\)) applications followed this treatment in both the years, respectively. The lowest yields (595 and 482 kg ha\(^{-1}\)) were obtained from Z1I50 treatments during the experimental years. In 2011, the highest Number of Pod was obtained from Z2I15 (46.14 pods per plant) treatment. There were not significant differences between that and using the Z3I100 (45.37 pods per plant) or Z4I100 (39.87 pods per plant) treatments. In 2012, the highest NP (36.30 pods per plant) was obtained from the Z4I100 treatment. Differences among Z1I100 (36.13 pods per plant), Z2I100 (35.68 pods per plant), and Z3I100 (34.81 pods per plant) treatments were significant. In both the years, TGW of 416 and 346 g, respectively, were obtained from Z2I15 treatment (p< 0.05). The yield obtained from zeolite treatment, Z4I100, exceeded 26.6–31.7% compared to that without zeolite application (Z1I100). Zeolite and irrigation applications affected yield and yield components positively. Similar results about the positive effects of zeolite on different crops were found by Valente et al. (1982), Polat et al. (2004) [12], and Gül et al. (2005). This study is in agreement with Mazur et al. (1984) who also found significant yield increases for carrots, eggplant, and potatoes when these crops were grown in soil mixed with zeolite. The best results were observed from zeolite application of 5 t ha\(^{-1}\). WUE values changed depending on the irrigation level and zeolite dose. In general, WUE increased with the increase in irrigation and zeolite. Similar results were found by Abdi et al. (2006). They determined that 3 g zeolite per kilogram of soil increased WUE in comparison to the control.

Junlin Zheng et al., 2019 carried out an experiment on “Influence of Zeolite and phosphorus applications on water use, P uptake and yield in rice under different irrigation management” during the 2016 and 2017 growing seasons (May–October). The analysis of variance indicated that irrigation regime (I) had no significant effect on grain yield or yield components. Phosphorus application (P) had a significant effect on grain yield, effective panicles, and spikelets per panicle, while zeolite application (Z) had a significant effect on grain yield and yield components except for grain filling percentage. Furthermore, a significant P and zeolite interactions occurred for spikelets per panicle, and irrigation, P, and zeolite interactions for grain yield. The ICFP60Z15 (continuous flooding with phosphorus rate of 60 kg ha\(^{-1}\) and zeolite rate of 15 t ha\(^{-1}\)) and IIAWD6P0Z15 treatments produced the highest grain yields in both years, being 12.0% and 8.9%, and 8.6% and 7.7% higher than the conventional management practice (ICFP60Z0) in 2016 and 2017, respectively. Regardless of the irrigation regime and zeolite application, the P application increased the grain yield by 17.2% in 2016 and 13.2% in 2017, relative to the non-phosphorus treatment.

Yidi Sun et al., 2019 reported that residual mineral N (RMN) in soil at harvest period was significantly affected by irrigation regime and Z amendment. AWD significantly increased RMN in soil at depths of 0–30 cm. For the depth of 0–30 cm, the addition of 5 and 10 t Z ha\(^{-1}\) increased RMN in soil by 13% and 21% in 2016, and 12% and 19% in 2017, respectively, as compared to no Z application. N uptake showed a significant difference in Z amendment, but not in irrigation or I X Z interaction in both years. Compared with zero Z amendment, the addition of 5 and 10 t Z ha\(^{-1}\) increased N up- take by 12 and 17% in 2016, and 12 and 18% in 2017, respectively, but there was no significant difference between 5 and 10 t Z ha\(^{-1}\) amendment. Rice yield was significantly affected by Z amendment and I X Z interaction in both years. Compared with CF, AWD reduced grain yield in 2017 but not 2016 without Z application. Zeolite amendment significantly improved grain yield regardless of irrigation regime. Under CF, addition of 5 and 10 t Z ha\(^{-1}\) increased yield by 9 and 8% in year 2016, and 6% in year 2017, respectively, as compared to no Z application. While under AWD, 5 and 10 t Z ha\(^{-1}\) amendment increased grain yield by 8 and 13%, respectively in both years. Water productivity (WP) was significantly affected by I, Z and their interaction in both years. Though alternate wetting and drying irrigation resulted in higher water productivity, yield and economic benefit for AWD were not higher than CF without or with Z amendment.

Impact of Zeolite alone

Swati Sembiring et al., 2017 [15] reported that application of zeolite different doses significantly different effect on height, leaf area, yield per plant and yield per plot of corn. But the differences are not significant on the number of leaves, stem diameter and the diameter of the cob. The corn crop vegetative growth period is in need of Nitrogen supply in large quantities for the formation of biomass. Corn crop yield in the form of seeds, provision of appropriate zeolite using 315 g / plot of 300 kg / ha, according to the research results Widyanto et al., (2013) high production and a recommended dosage for corn growth and yield of 300 kg / ha. In agriculture, zeolites is used as an absorbent, ion exchangers and reverting of soil fertilizer efficiency and lead to increased production (Anonymous, 2011). Giving Zeolite one of the factors increasing plant growth and production. Nutrient availability can be improved planting progress and results that their response to nutrient uptake by plant roots which can promote the growth and yield with increased concentrations of fertilizers applied on corn. The low zeolite supplied to the plant nutrients in the soil resulted into low will result in poor growth and development of plants once lowered maize production, especially compared to the higher concentration of fertilizer. Zeolites have a very high CEC. This is because the zeolite has a cavity that relate to one another, which is empty channels in all directions in which there are ions are easily confused. The use of zeolites can improve efficiency and reduce the damage will fertilization intensity excessive watering. This is due zeolite able to absorb nutrients and distribute them back and it maintains the humidity in a longer time.

A laboratory study was undertaken at the Department of Nano Science & Technology, Tamil Nadu Agricultural University, Coimbatore. During the experimentation, synthesis, characterization, Zn release pattern and Zn fractionation pattern were studied in nano size zeolite fortified with or without Zn. The results indicate that the zeolite may act as a superior substrate or carrier for the nutrients to be loaded. It has the properties of slow-release source of Zn nutrients to plants assuring higher yields. This minimizes losses of fertilizer added. The zeolite reduced to the nano-dimension
increases the surface area and maximum loading of nutrients. Thus, it can be used as a nano-fertilizer for rice crop to enhance the productivity and ensuring environmental hazard and safety as reported by Yuvaraj et al., 2018 [23].

Summary
There is an increasing interest in the utilization of nanoporous zeolites in farming over the years because of current public concern about the adverse effects of chemical fertilizers on the agro-ecosystem. Ion-exchange properties of zeolites are recognized as important for plant nutrition due to their high cation exchange capacity and porosity. Both ion exchange and porosity are relevant to agronomy and soil science. The specific structure and diversity of the zeolites vary as also their application. They can be used either as carriers of nutrients and/or a medium to free the nutrients. Several applications have been identified in zeolite research and attempts are being made worldwide. Considerable research has been carried out globally to exploit the potential of zeolites in the perpetual maintenance of soil productivity. The current growing awareness of the phenomenon and availability of inexpensive natural zeolites has aroused considerable commercial interest. Also, a number of issues have been identified for future research.

Conclusion
Zeolites can be used as a potential source of soil conditioner which helps in improving soil physico - chemical properties and Biological properties in one way, improving the crop production in others.

The Way Forwarded
The following issues have been identified for further research in soil and plant management:
1. To characterize the available zeolite deposits in each country.
2. To probe whether zeolite amendment will reduce the potential for nitrate leaching in agriculture.
3. To develop methodologies for organo-zeolitic manure/fertilizers.
4. To characterize the nutrient release pattern from organo-zeolites.
5. To probe the physical stability of zeolites in a variety of soil environments.
6. To probe the long-term impact of zeolites on soil flora and fauna.
7. To develop zeolitic herbicides to minimize herbicidal residues.
8. To carry out field testing of zeolites on soil and plant systems.

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