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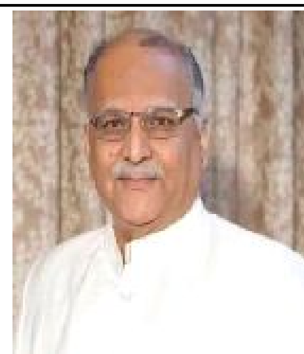
INVITED ARTICLE

Rejuvenation of Soil Properties with use of Zeolite



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Dr. K. Jeevan Rao published 271 research papers in national and international reputed high NAAS rated peer reviewed journals and he published 26 book chapters and 80 popular articles. He worked in various capacities as Head of the Department of Soil science, Dirctor, International Programmes of PJTSAU. He had more than 30 years of service in ANGRAU and PJTSAU. He aslo done additional duties as UG Academic In-Charge, Chairman, Educational Technology Cell and Officer,Placement Cell.

Dr. K. Jeevan Rao received more that 25 awards and Recognitions. Out of which some are Raman Prize (1979), Vidya Prakashan Silver Medel (1980), Vasant Rao Naik Memorial Prize (1980), State Meritorious Teacher Award (2010), Green Leaf Award (2011), Andhra Pradesh Scientist Award (2011), Life Time Achivement Award (2011) and Eminent Educationist Award (2011). He is having membership in many professional Societies like ISSS, New Delhi, IAFEM, NEERI,, Nagpur, ISCA, Kolkata and TSAS, Hyderabad.

Dr. K. Jeevana Rao visited Belgium, USA and France. He completed several research projects i.e. Urban Solid Waste Management, (1997-2000), Bioconversion of Urban Solid Wastes and Agricultural Wastes (2001-05) and developed Soil and Water Pollution laboratory in the College with private funded project.

Dr. K. Jeevan Rao guided 35 M.Sc/Ph. D students as chairman and he attended more that 75 conferences, Symposia, seminars at India and Abroad.

At global level, soil quality improvement, environment pollution and climate change is a big challenge, which is affecting food security. Ammonia volatisation, nitrate leaching, and waste water use are making unwanted changes in climate, ground water quality and soil. Excessive fertilizer use and pesticide use are increases cost of cultivation and degrade soil quality. Therefore, there is a need to add soil amendment that will increase soil quality. Zeolite is a aluminums silicate mineral found in volcanic rock. High CEC, porosity, adsorption efficiency, nutrient carrier, slow release pattern of fertilizer and open channel network are making unique to zeolite. The unique characteristic of zeolite will increase nutrient use efficiency, soil water content, increase heavy metal adsorption and pesticide adsorption and decrease heavy metal content in plant, pesticide residues in soil solution, leaching of nutrient. Zeolite application will increase soil microbial population and enzyme activity.

When soil quality is defined from an environmental perspective as "the capacity of the soil to promote the growth of plants, protect watersheds by regulating the infiltration and partitioning of precipitation, and prevent water and air pollution by buffering potential pollutants such as agricultural chemicals, organic wastes, and industrial chemicals" (Sim *et al.*1997). To manage soil quality is most important to get maximum agriculture production, reduction of greenhouse gas emission and cultivation with less input. Poor soil texture, structure, water movement are creating problem to the soil productivity. Now a day, use of wastewater and sewage water is increased because of less availability of water for farming. This black water is more dangerous to soil health and human health. Heavy metal toxicity in soil and food causing cancer in human and also drastically changing soil biology. Soil fertility and nutrient use efficiency is a big issue in front of chemical industry and soil specialist. Use of conventional fertilizer are not increasing nutrient use efficiency, just increasing ground water pollution and greenhouse gas emission percent. To manage this entire problem is a big problem in front of soil scientist. Soil amendment is one option to reduce above soil related issue like soil pollution, soil fertilizer, water management, Nutrient use efficiency, and exchange properties of soil etc. Zeolite is available in soil and also in market can be remediate new issue in the soil. Zeolite is an aluminum silicate mineral can use as soil amendment. The unique properties of zeolite are higher surface area, cation exchange property (150–250 cmol(p+) kg^{-1}), adsorption efficiency, porosity (~ 50%) and open channel network (Ramesh *et al.* 2010). Open channel network and pore structure of zeolite are responsible for higher nutrient use efficiency and water use efficiency. Soil fertility status of soil and uptake of heavy metals in plant can be improve with increasing exchange capacity and adsorption capacity of soil that increase with zeolite application. Zeolite is a simple mineral which not harmful to soil, plant, and human being, but act as soil amendment, slow release fertilizer, soil solidificant and stabilizer. Zeolite has capacity to restore soil properties and improve soil quality.

Zeolite availability and classification

Zeolite is a Greek word which means that boiling stone and identified by Swedish mineralogist, Alex Fredrik Cronstedt in 1756 from copper mine in Sweden. Zeolite minerals were found in volcanic rocks and its commercial production and use started in 1960s (Polat *et al.,* 2004). A global level, zeolite deposits are found more extensively in western USA, Bulgaria, Hungary, japan, Australia and Iran (Mumpton and Rocamagica, 1999). In India, zeolites are found in Maharashtra, Madhya Pradesh, Andhra Pradesh, Tamilnadu and Karnataka. Zeolite contain in Deccan plateau of Black soil and Indo Gangetic plain region near about 98% and 2% of the area respectively which is approx. 2.8 million (Bhattacharyya *et al.,* 2015) . Zeolite deposits mostly found in western part of India particularly Pune, Nashik, Mumbai and Baroda. Total 80 different species identified under zeolite mineral group and some more are coming to be identified (Ramesh *et al.,* 2015). Zeolites mineral are classified under different group on the basis of their morphological characteristics, crystal structure, chemical composition, effective pore diameter, natural occurrence, etc. In 1997, International Mineralogical Association Commission was recommended zeolite as New Minerals for nomenclature (Ramesh and Reddy 2011).

Zeolite Structure

Zeolite is an aluminium silicate mineral like other clay mineral i.e. smectite, illite and kaolinite. In zeolite mineral, aluminosilicate tetrahedron share charge with twelve other tetrahedron and formed three dimensional frameworks. Zeolite is composed of pores and open channel. This channel is interconnect with each other and formed a special honey comb like structure. Zeolite mineral allow the entry water and nutrient inside the honey comb structure due to creation of partial pressure difference between soil pore and zeolite pore. The general formula of zeolite mineral: $MxDy[Al(x+2y)+2ySin\text{-}(x+2y)O2n]mH2O$, where x is the number of monovalent cations (K and Na), y the number of bivalent cations (Ca and Mg) , n the cation valence and m the number of water molecules in the formula (Ramesh *et al.*2010).

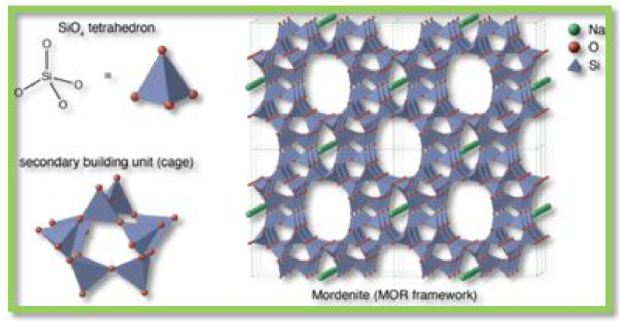
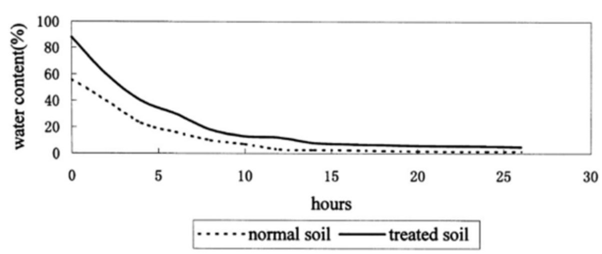


Figure 1. Zeolite structure

Effect of zeolite on soil properties

Soil water content

Soil water content is defined as the amount of water present in soil at particular time of time. Soil water content is mainly depending on the soil texture, bulk density and porosity of soil. Soil water content is an important factor for higher crop growth and yield. Length of growing period of crop is mainly depending on the availability of water for longer time. Presently, Maintain of soil water content for longer time mostly in the light texture soil under climate change is a great challenge. Zeolite is aluminum silicate mineral have capacity to increase water content in soil due to lower bulk density and porous structure of zeolite. Porous channel network of zeolite are responsible to the retention of water inside zeolite structure. Bulk density and porosity of light texture can modify with zeolite application. Application of zeolite at higher dose can increase soil water content period that improve water use efficiency.



The percent increase of water content in soil is also varies with zeolite size. Water holding capacity of soil was higher with nano zeolite than that of ordinary zeolite. Zeolite is considered as permanent water reservoir that provides water for longer period that will help to plant to withstand in dry spell. Application of zeolite in sandy soil was increases availability of water to plant by 50% (Voroney and Van Straaten 1988). In a study, it is reported that mixing of zeolite at 15 cm increased water holding capacity than that of placement of zeolite at proper depth. Ippolito *et al.* (2011). In another study, water holding capacity was increase with zeolite doses due to the decrease of bulk density of soil (Pandit *et al.,* 2019). Some studies found that application of zeolite in calcareous loess soil enhanced water retention upto 0.4 – 1.8 % compared to non zeolite treated soil in drought condition while in normal condition water content in zeolite treated soil was increased by 5– 15 %. Some authors studies the interaction of zeolite and nitrogen on water use. Highest water saving was recorded in 8 t ha $^{-1}$ zeolite along with different nitrogen rate viz.20, 40 and 80 kg N ha $^{-1}$. At 20 kg N ha $^{-1}$, seasonal water use in 0, 2, 4, and 8 t ha $^{-1}$ zeolite was 2098, 2217, 1954 and 1605 mm. These result showed that more water saving was observed in 8t ha $^{-1}$ zeolite treatment. At 40 kg N ha^{-1}, seasonal water use in 0, 2, 4 and 8 t ha^{-1} zeolite was 2124, 2233, 1864 and 1685 mm. At 80 kg N ha^{-1}, seasonal water use in 0, 2, 4, and 8 t ha^{-1} zeolite application rates was 2161, 2277, 1916 and 1666 mm. These result showed that highest water saved in 8t ha $^{-1}$ zeolite dose. Application of zeolite as agriculture amendment to improve the water saving in summer. The residual soil moisture in summer was increase by 1.4 % with application of 7 kg m $^{-2}$ zeolite compared to control. Maximum soil water holding was found in mixed applied zeolite than band placed zeolite. Zeolite was applied in soil by mixed method absorbed more soil moisture by 1.3% (wt. basis) than band placement. On averaged, band applied zeolite contained less soil moisture by 2.6% than mixed applied zeolite. 44.8 Mg ha^{-1} mixed applied zeolite absorbed 2.1% more water than control treatment. The maximum soil water was retained at – 100 and -300 Kpa in 44.8 Mg ha $^{-1}$ zeolite treatment compared to control and 13.4 Mg ha $^{-1}$. The research reveals that soil water retaination were increases with increasing zeolite application rate. Zeolite application was decline volume of irrigation. It examined that 40% depletion of water received more irrigation compare to 50% depletion of water due to presence of zeolite.

Exchange capacity

Cation exchange capacity is one of the important property of soil that decide fertility status of soil. Nutrient availability, nutrient movement and its losses are depend on the exchange property of soils. Exchange capacity of sandy and silt containing soils are very low than that of clay containing soils due to the small surface area. Higher surface area and charge density of clay particle will show maximum exchange capacity. Smectite and vermiculite containing soil are having higher exchange capacity than kaolinite and illite containing soils. Zeolites have higher exchange capacity than smectite and vermiculite due to the higher surface area. The experiment revealed that CEC of soil contained kaolinite, smectite and allophane increased by 3.8, 1.9 and 3.9 time respectively than original soil due to addition of 10% artificial zeolite (Moritani *et al*., 2010). Some other experiment also revealed that CEC of soil was increases significantly by addition zeolite at 5, 10 and 15 t ha^{-1} zeolite by 22.2 %, 40.8 %, and 51.4% respectively (Taotao *et al.,* 2017). Tsadilas and Argyropoulos (2006) reported that CEC of soil were increase significantly due to addition of zeolite to soil. Lowest value of CEC was observed in control pot (9.5 cmol(p+) kg^{-1}) while highest value was observed in 60 ton ha-1 zeolite dose (13.6 cmol(p+) kg^{-1}) followed by 45 ton ha-1 zeolite dose (13.4 cmol(p+) kg-1), 30 ton ha-1 zeolite dose (12.5 cmol(p+) kg^{-1}) and 15 ton ha^{-1} zeolite dose (11.4 cmol(p+) kg^{-1}) .After addition zeolite in soil, CEC of soil was increase by 43% compare to without application of zeolite.

Detoxification of soil

Detoxification of heavy metals

Soil pollution is a big challenge which increasing due to domestic waste, municipal waste, mining activities and industrial activities etc. Contaminated soil contained higher concentration of heavy metals like cadmium, lead, arsenic, nickel, mercury etc. Heavy metal content in soil is increasing with the use wastewater as irrigation water, use of fertilizer and use of water from industrial water bodies. Contaminated soil contained heavy metal will create serious problem for crop and human health due to toxic effect of heavy metal. Therefore, there is a need of remediation of contaminated soil with use of soil amendment like organic residue, phosphorus fertilizer, calcium carbonate, gypsum and zeolite. Zeolite is an aluminum silicate mineral that reduced toxicity of bioavailability of heavy metal through stabilization and solidification processes. Zeolite is immobilized heavy metal by chemical processes (complex speciation reactions) and physical processes based on the sorption of an element on material surfaces or encapsulation in the matrix. Complexation, ion exchange, precipitation, and adsorption are the major mechanisms involved in the transition of soluble forms of heavy metals to geochemically stable solid phases, thus reducing the heavy metal available for uptake by plants in soils (Cao *et al*., 2019). The application of modified halloysite was shown to be the most effective and decreased the average nickel content by 12%. The application of natural zeolite to soil reduced the nickel content in the soil by 13% (Radziemska and Mazur, 2016). Hasanabi and coworkers (2019) reported that application of natural zeolite significantly reduced concentration of lead and cadmium in root and shoot of plant and lower concentration in shoot and root of plant achieved with higher zeolite dose. Antoniadis and Damalidis (2014) studies the adsorption behavior of zeolite having 226 cmol (p^+) kg^{-1} cation exchange capacity in cu pollutant soil. The result indicated that zeolite was reduce available cu by 56 % and application of lime with zeolite increased adsorption of cu on zeolite by 72%. Panuccio and his coworker (2009) investigated the cadmium adsorption on vermiculite, pumice and zeolite. The result showed that zeolite adsorbed 70 % cadmium on surface which higher than vermiculite and pumice. Hu and coworker (2018) revealed that ordinary and nano zeolite significantly increased pH and reduced available cadmium. The result showed that application of ordinary and nano zeolite reduced the available Cd contents at 19.3% - 32.7% and 23.2% - 40.5%, respectively. Nano zeolite significantly reduced Cd content in tobacco compared to ordinary zeolite. Li and coworker (2009) study the remediation of lead polluted soil with natural zeolite. Natural zeolite was added in the lead polluted soil that increased pH and CEC of soil. Application of zeolite at 10 g kg^{-1} was significantly reduced lead content in contaminated soil contained > 1000 mg kg^{-1} lead. The reduction of lead from polluted soil because of increased of soil pH with application of zeolite only. In lead polluted soil (>2000 mg kg^{-1} lead), uptake of lead in rape crop reduced by 30% with 20 g kg^{-1} dose of zeolite.

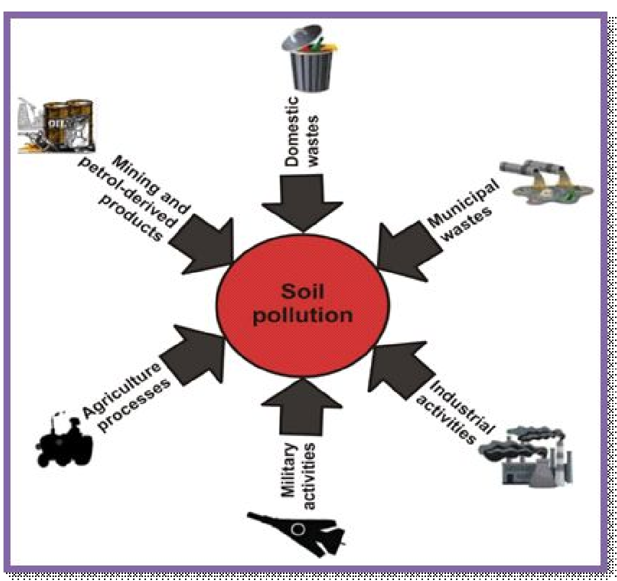


Figure: Main anthropogenic sources of soil pollution

Detoxification of Pesticide

Excess use of pesticide cause problem to soil biodiversity. Soil quality could be degrading by pesticide uses that drastically affect soil microorganism population and soil enzyme. Indirectly, excess pesticide usages are degrading soil fertility. Pesticide and its residues present in soil can be adsorbed on the clay, activated carbon, and zeolite. The unique properties of zeolite are higher surface area and CEC that responsible for higher adsorption of pesticide on zeolite. The sorption of pesticide on zeolite reduced the harmful or toxic effect of pesticide on soil microorganism. Zeolite is mostly used to remove the pesticide residues from waster. Pucarevic and his coworkers investigated the effects of pH, particle size and amount of zeolite on the amount of adsorbed atrazine. The highest atrazine adsorption was 73 % at high pH values with a use of 15g zeolite. At high pH value (pH=10), largest amount of atrazine adsorption was achieved with zeolite having particle size of 1-2 mm. At low pH, Atrazine adsorption on zeolite of 1-2 mm size was decrease due to protonation of zeolite. At low pH condition, Adsorption of atrazine can increases with decrease of particle size. The adsorption of efficiency of zeolite was increase with decrease of zeolite particle size (Pucarevic *et al.,*2017).

Nutrient interaction with zeolite

Nitrogen

Nitrogen is present in anion (NO^-_3) and cation (NH^+_4) form in soil. Both nitrogen forms are actively interact with zeolite because of high surface area for adsorption and presence of pore canal network in zeolite. Nitrogen is interact with zeolite by two ways i.e. adsorption on surface and absorption inside zeolite channel. Ammonium nitrogen is interacting with two ways but maximum amount of ammonium nitrogen can interact with zeolite by adsorption mechanism. Nitrate nitrogen is a anion form which interact with zeolite by absorption mechanism. Adsorption and absorption mechanism will release nitrogen in soil by slow release pattern. Therefore, sometime zeolite is called slow release nitrogenous fertilizer. Zeolite can reduce the nitrate leaching, ammonium fixation, and denitrification of nitrate. Application of surface modified clinothoptile and zeolite clinoptilolite at higher rates was reduced nitrate leaching by 26% and 22 % compared to control (Malekian *et al*., 2011). Available nitrogen content at start and end of experiment was more observed in 5% compost + 2% zeolite treatment (75 mg kg $^{-1}$ and 35 mg kg $^{-1}$ respectively) compared to control (22 mg $kg^{-1}$and 31 mg kg^{-1} respectively) (Litaor *et al*.,2017). Malekian *et al*. (2011) reported that clinothoptile and surface modified clinothoptile showed significant effect on inorganic nitrogen content in soil. Highest ammonium- N content in 0- 30 cm depth after harvest was recorded in 27 t ha $^{-1}$ zeolite level (28 – 33 mg kg $^{-1}$ soil) followed by 9 t ha $^{-1}$ zeolite level (28 mg kg $^{-1}$

soil) while Highest ammonium- N content in 30-60 cm depth after harvest was recorded in 27 t ha^{-1} zeolite level (25 mg kg^{-1} soil) followed by 9 t ha^{-1} zeolite level (23 mg kg^{-1} soil). Highest nitrate- N content in 0- 30 cm depth after harvest was recorded in 27 t ha^{-1} zeolite level (35 – 38 mg kg^{-1} soil) followed by 9 t ha^{-1} zeolite level (25 -28 mg kg^{-1} soil) while Highest nitrate- N content in 30-60 cm depth after harvest was recorded in 27 t ha^{-1} zeolite level (28-30 mg kg^{-1} soil) followed by 9 t ha^{-1} zeolite level (30-32 mg kg^{-1} soil).

Phosphorus

Phosphorus availability is very low in any type of soil. The reason of low availability of phosphorus is the formation of insoluble complex with calcium, aluminum and iron. In submerged condition, phosphorus availability is increases first then decreases by the formation of insoluble complex with iron and aluminum. Zeolite can constantly increase availability of phosphorus in submerge soil. Zeolite was adsorbed micronutrient on the surface and reduces the formation of insoluble complex. In normal condition, zeolite treated soil have higher phosphorus in available form. Modification of zeolite is require to increase cation exchange capacity of zeolite. Ammonium saturated zeolite and high temperature modified zeolite have more CEC than zeolite. Modified zeolite has more capacity to adsorbed micronutrient than ordinary zeolite due to higher CEC and surface area and reduce phosphorus fixation. The absolute increments of available phosphorus with high-temperature modification of ammonium saturated zeolite were 23.48 mg·kg"1, 15.10 mg·kg"1 and 7.92 mg·kg"1 in high phosphorus, medium and low phosphorus soil respectively. Solubilizing effect of the ammonium saturated zeolite was also evident, the absolute increments of its available phosphorus were 20.30 mg’”kg"1, 12.35 mg·kg"1 and 6.13 mg·kg"1 1in high, medium and low phosphorus soil respectively. Solubilizing effect of the high-temperature modified zeolite was better than the zeolite, and the absolute increments of its available phosphorus were 7.20 mg·kg"1, 6.90 mg·kg"1 and 3.49 mg·kg"1 in high, medium and low phosphorus soil respectively. The absolute increments of ordinary zeolite were 1.10 mg’”kg"1, 2.11 mg’”kg"1 and 0.35 mg’”kg"1 in high, medium and low phosphorus soil respectively (Jing *et al.*, 2016).

Potassium

The interaction of potassium with zeolite is same like Nitrogen – zeolite interaction. Potassium is cations which easily adsorb and absorb on zeolite. Potassium is enter in to the zeolite porous canal network and adsorb on surface due to higher CEC and surface area. Zeolite will reduce leaching and fixation of potassium. The adsorb and absorb potassium will release from zeolite in the slow rate. Therefore, zeolite is also called slow release potassium fertilizer.

Role of zeolite in Nutrient use efficiency

Nitrogen use efficiency

Nitrogen use efficiency is depend on many factor like crop, climate, soil and fertilizer etc. Nitrogen use efficiency of crop is varies between 30 – 50%. Fertilizer management like right time, right place, right fertilizer and right dose is most important practice for the improvement of use efficiency of nitrogen. Improvement in NUF will reduce fertilizer use, groundwater pollution and also decrease crop cultivation cost. Different kinds of fertilizer or other materials are available in the market that will increase fertilizer use efficiency or Nitrogen use efficiency. Conventional fertilizer like Urea, DAP and Ammonium Sulphate have less use efficiency in field. Fertilizer management practices can improve the nitrogen or fertilizer use efficiency, but in small percent. Smart fertilizer like slow release fertilizer, coated fertilizer and Nano fertilizers are have great potential to increase nitrogen or fertilizer use efficiency. Zeolite is an aluminum silicate clay mineral has capacity to increase nitrogen use efficiency due to the higher surface area and presence of canal like micro structure that mechanism releases nitrogen from zeolite in slow release pattern. Application of zeolite with Nitrogen fertilizer significantly improved the Nitrogen use efficiency. Taotao *et al.* (2017) studied that addition of 5 to 15 t Z ha^{-1} to the soil improved NUE by 24.6 to 88.2% at 52.5 kg N ha^{-1}, 68.7 to 78.2% at 105 kg N ha^{-1}, and 15.4 to 23.6% at 157.5 kg N ha^{-1}, which suggests the potential of agricultural application of Z for improving the NUE in lowland rice production systems. Application of zeolite at 8 and 16 t ha^{-1} with 60 kg N ha^{-1} improved N recovery up to 65% and agronomic use efficiency to 22 kg grain kg^{-1} N applied (Kavoosi, 2007). Sepaskhah and barzegar (2010) revealed that application of nitrogen along with zeolite was significantly increased agronomical nitrogen use efficiency in rice. A higher zeolite dose with lower nitrogen doses observed increasing trend of Agronomic NUE. Among four nitrogen levels, highest agronomical nitrogen use efficiency found in 20 kg ha-1 N at 2, 4 and 8 t ha^{-1} zeolite was 33, 37.7 and 58.8 kg grain kg^{-1} N respectively compared to other nitrogen doses. Aghalikhani *et al.* (2012) also reported highest NUE in N270Z9 (29%) treatment followed by N180Z9 (23%) treatment and N90Z9 (4%) treatment in canola.

Phosphorus use efficiency

Application of conventional phosphorus fertilizer will get maximum less than 20% phosphorus

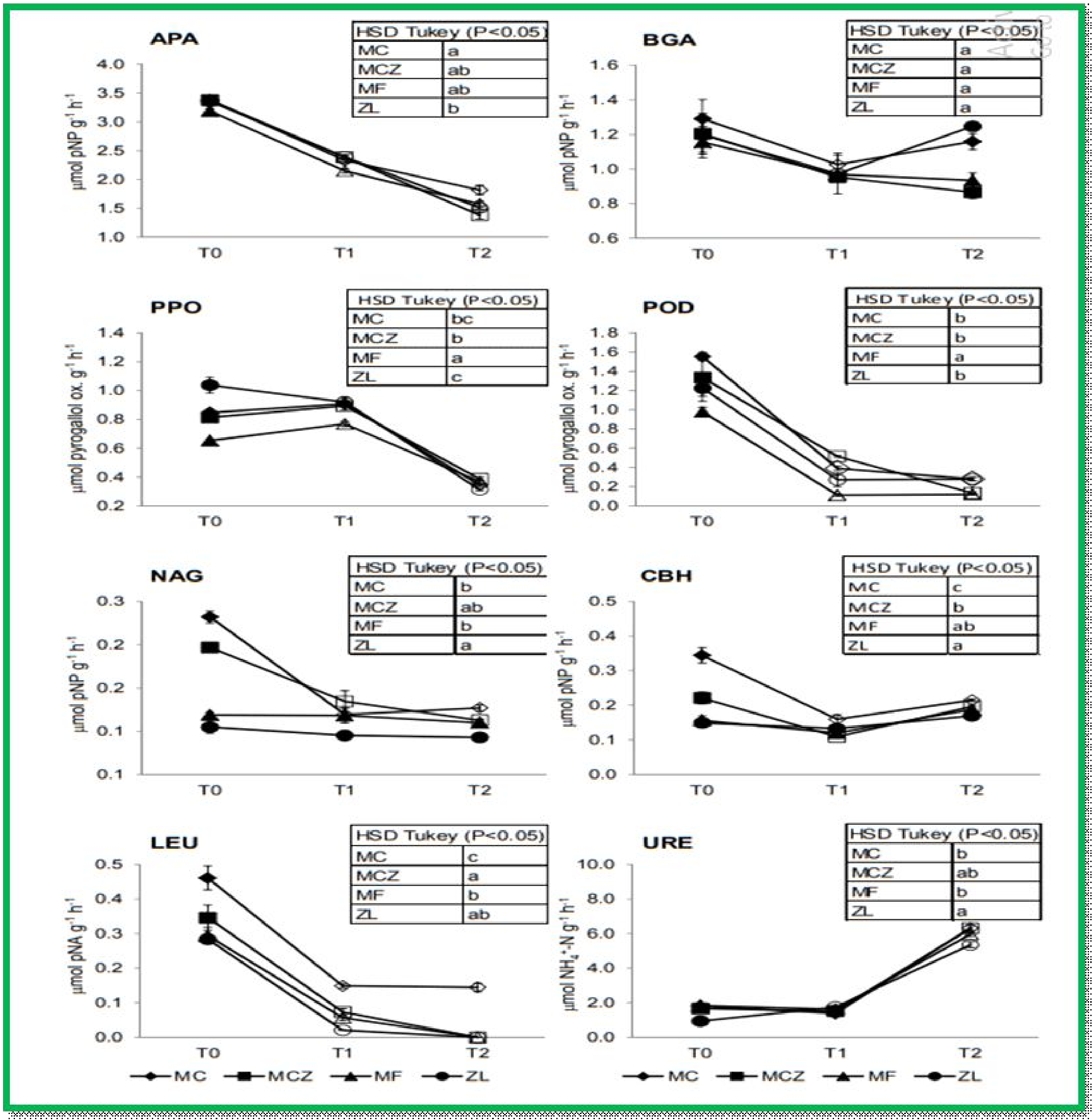


Figure. Influence of zeolite, manure compost, Fertilizer and Leonardite on soil enzyme activities.

use efficiency. Phosphorus use efficiency can be increase with application of organic residues, nano phosphorus fertilizer and also increase with the application of zeolite. 4 R's practices are also important to improve phosphorus efficiency. Zeolite and Nano zeolite Phosphorus fertilizer have a great potential to increase phosphorus use efficiency more than 30% (Hagab *et al.,* 2018). Hagab *et al.* (2018) reported that the apparent recovery efficiency of P at a rate of 100% was 18.40, 32.90 and 23.70% for Super phosphorus, Nano Zeolite Phosphorus and Zeolite Phosphorus, respectively. When only a rate of 50% of the recommended rate from nano source was used, the recovery efficiency was higher than applying 100% of the ordinary source. This indicates that nano zeolite phosphorus can be used as a potential and economic alternative source to other sources. Therefore, using nano zeolite phosphorus would help in reducing the quantity of the applied fertilizers and consequently the farmers' profitability.

Effect of zeolite on soil microbial population and Enzyme activities

Bacteria population, mould growth and ammonifiers were significantly increases with the application of ammonium loaded zeolite than that of mineral fertilizer and control. Dehydrogenase activity was significantly higher in ammonium loaded zeolite than mineral fertilizer application and control (Karlicic *et al*., 2017). Jose *et al*. (2017) investigated effect of manure compost, manure compost and zeolite and Fertilizer on soil enzyme activities. The results indicate that soil enzyme activities i.e. Urease activity, alkaline phosphatase activity, polyphenol oxidase, PPO, and peroxidase, POD and cellobiohydrolase activity (CBH) were significantly increased with manure compost and manure compost plus zeolite application than fertilizer application.

CONCLUSION

There is increase of zeolite use in agriculture because of positive response of zeolite on soil, plant and fertilizer. Special structure (Pore and channel network) and unique properties of zeolite like high CEC, low bulk density, high adsorption efficiency are responsible for improvement of soil fertility. Zeolite use is reducing heavy metal content, ground water pollution, and fertilizer use. Zeolite is act as nutrient carrier that increases soil productivity.

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