Brazilian sedimentary zeolite use in agriculture

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Abstract
Zeolites are hydrated crystalline aluminosilicate minerals of alkaline and alkaline earth metals, structured in rigid three dimension nets, organized by AlO_4 and SiO_4 tetrahedral and are of natural occurrence. This report describes the characterization and application of the Brazilian zeolitic sedimentary rock as a release fertilizer and soil conditioner. The characterization of the head samples showed that it is composed of the zeolite stilbite intermixed with a smectitic clay mineral, and quartz. A low-cost quartz separation technique was established. Enrichment of concentrated natural zeolite was carried out: zeolite + KNO_3, zeolite + K_2HPO_4 and zeolite + H_3PO_4 + apatite and the concentrated zeolite. These materials were tested with Rangpur lime rootstock and an experiment was also carried out with successive crops grown on the same substrate: lettuce, tomato, rice, and Andropogon grass. The results indicated that N, P and K enriched zeolite was an adequate slow-release source of nutrients to plants. Other green house and field experiments with concentrated zeolite applied with urea showed reduction of losses of ammonia by volatilization and improved in N use efficiency by maize. Concentrated zeolite also increased water retention and the available water capacity of a sand soil.

Key Words
Stilbite, slow-release fertilizer, N losses, water retention curve, available water capacity.

Introduction
The use of minerals for agricultural purposes is becoming widespread (Van Straaten 2006), and zeolitic concentrates have a special niche in this category. Zeolite minerals are crystalline hydrated aluminosilicates of alkali or alkaline-earth metals, structured in three-dimensional rigid crystalline network, formed by the tetrahedral AlO_4 and SiO_4, which come together to compose a system of canals, cavities and pores (Ming and Mumpton 1989). The worldwide number of identified natural zeolite – about forty –demonstrates both their great variety and the present-day interest on their potential applications in the industry and the agriculture (Ming and Dixon 1987). These minerals have three main properties, which are of great interest for agricultural purposes: high cation exchange capacity, high water holding capacity in the free channels, and high adsorption capacity (Mumpton 1999). Sediment occurrences of this aluminosilicate are known to exist in northern areas of Brazil (Rezende and Angelica 1999).

Zeolites improves the efficiency of nutrient use by increasing the availability of P from phosphate rock, the utilization of $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ and reduced losses by leaching of exchangeable cations, especially K^+ (Barbarick *et al.* 1990; Allen *et al.* 1995; Williams and Nelson 1997; Leggo 2000; and Pickering *et al.* 2002). Zeolites mixed with phosphate rock, can act as controlled delivery system and renewable source of nutrients for plants (Allen *et al.* 1995; Barbarick *et al.* 1990). The increased efficiency of N utilization when urea is used together with zeolite was demonstrated by Crespo (1989), Bouzo *et al.* (1994), Carrion *et al.* (1994) and He *et al.* (2002) that achieved increasing of N use efficiency, N uptake and dry matter yield and reductions of losses by ammonia volatilization. Zeolites also improves the efficiency of water use by increasing the soil water holding capacity and its availability to plants (Xiubin and Zhanbin 2001; Bernardi *et al.* 2008). While literature shows that zeolites are useful for increasing nutrient use efficiency in a range of crops, little information exists on the use of stilbite, in agricultural systems especially on acid soils. The objective of this report was to characterize and test the application of Brazilian zeolitic sedimentary rock as a slow release fertilizer and soil conditioner.

Methods
Zeolite used was collected in the north of the State of Tocantins, Brazil, in the basin of the Parnaiba river (Rezende and Angelica 1999). It had 470 g/kg of stilbite. The material was crushed and part of it was

concentrated, separating contaminants (quartz and iron oxides and hydroxides) from zeolite by means of gravitational concentration, using the Humphrey spiral, resulting in material with 650 g/kg of stilbite. The mineral was classified by sieving followed by Tyler-series grain size selection from 295 to 37 μm. All fractions were analysed by X-Ray diffraction (XRD). Nutrient adsorption and release properties matched those reported for similar commercial zeolitic products (Monte *et al.* 2009).

A greenhouse experiment was carried out with 3 kg pots with an inert substrate with an experimental design of randomized block with three replications. Four levels of enriched zeolite were tested: 20, 40, 80 and 160 g/pot. And four successive crops were obtained on the same substrate of each pot: lettuce, tomato, rice and Andropogon grass. In another experiment Rangpur lime (*Citrus limonia* Osbeck) rootstocks were cultivated during 93 days in 150cm^3-dibble tubes containing composted organic substrate of cocopeat and vegetal coal (3:1) with zeolite addition. Treatments comprised four types of enrichment of concentrated natural zeolite: only concentrated zeolite (Z), zeolite + KNO_3 (ZNK), zeolite + K_2HPO_4 (ZPK) and zeolite + H_3PO_4 + apatite (ZP) prepared as described by Monte *et al.* (2009). These treatments were also compared with adequate available nutrient supplied by complete nutrient solution. The N-urea losses were evaluated with collectors for volatized ammonia capture with phosphoric acid solution (0.5 N), changed every two days to determine the volatilized ammonia, with 11 samples taken in a period of 22 days.

Evaluation of the mineral as a soil conditioner was undertaken with three levels of zeolite 33.3; 66.7 and 100.0 g/kg and a control applied to a sand soil. Samples for the soil water retention were collected with stainless steel cylinders. the water retention curve was determined in a Richard´s pressure chamber and the equation of soil volumetric water content as a function of matric potential were adjusted with the van Genuchten model. All data were tested for differences among treatments using an analysis of variance. Response function and equations were adjusted as a function of treatments.

Results

Characterization analyses demonstrate that the zeolitic sediment and quartz are the major components of the head samples. The head sample contained zeolite stilbite mixed with smectitic clay. A characterization with X-Ray diffraction showed the presence of stilbite (ideal formula, $(Na,K)Ca_2[Al_5Si_{13}O_{36}]\ .14H_2O$) as one of main mineral components (Figure 1). The slow-release fertilizer effects of zeolite are a result of ion-exchange reactions with the zeolite, or through a combination of ion-exchange and mineral-dissolution reactions. Results of the successive crops of lettuce, tomato, rice and andropogon grass carried out on the same substrate of each pot indicated that N, P and K enriched zeolite was an adequate slow-release source of nutrients to plants (Figure 2A). The experiment also demonstrated the enhanced P availability from phosphate rock when applied in combination with zeolite, P availability presented a trend of increasing, especially after the second and third crops unlike the soluble P source (Figure 2 B and 2C).

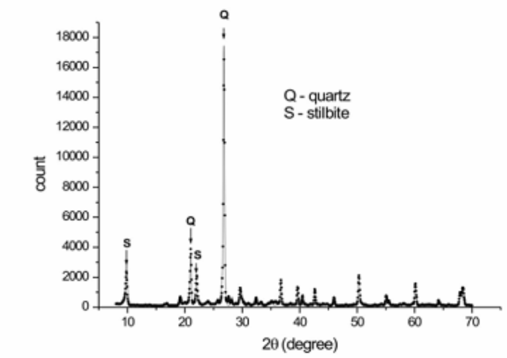

Figure 1. X-Ray diffraction of zeolite stiltbite. Source: Monte *et al.* (2009).

Figure 3 illustrates that the supply of nutrients through the mineral zeolite enriched with NPK added to the organic substrate was a viable alternative for Rangpur lime citrus rootstock production in protecting the environment since significantly increased dry matter production (3A), height and stem diameter (3B). Evaluation of the mixture of urea and zeolite to avoid ammonia volatilization in pot with soil and Tanzania-grass pasture are illustrate in Figure 4. The smallest losses by volatilization occurred at the proportions of the mixture of 25% of zeolite to urea and lead to a loss reduction from 33.5 to 7.6 kg/ha. Dry matter yield of silage corn as a function of N fertilizer level and zeolite ratio and type is illustrated in Figure 1. The highest

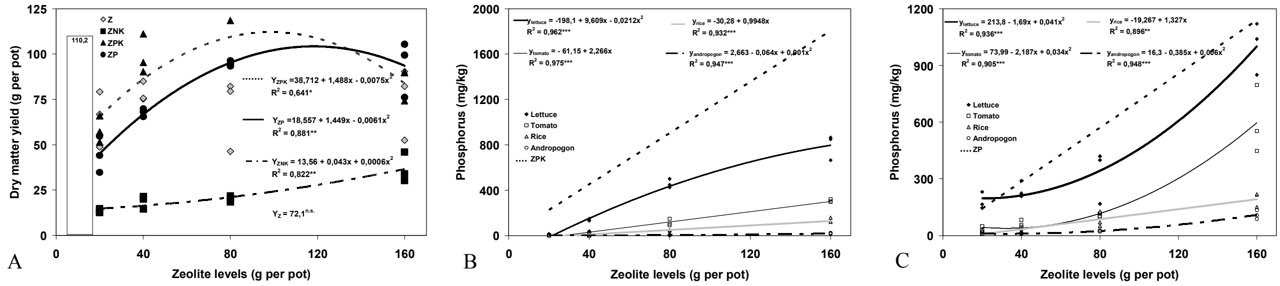

Figure 2. Dry matter yield of successive crops of lettuce, tomato, rice and Andropogon grass with N, P and K enriched zeolite stilbite (A) and P availability of ZPK (B) and ZP (C) after each crop. Source: Bernardi *et al.* (2009b).

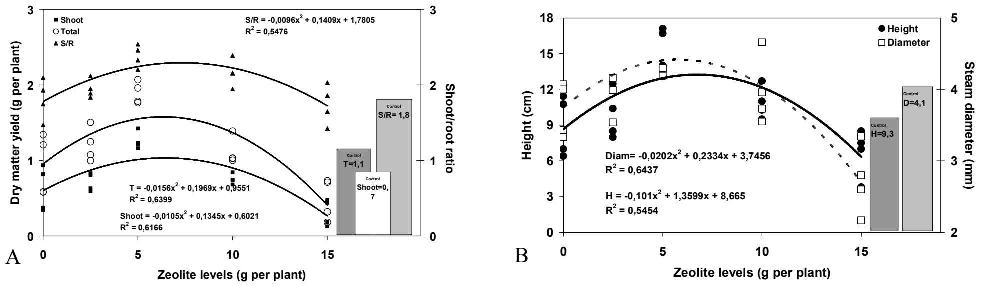

Figure 3. Dry matter yield, shoot/root ratio (A), plant height and stem diameter (B) of Rangpur lime rootstock according to level of zeolite stilbite. Source: Bernardi *et al.* (2008).

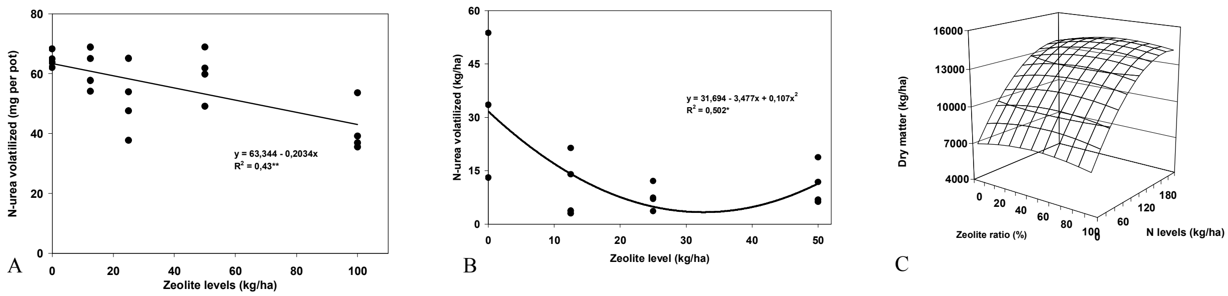

Figure 4. Losses of N-urea in pot (A) and Tanzania-grass pasture (B) experiments and silage corn dry matter yield (C) according to addition of zeolite stilbite. Source: Campana *et al.* (2009).

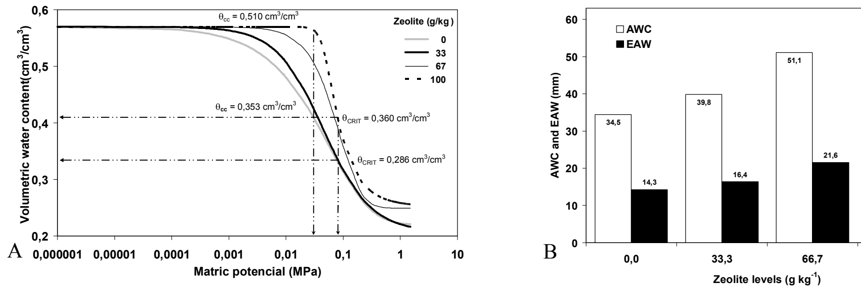

Figure 5. Water retention curve (A) available water capacity (AWC) and easily available water (EAW) (B) according to level of stilbite. Source: Bernardi *et al.* (2009a).

silage corn dry matter yield (14.5 kg/ha) was obtained with 183 kg/ha of N plus 59.6% of concentrated zeolite (Figure 4C). The highest values of DM yields were approximately 48% higher than those obtained without nitrogen fertilizer, and only 5.5% higher than DM yield obtained with N fertilizer but without zeolite. Zeolites are also an alternative to improve soil water retention when used as soil amendments. Results shown in Figure 5 indicate the change of water retention curve with zeolite amendment and on available water capacity increased 10, 38 and 67% and easily available water increased 15, 51 and 111% in relation to the control with the use of 33.3; 66.7 and 100.0 g/kg of zeolite. The present results indicate that despite their high-impurity content; applications of natural Brazilian zeolitic concentrates in agriculture present no major obstacle. And the addition of the zeolite - stilbite concentrate should increase the agronomic efficiency of fertilizer.

1 – 6 August 2010, Brisbane, Australia. Published on DVD.

Conclusion

The results indicated that concentrated zeolite enriched with N, P and K was an adequate slow-release source of nutrients to plants. Zeolite applied with urea improved N use efficiency and when applied with phosphate rock increased the P availability to plants and also increased water retention and the available water capacity of a sand soil when use as a soil conditioner.

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