The Organo-Zeolitic-Soil System: A New Biological Approach to Plant Nutrition

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Abstract: - A highly effective biological fertilizer (bio-fertilizer) can be produced cheaply in countries that have a source of a suitable type of zeolitic rock (tuff). Such rocks occur worldwide in areas of past or current volcanism. In the event of explosive volcanic activity huge volumes of silicic glass and other debris are projected into the atmosphere. Reaching high altitude the fine material is separated forming ash clouds of fine grained glass shards. On entering water they become thick beds of sediment producing a rock having a high abundance of zeolite. On uplift they are available for open cast quarrying. When mixed with organic waste, either animal or plant, a biological fertilizer is produced. Ammonium ions, from the decomposing organic waste, are captured by the zeolite. When the fertilizer is added to the soil the ammonium ions become oxidised by soil micro-organisms (Crenarchaeota) to nitrate together hydrogen ions. The hydrogen ions, reacting with the substrate, provide a range of essential and beneficial plant nutrients. Unlike chemical fertilizers (NPK) the nutrients are delivered slowly as the plant grows and there is little surplus to leach into the ground and thus the bio-fertilizer is not highly susceptible to leaching by rainfall. Adequate phosphate ions are available from the organic waste and potassium, being a more ubiquitous element is present in the soil / organic mixture and acts to back exchange ammonium ions that are oxidized to nitrate as mentioned above.

Key-Words: - zeolitic tuff, organic waste, ammonium ions, nitrate, crenarchaeota, phosphate, potassium.

1 Introduction

Zeolites are framework alumino-silicates that have a unique property in that they possess open channels (pores) and cavities present throughout the lattice. The basic building block is a tetrahedral unit with a silica atom at its centre surrounded by four oxygen atoms in corner positions; the sharing of which form the crystalline lattice. It is the substitution of silica by aluminium that imparts a negative charge to the zeolite surface which in turn is compensated by the uptake of cations and water molecules.

Often the cations are weakly bound and can be exchanged by other cations.

Water molecules, acting as cations are always present in the natural zeolite lattice, and are susceptible to loss and gain, on heating and cooling which accounts for their well-known desiccant property. The bio-fertilizer is made of the crushed zeolitic rock (tuff) and an organic component, either animal or plant waste. The function of the common zeolite mineral, either clinoptilolite or mordenite, is to adsorb ammonia made available from the decomposition of the organic waste. Without the presence of the zeolite, the ammonia would be volatilised into the atmosphere and lost.

When soil is amended with the bio-fertilizer the ammonium ion (NH4+) is back exchanged into the soil pore water and oxidised to nitrate by nitrifying soil microorganisms. Due to its higher selectivity, in both clinoptilolite and mordenite, [1] and its ubiquitous nature potassium (K+) is the most likely ion to replace NH4+.

Molecular biological work on aqueous extracts from soils amended with the biofertilizer has shown the ammonium oxidizer to be Crenarchaeota. rather that nitrifying Bacteria [2]. Protons from the ensuing enzyme reactions protonate the soil pore water producing hydronium ions which are very unstable and react with the soil to dissociate cations. Phosphorus and other nutritional anions are present in the organic component and essential cations are available for plant uptake in the amended soil.

The bio-fertilizer has been developed at Cambridge University over the last decade.This work concentrated on the re-vegetation of barren contaminated land and has constantly demonstrated its efficacy. Plants such as Arabidopsis, Miscanthus, Osier Willow, Oil Seed Rape, Linseed, Maize and Sugar Beet have all shown enhanced growth on contaminated soils such as mine and coal waste. The work has also demonstrated that both components, crushed zeolitic tuff and organic waste, mixed together are required to produce the enhanced growth performance. Experiments with spring wheat, peppers, chili, tomatoes, lettuce and various herbs have also shown the same effects and it is now clear that countries that have suitable zeolitic tuff will be able to sustain their food crops very economically.

Use of the bio-fertilizer does not suffer from the long term problem of artificial chemical fertilizer which causes groundwater pollution and the loss of soil carbon. The application of chemical salts is known to cause nutrient limited soil microbes to rapidly decompose the soil organic matter (SOM) which can lead to a loss of soil structure with less capacity to hold water [3]. Thus, the bio-fertilizer has the advantage of being potentially less expensive, far easier to produce in terms of energy cost and greater benefit to soil health.

2 Plant Growth

The initial research was aimed at environmental protection as if contaminated land could be vegetated and thus stabilized then the transport of pollutants can be controlled. Work with pot plants growing in acid sulphide mine waste [4] was successful, see Fig.1. The same degree of success was obtained using mine waste from a demolished coal mine in the Nottinghamshire coal field [5], Figs. 2, 3 and 4. An image of mature Corn ears, (Zea m*aize*) are shown in Fig. 3. The plant substrate is a mixture of coal waste and debris from the demolition of the mine buildings. This material has a very low nutritional value being high in Al, Si and Fe but relatively low in K and very low in P, see Table 1. The nitrogen concentration was not analyses but is assumed to be very low. Other plants grown on the coal waste included Oil Seed Rape (*Brassica napus*), Tall Grass *(Miscanthus giganteus*) and Osier Willow (*Salix viminalis*) were also greatly enhanced by the addition of the bio-fertilizer. Wheat (*Triticum aestivum*), Rye Grass, (*Lolium perenne*) , Creeping Red Frescu (*Frestuca rubra*), Timothy (*Phleum ptatense*) and Red Clover (*Trifolium pratense*) in other studies behaved likewise. Tomato, Chiles , Peppers and various herbs have also shown considerable growth enhancement when their various substrates have been amended with the biofertilizer.

3 Methods, Experimental Studies and Results

Throughout the work use was made of the departmental SEM, XRD and ICMS for the morphological and structural analysis of the zeolitic tuff and analysis of plant tissue chemistry. The University of Cambridge Botanic Garden soil was used for all the pot plant work. This soil can be described as a dark grey clayey silt containing fine to medium grained sand together with some fine to medium gravel. The pH of aqueous soil extracts varied between 7.0 and 8.0. The organic material, used in the preparation of the bio-fertilizer , was poultry manure which was mixed with the zeolitic rock (tuff) in the ratio 2 : 1 by volume. This material was composted until a temperature of 70^{o}C was reached, after which it was shown to be free of pathogenic organisms. The mixture, lacking malodour, was added to the soil substrate in the ratio of 1:5 by volume; the un-amended soil being used as the control. Aqueous leachates of the substrates were prepared systematically by watering to field capacity and allowing the substrates to drain freely. In this way repeated analyses of electrical conductivity and pH were found to have low experimental variation. Shoots and stems were dried at 65^{o} C and used for the comparison of plant growth between different substrates, being cut at soil level when the plants reach maturity.

Molecular biological study of substrate pore water identified a novel group of ammonia oxidizers, previously found in saltwater in the late 1990’s, known as Crenarchaeota. a phylum of the Kingdom Archeae now considered to be the dominant ammonium-oxidizing prokaryotes in soils [6]. These prokaryotic cells can function in conditions of extreme temperature, as high as 97^{o}C in hot springs, and pH values as low as 2.5, existing in habitats that far exceed those of bacterial ammonium-oxidising microbes. Time-course experiments show the concentration of NH4+ ions adsorbed to the zeolitic tuff grains, separated from amended substrates and analysed using an ammonium selective electrode, reach a maximum in 50 – 60 days after which the concentration falls dramatically [7]. It is now understood that the development of Crenarchaea controls the oxidation rate of the NH_4^+ ions providing nitrate over this Period. However, four nitrogen fixing bacteria, Bradyrhizobiumjaponicum, Rhodopseudomonaplaustris, Azospirillum brasile and Frankia alni, were also found to be present but what degree of effect they have on the degree of nitrification is currently unknown. The variation of nitrate concentration of aqueous leachates taken from the pot plants during the time-course experiments, show that the substrates amended with the organo-zeolitic material have nitrate concentrations that far exceed those having only an organic amendment. This feature has been seen elsewhere as controls have shown that both components must be present to produce the high degree of plant growth enhancement found. A linear relationship exists between the nitrate concentration of aqueous leachate from the amended substrates and electrical conductivity. Such a relationship would be expected if the enzyme reactions involved in the nitrification was protonating the substrate pore water [8] .

4 The use of the bio-fertilizer to stabilise industrial waste deposits.

Mining of nickel-copper sulphides at Lynn Lake in Manitoba, Canada has produced some 22 million tonnes of waste spread over 213 hectares of deforested land, which is now barren of vegetation . These tailings contain toxic metals such as lead, copper and zinc together with other trace elements such as arsenic, nickel, chromium. The site is prone to wind and water erosion. In high winds clouds of toxic dust occur which endangers inhabitants of the local township. As the chemical composition of the waste is not compatible with plant growth it was decided to use the bio-fertilizer to attempt to establish vegetation on the site in order to stabilize the waste and stop its transportation.

Private funding from Mr Stephen Dunn of Edmonton Alberta enabled the use of the organo-zeolitic bio-fertilizer to try and revegetate the damaged land. After a series of pot experiments at Olds College,Alberta [9]] a trial was performed on part of the site where test strips were sown on amended mine waste. The result is shown in Fig 5 where a photograph was taken of the after seed germination. The plants were self-sustaining for over a decade. The success of this experiment was followed by an even more ambitious experiment.

A large metal refinery in the North of France had deposited fine sulphide ore concentrate on an area of 10 –11 hectares which has since become barren of vegetation. Careful sampling confirmed the average concentration, at the surface, of Pb, Zn and Cd to be in the order of weight percent (Pb 9.2%., Zn 6.8%., Cd 0.5%) [10]. The zinc hyperaccumulater plant Arabidopsis halleri was used in this experiment and grown in pots under stable greenhouse conditions. The un-amended ore concentrate was used as a control against a substrate of the concentrate amended with the bio-fertilizer. It was a great surprise to find that luxuriant plant growth occurred in the amended substrate, Fig. 6 and it is assumed that the presence of an Archaeal ammonium oxidizer is again functioning in the amended ore concentrate, as a Bacterial ammonium oxidizer would be unlikely to survive in such high concentrations of base metals at a pH value of 4.0.

Work in the Almeria region of the South East Coast of Spain has shown that the growth of indigenous plants can be sustained by the use of the bio-fertilizer. This area has an average annual rainfall of 200 mm per year and in this semi-arid climate only special plants, adapted by nature, can grow. It was decided by local environmental scientists to make tests with the bio-fertilizer to see if plant growth could be sustained on barren industrial waste sites in this area. This test again, most surprisingly, was successful, Fig. 7. Shallow pits were dug in the surface of the industrial waste and filled with amended waste. Various indigenous plants, from a local botanic garden, were then transplanted into the pits. Once planted these were watered and then left unattended. Some 60% of the plants survived and it is thought that the zeolite component, with its affinity for water, retained dew on its mineral surface; desorbing water during the day as the temperature climbed and resorbing water at night, especially from early morning dew; as earlier work had shown that a soil amended with the biofertilize sustained its soil moisture longer than an unamended soil [11]. This suggestion is speculative and it is clear that more research work is needed to resolve this phenomenon.

4 Concluding Remarks

The use of the bio-fertilizer on waste sites and marginal soils will enable the growth of feedstock for the bio-fuel industry. Considering the large area needed to grow these crops its employment will avoid the necessity to use valuable arable land.

The plant growth studies have shown that together with an organic component, either animal or plant waste, zeolitic tuff can be used to great advantage as a biological plant fertilizer. Experiments have shown that NH4+ ions produced during decomposition of organic waste are bound to the zeolite surface. During preparation and use ammonium ions (NH4+) are back exchanged by potassium ions (K+) and oxidized by soil micro-organisms. Molecular biological technology has shown that Crenarchaeota appear to be the main ammonium oxidizing organisms in the organo-zeolite-soil system. This process greatly sponsors nitrification and hydrogen ions, liberated by the ensuing enzyme activity, dissociate cations from the plant substrate providing ionized elements, in trace concentrations, which are both essential and beneficial for plant growth. The organic material provides phosphorus but it is not entirely clear how this element is ionized; most likely due to the activity of mycorrhizal fungi.

When one considers the damage done to arable farmland due to the long and over use of chemical fertilizers it is time to use a new scientific approach and bio-fertilizers, of the type described here, will be of great advantage in providing plant nutrition in the future.

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Fig 1. Oil Seed Rape (Brassica napus) LHS plant growing in un-amended acid mine waste,

RHS plant growing in amended acid mine waste.

Fig 2. Linseed (*Linium usitatissiumum*) LHS plant growing in Garden soil, Centre plant growing in coal waste , RHS plant growing in amended coal waste.

Fig 3. Maze (*Zea mays*) ears from mature plants, in triplicate, from coal waste study. Large ears from plants grown in amended coal waste are shown below those from the un-amended coal waste.

Fig 4. Triplicate plants grown at the same time as the above, under identical green-house conditions. Upper roots are from plants grown in the amended coal waste and lower roots are from plants grown in the un-amended coal waste.

Fig 5. Lynn Lake Manitobe, Canada test site. This site here sown in 2001 has been self sustaining for more than a decade. Plants used were Red Fescue (Festuca *rubra*), Timothy (Phleum *pratense*) and Red Clover (*Trifolium pratense*).

Fig 6. Arabidopsis (*halleri*) experiment with plants grown in sulphide refinery concentrate. Upper image showing plants in un-amended concentrate and lower image plants grown in amended concentrate. In both cases the experimental plants are shown against those grown in clean soil.

Fig 7. Almeria test site, South East Spain. Plants in the foreground are growing in industrial waste amended with the bio-fertilizer. This part of Mediterranean Spain has an annual rainfall of approximately 200 mm per year, making it