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Synthesis of zeolites and their application as soil amendments to increase crop yield and potentially act as controlled release fertilizers

A thesis presented for the degree of
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by

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requirements of the University of Wolverhampton
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Abstract

Zeolites have been used in agriculture since the 1960s, due to the effectiveness of these crystalline microporous solids as soil amendments for plant growth, their cation exchange capacity (CEC) and slow-release fertilizer properties. Most work on slow-release fertilizers has focused on natural Clinoptilolite, Phillipsite and Chabazite. The aim of this study was to synthesize zeolites, study their effectiveness as soil amendments and their ability to act as controlled release fertilizers to decrease nitrate leaching. Nitrate pollution of groundwater is a major agro-environmental concern.

The zeolites Phillipsite and Linde-type F were synthesized from aluminosilicate gels; ion exchanged to introduce ammonium and characterized using X-ray diffraction (XRD), X-ray fluorescence (XRF), Thermo-gravimetric analysis (TGA) and Scanning electron microscopy (SEM) techniques, both before and after ion exchange. Ammonium-exchanged Phillipsites (natural and synthetic), ammonium-exchanged synthetic Linde-type F (the zeolite having highest affinity towards ammonium) and ammonium exchanged Phillipsites (high crystalline and high aluminium) were compared with conventional NPK fertilizer.

Three glasshouse experiments were performed to study the effects of zeolite-amended soils on maize growth. Ion exchanged synthetic and natural Phillipsites were first used as soil amendments (w/w 2, 4, 8% zeolite to soil). Synthetic Phillipsite, at 2% loading, resulted in the most significant improvement in both plant growth and phased ammonium release. The synthetic ammonium-exchanged zeolites Phillipsite and Linde-type F (at w/w 1, 2, 4%) were then compared; synthetic Phillipsite, at 2% loading, again resulted in the most significant plant growth response with an increase (≥15%) in shoot dry weight and a decrease (≥30%) in nitrate leaching. Experiments using unexchanged synthetic

Phillipsite (at w/w 2%), but with added NPK fertilizer, showed increased plant growth and decreased nitrate leaching, compared with parallel experiments containing unexchanged synthetic Linde-type F (at w/w 2%) and a conventional fertilizer amended soil. This revealed the beneficial effect of Phillipsite for soil amendment, even without ion exchange to the ammonium form.

To study the physico-chemical properties affecting the release of ammonium from the Phillipsite framework; high crystalline/low aluminium and low crystalline/high aluminium forms were synthesized and ion exchanged. Both forms were introduced as soil amendments (at w/w 1 and 2%) and experiments showed that the lower zeolite crystallinity decreased cation exchange and therefore decreased nitrate leaching.

Experimental results from the glasshouse experiments and cation exchange capacity (CEC) experiments suggest that synthetic Phillipsite, at lower loadings (1 and 2% w/w zeolite to soil) have most potential as soil amendments for both plant growth and controlled-release applications. This conclusion is supported by soil leachate and shoots dry weight analysis. Furthermore, Phillipsite, synthesized in a low crystalline and low ammonium form, may be an even better soil amendment for controlled release of ammonium, which will thereby further decrease nitrate pollution.

Chapter 1

Introduction and Literature Review

Introduction

This study focuses on application of zeolites (alumino-silicate minerals) as soil amendments, to study plant growth responses from the slow/controlled release of ammonium from ion-exchanged zeolites used as fertilizer substitutes. Chapter 1 gives a brief overview of zeolites in general, their background, classification, application and ion exchange properties. A general overview of maize along with its nutrient requirements and aspects of nitrate pollution are also discussed in this chapter.

1.1. Zeolites

1.1.1. Historical Perspective

The study of zeolites dates back to the 18th century, with the discovery of the mineral Stilbite by a Swedish mineralogist, A.F. Cronstedt in 1756 (Mumpton, 1978). The mineral lost water when heated with a blowpipe flame, a process now known as intumescence. He called this mineral “zeolite” from the Greek ‘zeo’, to boil and ‘lithos’, stone (Gottardi and Galli, 1985). Since then, zeolites have been recognized as a separate group of minerals, one of the most abundant on earth. Following their discovery, work has been performed on the hydration, dehydration, synthesis and ion exchange of these minerals. As cited in Van Bekkum *et al.* (2001), Eichhorn (1858) first reported reversibility of ion exchange on zeolite minerals and Damour (1840) showed that zeolite could be reversibly dehydrated with no apparent change in their transparency or crystal morphology.

As cited in Szostak (1989), Friedel and Bull (1896) proposed that the structure of dehydrated zeolites consists of open porous frameworks. This was confirmed by occlusion of liquids, such as alcohol, benzene and chloroform, by dehydrated zeolites. Grandjean (1909) demonstrated that dehydrated Chabazite adsorbs ammonia, air, hydrogen and other molecules. The first molecular sieve effect was reported by Weigel and Steinhoff (1925), who observed that dehydrated Chabazite crystals rapidly absorbed water, methyl alcohol, ethyl alcohol and formic acid, but essentially excluded acetone, ether or benzene. As cited in Van Bekkum *et al.* (2001), Schafhautle (1845) reported the hydrothermal synthesis of quartz by heating ‘gel’ silica with water in an autoclave. Levynite was the first hydro-thermally synthesized zeolite, as reported by St. Claire Deville (1862), who claimed to have made this zeolite from a solution of Na and K-silicates heated in a sealed glass tube to 170°C. The tubular hexagonal crystals formed had the composition:

$$Ca_{0.25}Na_{2.68}K_{2.80}[(AlO_2)_{6.5}(SiO_2)_{11.5}].\ 16.8\ H_2O \tag{1.1}$$

Although the synthesis of zeolites has been reported from 1862 onwards, it was only after 1930 with the availability of X-ray diffraction techniques, that the synthesised products could be assigned complete based on their crystalline structure. As cited in Occelli and Robson (1992), Leonard (1927) first described the use of X-ray diffraction for identification purposes of mineral synthesis. Professor R.M. Barrer and his researchers early pioneering work in adsorption and synthesis began the era of synthetic zeolites in the mid-1930s. Barrer (1948) reported the first definitive synthesis of zeolites, including the synthetic analogue of zeolite mineral mordenite. The starting composition for this zeolite was Na_2O: Al_2O_3: 8.2-12.3 SiO_2. From this, Barrer explored the composition range to optimize the SiO_2/Al_2O_3 ratio that would produce mordenite topology (Barrer, 1982).

Inspired by Barrer’s work, studies were carried out on zeolite synthesis by both individuals as well as industries in search of new approaches for separation and air purification. In a span between 1949-1954 Milton and co-worker Breck discovered several zeolite types, zeolites A, X and zeolite Y were some of the important ones among them. Based on the properties of synthetic zeolites Union Carbide commercialized them as a new class of industrial materials for separation and purification in 1954. Mobil Oil introduced synthetic zeolite X as a cracking catalyst (breaking up large hydrocarbon molecules into smaller and more useful bits) in 1962. As cited in Barrer (1982), Zeolite Y was modified to “ultrastable zeolite Y” based on modification chemistry of steaming the zeolite (Grace, 1969). Henkel (1974) introduced zeolite A in detergents as a replacement for phosphates. More than 70 novel distinct framework structures of zeolites have been synthesized in recent decades. Some of the more important zeolite types that have been used in commercial applications include natural minerals Mordenite, Chabazite, Phillipsite, Erionite and Clinoptilolite, and synthetic zeolites type A, X, Y, L, Mordenite, ZSM-5, Beta, MCM-22, and zeolite F and W.

1.1.2. Introduction

(a) Background

After the discovery of zeolites, work was carried out to study their physical and chemical properties. In the 1930s a new term "molecular sieves" was introduced. McBain (1932) defined the term "molecular sieve" to describe a class of materials that exhibited selective adsorption properties. These materials contain other elements in addition to, or in lieu of, silicon and aluminium. Only two classes of zeolite based molecular sieves zeolites and microporous charcoals were known at that time. Later work introduced different classes of molecular sieves, such as silicates, metallosilicates, metalloaluminates, $AlPO_4S$ and silico- and metalloaluminophosphates, as well as zeolites (Figure. 1.1).

As by definition "*Zeolites are crystalline framework materials that are composed of TO_4 tetrahedra linked with oxygen sharing* " the negative charge created by the presence of AlO_2^- is balanced by cations that neutralize the charge deficiency. These cations include: the alkaline (Na^+, K^+, Rb^+, Cs^+), the alkaline earth (Mg^{2+}, Ca^{2+}) cations, NH_4^+, H_3O^+ (H^+), TMA^+ (Tetramethylammonium) and other nitrogen containing organic cations, and the rare earth and noble metal ions. Cations presently known to occupy framework sites within the molecular sieve structures are reported in Table 1.1.

Table 1.1. Cations that may form molecular sieve framework structures and the metal oxide charge possible (Szostak 1989).

Metal Oxide Charge	Cations
$(M^{+2}O_2)^{-2}$	Be, Mg, Zn, Co, Fe, Mn
$(M^{+3}O_2)^{-1}$	Al, B, Ga, Fe, Cr
$(M^{+4}O_2)^{0}$	Si, Ge, Mn, Ti
$(M^{+5}O_2)^{+1}$	P

(b) Nomenclature

There is no systematic nomenclature developed for molecular sieve materials. To each unique structure type, which has been established based on the characteristic X-ray powder diffraction patterns irrespective of their chemical composition, the IZA (International Zeolite Association) *Atlas of zeolite structure types* has assigned a code composed of three capital letters. Illustrative codes are LTA for Linde zeolite A, FAU for molecular sieves with a faujasite topology, e.g. Zeolites X and Y, MOR for the mordenite topology, MFI for the ZSM-5 and silicalite topologies and AFI for the aluminophosphate $AlPO_4$-5 topology. For this research project, zeolites Phillipsite and Linde type F have been studied and they have been assigned with three letters abbreviations as PHI and EDI. There have been 157 framework type codes assigned to date, more recently four new framework type codes have been approved namely: CDO, GIU, SFO, SOS. The acceptance of a newly determined structure of a zeolite or molecular sieve for inclusion in the official *Atlas* is reviewed and requires acceptance by the IZA Commission.

(c) Classification

Zeolites and zeolite related materials are classified according to their framework structure, in addition to their chemical composition that can usually be considered variable. Each framework type can be described by their secondary building units, framework density, channel system, crystal symmetry and unit cell constant (Nagy *et al.* 1998). Different classes of molecular sieves are listed in Figure 1.1. All of these are molecular sieves and their regular framework structure separates components of a mixture on the basis of size and shape. As most of them are structurally analogous, the difference lies not in the structure of these materials, but in their elemental composition.

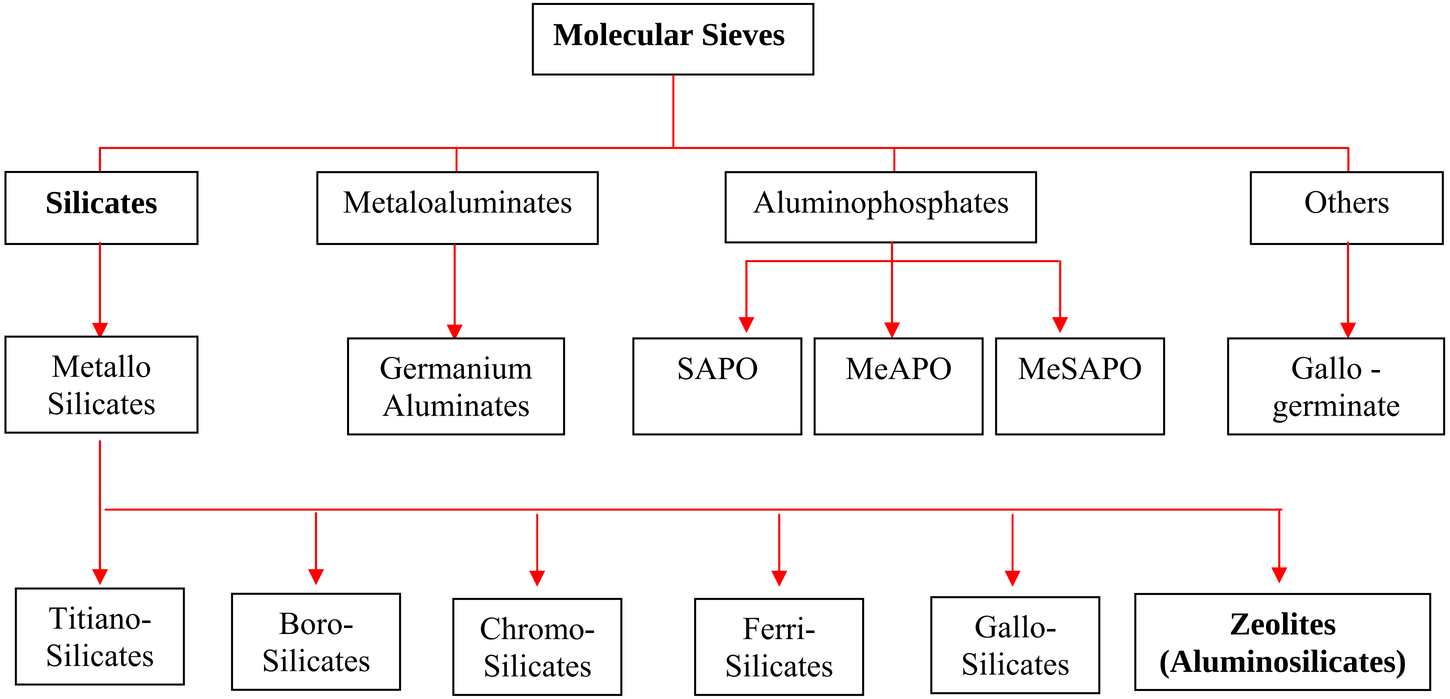


Figure 1.1. Classification of molecular sieve materials indicating the extensive variation in composition (Szostak, 1989).

1.1.3. Structure of zeolites

Zeolites are crystalline alumino-silicate minerals of the alkali and alkaline group elements and have a molecular sieve action due to their open channel network, thereby allowing some ions to pass through while blocking others. All zeolite framework structures have a three dimensional arrangement of TO_4 tetrahedra (T= tetrahedrally co-ordinated atom, usually Si^{4+}, Al^{3+}). These tetrahedra are linked together by the sharing of oxygen atoms and result in an open and stable three-dimensional honeycomb structure with an overall negative charge, which is balanced by the cations that move freely in and out of its framework (Figure 1.2).

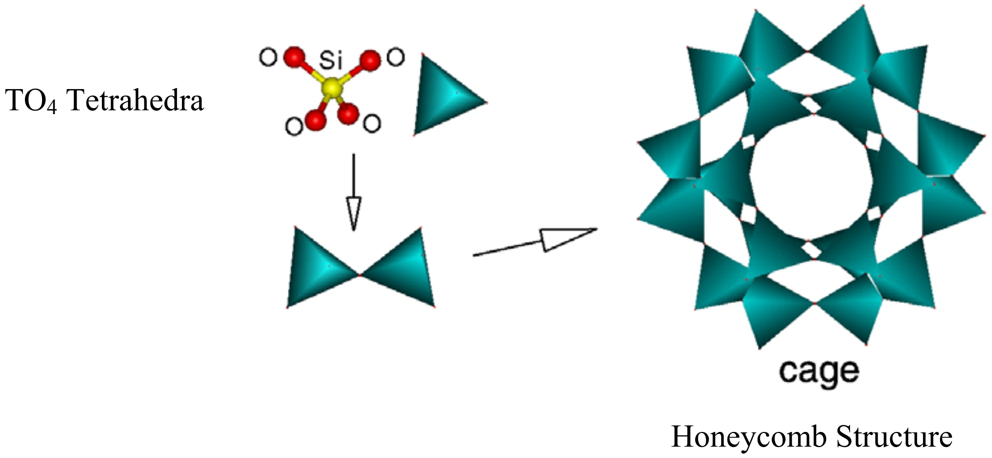


Figure 1.2. Tetrahedral framework structure of a zeolite

Source: **http://www.bza.org/zeolites.html**

Zeolite minerals are generally assigned with a unit cell formula as proposed by (Barrer, 1982). Chemically, they are represented by the empirical formula:

$$(M_x^{+}, M_y^{2+})[Al_{(x+2y)}Si_{n-(x+2y)}O_{2n}].mH_2O \tag{1.2}$$

Where atoms in the tectosilicate framework structure are represented within the brackets, the monovalent and the divalent cations that neutralize the structural negative charge are represented within the parentheses by M^+ and M^{2+}, and water molecules represent adsorbed or zeolitic water. The total number of tetrahedral cations (Al + Si) in a unit cell is n, while the number of oxygen atoms is $2n$.

(a). Pores and Channels

Zeolite structures are always described according to their framework type in terms of size of pore openings and dimensionality of the channel system. These pore openings are characterized by size of the ring that defines a pore, usually designated as n-ring, where n is the number of T-atoms in a ring. Different pore openings are assigned for different ring sizes. An 8-ring is considered to be a small ring opening, a 10-ring a medium one, and a 12-ring a large one. Various methods have been proposed to examine pore size; the simplest of which involves selecting the proper molecular probes and examining ability of the zeolite to adsorb these probes.

Molecular probes such as methane, *n*-hexane, 2-methylpentane, cyclohexane, *o*-xylene, and mesitylene are commonly applied for determining pore size. Erionite, Chabazite, and type A (Ca^{++} exchanged form) 8-ring zeolites adsorb methane, but not cyclohexane. ZSM-5, ZSM-11, EU-1, and theta-1 (10-ring zeolites) all adsorb methane, n-hexane, and alkanes readily, while adsorbing cyclohexane slowly. These 10-member ring zeolites will not adsorb mesitylene. Finally, 12-member ring zeolites such as Type-Y, Mordenite (synthetic), ZSM-12, and zeolite Beta readily adsorb all the probe molecules. The size and shape of pore opening depends on five important factors:

a) Configuration of the T and O atoms relative to each other.
b) Silicon/Aluminium ratio.
c) Size of the cation.
d) Location of the cation.
e) Temperature.

Along with pore size it is important to consider the channel system within a zeolite framework. Instead of visualizing zeolites in terms of interconnection of voids by these 8, 10, and 12 ring pore openings; the structure can be viewed in terms of one, two or three dimensional tubes or channels. For some zeolites "channels" are very short, similar to portholes or windows connecting large cavities within the structure. Examples of some zeolites with their channel systems are shown in Table 1.2.

Table.1.2. Various zeolites with their channel systems.

Channel System	**Zeolites**
One-Dimensional	Analcime
Two-Dimensional	Mordenite, Phillipsite
Three-Dimensional	Paulingite, ZSM-5, ZSM-11

(b). Secondary Building Unit (SBU)

The various secondary building units needed for the reconstruction of zeolite framework are presented in Figure 1.3.

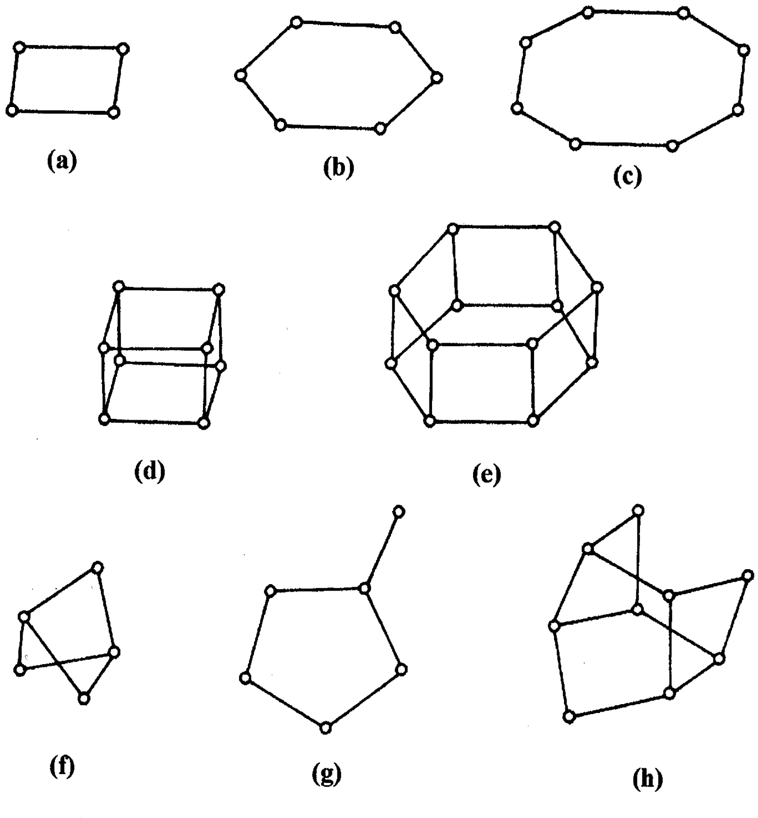


Figure 1.3. Secondary building units recognized in zeolite frameworks (a) Single four ring (S4R), (b) Single six ring (S6R), (c) Single eight ring (S8R), (d) Double four ring (D4R), (e) Double six ring (D6R), (f) Complex 4-1, (g) Complex 5-1 and (h) Complex 4-4-1 (Szostak, 1989).

It is simple to compare adsorptive and catalytical properties of zeolites by describing them in terms of their pore openings and channel systems. A need to relate and compare structural properties of a large number of zeolite structures has led to development of secondary building units (SBU). These units are also used in efforts to understand formation of individual structures from complex mixtures used in the synthesis. As the individual tetrahedral TO_4 unit is the basic building unit of a zeolite, a secondary building unit (SBU) consists of selected geometrical groupings of those tetrahedrons. There are various building units, which can be used to describe zeolite structures. The topologies of these units are shown in Figure 1.3.

1.2. Structures studied in this work

1.2.1. Phillipsite

As cited in Meier and Olson (1987), Steinfink (1962) first reported the structure of Phillipsite (Figure 1.4), a naturally occurring zeolite with a similar framework to that of Harmotone, reported by Sadanaga *et al* (1961). On the basis of structural and crystallographic data, both Phillipsite and Harmotone can be described as a single zeolite species.

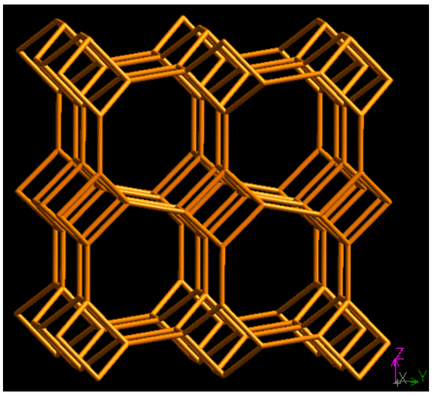


Figure 1.4. Framework structure of Phillipsite (PHI).

Source: **http://www.iza-structure.org/databases**

Phillipsite contains a two-dimensional channel system similar to harmotone, differing only in their chemical composition and symmetry. Phillipsite is a monoclinic zeolite with pseudo-orthorhombic framework. The main channel of the zeolite is an 8-membered ring with a free aperture ~3.8 $\mathring{A}$.

The unit-cell parameters ranges for Phillipsite are as follows: $a = 9.81\text{-}10.01\ \mathring{A}$ (1.3)

$b = 14.10\text{-}14.34\ \mathring{A}$

$c = 14.16\text{-}14.42\ \mathring{A}$

1.2.2. Linde type-F

As cited in Meier and Olson (1987), the structure of Linde type F (Figure 1.5) also known as Edingtonite (EDI) was solved by Taylor and Jackson (1933) and refined by Mazzi *et al.* (1984).

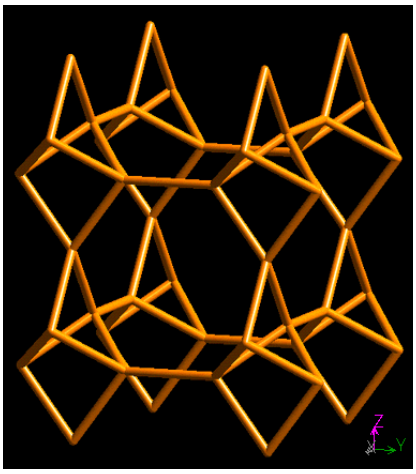


Figure 1.5. Framework structure of Edingtonite (EDI).

Source: **http://www.iza-structure.org/databases**

The framework structure of Edingtonite consists of the simplest method of cross-linking the chains of 4-1 units of tetrahedra. Edingtonite is a tetragonal zeolite and can also be orthorhombic, the difference between the orthorhombic (O) and tetragonal (T) Edingtonite is due to Si/Al-ordering in the tetrahedral sites of the framework. The main channel of the zeolite is an 8-membered ring with a free aperture ~2.8 Å .

The unit-cell parameter ranges for Edingtonite are as follows: $a = 9.550$ Å (1.4)

$b = 9.665$ Å

$c = 6.523$ Å

1.3. Synthesis of zeolites

(a) Introduction

Generally, synthesis of a zeolite involves preparation of a homogenous gel obtained by combining a silica source and an aluminium source in water under basic pH. Other additives that can be added to the gel includes; alkali or alkaline earth cations introduced as their oxide, hydroxide or salts, ammonia or ammonium salts and alkylamines or alkyl ammonium compounds. During synthesis, these compounds act as OH^- ion sources, as electrolytes, as counter ions of the formed anionic framework, or as structure directing agents.

(b) General conditions

The three main factors influencing zeolite structure formation are composition of reaction mixtures, temperature and time. Along with these factors, seeding, ageing, stirring, nature of mixing and order of mixing can all play a vital role in zeolite formation and crystallization (Table 1.3).

Table 1.3. Sub-factors influencing zeolite crystallization.

Gel/Reaction composition	• SiO_2/Al_2O_3 sources • $[OH^-]$ concentration • Cations both organic and inorganic • Anions other than OH^- (i.e. F^-) • Water concentration
Time	• Varies depending on zeolite type
Temperature	• Varies depending on zeolite type (a) Ambient (25-60°C) (b) Low (90-120°C) (c) Moderate (120-180°C) (d) High ($\geq$250°C)

(c) Seeding

Studies have shown that adding seed crystals to the crystallization system has typically resulted in increased crystallization rates. Seeding the synthesis mixture allows accelerated synthesis processes and directed synthesis to a given direction, provided the seed crystals are stable in the synthesis media and conditions. The enhanced rate might be due to simply increasing the rate at which the solute is integrated into the solid phase from solution due to increased availability of surface area, but may also be due to the enhanced nucleation of new crystals. Work to understand the role of seed crystals is an area of ongoing investigation.

(d) Ageing

Time is a very important factor for the control of zeolite synthesis. In addition to time required to crystallize a zeolite at a high temperature, dissolution of gel at room temperature is often required. It is believed that by ageing gel at room temperature the development of nuclei of metastable zeolites is encouraged. Ageing of the composition gel has been practiced for years since the first reported synthesis in 1862.

(e) Crystallization

A zeolite formed from a reaction gel composition can be highly crystalline or very low in crystallinity. Zeolite crystallinity is defined by powder X-ray diffraction (XRD). The different factors that can operate in a crystallization mixture can be summarized as follows (Szostak, 1992):

- Precipitation of an initial gel phase.
- Dissolution with time of that gel.
- Zeolite nucleation from gel or solution phase.
- Crystallization and crystal growth of these structures from the gel or solution.
- Dissolution/recrystallization of metastable phase, and crystallization of a new, more stable crystalline phase.
- Successive nucleation, crystallization and dissolution of further nucleation phases.
- Finally, formation of the equilibrium phase.

Different zeolites have different crystallization times; optimum crystallization time can be several hours (Zeolite type A) to several weeks (Zeolite Beta), synthesis recipe can be optimized to produce highly crystalline zeolites within several days. Crystallization is vital for zeolite synthesis as a zeolite framework can be said to be formed if it is crystalline and not formed if it is amorphous, when observed under X-ray diffraction. Szostak (1989) proposed a method for the calculation of crystallinity. According to this method, crystallinity of a zeolite can be calculated by measuring the area of the peaks at an angle $2\theta^{o}$ range (from XRD) where the most intensive peaks are produced after baseline correction. The sample that presents the largest area is considered as 100% crystalline, and areas of other samples are normalized accordingly.

1.4. Properties of Zeolites

Some of the physical and chemical properties of zeolites are morphology, particle size, thermal expansion, density, hardness, dehydration, cation hydrolysis and stabilization. The unique physio-chemical property of zeolites makes them suitable for agricultural use (Barbarick and Pirela, 1984; Allen and Ming, 1993). Some of the effects of zeolites which make them unique soil amendments are: decreased soil acidity; activating nutrients from soil reserves and decreasing the need for mineral fertilizers, thereby eliminating their adverse acidifying effects; antitoxic effects (eliminating the impact of free ions such as aluminium, manganese and iron) and increasing drought resistance by binding water molecules (Pisarovic *et al.*, 2003).

1.5. Applications of Zeolites

Zeolites have numerous applications. Some of the most important applications are in catalysis, gas adsorption, industrial gas separation, water treatment (wastewater and drinking water), agriculture, and metal immobilization in soils, ion exchange, aquaculture, odour control, and desiccation and as phosphate substitutes in detergents. Based on cost effectiveness, four main areas where zeolites are finding application as ion-exchangers are: in detergents; in ammonia/ammonium removal from wastewater effluent; in radioactive isotope removal from spent pile effluent and in agriculture. By far the most important of these is in detergents, where zeolites are employed as water softeners, partially replacing tri-polyphosphate builders (Flanigen, 1980). The annual turnover of Zeolite A for this purpose alone in the U.S is several billions of dollars.

Many authors have studied the possibilities of separation of ammonium ions from drinking water and from wastewaters by zeolites (Hagivara and Uchida, 1978; Ciambelli *et al.,* 1988; Colella and Aiello, 1988). The application of synthetic Phillipsite prepared by hydrothermal alteration of power plant ashes, when compared to a natural Slovakian Clinoptilolite, showed that the former significantly reduced the concentration of ammonium ions in wastewaters (Kovanda *et al.,* 1994). A pilot project near Denver, Colorado (USA) uses natural zeolites for removal of ammonium in potable water systems. Similar systems are now in production to remove various pollutants, including heavy metals and radioactive ions from industrial effluents. Since synthetic zeolites were first used commercially, they have found many uses in adsorbent and catalytic applications based on their unique physical structure. As adsorbents, zeolites have found wide use in drying and purifying both gaseous and liquid streams in chemical, petroleum and natural gas operations. Many bulk separations, such as separating olefins from paraffins, oxygen from air and paraxylene from mixed xylenes, also utilize zeolite adsorbents.

Natural zeolites like Mordenite, Chabazite, Clinoptilolite, Ferrierite and Phillipsite, have been tested for their adsorption selectivity for ammonia over methane in the gasification procedure. It was evident that Phillipsite has a particular potential applicability in this process, as it would not adsorb significant amounts of most reactants in a gasification stream, including CO, CO_2 and CH_4 (Hayhurst, 1978). The results also showed that at 25^0C, Phillipsite adsorbs NH_3 rapidly. Synthetic zeolites are potentially useful additives to bind heavy metals. Zeolites such as Mordenite, Faujasite, Zeolite X, Zeolite P and Zeolite A were studied to evaluate their effectiveness in binding Cadmium and Zinc in the soil. The results showed that Zeolite A has the highest capacity to bind heavy metals. Zeolite A has the highest binding capacity between pH 5 and 6.5 and was stable > pH 5.5 (Leonard *et al.,* 2002).

Soils throughout the world have been contaminated with heavy metals (i.e. Cu, Cd, Pb and Zn) and with radionuclides (i.e., ^{134}Cs, ^{137}Cs and ^{90}Sr). Zeolite addition to metal contaminated soils resulted in a significant decrease in the metal uptake by plants grown in these soils. In some notable cases, soils treated with zeolite-like materials completely eliminated metal phytotoxicity and allowed establishment of vegetation on previously bare contaminated soil (Gworek, 1992; Rebedea and Lepp, 1995; Vangronsveld *et al.,* 1995). The use of zeolites in soils causes general alkalization of treated soils and may help to reduce metal mobility and phytotoxicity. However, it also depends on the ion-exchange capabilities of the zeolite-treated soils.

Zeolites can serve as both oxidation and reduction catalysts, often after metals have been introduced into the framework. Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. In principle the high internal surface area allows high reactivity and the cation exchange capacity of zeolites permits facile introduction of acidic or transitional metal catalytic function (Howe, 2004). Some examples of catalysis uses are: titanium ZSM-5 in the production of caprolactum, and copper zeolites in NO_X decomposition. As heterogeneous catalysts, zeolites have proved to be much improved over the amorphous catalysts originally used in cracking and alkylation processes. New uses in hydrocracking, toluene alkylation, and methanol dehydration (for gasoline or light olefin production and other processes) are expected for zeolites, because of their shape selectivity.

Due to the ban on production and use of chlorofluorocabons (CFCs) and Halons, which resulted in ozone depletion, there is a greater need for safe disposal of these banned materials and/or their conversion into alternative materials, which are environmentally acceptable. Development of zeolite-based catalysts can act as potential agents for dehalogenation processes for environmental protection (Howe, 2004). A zeolite based catalyst for atmospheric hydrocracking was developed (Ohshio *et al.,* 2003) and its production on an industrial scale was successfully accomplished. Its high and stable performance as hydrocracking catalyst in a Atmospheric Residue Desulphurization (ARDS) unit was confirmed.

Along with copper loaded zeolites used in NO_X decomposition, Fe-ZSM-5 zeolites of different Si/Al ratio prepared by means of ionic exchange from aqueous solution and solid state were used as catalysts for N_2O decomposition in the 300-500^oC range (Waclaw *et al.,* 2004). Results showed the samples with high concentration (3-15 wt% of Fe), both calcined at 550 and 900^oC, have a very high activity for N_2O decomposition. On examining IR spectra of adsorbed N_2O, it was concluded that N_2O was bonded to zeolite structure both through Oxygen and Nitrogen atoms. More recent work involved substituting Scandium (Sc) (Brigden *et al.* 2004) and Rhodium (Rh) into the ZSM-5 framework to study their NO_X decomposition properties.

1.6. Ion exchange in zeolites

The simplest case in any ion exchange system consists of three phases, namely the exchanger, external solution and vapour, however for most systems vapour can be ignored. Ion exchange is a stoichiometric reaction, which in general terms can be written:

$$Z_a \overline{M_b} + Z_b M_a == Z_a M_b + Z_b \overline{M_a} \qquad (1.5)$$

M_a & M_b are the two cations or anions involved; Z_a & Z_b are the valences of these ions. The characters with a bar indicate the particular cation or anion in the exchanger phase.

There are a various materials used as ion exchangers, including organic based resins, zeolites, $AlPO_4$-n S (including the SAPOs) and double-layered metal hydroxides. An organic based resin usually consists of a cross-linked co-polymer containing carboxylate, quaternary ammonium or sulphonate groups. The carboxylate and sulphonate group resins are used as cation exchangers, while the quaternary ammonium groups are used as anion exchangers.

Ion exchange is an intrinsic property of most zeolites. The cation exchange capacity of a zeolite is a consequence of the degree of substitution of Al for Si in the framework. The greater the substitution, the greater the number of cations necessary to maintain electrical neutrality (Sheppard and Arthur, 1982). These charge balancing cations are generally exchangeable, and channel structure of zeolites is responsible for their function as a “molecular sieve”. The channels and cages of a particular zeolite are clearly defined in their dimensions and shape, owing to high crystallinity of these materials. The open channels thereby allow ions to pass through very freely. On the other hand, it is possible for ions to exchange only partially, because the volumes of the ions are such that these completely fill the intra-crystalline space in the channels before 100% exchange is attained (Townsend, 1984).

The selectivity of zeolites for different ions is determined by several factors (Dyer, 1988). These include size and state of solvation of the ions, the charge (Si to Al ratio), framework geometry, number of cation sites available for occupation inside the framework and temperature. A particular ion can therefore be excluded from the exchanger because of its size. Along with the size of pore apertures the hydrophilic or hydrophobic character of zeolite greatly influences ion-sieving selectivity. For example, highly negatively charged framework of zeolite X (Si/Al ~ 1-1.5) prefers smaller cations in the order: $Na^+ > K^+ > Rb^+ > Cs^+ > Li^+$, whereas zeolite Y with a lower anionic charge (Si/Al ~ 1.5-3) takes up preferentially larger cations in the order: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ (Nagy *et al.,* 1998). Adabbo *et al.* (1998) also reported that ion exchange selectivity depends on the anionic strength of zeolites, in that siliceous zeolites with low field strength prefer larger cations, e.g. Cs^+, characterized by a lower charge density, whereas aluminous zeolites are more selective for cations with a higher charge density, e.g. Sr^{2+}.

Exchange behaviour for a range of zeolitic compositions can be predicted under the following conditions:

a) In relatively dilute solutions at constant temperature.

b) In more concentrated solutions (>0.5 molar) at constant temperature.

c) Over a range of temperatures for a given solution concentration.

Apart from the original liquid phase ion exchange Huang *et al.,* (1998) studied solid-state ion exchange using the FT-Raman technique, and termed the exchange as contact-induced ion exchange. The exchange between zeolite and metal salt was achieved by grinding together zeolite with a salt of the in-going cation. This mixture was then heated in a furnace at different temperatures for various periods. The FT-Raman technique was then applied to follow up the exchange of cation species between different zeolites caused by physical contact between crystals, and also exchange between metal salts and zeolites by directly monitoring the zeolite framework vibrations.

In order to establish exchange kinetics in zeolites, a series of studies carried out by Barrer (1982) on natural zeolites threw light on one important aspect of the subject i.e., intra-crystalline diffusion and this is discussed in more detail in Section 1.7. Most of the experimental and theoretical work on zeolites has been on ion exchange equilibria that involve just two exchanging ions. Fletcher *et al.* (1984) investigated multicomponent ion exchange equilibria, although many natural and industrial processes involve more than two types of exchanging ions. Detailed studies on multicomponent exchange equilibria in resins have been in progress for some time (Soldatov and Bychkova, 1971). Resins have being widely used as ion exchangers in the past and are still in use. Zeolites have replaced resins as ion exchangers only in those ‘niches’ of the market where resins are unsuitable, although there are wide variations in the properties of these two materials (Table 1.4) (Townsend, 1984).

Table 1.4. Comparison of resins and zeolites

Property	Resin	Zeolite
Chemical nature	Organic co-polymer	Aluminosilicate-crystals
Structure	Amorphous	Crystalline
Porosity	Disperse, about 10 nm	Specific, < 1 nm
Particle size	Variable, up to several mm	0.1-50 μm
Ion sittings	Non-specific	Clearly defined sets of sites
Thermal stability	Low	Usually high
Solution stability	High	Usually low
Radiation stability	Usually low	High
Mechanical Strength	Variable	Usually High
Attrition Resistance	High	Variable
Cost	High	Usually low

1.6.1. Ion exchange in Phillipsite

Ion exchanged natural Phillipsite has been used in various applications, especially in pollution abatement and agriculture. As natural Phillipsite occurs in the form of sedimentary zeolitized tuffs, it becomes essential to identify the percentage of Phillipsite along with various other phases attached to it. Garcia *et al.* (1993) proposed a method for quantitative determination of Phillipsite in tuffs based on its CEC. The study involved comparing CEC results with X-ray diffraction data (Chung, 1974) and thermo-gravimetric analysis data (De'Gennaro and Colella, 1989). Results showed optimum correlation co-efficient between percentage Phillipsite obtained by X-ray diffraction, thermo-gravimetric analysis and CEC.

Natural zeolites, such as Clinoptilolite and Phillipsite entrap NH_4^+ ions, which can be advantageous in wastewater treatment (Ciambelli *et al.,* 1988). On the other hand, it would also be advantageous to saturate/enrich/exchange, natural/synthetic Phillipsite with NH_4^+ by ion exchange. This would enable observation of the kinetics of NH_4^+ exchange with other cations present in the soil when introduced as a soil amendment and to evaluate the potential of a particular zeolite as a slow/controlled-release fertilizer. Kovanda *et al.* (1996) carried out pot experiments under laboratory conditions to study changes in ion concentrations in soil solutions after the addition of NH_4^+ exchanged natural Phillipsite as a soil amendment. For this ion exchange study zeolite and reagent (5M NH_4Cl) suspension was stirred for 24 hours, filtered and washed with distilled water. This procedure was repeated six times, until maximum exchange was attained.

Studies on ion exchange in Phillipsite (natural and synthetic) vary, from identifying its selectivity towards various cations, to evaluating its potential as a cation exchanger. Gualtieri *et al.* (1999) showed that natural Phillipsite is a potential cation exchanger for $^{137}Cs^+$ in nuclear wastes, like any other commercially available zeolite such as Clinoptilolite. On evaluating the cation exchange properties of Phillipsite-rich rock obtained from a quarry in Chiaiano (Naples, Italy) on addition to simulated Pb containing wastewaters, elevated selectivity of this zeolite towards Pb was observed. Further investigations by Pansini *et al.* (1996) strongly supported possible utilization of Phillipsite from this region in its Na form (obtained upon ion exchange with 0.5M NaCl), for removing Pb from water. Colella *et al.* (1998) investigated the selectivity of natural Phillipsite obtained from volcaniclastic deposits in central-southern Italy and recommended not to use Phillipsite-rich materials in removal of Cu and Zn from water, due to its incompleteness of exchange, poor selectivity and low exchange rate (reduction of about 25% of either Cu or Zn exchange capacity with respect to total CEC), especially if compared to other cations, such as Pb.

On studying exchange properties of a natural Phillipsite tuff obtained from the Aritian area of Jordan under the NH_4^+-Na^+ system, exchange isotherms at 18, 35 and 50^0C showed that Phillipsite exchanged NH_4^+ preferably over Na^+ at all temperatures. However, the selectivity co-efficient for NH_4^+ decreased with decreasing temperature (Dwairi, 1998). Selectivity sequences towards cations have been proposed for Phillipsite, based on their framework composition and also their origin. For instance, on comparing two natural Phillipsites from different origins (sedimentary Phillipsite from Neapolitan yellow tuff (Marano, Naples), hydrothermal Phillipsite from a basalt

(Vesuvius, Naples) and one synthetic Phillipsite (hydrothermally synthesized, stirring under pressure) for their ion exchange selectivity towards Cs and Sr, it was of the order of Cs > Na > Sr for all three Phillipsites, irrespective of their framework composition and origin (Adabbo *et al.* 1998). Garcia Hernandez *et al.* (1994) studied the selectivity sequence of Phillipsite in Na^+ exchanged form as well as the acid-treated form. Exchange reactions involving a series of cations were investigated. The selectivity sequence for Na^+-exchanged Phillipsite was $Ba^{2+} >> Pb^{2+} >> Cd^{2+} > NH_4^+ > Cu^{2+} \sim Zn^{2+} \sim K^+ > Na^+ >> Li^+$, and for acid-treated Phillipsite the selectivity sequence was $Ba^{2+} \sim Pb^{2+} > Cd^{2+} \sim NH_4^+ > K^+ \sim Cu^{2+} \sim Zn^{2+} > H_3O^+ >> Li^+$. Gottardi and Galli (1985) published the selectivity sequence of natural Phillipsite as: Cs ~ Rb ~ K > NH_4^+ > Na > Li and Ba > Ca ~ Na ~ Sr.

In order to examine the influence of these exchangeable cations on the character of dehydration of Phillipsite, Guliev *et al.* (1999) investigated various forms of Phillipsite (Phi), i.e., Na, K-Phi and NH_4-Phi, mainly focusing on NH_4^+-Phi. Results indicated that on insertion of ammonium ions into the Na, K-Phi structure there is a substantial change in the pattern of dehydration, rehydration and heats of immersion as a function of the temperature of evacuation. There was no low temperature deformation for NH_4-Phi, which is common for Na, K-Phi and K-Phi. When compared to alkali-cationic forms of Phillipsite, loss of rehydration capacity of NH_4-Phi were initiated at a lower temperature and are accompanied by a greater decrease in adsorption capacity. NH_4-Phi ~40% of adsorbed water following evacuation at room temperature, and that is 15 and 20% less than the water loss from Na and K-Phi. The heat of rehydration of NH_4-Phi is 90 Jg^{-1}, which is also lower than the heat measured for alkali-cation forms of Phi.

1.6.2. Ion exchange in other Zeolites

Other zeolites widely studied for their ion exchange properties include Clinoptilolite and to a lesser extent Chabazite. Clinoptilolite is one of the most abundantly available natural zeolite. Properties such as pozzolanic (Sersale, 1995), cation exchange (Collela, 1996) and adsorption (Caputo *et al.,* 1999) makes this zeolite of great technological interest. Ames (1960) showed that Clinoptilolite prefers K to NH_4 on its exchange sites. Pansini *et al.* (1996) examined the cation exchange properties of Clinoptilolite-bearing materials and used them primarily to remove NH_4^+ from municipal wastewaters and Cs^+ from nuclear power plant station wastewaters. These applications are based on high selectivity of Na-Clinoptilolite towards NH_4^+ and Cs^+.

Colella *et al.* (1982) proposed two methods to characterize the CEC of zeolites; these are the Cross Exchange Method (CEM), and the Batch Exchange Method (BEM). Although the CEM method has successfully determined the CEC of Phillipsite and Chabazite bearing material, BEM was found to be the most reliable and effective method for determining the CEC of Clinoptilolite-bearing materials, due to its simplicity and non-requirement for time-consuming pre-conditioning treatments. In addition to exchangeable cations, natural zeolites such as Chabazite, Clinoptilolite, Erionite and Phillipsite have extra capacity to store a considerable amount of nutrients, like NH_4NO_3 and KNO_3 by salt occlusion. These zeolites can then be used as K and ammonium enriched slow/controlled release fertilizers (Komarneni and Park, 1998).

1.6.3. Salt occlusion or imbibition

Mineral and synthetic aluminosilicates of the feldspathoid type are framework structures, and contain within the cavities of the anionic framework various species of inorganic compounds i.e., NaCl in Sodalite and $CaCO_3$ in Scapolite. The occlusion of NaCl from aqueous solution in Zeolite X is significant only at high salt concentrations. Zeolites with more open structures such as chabazite and Zeolite A may occlude the salts within the larger cages after dehydration. The cation exchange of various uni- and divalent cations in nitrate melts has been studied with $LiNO_3$, $NaNO_3$, and KNO_3. Although related to a size-charge effect, the selectivity sequence varies with the salt. The size of the cation, the size of the solvent (salt) cation, and the size of the zeolite channels were all deemed important in determining the exchange behaviour (Breck, 1974).

1.7. Diffusion in Zeolites

Diffusion plays an important role in catalysis and selective adsorption/separation. Diffusion in zeolites differs from ordinary diffusion in the sense that molecules have to move through channels of molecular dimensions, as a result there is a constant interaction between the diffusing molecules and the zeolite framework. The molecular motion is strongly influenced by the exact size and shape of these molecules along with temperature and concentration as in the case of gases. Diffusion can therefore be described as "*migration of adsorbed molecules through the pores, cages and channels within the crystals*" (Van Bekkum *et al.* 2001).

Different types of diffusion as distinguished by (Weisz 1962) are molecular diffusion (pore sizes 800-10,000 A^o), Knudsen diffusion (10-80 A^o) and intracrystalline or configurational diffusion (3-10 A^o). Intracrystalline diffusion is an activation process, the energy of activation arising largely from steric hindrance. Intracrystalline diffusion is a surprisingly rapid process, except when the zeolite crystals are large, or the diffusing species are bulky, adsorption/desorption rates are generally controlled by processes other than intracrystalline diffusion. Diffusion of molecules through the pores of zeolite crystals (Figure 1.6) differs greatly from gaseous diffusion. In gases diffusion is controlled by the interactions (collisions) between different molecules due to their thermal motion.

The diffusion of molecules in zeolites can be classified in several different regimes depending upon the pore diameter. For large pore diameters of the order of $\geq 1\mu m$ usually called "macropores", collisions between the molecules occur much more frequently than the collisions with walls and molecular diffusion is a dominant mechanism. As the size of the pore decreases the number of collisions with the wall increases, until it becomes smaller than the mean free path (the average distance travelled by a molecule between two collisions) of the gas molecules. At this moment "Knudsen diffusion" takes over and the mobility starts to depend on the dimension of the pore. At even smaller pore sizes (when the pore diameter becomes comparable to the size of the molecules) these will continuously interact with the wall. Diffusion in the "micropores" of a zeolite usually takes place in this regime and is called "Configurational diffusion" (Karger and Ruthven, 1992).

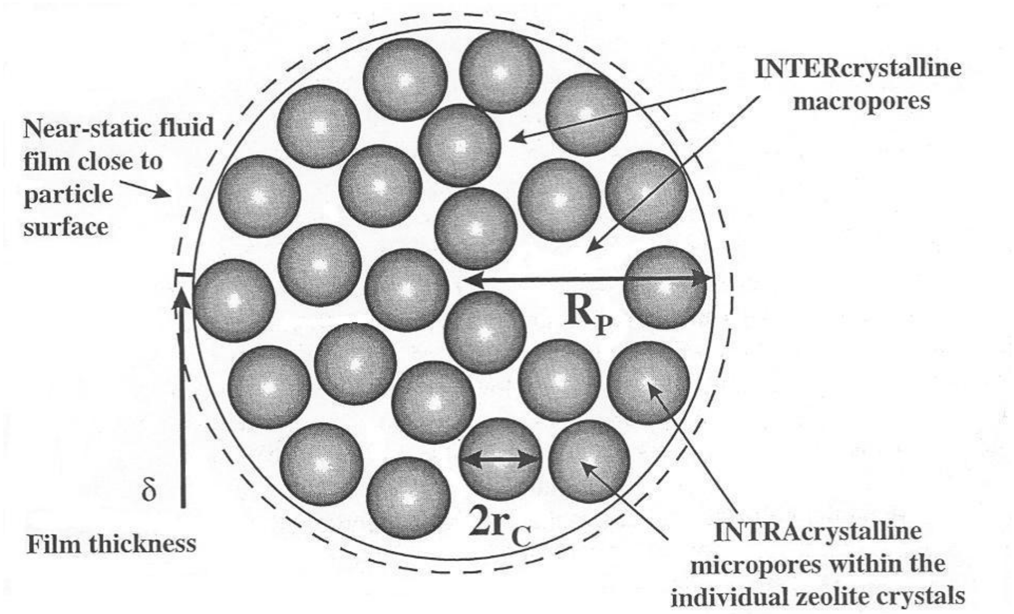


Figure.1.6. An idealized agglomerate of zeolite crystals where the various hierarchical levels of diffusion resistance are apparent (film diffusion, inter-crystalline transport and intracrystalline diffusion). R_p – Radius of agglomerate or pellet; r_c – Radius of zeolite crystallite. (Van Bekkum *et al.*. 2001).

The mechanism by which the molecules move through the pores in a configuration regime is comparable to that of surface diffusion of adsorbed molecules on a surface. Due to the small distance between the molecules and the pore wall, the molecules are physically bonded to it. The diffusivity in this regime will depend strongly on the pore diameter, the structure of the pore wall, the interactions between the surface atoms and the diffusing molecules, the shape of the diffusing molecules and the way the channels are connected.

1.8. Use of zeolites in Agriculture

Nitrogen loss from irrigated cropland, particularly sandy soils, significantly contributes to nitrate contamination of both underground and surface waters. Zeolites (both natural and synthetic) when added as a fertilizer amendment to soil can increase crop yield and prevent water pollution from nitrates and heavy metals, thereby saving the cost for future improvement. The use of natural zeolites for plant growth was first reported in Japan (Minato, 1968). Previous studies (Allen *et al.,* 1995ab, 1996) showed that the most important plant nutrients, like Nitrogen and Phosphate, could be supplied to plants by exchanging ammonium (NH_4^+) and Phosphate (P) into zeolites and applying the ion exchanged zeolite to soil to act as a nutrient supplement.

One of the most important applications of zeolites in agriculture is the slow/controlled-release fertilizer aspect. Slow release is a term that is interchangeable with delayed-release, controlled-release, controlled-availability, slow acting and metered-release (Ming and Allen, 2001). Some of the natural zeolites that have been studied for slow-release fertilizer aspects are Clinoptilolite, Chabazite, Phillipsite and Mordenite. The widespread abundance of these zeolites in nature and their selectivity for certain cations (i.e. NH_4^+ and K^+) makes them suitable for this purpose.

Slow-release synthetic zeolite-bound Zinc and Copper fertilizers were used to study the influence of these cations on Cadmium (Cd) uptake of wheat and spinach, two crops with a high tendency to accumulate Cd. The study concludes that application of zeolite-bound Zn or Cu may help to reduce Cd accumulation in edible parts of crops (Puschenreiter and Horak, 2003). Most of the previous studies carried out on the slow/controlled release fertilizer aspects of zeolites were focused on natural Clinoptilolite and to a certain extent on natural Phillipsite.

Application of zeolite to soil is beneficial in spinach (*Spinacia oleracea*) cultivation and leads to an increase in seed germination and an overall increase in yield, when applied in conjunction with conventional fertilizer application (Burriesci *et al.,* 1983). On adding zeolites to traditional fertilizers in trials on plums (*Prunus persica*) and vines (*Vitis vinifera*) in southern Italy, increases in fruit size and yields were noted (Burriesci *et al.,* 1984). Jordanian zeolite tuffs have been used for various applications. Studies of Jordanian Chabazite-Phillipsite tuff effects on yield and nutrient concentration of strawberries (*Fragania xananassa*) showed that a zeolite tuff-soil mixture with 2:5 ratio increased yield and plant height and decreased mortality. The effective increase in total yield of strawberry reached ≤ 72% (Ibrahim *et al.,* 1996).

1.8.1. Use of Clinoptilolite in Agriculture

The pronounced selectivity of Clinoptilolite for NH_4^+ and K^+ was exploited in Japan in slow-release chemical fertilizers. The high cation exchange property of

Clinoptilolite towards NH_4^+ makes it particularly valuable when applied to finely textured sandy soils to restrict leaching of NH_4^+, as high retention of this ion would control its accessibility to nitrifying bacteria (Andronikashvili *et al.,* 1995). Other studies by Leggo (2000) showed that an organo-zeolitic substrate incorporating a composted mixture of poultry manure and Clinoptilolite-zeolite tuff is an effective fertilizer and soil conditioner. Therefore, Clinoptilolite, when incorporated as part of organic fertilizers, improves soil quality by improving structure, ion exchange capacity, moisture and nutrient retention. Zeolites also help in controlling and managing valuable nutrient assets, by inhibiting release and loss to the environment.

Lewis *et al.* (1984) and Pirela *et al.* (1984) showed that Nitrogen can be supplied to plants from soils amended with ion exchange form of NH_4^+- saturated Clinoptilolite. A substantial reduction of NO_3^- leaching and increased uptake of N-fertilizer was observed on addition of 10% (w/w) Clinoptilolite to sand used in the construction of golf-course greens (Mumpton, 1999). Studies by Perrin *et al.* (1998) on sweet corn (*Zea mays*) showed that amending soils with ammonium-Clinoptilolite, reduced N leaching considerably, while sustaining plant growth and increasing N-use efficiency, when compared to ammonium sulphate amended soils. Also sweet corn grown in soil amended with ammonium-Clinoptilolite assimilated significantly more N than sweet corn grown in soil amended with ammonium sulphate. (Allen *et al.,* 1995) developed a kinetics theory that, controlled release of P, NH_4^+ and K^+ can be accomplished in synthetic soil through dissolution and cation exchange reactions between phosphate rock and Clinoptilolite. On the other hand, mixing NH_4^+- saturated Clinoptilolite with phosphate rock can act as a supplement of N and P to plants (Chesworth *et al.,* 1987; Barbarick *et al.,* 1990).

1.8.2. Use of Phillipsite in Agriculture

The exchange properties of natural Phillipsite tuff obtained from the Aritain area of Jordon were evaluated by studying the exchange properties of this zeolite in the NH_4^+-Na^+ system. The tuff has a higher selectivity for ammonium ions than sodium ions (Dwairi, 1998). Studies on tuff revealed that release of NH_4^+ from the saturated tuff occurs over a long period of time (630 days) (Dwairi, 1998). These properties are favourable for using Jordanian Phillipsite tuff as a potential ammonium based slow-release fertilizer.

Studies were also carried out on potassium phosphate (KH_2PO_4) saturated Phillipsite tuff from Tenerife, to study the supply rate of P from this fertilizer compared with KH_2PO_4 alone. Results indicated that zeolite fertilizers supply available P after 70 days of continuous percolation, whereas P from KH_2PO_4 is exhausted after 50 days. Both fertilizers supplied available K throughout the whole experiment period; unlike KH_2PO_4, zeolite fertilizer provided controlled potassium release (Notario del Pino *et al.,* 1995).

1.8.3. Zeoponic Substrates

Co-operative programmes between NASA and industry have developed zeoponic plant growth media and fertility systems. A zeoponic plant growth system is defined as cultivation of plants in artificial soils, which contain zeolites as a major component (Parham, 1984; Ming, 1999). Zeoponic materials consist of (a) plant nutrient ion exchanged natural/synthetic zeolites and (b) synthetic apatite, a phosphorus and trace element fertilizer constituent. Zeoponic substrates have been used on the Russian Mir Space Station and U.S. Space Shuttles to grow various plants, including radishes, wheat and brassicas. Space gravitational biologists have considered Zeoponic substrates as preferred material for plant growth in a microgravity environment. However, the effectiveness of zeoponic substrates for plant growth in macrogravity is unclear. Between 1994-1997, Zeoponix, Inc (USA) and NASA, conducted experiments on zeoponic materials as soil amendments for plant growth, studying seed germination, root development, fruit development, fruit quality and yield. Work was carried out on horticultural species and cereal crops. According to results claimed virtually all plants tested had improved yield or quality of growth when growing in soil-less media containing 5-30% by volume zeoponic fertilizer-amendments (Ming and Allen, 2001). With rising world populations, potential improvements in crop yield indicated with zeoponic systems are of particular importance in meeting rising food demands.

1.8.4. Zeolites as Soil Conditioners

Zeolites have also been used as soil conditioners to improve soil physio-chemical properties (Kralova *et al.*, 1994). On adding Clinoptilolite to slightly alkaline or acidic soils, there is an increase in soil pH and exchangeable K, but it does not influence humus content and soil chemical composition (Filcheva and Tsadilas, 2002). Farmers add zeolites to soil to control soil pH and improve ammonium retention (Dwyer and Dyer, 1984).

Zeolites can increase soil CEC, act as a reservoir of K^+ (Hershey *et al.*, 1980) and increase the water-holding capacity of loamy sand soils if very large amounts are added (Huang and Petrovic, 1994). Studies by Kralova *et al.* (1994) on synthetic Phillipsite and natural Clinoptilolite supplemented soils showed an increase in water holding capacity and CEC. Natural zeolite-enriched soils increased water holding capacity from (18-19%) and CEC from 30-40%, whereas the synthetic zeolite enriched soils increased water-holding capacity from 3-30% and CEC from 10-50%. Soils supplemented with both synthetic and natural zeolites can be used as effective fertilizers on saturating the zeolites with ammonium. This can be achieved by ion exchange reactions, whereby ammonium is exchanged for cations present in the zeolite framework. Ammonium exchanged zeolites can potentially be a valuable source for controlled release of N and can replace the use of conventional fertilizers used intensively by farmers for increased crop production. With respect to conditioning soils low in potassium, zeolites such as Linde type F synthesized in K form can be used for replenishing K in these soils.

1.9. Maize growth: An overview

Maize (*Zea mays*) is one of the most important commercial crops, grown widely throughout the world. For the current study, maize was selected over other crops in view of its rapid growth cycle and responsiveness to changes in the availability of nutrients. It has the potential to show growth responses over short harvest intervals. Maize grows best and is most easily handled on fairly flat, well-drained, fertile land. Continuous cropping with maize is feasible, but requires close attention to the build-up of pathogens and pests. Maize can also be grown under glasshouse conditions by following good cultural practices; it grows best in a glasshouse ground bed, but can also be grown in pots. The following conditions should be maintained in the glasshouse for cultivating maize. The soil should be fertile, well drained and not too high in organic matter. The temperature should not be $<19^{o}C$ or $>32^{o}C$. The best growth temperatures are between 20-25^{o}C during the night and 25-30^{o}C during the day. Higher temperatures should be accompanied by higher light intensity. The most critical factor in growing maize in the glasshouse is light intensity. High-pressure sodium vapour lamps are recommended to give a minimum of 12 hours of light during winter months (Sheridan, 1982). The current project focused on growing maize in pots under glasshouse conditions for two reasons. First to limit the amount of zeolite required, as much larger amounts of zeolite would be needed if grown in the field. Second, for collecting leachates, pots were a better option, allowing individual or grouped leachates to be collected.

Before considering the macro- and micro- nutrient requirements of maize, it is necessary to give a brief overview of maize growth and physiology. *Zea mays* is a member of the Gramineae family, but unlike other grasses which produce perfect bisexual flowers, maize produces male inflorescences (tassels) which crown the plant at the stem apex, and female inflorescences (ears) which are borne at the apex of the condensed lateral branches protruding from leaf axils (Salvador, 1997). The male (staminate) inflorescence produces pairs of free spikelets, each enclosing a fertile and a sterile floret. The female (pistillate) inflorescence produces pairs of spikelets on the surface of a highly condensed rachis (central axis or cob). Each of the female spikelets encloses two fertile florets, one of whose ovaries will mature into a maize kernel once sexually fertilized by wind-blown pollen (Figure 1.7). All three-glasshouse experiments reported in this study investigated the effects of zeolites on vegetative growth. The final experiment also measured effects on reproductive growth, up to cob formation. Therefore both these growth phases must be considered.

1.9.1. Vegetative growth of maize

Plant development involves both growth and differentiation. The term growth is applied to quantitative changes occurring during development and it may be defined as an irreversible change in the size of a cell, organ or whole organism. Primary growth involves the increase in the size of the primary plant body, such as increases in the height of the stem, number and size of leaves, and growth of roots (Wareing and Phillips, 1981). Above-ground vegetative growth stages involved in the development of maize can be classified into (a) Seed germination and seedling growth, (b) Leaf emergence, (c) Main shoot growth and formation of axillary shoots and (d) tasseling.

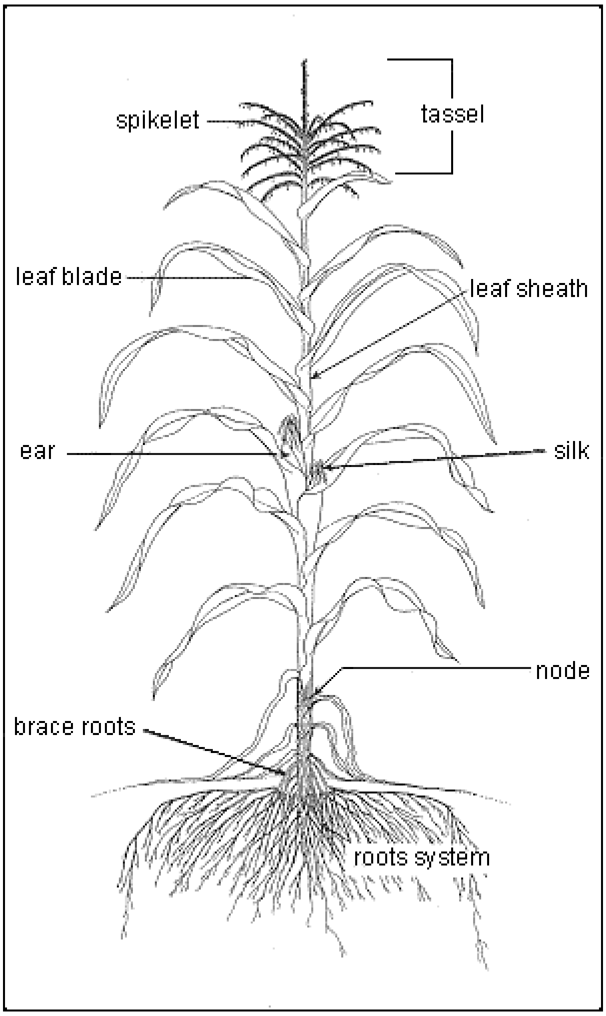


Figure 1.7. The mature maize plant

Source: Crop Physiology (Evans, 1975).

(a) Seed germination and seedling growth

The germination of maize seed is similar to that of many grasses except for scale differences resulting from the relatively large endosperm and embryo. The large size of the endosperm and embryo permits emergence from considerable depths. Under good field conditions, the seed absorbs water and begins germination. The radicle is first to begin elongation; followed by the coleoptile with the enclosed plumule (embryonic primary leaf), and then the three to four lateral seminal roots. Emergence is finally attained by the rapid elongation of the mesocotyl, which pushes the growing coleoptile to the soil surface (Figure1.8, Aldrich and Leng, 1976).

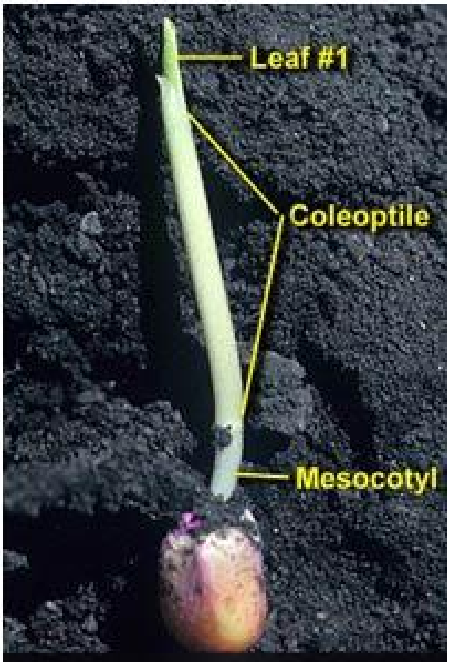


Figure 1.8. Germinating seed

Source: Plant physiology (Taiz & Zeiger, 2002).

The first permanent roots emerge at the node joining mesocotyl and coleoptile. Upon emergence and exposure of the coleoptile tip to sunlight, coleoptile and mesocotyl elongation stops and the primary leaf grows through the coleoptile. This leaf starts to turn green, through the light stimulated synthesis of chlorophyll from proto-chlorophyll. Photosynthesis begins shortly after this stage (Hanway, 1971).

(b) Leaf emergence

The leaves of the maize plant are the first to emerge from the soil after the tip of the coleoptile and remain the only aboveground plant part for a considerable time. The first leaf always has a rounded tip. At this stage the collar of leaf number "n" is visible ("n" is equal to the final number of leaves the plant has, and is usually between 16-22, but by flowering the lower 4 to 5 leaves will have been lost). The nodes from which the leaves arise develop in rapid succession above the mesocotyl, but elongation of the internodal tissue is delayed, often until primordial development is complete (Evans, 1975).

(c) Main shoot growth

The sequence of development of the shoot may be described as a repeating unit structure consisting of a leaf blade, a leaf sheath, a disk of insertion or node and an internode. This structural unit is repeated, with variations in relative dimensions of the component parts, to make up the entire vegetative shoot, except the tassel and its stem. Each of the structural unit develops as a wave of growth and elongation that commences in the leaf blade and moves down so that sheath development follows that of the leaf blade and growth of the unit terminates with elongation of the internode. The successive elongation of the lower internodes forms the stalk that rises through the tube formed by the leaf sheaths, which developed earlier. The relatively late elongation of internodes in relation to leaves and sheath means that stalks are more affected than leaves by stresses or deficiencies that increase during vegetative plant development (Aldrich and Leng, 1976). The final stage of development for each structural unit is the formation of roots or root initials at the lower part of the internode and the hardening of the meristematic tissues. The height of the final plant, diameter of its stalk, and to some extent its yield potential are strongly influenced by environmental conditions during stem elongation, including the availability of plant nutrients. Studies by Hozumi *et al*. (1965) noted that in closely spaced plants of different initial heights the shorter plants elongated more rapidly than the taller ones. Although the shorter plants elongated more rapidly, their rate of dry weight gain was less, so their stalks were lighter and smaller in diameter.

(d) Tasseling

The termination of the vegetative development in maize is signalled when the apical meristem of the stem, which has a hemispherical form when leaves are being formed, begins to elongate and initiate the primordia of the staminate flower or tassel. The development of the tassel proceeds as the internodes of the stalk elongate so it is almost fully developed when it emerges from the leaf whorl at anthesis. From emergence of the tassel to its full development and shedding of the pollen may take ≤ 10 days during which the supporting stalk elongates and the vegetative plant growth is completed (Reeves, 1970). The shedding of pollen by an individual tassel usually starts near the tip and proceeds both upward to the tip and down and out along the branches to their tips, although there may be considerable variation in this sequence. It is incorrect to say that reproductive development begins with the initiation of the tassel because the early initials of ears are visible as buds at the axils of the lower leaves before the tassel is differentiated. An axillary bud develops into an ear shoot at each node of the stem up to the one, which bears the uppermost ear. Several ears in lower positions of the plant may attain considerable size, but those that do not reach the fertilization stage regress.

1.9.2. Reproductive growth of maize

Reproductive growth is the stage when reproductive structures are being produced. Reproductive growth stages of maize can be classified into (a) Silking, (b) Blister, (c) Milk, dough and dent and (d) Physiological maturity.

(a) Silking stage

The ear shoot mentioned earlier starts development by enlargement of the prophyllum, which eventually becomes a husk. This is accompanied by the growth of the branch or shank, which differs from ordinary stems in remaining slender with usually short internodes. This enables sheaths of the leaves that develop at each node to surround the ears as husks. Rapid development of ear shoots appears to start at about the time the tassel emerges, and growth of the husks is well advanced at anthesis (Kiesselbach, 1979). The earliest development of the ear consists of the formation of a structure with two-lobed protuberances from base to tip. Each of these lobes develops into a spikelet with two flowers, only one of which commonly persists. The pistil of the female flower known as the silk develops from the growing point of the flower. The stage of silking occurs when silks are visible and pollination occurs. Pollination occurs when newly formed moist silks catch the fallen pollen grains. A pollen grain grows down the silk and fertilizes the ovule in ~ 24 hours. Upon this fertilization, the ovule is a kernel. Normally, it takes two to three days for all silks on a single ear to emerge and be pollinated. In maize plant the number of kernels per ear and the number of ears that can develop is established at or shortly after pollination and no more can develop later (Aldrich and Leng, 1976).

(b) Blister stage

Kernels are white on the outside and resemble a blister in shape. The endosperm and its available fluid are clear in colour, and starch just begins to accumulate in the watery endosperm. Although the embryo is still developing at this time, the radicle, coleoptile, and first embryonic leaf have already formed. Thus, within the developing embryo is a developing miniature maize plant. By this stage, much of the kernel has grown out from within the surrounding cob material and the cob is close to or at full size (Kiesselbach, 1979).

(c) Milk, dough and dent stage

By this stage kernels begin to yellow on the outside but contain a milky white inner fluid (starch accumulation—kernel is now at ~ 80% moisture). Most of the kernels have grown out from the surrounding cob material. The endosperm cell division in each seed is complete and growth will now be due to cell expansion and starch accumulation. The kernel has thickened to a pasty (doughy) consistency from the earlier milky state (starch has continued to accumulate and kernel moisture content has decreased). The embryo of the seed is growing while the kernels are just beginning to dry at the top (dent). Kernels have now accumulated 50% of their dry weight and have a moisture content of about 70%. Drying kernels show a small, hard, white layer on top. A white line (known as the milk line or starch line) can be seen across the kernel shortly after denting (starch line indicates maturity—it will advance toward the kernel tip with maturity). Kernels at this stage have ~ 55% moisture. At ~ 48 days after silking, all the kernels should be fully dented. Each seed embryo is morphologically mature, and dry matter accumulation in the kernels will cease (Daynard *et al*., 1989).

(d) Physiological maturity

All kernels have attained maximum dry weight. The starch line has advanced completely to the kernel tip and a brown or black layer is present (black layer progresses on the ear from the tip kernels to the basal kernels in about 10 days). Harvest for silage can be done now or slightly earlier, but grain harvest will require more drying. Husks and many of the leaves are no longer green, but the stalk may be green. At black layer stage the average kernel moisture is 30-35% (varying with hybrids and environmental conditions). At 20-26% moisture, harvested grain will still need artificial drying to store safely, thus more field dry down is often used (rate of field dry down varies with hybrid and environmental conditions). Shelled maize can be safely stored at 13-15% moisture (Hatfield, 1987).

1.10. Maize growth as influenced by soil physical properties

Various factors influence maize growth and nutrient uptake. Some of the most important soil properties that influence seed germination, growth and development are: (a) soil compaction (b) temperature and (c) moisture content.

(a) Soil Compaction

The growth and development of roots depend on soil physico-chemical properties. Normally, roots grow downwards but when they encounter a compacted zone, the direction and growth form of the roots can be changed. The degree to which a soil restricts water movement and root penetration depends on the degree of compaction (Sene *et al.*, 1985). The resistance to a cone penetrometer is used to measure soil compaction. Penetrometer resistance > 2.0 Mpa severely impedes root growth (Ehlers *et al.,* 1983). Sub-soiling can reduce soil compaction. Kamprath *et al.* (1979) showed increased maize yield on soils with root restricting layers following sub-soiling, which was attributed to greater utilization of subsoil moisture by crops. The most effective way to reduce compaction is through tillage. Deep tillage breaks up high-density soil layers, improves water infiltration and movement in the soil, enhances root growth and development and increases crop production potential (Bennie and Botha, 1986).

(b) Temperature

Soil temperature plays a vital role in germination and speed of coleoptile elongation (Blacklow, 1974). Soil temperature usually decreases with depth and for this reason the period of time to obtain a given number of growing degree-days is longer for more deeply sown seeds. Furthermore, the distance to be covered by the coleoptile to reach the soil surface is longer, one more day being necessary for each 2.5 cm increase in sowing depth (Alessi and Power, 1971). Thus variations in sowing depth and surface residues cause heterogeneities in time of seedling emergence, due to variations in seed temperature (Hayhoe and Dwyer, 1990). Although effects of air temperature on maize seedlings have been studied to a greater extent than the effects of soil temperature, the latter plays a more important role in early maize growth and development. Maize seeds germinate when the soil temperature reaches 15^{o}C at 5 cm depth. After this, a soil temperature of 20^{o}C is optimal in terms of dry matter accumulation, although many other factors also influence dry matter content. With pots in a glasshouse, it is assumed that the soil temperature in the pot equilibrates with the air temperature, except after watering when high ratio of evaporation from the soil surface causes cooling.

(c) Moisture Content/Water availability

Maximum maize yields can only be achieved under conditions of adequate water availability. Water stress in early growth can delay flowering, and therefore reduce yield (Wrigley, 1969). Apart from germination, the most crucial times in terms of water availability are during flowering and grain formation (Classen and Shaw, 1970). Macronutrients, such as N, P, and K, are transported conventionally with water through the xylem, driven by the gradient of water potential via the soil-plant atmosphere system (Novak, 1994). Franko *et al.* (1995) showed that the above approximation is less successful in poor, dry soils when the plants experience nutrient stress.

1.11. Maize growth as influenced by soil chemical properties

Nutrients that are mobile in plants such as N, P, K and Mg, can be re-translocated from old tissue (bottom of the plant) to young growing tissue (top of the plant). Deficiency symptoms for these nutrients occur first on lower, older leaves. Immobile nutrients such as B, Ca, Cu, Fe, Mn, Mo, S and Zn are not easily re-translocated and deficiency symptoms occur on upper, new leaves (Mengel and Kirkby, 1987). Depending on the magnitude of the growth requirement for a given nutrient, the nutrient is referred to as either a macronutrient or a micronutrient. Maize plants require all the essential macronutrients (N, P, K, Ca, Mg and S) for growth, along with the micronutrients Fe, Cu, Zn, Mn, Ni, Mo, Na, B and Cl.

Nitrogen (N)

Nitrogen is a major constituent of several of the most important substances that occur in plants. Among all the essential elements for plants, N is most important in that N compounds comprise from 40-50% of the dry matter of protoplasm, the living component of plant cells (Levin *et al.*, 1989). N serves as a constituent of many plant cell components, such as amino acids, amides, alkaloids and nucleic acids, and is a component of many important structural, genetic and metabolic compounds in plant cells. N is a basic component of amino acids, which are the building blocks of proteins. Proteins can be structural or functional as enzymes. Chlorophyll the green colouring matter of the leaves, also contains nitrogen. N is a part of energy-transfer compounds such as ATP (Adenosine triphosphate), which allows cells to conserve and use the energy released in metabolism. Finally, N is a significant component of nucleic acids such as DNA and RNA (Wallace, 1961). Depending on the plant species, development stage and organ, the N content required for optimal growth varies between 2-5% of plant dry weight (Marschner, 1997).

Nitrate (NO_3^-) and ammonium (NH_4^+) are the major sources of inorganic N taken up by the roots of higher plants. Most of the ammonium has to be incorporated into organic compounds in the roots, whereas nitrate is readily mobile in the xylem and can also be stored in the vacuoles of roots, shoots and storage organs. Nitrate accumulation in vacuoles can be of considerable importance for cation-anion balance, osmoregulation and for the quality of vegetable and forage plants (Smirnoff and Stewart, 1985). In those plant species where most or all nitrate assimilation occurs in the shoots, organic acid anions are synthesized in the cytoplasm and stored in the vacuole. However, in order to be incorporated into organic structures and to fulfil its essential functions as a plant nutrient, nitrate has to be reduced to ammonia (Raven and Smith, 1976). The importance of the reduction and assimilation of nitrate for plant life is similar to that of the reduction and assimilation of CO_2 in photosynthesis.

Nitrate reduction in higher as well as in lower plants follows the reaction:

$$NO_3^- + 8H^+ + 8e^- \longrightarrow NH_3^- + 2H_2O + OH^- \qquad (1.6)$$

Two enzymes mediate the reduction of nitrate to ammonia: nitrate reductase (NR), which involves the two-electron reduction of nitrate to nitrite, and nitrite reductase (NiR), which transforms nitrite to ammonia in a six-electron reduction. The principal steps in the assimilation of ammonium ions supplied to the roots are uptake into the root cells and incorporation into amino acids and amides with a simultaneous release of protons for charge compensation. As shoots have a rather limited capacity for disposal of protons, nearly all of the ammonium taken up has to be assimilated in the roots, and the assimilated nitrogen transported in the xylem as amino acids and amides to the shoot (Raven, 1986).

N is the most important nutrient required for maize growth. The amount of N needed is based on the expected yield, the amount of residual soil nitrate-N (NO_3-N) and soil organic matter. It has been estimated that under intensive cultivation a hectare of maize producing 5000 kg of grain will take ≤ 105 kg of N. Addition of N fertilizer to crops in temperate and the tropical countries is very similar, between 30-160 kg ha^{-1} in the USA and 88-132 kg ha^{-1} in India (Department of Environment and Rural Affairs, (DEFRA), 2002). The high N requirement of maize plants was demonstrated at the Continuous Maize Experiment at the Illinois Agricultural and Experimental Station, USA. Experiments were carried out by growing maize for several years continuously without fertilizer addition, results showed severe depletion of N levels after the first year alone (Purseglove, 1979).

N deficiency will rapidly inhibit plant growth. Under N deficiency, most plant species show chlorosis (yellowing of the leaves), especially in the older leaves near the plant base. Under severe N deficiency, these leaves become completely yellow (or tan) and fall off the plant. Younger leaves may not show these symptoms initially because N can be mobilized from older to younger leaves (Bauer and Carter, 1986). Symptoms of N deficiency are shown by withering in a V shape towards the midrib of the leaf, which is often accompanied by yellowing in this area, and low N can result in a low grain protein content (Bauer and Carter, 1986). Thus N-deficient plants may have light green upper leaves and yellow or tan lower leaves. When N deficiency develops slowly, plants may have markedly slender and often woody stems. This feature may be due to a build up of excess carbohydrates that cannot be used in the synthesis of amino acids or other N compounds. Carbohydrates not used in N metabolism may be used in anthocyanin synthesis, leading to the accumulation of this pigment. This condition is revealed as a purple coloration in leaves, petioles and stems of some N-deficient plants, such as tomato and maize (Taiz and Zeiger, 2002).

In agricultural practices for maize production, N fertilizer is added to the soil at sowing. However, different approaches have been suggested for the addition of fertilizer. Bacon and Thompson (1984) found a one-off early application of N fertilizer produced higher yields than continuous or late applications, whereas Murwira and Kirchmann (1993) found a late application produced better results. Studies were carried out in the US to investigate maize production under different tillage methods and rates of N application. Studies showed NH_4 to be higher in the soil surface under no-tillage and levels of NO_3 were higher in the surface under conventional tillage. This greatly influences the availability and leaching of NO_3, due to its solubility in liquid surrounding the roots (Staley, 1988). Excess nitrate present in the soil leaches out into the underground water and is a major concern, especially in regions of high fertilizer application.

Maize root reaction to N fertilizer was considered in some detailed study in The Netherlands (Schroder *et al*., 1996). Maize plants were grown in purpose built rhizolabs where root growth could be observed. One of the findings was that at low temperatures, root growth and activity are restricted, possibly limiting the ability of the root system to efficiently take up N. The effects of root zone temperature on the form of N taken up by maize roots have also been studied, maize roots take up NH_4^+ and NO_3^- through different mechanisms, and ammonium is assimilated into organic compounds in the root, unlike NO_3^-. Soil pH can also play a role in the uptake of N by maize roots. Alkaline to neutral conditions have a stimulatory effect on nitrate reductase activity, which will increase NO_3^- uptake, whereas presence of NH_4^+ or acid conditions has an inhibitory effect (Mengel *et al*., 1983). Conversely, McClure *et al.* (1986) claimed that NO_3^- uptake is favoured by more acidic soils.

Phosphorus (P)

Phosphorus like N, is closely concerned with many vital growth processes in plants, it is a constituent of nucleic acids, and nuclei in which these occur are essential parts of all living cells. P (as phosphate, PO_4^{3-}) is an integral component of important compounds of plant cells, including the sugar-phosphate intermediates of respiration and photosynthesis and the phospholipids that make up plant membranes (Taiz and Zeiger, 2002). P is involved in many of the biochemical reactions concerned in the metabolism of carbohydrates, fats and proteins in which phosphorylated compounds act as intermediates.

It is also a component of nucleotides used in plant energy metabolism (such as ATP) and in DNA and RNA. In both DNA and RNA, phosphate forms a bridge between ribonucleoside units to form macromolecules (Marschner, 1997). P is a vital component of ATP (the energy unit of plants). ATP forms during photosynthesis, has

P in its structure, and processes from the beginning of the seedling growth through to the formation of grain and maturity. P is of special importance in the germination of seeds, in the ripening processes of seeds and fruits and in root development. P requirement for optimal growth is in the range of 0.3-0.5% of plant dry matter during the vegetative growth stage (Wallace, 1961).

In plants suffering from P deficiency, reductions in leaf expansion and leaf surface area, and also number of leaves are the most striking effects (Fredeen *et al.*, 1989). Leaf expansion is strongly related to the extension of epidermal cells, and this process may be particularly impaired in P-deficient plants, due to low P content of epidermal cells (Treeby *et al.*, 1987) and decrease in root hydraulic conductivity (Radin, 1990). In contrast to the severe inhibition in leaf expansion, the contents of protein and of chlorophyll per unit leaf area are not much affected. However, the photosynthetic efficiency per unit of chlorophyll is much lower in P deficient leaves (Lauer *et al.*, 1989). Characteristic symptoms of P deficiency include stunted growth in young plants and a dark green coloration of the leaves, as cell and leaf expansion are more retarded than chloroplast and chlorophyll formation (Wallace, 1961). The part played by P in the efficient functioning and utilization of N probably accounts for the fact that several of the important symptoms of P deficiency are identical with or similar to those that result from N deficiency. As in N deficiency, some species may produce excess anthocyanins, giving the leaves a slight purple coloration. In contrast to N deficiency, the purple coloration of P deficiency is not associated with chlorosis; in fact the leaves may be a dark greenish purple. Additional symptoms of P deficiency include the production of slender (but not woody) stems and the death of older leaves. Maturation of the plant may also be delayed (Taiz and Zeiger, 2002).

P requirement for maize growth remains consistent throughout the plant’s life. It has been estimated that 1 hectare of maize producing 5000 kg of grain will take up 50 kg of P_2O_5 during its life cycle (DEFRA, 2002). P requirement in the form of P fertilizer varies according to soil type and cultivar. It is also highly dependent on the system under which maize is produced. In tropical soils the sub-soil is often low in P, therefore crops take most of their P requirements from the surface. In the case of maize this does not present any problems, as the plant has extensive lateral roots and can adapt its root system to P availability. The relationship between P distribution in the soil and maize root distribution was studied by Zhang and Barber (1992). Studies showed that maize plants take up more P when fertilizer was added to a portion of soil, rather than uniformly in the soil. It therefore appears that smaller pockets of concentrated P fertilizer are more beneficial. Soil chemical conditions can have significant effects on the ability of maize to take up P, because they can change the form in which P occurs in soil. Maize takes up P mainly in the form of dihydrogen phosphate (H_2PO_4), which is taken up 10 times more rapidly than hydrogen phosphate (HPO_4), which is also present in soil (Chen and Barber, 1990). P uptake by the root system of maize is also influenced by mychorrizae. Kothari *et al*. (1990, 1991) gave an overview of maize root/mycorrhiza interactions.

Potassium (K)

Unlike all the other major elements, potassium does not enter into the composition of any of the important plant constituents, such as proteins, chlorophyll, fats and carbohydrates, concerned in plant metabolism (Wallace, 1961). It is of special importance in leaves and at growing points, as these are rich in K. It has been shown in many instances that the K content of plants is frequently much higher than is necessary for healthy growth. In plants, K is present in soluble form, and most of it seems to be contained in the cell sap and cytoplasm. As a cation, K^+ plays an important role in regulation of the osmotic potential of plant cells (the regulation of water conditions within the plant cell and water loss by transpiration); and activates many enzymes involved in respiration and photosynthesis, especially under conditions of low light intensity (Taiz and Zeiger, 2002).

K is remarkable among the nutrient elements for its mobility and solubility within plant tissues, and these properties account for the way in which K can be re-utilized by young tissues when the element is in short supply. Therefore, when K is moderately deficient, the effects are first seen in the older tissues and progress from these to the growing points, but when the deficiency is acute, growing points are severely affected and die back and general collapse of the plant commonly occur. Next to N, K is the mineral nutrient required in the largest amount by plants. The K requirement for optimal plant growth is in the range 2-5% of the plant dry weight of vegetative parts, fleshy fruits and tubers (Marschner, 1997).

When K is deficient, growth is restarted, and net retranslocation of K is enhanced from mature leaves and stems, and under severe deficiency these organs become chlorotic and necrotic. The first observational symptom of K deficiency is mottled or marginal chlorosis, which then develops into necrosis, primarily at the leaf tips at the margins, and between veins (Marschner and Cakmak, 1989). Because K can be mobilized to the younger leaves, these symptoms appear initially on the more mature leaves toward the base of the plant. The leaves may also curl and crinkle. Symptoms of K deficiency are whitish yellow spots on the leaves, followed by scorching or browning of leaf edges. The stems of K deficient plants may be slender and weak, with abnormally short internodal regions. In potassium-deficient corn, the roots may have an increased susceptibility to root-rotting fungi present in the soil (Marschner, 1997). This susceptibility, together with effects on the stem, results in an increased tendency for the plant to be easily bent to the ground (lodging). Plants receiving inadequate supplies of K are often more susceptible to frost damage (Larsen, 1976), which at the cellular level is related in some respects to water deficiency. When the soil water supply is limited, loss of turgid and wilting is typical symptoms of K deficiency.

Most soils are already rich in K, in cases where organic fertilizers, such as cattle manure, are added no K addition is required. Maize takes up less K than N, with a hectare producing 5000 kg of grain taking up 75 kg of K_2O (DEFRA, 2002). Soil moisture plays a major role in K uptake and root growth. The higher the soil moisture, the greater is the root growth and K uptake (Seiffert *et al.,* 1995). A study also revealed at low K concentrations, K uptake was independent of soil pH (Kochian *et al.,* 1989). However, this is not the case when K concentrations in the soil are high. This was because the system of uptake at low levels did not involve a H^+ exchange system. The mechanism of K uptake in maize roots has been the subject of several studies and is still poorly understood. It is, however, apparent that there may be more than one transport mechanism and that the one used depends on soil K concentration.

Magnesium (Mg)

Magnesium plays a vital role as a constituent of the chlorophyll molecule. Mg is concerned in numerous enzyme reactions, in which it is regarded as a most effective activator. In plant cells, magnesium ion (Mg^{2+}) has a specific role in the activation of enzymes involved in respiration, photosynthesis and the synthesis of DNA and RNA. Mg is closely associated with energy supplying P compounds, acting in the role of a carrier for the element. In this connection, it is considered of importance in the formation of seeds of high oil content, containing phospholipids (Taiz and Zeiger, 2002). The Mg requirement for optimal plant growth is in the range of 0.15-0.35% of the dry weight of the vegetative parts.

A characteristic symptom of Mg deficiency is chlorosis between the leaf veins, occurring first in the older leaves because of the mobility of this element. Symptoms of Mg deficiency can be seen as whitish or yellow strips between the leaf veins and this can be accounted for by chlorophyll deficiency. This pattern of chlorosis results because the chlorophyll in the vascular bundles remains unaffected for longer periods than the chlorophyll in the cells between the bundles. If the deficiency is extensive, the leaves may become yellow or white. An additional symptom of Mg deficiency may be premature leaf abscission (Wallace, 1961).

Mg is an essential element for maize growth. In maize plants, Mg is needed as an enzyme activator in phosphate transfer. By adding Mg, K concentration decreases in plant material, suggesting these two nutrients are competing for uptake sites or interfering with each other’s solubility. In tropical soils, Mg can often be the limiting nutrient to maize production, especially if N, P and K are added in substantial amounts. Mg deficiency is associated with acidic, sandy or highly leached soils. It is, therefore, particularly relevant to soils which may be subject to erosion (Landon, 1991).

Calcium (Ca)

Calcium occurs in plants chiefly in the leaves and the amounts present in seeds and fruits are relatively low. Calcium ions (Ca^{2+}) are used in the synthesis of new cell walls, particularly the middle lamellae that separate newly dived cells (Taiz and Zeiger, 2002). This function appears to be of fundamental importance, since if any other of the essential elements, such as Mg or K replaces Ca the organic materials and mineral salts in the cells are readily leached through the walls. Ca is also used in the mitotic spindle during cell division. Ca is required for the normal functioning of plant membranes and has been implicated as a second messenger for various plant responses to both environmental and hormonal signals (Sanders *et al.*, 1999). Ca is intimately concerned in the activities of growing points (meristems), and is of special importance in root development, in which it has been shown to exercise a three-fold function, in cell division, cell elongation and the detoxification of hydrogen ions. Other functions attributed to Ca are that it provides a base for the neutralization of organic acids; it inhibits and thus may regulate some K-activated functions, and may be of importance in N absorption. The Ca content of plants varies between 0.1 and >5.0% of dry weight depending on the growing conditions, plant species and plant organ (Kirkby and Pilbeam, 1984).

Characteristic symptoms of Ca deficiency include necrosis of young meritematic regions, such as the tips of root or young leaves, where cell division and wall formation are most rapid. Necrosis in slowly growing plants may be preceded by a general chlorosis and downward hooking of the young leaves, the leaves may also appear deformed. The root system of a Ca-deficient plant may appear brownish, short, and highly branched. Severe stunting may result if the meristematic regions of the plant die prematurely (Hanson, 1984).

Micro-nutrients

Iron (Fe) is an essential trace element for maize as it is directly linked to chlorophyll levels. Fe has an important role as a component of enzymes involved in the transfer of electrons (redox reactions), such as cytochromes. Maize in common with other graminaceous species, can release phytosiderophores from its roots, which aid Fe uptake (Von Wiren *et al.*, 1993). Zinc (Zn) deficiency can occur in temperate and tropical maize production. Zn deficiency in maize occurs most often where subsoil is exposed on soils levelled for irrigation. Zn deficiency can be caused by several factors including: soils low in organic matter, low temperatures, high sodicity, high soil phosphate, large applications of N and a restricted root zone (Kayode, 1985). Soil pH determines the availability of soil macro- and micronutrients to plants. Acidity promotes the weathering of rocks that release K, Mg, Ca and Mn and increase the solubility of carbonates, sulphates and phosphates. Therefore, increasing nutrient solubility facilitates their availability to roots.

1.12. Nitrate Pollution of Groundwater

Nitrogen is the main constituent of the Earth's atmosphere and occurs in many different forms, such as elemental N, nitrate and ammonia. There are many sources of N (both natural and anthropogenic) that could potentially lead to nitrate pollution of groundwater. Natural reactions of the atmospheric form of N with rainwater results in the formation of nitrate and ammonium ions. Anthropogenic sources most often cause the amount of nitrate to rise to dangerous concentrations. The largest anthropogenic sources are septic tanks, application of N-rich fertilizers to turf grass and agricultural processes. In the atmosphere, major sources of nitrate include reactions caused by lightning, photochemical oxidation in the stratosphere, chemical oxidation of ammonia, soil production of NO by microbial process, and fossil fuel combustion (Figure 1.9). Nitrate that leaves the atmosphere can be converted back into elemental N through the process of denitrification. This process takes place in soil through the activity of nitrifying bacteria. Ammonium in soil can undergo the process of nitrification, which is an oxidation reaction that converts it to nitrate. Through this mechanism N in the ammonium ion is released back into the atmosphere (Berner and Berner, 1987).

Nitrification of ammonium N is a two-step process:

$$2NH_4^+ + 3O_2 \longrightarrow \underset{\text{Nitrite}}{2NO_2^-} + 4H^+ + 2H_2O \qquad (1.7)$$

$$2NO_2^- + O_2 \longrightarrow \underset{\text{Nitrate}}{2NO_3^-} \qquad (1.8)$$

Nitrate leaching from fertilizer use depends upon the fertilizer types (ammonical, nitrate or organic), method of application and climatic conditions. Nitrate leaching may be greater for fertilizers containing nitrate compared to ammonical N as a major component. Hence, ammonium exchanged or saturated zeolites can be of potential use in controlling nitrate pollution. Some of the nitrate fertilizers widely used are calcium nitrate ($Ca(NO_3)_2$), potassium nitrate (KNO_3) and sodium nitrate ($NaNO_3$). Controlled release (slow-release) fertilizers have also been manufactured, but due to their high cost, these fertilizers are not used extensively, but do have some specific applications. Some of the urea-based controlled release fertilizers are methylene diurea, dimethylene triurea, sulphur-coated urea (SCU) and polymer-coated urea (PCU).

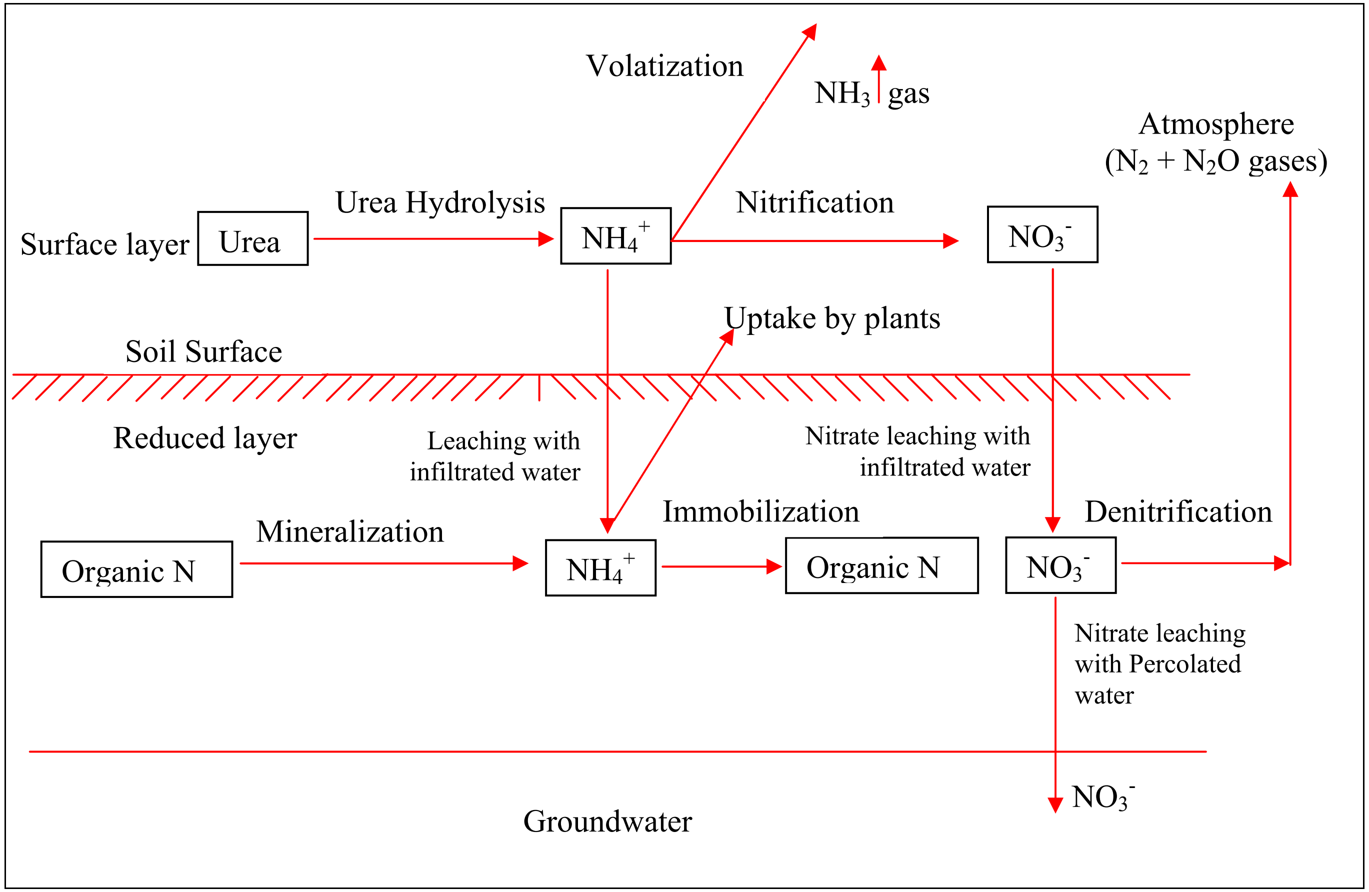
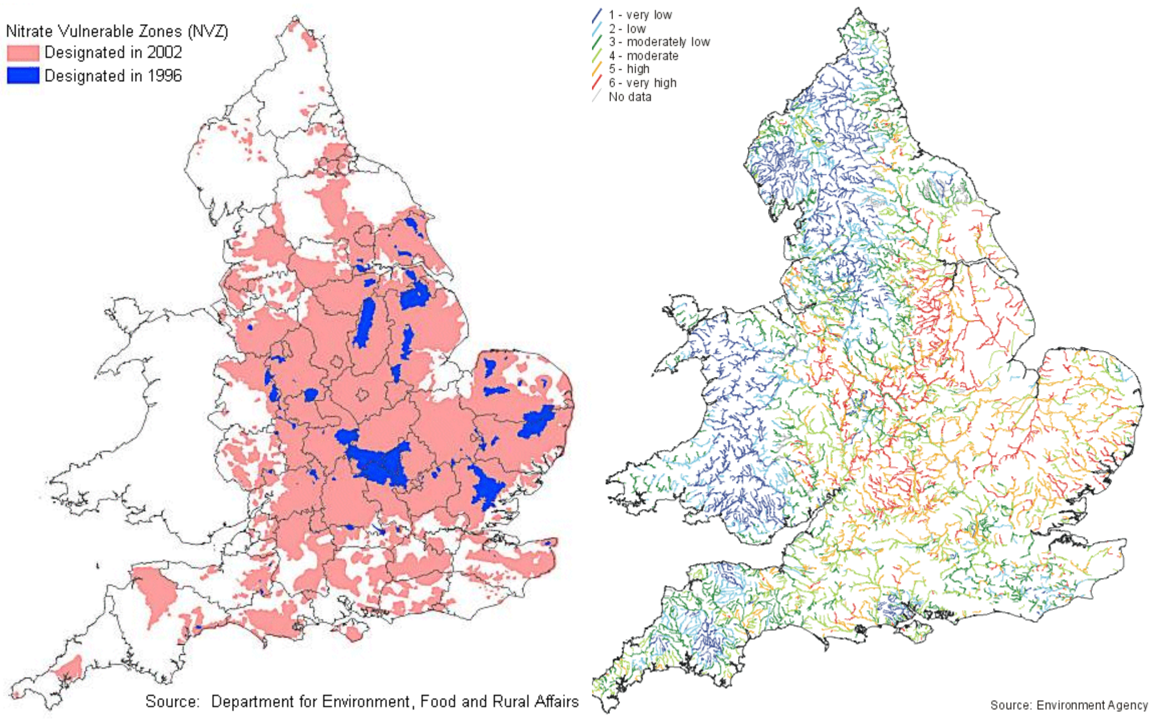


Fig.1.7. Schematic representation of the N-transformations in a soil-water-plant-atmosphere system, adapted from Chowdary *et al.* (2004).

Agricultural groundwater pollution from nitrate is a worldwide problem that has economic, ecosystem and human health impacts (O'Neil and Raucher, 1990; Spalding and Exner, 1993). Besides degrading drinking water resources (Hamilton and Helsel, 1995), aquatic ecosystems are affected when pollutant-bearing groundwater discharges to surface water. Nitrate can harm the eggs and young of some salmonids and amphibians (Kincheloe *et al.,* 1979; Hecnar, 1995; Marco *et al.,* 1999; Rouse *et al.,* 1999), promote eutrophication in N-limited freshwaters and increase the growth of rooted aquatic plants (Rodgers *et al.,* 1995). Nitrate export from freshwater basins can also cause eutrophication in saltwater bodies. Nitrate vulnerable zones in the U.K are shown in Figure 1.10.

(a) (b)



Source: Department for Environment, Food and Rural Affairs

Source: Environment Agency

Fig.1.10. (a). Nitrate vulnerable zones and (b) Nitrate levels of rivers in U.K. Source: **http://www.defra.gov.uk/environment/water/quality/nitrate**

Human interest is of primary concern when setting guidelines for acceptable nitrate levels and proper agricultural practices. The United States Environmental Protection Agency (USEPA) established the current drinking water standard and health advisory level of 10-mg/L nitrate-nitrogen based on the human health risks due to nitrate consumption (Kross *et al.,* 1993). Although there have been studies attempting to link nitrate consumption to various illnesses, only methemoglobinemia (also known as infant cyanosis or blue-baby syndrome) has been proved to result from ingestion of water containing high nitrate concentrations (>10 mg/L). Although many studies have been performed attempting to link stomach and gastrointestinal cancer to nitrate intake, there is no conclusive evidence that there is a correlation. At present, no other toxic effects have been observed under conditions of high nitrate levels. Even at exposure to levels of 111 mg/L there was no adverse condition in infants, except for methemoglobinemia (Gustafson, 1993).

There are various ways of reducing nitrate contamination of groundwater, including:
(1). Use of phased application of N fertilizer, thus avoiding a high application rate at one time.
(2). Use of slow-release or controlled release fertilizers, which release N progressively into the soil.
(3). Removal of nitrates from water by large-scale water purification using low cost ion exchange resins. This process involves several steps for successful decontamination. The entire process is composed of four major steps to remove selected ions from the solution. They are (a) resin recharge; (b) anion exchange; (c) resin becomes exhausted; and (d) resin regeneration.
(4). Use of biochemical denitrification via denitrifying bacteria. By using denitrifying bacteria, the nitrate ion can be reduced to its original elemental state of N_2. These organisms are able to carry out this process through a reaction such as:

$$6H^+ + 6NO_3^- + 5CH_3OH \Longrightarrow 3N_2 + 5CO_2 + 13H_2O \text{ (Zajic 1971).} \qquad (1.9)$$

All of these approaches are of limited effectiveness; therefore this project will examine, the use of zeolites as controlled-release (slow-release) fertilizer amendments. The rationale for using zeolites as alternative fertilizer soil amendments is discussed in Section 1.13.

1.13. Rationale

From the roles of soil physical and chemical properties described above, an ion-exchanged zeolite with a high absorption/release capacity could amend soils in several ways. Zeolite with their open structures containing large cavities filled with water molecules can be an alternative solution to excessively wet and/or dry soils, due to their water holding/retention capacity. Zeolite addition to soil can result in an effective pH buffering, since their alkaline nature neutralizes the hydrolytic and exchangeable acidity of soils and increases the soil fertility in the rhizosphere. Due to the high affinity and selectivity of zeolites towards certain cations, they can be effective in both release and removal of ions, depending on the chemical environment of the soils.

Ion exchanged natural zeolites are effective slow-release fertilizers (Section 1.8). Natural zeolites upon introduction as soil amendments in either ammonium or K saturated forms, were potential slow-release fertilizers along with increasing crop productivity. However, the impurities and phases associated with natural zeolites may hinder plant growth and might even affect the release of cations from these materials. An alternative is to use tailor made synthetic zeolites. Work has not been carried out comparing synthetic zeolites with natural zeolites. Therefore, this project involves initially synthesizing pure crystalline zeolites and comparing them with their natural counterparts as soil amendments.

The study will help in understanding the diffusion rate and CEC of both natural and synthetic zeolites, and will identify the problems associated with both forms of zeolites to select a potential soil amendment, either in the form of synthetic or natural for further refinement. Zeolites such as Phillipsite (high crystalline and high Al) and Linde-type F were synthesized for this project. Literature review suggests that Linde-type F is being used for the first time as a soil amendment. Due to its high affinity for NH_4^+, Linde type F was considered as a potential soil amendment for the research study.

The research project involved studying slow release of N from the above zeolites by measuring the ammonium, nitrate and nitrite levels in zeolite-loaded soils at regular weekly intervals; and to compare the release with a conventional fertilizer in order to evaluate the most potential slow/controlled release N amendment. In doing so, N equilibrium in the soil is studied in detail. The effectiveness of both natural and synthetic zeolites with respect to their physico-chemical properties were studied, and the best potential zeolite selected based on plant growth, soil nutrient status and restricted nitrate leaching. The research study may therefore potentially propose an alternative fertilizer approach to counteract nitrate leaching from soils resulting from excessive use of conventional fertilizers.

Along with standard methods proposed by Allen (1989) and Rowell (1994) for determining ammonium and nitrate in soil, new extraction and leaching methods for ammonium, nitrate and nitrite are designed, which involved using anionic exchanger, cationic exchanger and ion selective electrodes. The study will therefore help in constructing a theory to evaluate release of N over a period of time for fertilizer, synthetic and natural zeolite loaded soils and may lead towards further refinement of zeolites as slow/controlled-release fertilizers.

1.14. Aim and objectives

The primary aim of this study was to synthesize zeolites and compare them with their natural counterparts when introduced as a soil amendment for maize growth. Secondly, the zeolite's ability to act as a controlled release fertilizer when added as an ammonium exchanged soil amendment was studied, with a view to selecting a potential zeolitic N-fertilizer. The key aim was to develop a zeolitic soil amendment (synthetic/natural), which has a possible advantage as a controlled release fertilizer over multiple conventional fertilizer applications, and also as means of supplying adequate plant nutrients over the growing season, while minimizing possible N losses through leaching.

Objectives

(1) Synthesizing Phillipsite in a (Na, K) system and comparing with its natural counterpart, to investigate their ability as potential soil amendments (Glasshouse Experiment 1). Ion exchange of both synthetic and natural Phillipsite to exchange ammonium into the zeolites and eliminate Na completely, to be used as N fertilizer soil amendments.

(2) In view of plant responses from Glasshouse Experiment 1, select the best potential ion exchanged zeolite (synthetic/natural) for Glasshouse Experiment 2. Synthesize and ion exchange zeolites that have a higher affinity towards NH_4^+ (i.e.

Linde-type F) and accordingly compare them with a standard conventional fertilizer amended soil and, the most promising active zeolite for plant growth from Glasshouse Experiment 1.

(3) From initial Glasshouse Experiments (1 and 2) based on the applicability of zeolitic soil amendments, select a zeolite that both increased plant growth and decreased N leaching and study its structural and physical characteristics in Glasshouse Experiment 3. The selected zeolite would then be tailored accordingly to improve its properties (high-crystalline/high-Al) to study plant growth response and controlled release of ammonium.

(4) To understand and expand knowledge of the structural properties of zeolites together with their physico-chemical properties when introduced as soil amendments, and construct a theory for environmental approach to control nitrate pollution of ground waters.

Chapter 2

Methodology and Experimental Design

Introduction

This chapter focuses on general methods involved in the synthesis of zeolites along with their characterization techniques. Experimental protocols for all three-glasshouse experiments and the plant, soil and leachate analysis carried out for this research project is also discussed.

2.1. Synthesis of Zeolites

As discussed in Section (1.3a), zeolite synthesis involves preparation of a homogenous gel obtained by combining a silica source, an aluminium source and suitable cation in aqueous media in the presence of water under basic pH. The reaction gel is then heated in a sealed reaction vessel under constant pressure, to the required temperature. Zeolite would then be expected to crystallize from the reaction mixture after a certain period of time (Van Bekkum *et al.,* 2001).

2.1.1. Synthesis of Phillipsite

Phillipsite was synthesized from the following gel molar composition:

6.95 Na_2O: 3.50 K_2O: 1 Al_2O_3: 18.5 SiO_2: 325 H_2O (Hayhurst, 1977)**.** (2.1)

At room temperature, sodium silicate solution (Na_2SiO_3) was added to potassium hydroxide (KOH) solution while stirring. The mixture was stirred thoroughly using a mechanical stirrer, sodium aluminate ($NaAlO_2$) powder was then added and stirring was continued, to form the reaction gel. The gel was then poured into PTFE-vessels and heated in an oven at 100^0C. Samples were taken out at regular intervals from 8-24 hours, filtered, washed repeatedly with ultra-pure water and dried at 40^0C for 24 hours. The pH of the reaction gel was measured both before and after synthesis. The most crystalline sample was obtained after 19 hours of incubation, which was calculated by making use of the peak intensities from the X-ray Diffraction (XRD) results (as discussed in Section 1.3e). Samples were then characterized by various techniques, including X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Thermo-gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). Once the zeolite was characterized and identified as Phillipsite on the smaller scale, bulk synthesis was carried out in 2 litre PTFE vessels making use of the same gel molar composition. The average yield of Phillipsite per batch (1250 g of reaction gel) was 110-120 g. Nearly 3.5 kg of Phillipsite was synthesized for Glasshouse Experiment 1 (Spring-Summer 2002) and another 3 kg of Phillipsite synthesized for Glasshouse Experiment 2 (Spring-Summer 2003).

2.1.2. Synthesis of Linde-type F

Linde-type F was synthesized from the following gel molar composition:

$5.26\ K_2O: Al_2O_3: 3\ SiO_2: 94.5\ H_2O$ (Warzywoda and Thompson, 1991). (2.2)

Potassium hydroxide (KOH) solution was prepared and divided into two equal halves. At room temperature, aluminium (Al) powder was added to the first half of KOH solution and silica (Ludox AS 40) to the second half of KOH solution, while stirring. The mixture was stirred thoroughly using a mechanical stirrer and poured into PTFE-vessels and heated in an oven at 80-90^{0}C. The resultant solutions were then mixed together while still stirring to form the reaction gel. The gel was then poured into PTFE-vessels and heated in the oven at 100^{0}C. Samples were taken at regular intervals from 90-100 hours, washed repeatedly with ultra-pure water and dried at 40^{0}C for 24 hours. The pH of the reaction gel was measured both before and after synthesis. The most crystalline sample was obtained after 96 hours of incubation. Samples were then characterized by XRD, XRF, TGA and SEM techniques. Once the zeolite was characterized and identified as Linde-type F on the smaller scale, bulk synthesis was carried out in 2 litre PTFE vessels making use of the same gel molar composition. The average yield of Linde-type F per batch (1720 g of reaction gel) was 165-175 g. Nearly 3 kg of Linde-type F was synthesized for Glasshouse Experiment 2 (Spring-Summer 2003).

2.1.3. Synthesis of high aluminium Phillipsite

High Aluminium Phillipsite was synthesized from the following gel molar composition:

$1.53Na_2O: 0.44K_2O: Al_2O_3: 5SiO_2: 82.7H_2O$ (Cichocki, 1991). (2.3)

At room temperature, sodium hydroxide (NaOH) solution was added to potassium hydroxide (KOH) solution while stirring. Silica (Ludox 30) solution was then added to the above mixture and stirred thoroughly using a mechanical stirrer. $NaAlO_2$ solution was then added slowly to the stirred silicate over a 10-minute period and stirring continued, to form the reaction gel. The gel was then poured into PTFE-vessels and heated in an oven at 100^0C. Samples were taken out at regular intervals from 8-24 hours, washed repeatedly with ultra-pure water and dried at 40^0C for 24 hours. The pH of the reaction gel was measured both before and after synthesis. The most crystalline sample was obtained after 24 hours of incubation. XRD, XRF, TGA and SEM techniques were used to characterize samples. Once the zeolite was characterized and identified as Phillipsite on the smaller scale, bulk synthesis was carried out in 2 litre PTFE vessels making use of the same gel molar composition. The average yield of Phillipsite per batch (1320 g of reaction gel) was 250-260 g. Nearly 2 kg of high-aluminium Phillipsite was synthesized for Glasshouse Experiment 3 (Spring-Summer 2004).

2.1.4. Synthesis of high crystalline Phillipsite

High Crystalline Phillipsite was synthesized from the following gel molar composition:

$\mathbf{6.95\ Na_2O: 3.50\ K_2O: 1\ Al_2O_3: 18.5\ SiO_2: 325\ H_2O}$ (Hayhurst, 1977). (2.4)

At room temperature, Na_2SiO_3 solution was added to KOH solution while stirring. The mixture was stirred thoroughly using a mechanical stirrer, $NaAlO_2$ powder was then added and stirring continued, to form the reaction gel. The gel was then aged for 2 hours at room temperature and poured into PTFE-vessels and heated in an oven at 100^0C. Samples were taken out at regular intervals from 8-24 hours, washed repeatedly with ultra-pure water and dried at 40^0C for 24 hours. The pH of the reaction gel was measured both before and after synthesis. The most crystalline sample was obtained after 19 hours of incubation. Samples were then characterized by XRD, XRF, TGA and SEM techniques. Once the zeolite was characterized and identified as Phillipsite on the smaller scale, bulk synthesis was carried out in 2 litre PTFE vessels making use of the same gel molar composition. The average yield of Phillipsite per batch (1250 g of reaction gel) was 110-120 g. Nearly 2 kg of high-crystalline Phillipsite was synthesized for Glasshouse Experiment 3 (Spring-Summer 2004).

2.2. Natural Phillipsite

Natural Phillipsite was obtained from Pine Valley, Nevada (U.S.A). Phillipsite obtained was in the form of tuff, so it was necessarily important to identify the other phases present in this mineral material. Quantitative phase analysis of a number of multi-component standard and mineral mixtures has been performed using an adaptation of the Reitveld method (Bish and Post, 1993). Quantitative analysis by the Rietveld method requires knowledge of the approximate crystal structure of all phases of interest (not necessarily all phases present) in a mixture. The input data to a refinement include space group symmetry, atomic positions, site occupancies and unit cell parameters. The required input data for both Phillipsite and Erionite was obtained from Inorganic Crystal Structure Database (ICSD). Hence, by applying Rietveld method natural Phillipsite was identified to be a tuff of Phillipsite and Erionite in the ratio of 92:8 weight %.

Principle

The drawback of conventional powder diffraction technique is data grossly overlap, thereby preventing proper determination of structure. The Rietveld refinement method refines a model crystal structure by comparing the measured diffraction pattern with that calculated from a known crystal structure. The structural model is then refined by varying the structure parameters to minimise the difference between the calculated and observed patterns at each point. As the method uses a whole pattern-fitting algorithm, all lines for each phase are explicitly considered, and even severely overlapping lines are usually not a problem. A least squares refinement is used to optimize the structure parameters.

The least squares procedure is carried out by minimising the residual R (equation 2.5), where w_i is a weighting function, calculated at each step i to account for estimated experimental error arising from counting statistics (X'pert plus, 1999).

$$R = \sum_{i} w_i (y_{io} - y_{ic})^2 \tag{2.5}$$

Where y_{ic} is the calculated intensity and y_{io} is the observed background intensity at point i in the calculated pattern. The least-squares minimisation is performed over all points in the diffraction pattern, so the fit is optimised with respect to both the peaks and the background.

Quantitative phase analysis using the Rietveld method

Quantitative Rietveld refinement was first performed using neutron powder diffraction data by Hill and Howard (1987), who derived the phase weight relationship given in equation 2.6. Information on the weight fractions (W_i) of phases present in a mixture is calculated from the scale factors for each phase obtained from the refinement. The weight fraction of the phase i is given by:

$$W_i = \frac{(SMV)_i}{\sum(SMV)_j} = \frac{(S\rho V)_i}{\sum(S\rho V)_j} \tag{2.6}$$

Where S is the Rietveld scale factor, M is the unit cell mass (ρ is density) and V is the unit cell volume, respectively of phase I, and the summation is over all phases present.

This is the equation used by the quantitative phase analysis algorithm of X'pert plus. Using this relationship, natural Phillipsite tuff was quantified. X-ray diffraction data for natural Phillipsite tuff were obtained on Phillips PW 1710 X-ray diffractometer. Copper K_α radiation with a graphite monochromator was used, operating at 40mV and 40mA. Data was collected using Philips PC-APD software. Conventional data measurement parameters were used in these analyses, usually scanning from 5^o 2θ to 50^o 2θ with a step width of 0.020 $^o2\theta$ and a count time of 0.40 seconds per step. Finally, the least squares structure and profile refinements were performed with the Rietveld analysis program in automatic mode by using a Philips X'Pert Plus version 1.0.

2.3. Basic techniques used before zeolite characterization

(a). Filtration

The synthesized samples from PTFE vessels were filtered using a Buchner funnel vacuum. Whatman No 1 filter paper was used for this purpose. The powder samples obtained were then washed with distilled water repeatedly until the filtrate was clear.

(b). Centrifuging

When the powder sample was too fine to be filtered by a filter paper, a centrifuge was used. Samples were filled into Teflon tubes, and centrifuged at full speed (100 rpm) for 10 minutes. Supernatant was then replaced with distilled water and powder settled at the bottom was re-suspended by stirring. The procedure was repeated three to four times, until a clear supernatant was obtained.

(c). Drying

Samples obtained after washing with distilled water were initially filtered (2.3a). The filtered samples were left in a 40^{o}C oven overnight, and in some cases for 24-30 hours to dry the sample by evaporating the excess surface water. However, as zeolites are porous materials, they do absorb water if they are left at room temperature, hence the samples were kept in desiccators.

(d). Grinding

As natural Phillipsite tuff was obtained as big lumps of rock material, ball milling was preferred for grinding natural Phillipsite. Grinding was carried out for 2-3 hours/until a fine powder was obtained. Ground material was then sieved by using a 1mm sieve.

2.4. Characterization of Zeolites

Various spectroscopic and thermal methods were used to characterize zeolites. Spectroscopic methods used in this work included X-Ray Diffraction (XRD) and X-Ray Fluorescence spectroscopy (XRF). The thermal method included Thermo-gravimetric Analysis (TGA) and the microscopy technique included Scanning Electron Microscopy (SEM). Zeolites were also analysed for their particle size and surface area, to establish their diffusion and ion exchange properties. Models used for these analyses are shown in section 2.13.

2.4.1. X-Ray Diffraction (XRD)

XRD has been one of the most conclusive means of identifying members of the zeolite group. The framework of a new material can be easily recognized by XRD from powder samples using Rietveld refinement techniques (Jentys and Lercher 2001). It is also used to determine the phases present, their crystallinity and the unit cell parameters of a sample. The considerably improved single crystal XRD techniques have been able to provide accurate information on bond angles and bond distance.

Principle of XRD

The theory is based on Bragg's Law: $2d\sin\theta = n\lambda$ (Jenkins, 1988) (2.7)

When a monochromatic X-ray beam with a wavelength λ is incident on lattice planes on a crystal at an angle θ, diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number n of wavelength. Rearranged, this equation relates the angle of diffraction of X-ray radiation of a particular wavelength to the distance between atomic planes of identical type in the unit cell (*d*-spacing) and the incident angle of radiation.

Bragg's Law gives the lattice spacing, which is unique for any crystalline phase, unit cell sizes and space groups may be readily determined and a scattering pattern will be observed for each crystalline phase. As a consequence of the Bragg Law, X-ray diffraction from a particular atomic plane in the crystal will give rise to a peak at a certain 2θ angle on the diffraction pattern. For zeolites the most intense peaks occur in the range $5^o\ 2\theta$ to $40^o\ 2\theta$ (Szostak, 1989). Unit cell dimensions may be calculated by computer analysis of the d spacing within the crystal. Crystallinity can also be calculated from the XRD data by comparisons of the d-spacing and line intensities (I/Io) with a standard data, or the direct comparisons of the intensities of characteristic lines for each phase (Jentys and Lercher, 2001). Data were processed with a search/match facility and compared with the reference pattern of that particular zeolite, as obtained from the ICDD (International Centre for Diffraction Data) database.

Method

Synthesized zeolite samples were ground first with a pestle and mortar, and pressed into standard sample holders with a volume of 0.1 cm^3. Samples were then scanned between 3 and 50 degrees 2-theta using a Phillips PW 1710 X-ray diffractometer with a step width of 0.020 $^{o}2\theta$ and a count time of 0.40 seconds per step to produce the XRD pattern. A glass slide was used if the amount of sample was too small to be pressed into sample holders; ethanol was used to moisten the powder sample in this case. Samples from each batch of the bulk synthesis were characterized both before and after ion exchange to check for their structure, crystallinity and reproducibility.

2.4.2. X-Ray Fluorescence (XRF)

XRF is used to analyse the elemental composition of zeolites. XRF analysis is a wavelength dispersive X-ray method (Dziunikowski, 1978). This technique is used to determine each element in solid or liquid samples from concentrations as low as 1 ppm to as high as 100% (Jenkins, 1988).

Principle

The method is based on the theory that each individual element produces a unique pattern of fluorescence spectra of specific wavelength. The technique bombards the sample with primary X-rays. This leads to elements fluorescing and generating secondary X-rays, which are then analysed using an artificial crystal with known atomic spacing, to determine X-ray wavelengths. These are characteristic for individual elements, being related to the energy wavelengths of different electron shells. The analysis gives data as the oxidized form of each element in % w/w Si:Al as well as any other elements present in the zeolite framework. With known unit cell dimensions and density of the crystalline material, the chemical composition of each unit cell can be calculated. Unit cell calculations for all zeolites synthesized and ion exchanged for this project are shown in Appendix 1.1.

Method

Samples are prepared by placing ground zeolite sample in between the gas permeable membrane (microporous film) and 6 μm X-ray transparent film (Mylar). The sample was then analysed by the Fisons ARL 84 10 XRF spectrometer. Before running the sample for XRF analysis, a predetermination of organic and water loss from the sample by TGA was necessary. Samples from each batch of the bulk synthesis were characterized both before and after ion exchange to check for their weight loss (TGA) and their chemical composition (XRF).

2.4.3. Thermogravimetric Analysis (TGA)

Thermo-gravimetric analysis records the loss in weight due to loss of material (water and/or loss of structure directing agent) from sample over a range of temperatures from ambient to 1000^{o}C in either oxygen or nitrogen to control the atmosphere. This method was useful to compare zeolites both before and after ion exchange to evaluate loss of NH_3^+ and water from the sample (Appendix 1.2).

Method

Samples ~15-20 mg were heated under nitrogen gas flow (20ml/min) between 40-900^{0}C at a rate of 20^{0}C/min. TGA can also be used to study the thermal stability of the zeolite framework, and loss of ignition (LOI), i.e. the total weight loss of non-framework material, which is an essential figure in XRF data interpretation. Araujo *et al.* (1999) showed TGA could be used to determine the crystallinity of microporous materials.

2.4.4. Scanning electron microscope (SEM)

SEM shows the morphology and particle size of crystalline samples. It is very useful in this research to compare zeolites both before and after ion exchange, to study changes in crystal morphology and to compare natural and synthetic zeolites of the same zeotype. The size of zeolites that can be studied with SEM varies between 20 nm and 20 μm.

Principle

A beam of electrons is directed at the specimen to study the surface or near surface structure of bulk specimens (Goodhew and Humphereys, 1998). The fine beam of electrons is scanned across the specimen by the scan coils, while a detector counts the number of low energy secondary electrons, or other radiation, given off from each point on the surface.

Method

Samples are prepared by spraying dry zeolite sample onto aluminium stubs coated with adhesive and gold coating to reduce static charging and then observing under SEM conditions (i.e. under vacuum (7.77e-004 Pa), aperture size 20 μm, and power 20.00 KV). Electron micrographs are obtained at various magnifications for different zeolites used for this project (Appendix 1.3). SEM can provide information on identifying phases of a composite sample; absolute phase purity and uniformity can also be obtained.

2.5. Ion exchange of Zeolites

As this research focuses on slow/controlled release fertilizer aspects of zeolites, ion exchange was carried out on Phillipsite (synthetic, natural, high-Aluminium, high-Crystalline), and also Linde type-F (synthetic). Exchange was carried out to introduce ammonium (NH_4^+) into zeolites and eliminate sodium (Na^+). Potassium (K^+) concentrations for zeolites were always kept at low concentrations as per the requirements of maize growth.

Due to the differences in the Si:Al ratio of zeolites and difference in their final K^+ concentrations as determined by XRF, ion exchange experiments were carried out by varying the concentrations of exchange reagent and also, by varying the time interval to match the final K^+ concentrations of any two zeolites used for a particular glasshouse experiment to as near as possible for comparative studies. Selecting a known concentration i.e. (0.1M NH_4NO_3) of exchange reagent and carrying out exchange for the same period of time i.e. 30 minutes was the first stage in optimizing ion exchange experiments. Based on the final K^+ concentrations in the sample as determined by XRF after ion exchange, a series of experiments were carried out with varying molar concentrations of NH_4NO_3 (0.1M-1M) and varying time interval (30 minutes - 6 hours) and repeated after the equilibrium was established. Thereby, by knowing the total K^+ content both before and after ion exchange at a particular concentration and time interval, as determined by XRF, bulk ion exchange experiments were carried out for all 5 zeolites and are discussed in the subsequent sections. All 5 zeolites exchanged NH_4^+ into their framework for Na^+ and K^+ present as counter balancing cations.

2.5.1. Ion exchange of Phillipsite

(a). Synthetic Phillipsite

Synthesized Phillipsite had a very high concentration of Na^+ (from XRF data). Ion exchange was carried out on synthetic Phillipsite, to eliminate Na^+ completely and to introduce NH_4^+ into the zeolite. 1M Ammonium Nitrate (NH_4NO_3) was used as the reagent to carry out ion exchange. A zeolite to reagent mixture of 1:20 (w/w) was stirred continuously in a plastic container for 3 hours at room temperature. The solution was then filtered and washed repeatedly with distilled water to wash off nitrate present on extra lattice framework. Once ion exchange was established on a small scale, bulk ion exchange was carried out and ~3.5 kg of Phillipsite was ion exchanged for Glasshouse Experiment 1. Another 3 kg of Phillipsite was ion exchanged for Glasshouse Experiment 2.

(b). Natural Phillipsite

As natural Phillipsite was obtained in high Na^+ and K^+-form (from XRF data), it was necessary to convert it to the NH_4^+-form by ion exchange, to eliminate Na^+ completely and match the K^+ concentration in both forms of Phillipsite. 0.5 M NH_4NO_3 was used as exchange reagent for ion exchange. A zeolite to reagent mixture of 1:20 (w/w) was stirred continuously in a container for 45 minutes at room temperature. The solution was then filtered and washed repeatedly with distilled water, to remove nitrate present on extra lattice framework. Once ion exchange was established on a small scale, bulk ion exchange was carried out and ~3.5 kg of natural Phillipsite was ion exchanged for Glasshouse Experiment 1.

(c). High-Aluminium Phillipsite

Synthesized high-aluminium Phillipsite had a very high concentration of K^+ (from XRF data), and Na^+ was also present in sufficiently high concentrations to be detrimental to plant growth. Ion exchange was carried out on synthetic high-aluminium Phillipsite, to eliminate Na^+ completely and to introduce NH_4^+ into the zeolite and to keep K^+ concentrations low. 1M NH_4NO_3 was used as the reagent to carry out ion exchange. A zeolite to reagent mixture of 1:20 (w/w) was stirred continuously in a plastic container for 4 hours at room temperature. The solution was then filtered and washed repeatedly with distilled water to wash off nitrate present on extra lattice framework. Once ion exchange was established on a small scale, bulk ion exchange was carried out and 2 kg of high-aluminium Phillipsite was ion exchanged for Glasshouse Experiment 3.

(d). High-Crystalline Phillipsite

Synthesized high-crystalline Phillipsite had a very high concentration of Na^+ (from XRF data), which is detrimental to plant growth. Ion exchange was carried out on synthetic high-crystalline Phillipsite, to eliminate Na^+ completely and to introduce NH_4^+ into the zeolite by keeping K^+ concentrations low. 1M NH_4NO_3 was used as the reagent to carry out ion exchange. A zeolite to reagent mixture of 1:20 (w/w) was stirred continuously in a plastic container for 3 hours at room temperature (similar to 3.5.1a). The solution was then filtered and washed repeatedly with distilled water to wash off nitrate present on extra lattice framework. Once ion exchange was established on a small scale, bulk ion exchange was carried out and 2 kg of high-crystalline Phillipsite was ion exchanged for Glasshouse Experiment 3.

2.5.2. Ion exchange of Linde-type F

As Linde-type F has a very high affinity towards NH_4^+, ion exchange was carried out with NH_4NO_3. The excess KOH involved in this zeolite preparation makes it highly alkaline with pH as high as 14. 1M NH_4NO_3 was used as the reagent to carry out ion exchange. A zeolite to reagent mixture of 1:10 (w/w) was stirred continuously in a container for 6 hours at room temperature. The solution was then filtered and washed repeatedly with distilled water to remove nitrate present on the extra lattice framework. Once ion exchange was established on a small scale, bulk ion exchange was carried out, and ~3 kg of Linde-type F was ion exchanged for Glasshouse Experiment 2.

2.6. Particle Size Analysis of Zeolites

Pre - and post-ion exchanged zeolite samples were all analysed for their particle size using a Mastersizer X analyser.

Principle

The particle sizers are all based on the principle of laser ensemble light scattering. They fall into the category of non-imaging optical systems, due to the fact that sizing is accomplished without forming an image of the particle onto a detector. The system inherently measures the integral scattering from all particles present in the beam. In a typical experiment the number of particles needed in the beam simultaneously to obtain an adequate measurement of the scattering would be 100-10,000 depending on their size. Three different types of lenses are used for measuring a range of particle sizes within a given sample they are for particle sizes ranging from: (a) 0.1-80 μm (b) 100-600 μm and (c) > 600-2000 μm.

Method

Representative samples of the bulk pre- and post-ion exchanged zeolites were selected for particle size analysis. As the sample may have a tendency to flocculate in some media and dissolve in others, water was used, as it is the most convenient media for zeolites. Sodium amalgam was used to disperse zeolites particles as they have the tendency to adhere to each other in water media. To ensure zeolite particles are not sticking to each other, the sample was loaded into MSX 15 sample handling unit that uses mechanical action of stirring the sample along with ultrasound.

2.7. Surface Area Analysis (BET) of Zeolites

Pre- and post-ion exchanged zeolite samples were all analysed for their surface area using a Beckman Coulter SA3100 analyser. The SA 3100™ with automated dewar lift is a complete system with integrated out gassing stations and vacuum pump and is highly accurate. It features continuous saturation pressure measurement, has a minimum manifold volume to enhance sensitivity, and to improve repeatability and accuracy.

Principle

One of the most important applications of Van der Waals adsorption is the use of adsorption measurements to determine the surface areas of finely divided and porous solids. The multi-molecular adsorption theory of Brunauer, Emmett and Teller referred to as BET is used to readily calculate surface areas and approximate heats of adsorption (Young and Crowell, 1962). The specific surface area Σ of a solid is defined as surface area per unit mass. It is usually expressed in square metres per gram. The specific surface area in square metres per gram and the monolayer capacity in cubic centimetres per gram are related as follows:

$$\Sigma = 0.269\ \sigma_m v_m \tag{2.8}$$

Where σ_m is the area in square angstroms which one adsorbed molecule would occupy in the completed monolayer. And the monolayer capacity, (v_m) is defined as the quantity of adsorbate, which would be required to cover the adsorbent with a monomolecular layer only (Langmuir, 1918).

Method

The gas adsorption technique is performed by the addition of known volume of gas (adsorbate), typically nitrogen, to a solid material (in this case zeolite) in a sample vessel at cryogenic temperatures. At cryogenic temperatures, weak molecular attractive forces cause the gas molecules to adsorb onto (attach to the surface of) solid material (zeolite sample). The adsorbate is added to the sample in a series of controlled doses. Samples were sent away for analysis to, the water science and technology (WatStech) group at the University of Wolverhampton.

2.8. Glasshouse Experiments

All three experiments were conducted in Cambridge Glasshouse 1 (Plate 2.1) on maize plants (*Zea mays*). AVENIR was the variety of maize seeds used for all three-glasshouse experiments, and were obtained from N.B. Camber Ltd, agricultural merchants, Harley, Shrewsbury.

Preparing the soil

Soil was obtained from the Plant and Environment Research Unit at Compton Park, Wolverhampton, UK. Soil was then tested for nutrient content by performing the rapid nutrient analysis test (Appendix 1.5). Soil was steam sterilized at 70°C for 24 hours (Bunt, 1976), and shredded to $\leq$10-15 mm using a Royer topsoil shredder before commencing glasshouse experiments.

Plate 2.1. Cambridge Glasshouse 1 at the Crop Technology Unit, Compton Park.

2.8.1. Glasshouse Experiment 1

Aim

This experiment focused on comparing natural Phillipsite with synthetic Phillipsite to study the potential utilization of these zeolites for plant growth and fertilization, when added as a soil amendment and compared with standard Nitrogen, Phosphorus, Potassium (NPK) fertilizer amended soil. The addition of fertilizer to soil in each individual pot corresponds to the calculations as shown in Appendix 1.5. The brand of fertilizer used for all three-glasshouse experiments was similar and their composition is described in section 2.14.

Plant material

Maize was used as the plant material for growth.

Treatments

A total of 8 treatments x 10 replicates each were used for this experiment

- C. High (Soil with high amount of NPK added fertilizer)
- C. Std (Soil with standard NPK added fertilizer)
- 2% w/w of NH_4^+- exchanged natural Phillipsite in Soil with added P fertilizer
- 4% w/w of NH_4^+- exchanged natural Phillipsite in Soil with added P fertilizer
- 8% w/w of NH_4^+- exchanged natural Phillipsite in Soil with added P fertilizer
- 2% w/w of NH_4^+- exchanged synthetic Phillipsite in Soil with added P fertilizer
- 4% w/w of NH_4^+- exchanged synthetic Phillipsite in Soil with added P fertilizer
- 8% w/w of NH_4^+- exchanged synthetic Phillipsite in Soil with added P fertilizer

Note: Control 1 (C. High) has the same amount of N in the form of ammonium nitrate as N (present as ammonium) in 8% w/w NH_4- exchanged Phillipsite added soils.

- Control 2 (C. Std) is a standard NPK fertilizer addition as to maize growth requirement (Appendix 1.5).
- Standard P fertilizer (as calculated in Appendix 1.5) was added to all the zeolite amended soils. Zeolites already have NH_4^+ and K^+ in their framework, therefore N and K fertilizers were not added to these soils.

2.8.2. Glasshouse Experiment 2

Aim

This experiment focused on comparing synthetic Phillipsite with synthetic Linde type F to study the potential utilization of these zeolites for plant growth and fertilization, when added as a soil amendment and compared with standard Nitrogen, Phosphorus, Potassium (NPK) fertilizer amended soil. The addition of fertilizer to soil in each individual pot corresponds to the calculations as shown in Appendix 1.5.

Plant material

Maize was used as the plant material for growth.

Treatments

A total of 11 treatments x 8 replicates each were used for this experiment

- C. Blank soil (with no added NPK fertilizer);
- C. High (Soil with high amount of NPK added fertilizer)
- C. Std (Soil with standard NPK added fertilizer)
- 1% w/w of NH_4^+- exchanged synthetic Phillipsite in Soil with added P fertilizer
- 2% w/w of NH_4^+- exchanged synthetic Phillipsite in Soil with added P fertilizer
- 4% w/w of NH_4^+- exchanged synthetic Phillipsite in Soil with added P fertilizer
- 1% w/w of NH_4^+- exchanged synthetic Linde-type F in Soil with added P fertilizer
- 2% w/w of NH_4^+- exchanged synthetic Linde-type F in Soil with added P fertilizer
- 4% w/w of NH_4^+- exchanged synthetic Linde-type F in Soil with added P fertilizer
- 2% w/w of Non-exchanged synthetic Phillipsite in Soil with added NP fertilizer
- 2% w/w of Non-exchanged synthetic Linde-type F in Soil with added NP fertilizer

Note: Control 2 (C. High) has the same amount of N in the form of ammonium nitrate as N (present as ammonium) in 4% w/w NH_4- exchanged Linde type F amended soils.

- Control 3 (C. Std) is a standard NPK fertilizer addition as to maize growth requirement (Appendix 1.5).
- Standard P fertilizer (as calculated in Appendix 1.5) was added to all the zeolite amended soils. Zeolites already have NH_4^+ and K^+ in their framework, therefore N and K fertilizers were not added to these soils.
- Both standard N and P fertilizers (as calculated in Appendix 1.5) were added to the Non-exchanged zeolite amended soils. As both these zeolites already have K^+ in their framework, K fertilizer was not added to these soils.

2.8.3. Glasshouse Experiment 3

Aim

This experiment focused on comparing synthetic high aluminium Phillipsite with synthetic high crystalline Phillipsite to study the potential utilization of these zeolites for plant growth and fertilization, when added as a soil amendment and compared with standard Nitrogen, Phosphorus, Potassium (NPK) fertilizer amended soil. The addition of fertilizer to soil in each individual pot corresponds to the calculations as shown in Appendix 1.5.

Plant material

Maize was used as the plant material for growth.

Treatments

A total of 6 treatments x 8 replicates each were used for this experiment

- C. Blank (soil with no added NPK fertilizer)
- C. Std (Soil with standard NPK added fertilizer)
- 1% w/w of NH_4^+- exchanged synthetic high-aluminium Phillipsite in Soil with added P fertilizer
- 2% w/w of NH_4^+- exchanged synthetic high-aluminium Phillipsite in Soil with added P fertilizer
- 1% w/w of NH_4^+- exchanged synthetic high-crystalline Phillipsite in Soil with added P fertilizer
- 2% w/w of NH_4^+- exchanged synthetic high-crystalline Phillipsite in Soil with added P fertilizer

Note: Control 2 (C. Std) is a standard NPK fertilizer addition as to maize growth requirement (Appendix 1.5).

- Standard P fertilizer (as calculated in Appendix 1.5) was added to all the zeolite amended soils. Zeolites already have NH_4^+ and K^+ in their framework, therefore N and K fertilizers were not added to these soils.

2.8.4. Experimental Design

The experimental design consisted of one (uniform) maize seed being planted in each pot of all replicated treatments. The numbers of replicates for each treatment were decided to be 8/10 at each harvest for the purpose of statistical analysis. Plants were harvested thrice during the growth phase at three regular weekly intervals (Weeks 3, 6 and 9 after plant emergence i.e., 7-8 days from the date of sowing). Pots were randomly arranged in the glasshouse Plate 2.2 and were re-randomized at every harvest to minimize the risk of differential sunlight affecting growth (i.e. pots nearer to the edges of the glasshouse getting more sunlight than pots at the far end). Table 2.1 illustrates the experimental design used for all three-glasshouse experiments.

Table 2.1. Experimental design for Glasshouse Experiments 1, 2 and 3.

	Glasshouse Experiment 1	**Glasshouse Experiment 2**	**Glasshouse Experiment 3**
Soil/Pot size	400g/pot	400g/pot	800g/pot
Design	Randomized	Randomized	Randomized
Treatments	8	11	6
Replicates	10	8	10
Harvests	3	3	3
Watering	45 cm^3/d	45 cm^3/d	90 cm^3/d
Glasshouse conditions: Day	25 ^oC	25 ^oC	25 ^oC
Night	10-15 ^oC	10-15 ^oC	10-15 ^oC
Leachates collected	———	Plastic trays 11 treatments x 2 replicates	Plastic Containers 6 treatments x 5 replicates

Plate 2.2. Pots with maize plants randomly arranged in Cambridge Glasshouse 1 (6 weeks) from the sowing date.

2.9. Leachate Experiments

As nitrate leaching into groundwater is a major concern, especially in regions where high doses of fertilizers are applied, this project focused on nitrate leaching from zeolite-amended soils versus fertilizer-amended soils under glasshouse conditions. Leachates were not collected for Glasshouse experiment 1, as the project originally focused on plant growth aspects of maize in respect to zeolite addition. In view of increasing demand for slow release fertilizers, work was carried out to study ammonium exchanged zeolite-amended soils for their potential use as slow/controlled release fertilizers, along with plant growth (Glasshouse Experiments 2 and 3).

2.9.1. Leachate Experiment 1

Leachates were collected from Glasshouse Experiment 2 by placing 2 replicate pots of each individual treatment in plastic trays (Plate 2.3). The leached water from these pots was collected every week and frozen and analysed for nutrient, nitrate and ammonium loss.

Plate 2.3. Pots arranged in plastic trays for leachate collection.

2.9.2. Leachate Experiment 2

Leachates were collected from Glasshouse Experiment 3 by placing 5 replicate pots of each treatment in individual plastic containers (Plate 2.4). The leached water from these pots was collected every week, frozen and analysed later for nutrient, nitrate and ammonium loss. The first leachate was collected at Week 1 (7 days after sowing seeds) for both Glasshouse Experiments 2 and 3. Leachates were collected at a regular basis thereafter. Leachate samples were analysed by ICP for nutrient losses; and IC for nitrite, nitrate and ammonium losses from the pots. All results were statistically analysed, including least significant differences (LSD) within treatments.

Plate 2.4. Pots arranged in individual plastic pots for leachate collection.

2.9.3. Analysis of Ammonium, Nitrite and Nitrate by Ion Chromatography (IC)

Ion chromatography is used for analysis of aqueous samples in parts-per-million (ppm) quantities of common anions (such as fluoride, chloride, nitrite, bromide, nitrate and sulphate) and for cation analysis (such as lithium, sodium, ammonium and potassium) using conductivity detectors. Its greatest utility is for analysis of anions for which there is no other rapid analytical method. It is also used for cations and biochemical species, such as amino acids and proteins.

Ion chromatography is the only technique that can provide quantitative analysis of anions at the parts-per-billion (ppb) level. This technique is used to determine ions in liquids and ionic contamination on the surfaces of waters. Aqueous solutions may require filtration, dilution and cleaning to remove interferences before analysis. Solid samples are extracted with water to remove ions from the sample surface, organic liquids may also be extracted with water to obtain an aqueous solution of ions for analysis.

Principle

Ion chromatography is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on their interaction with the resin.

Method

Samples collected from Leaching Experiments 1 and 2, and CEC Experiments 1 and 2 were analysed for nitrite and nitrate by anion exchange column, and ammonium by cation exchange column. ICS-90 ion chromatography system was used along with AS-40 auto sampler. 5 ml of filtered and diluted (accordingly to levels of anions or cations acceptable by detector) samples were loaded onto the auto sampler and run for 10 min on the anion column, and 20 min on the cation column, separately. The peak areas of nitrite, nitrate and ammonium obtained from IC traces, were then normalised according to their respective calibration curves to calculate the concentrations of these ions in the leachates. Calibration curves as obtained for both anions and cations, and are shown in Appendix 1.7.

2.10. Plant Growth Measurements

An overview of the development and growth stages of maize plant is given in Section 1.8. Measurements of plant growth were made for all replicates, of each individual treatment at all the 3 harvests, for Glasshouse Experiments 1, 2 and 3 (Table 2.2).

Table 2.2. Number of treatments *vs.* replicates of all three-greenhouse experiments.

Experiment	**Treatments**	**Replicates**	**Total plants harvested at each individual harvest**
Greenhouse experiment 1	8	10	**80 x 3 = 240**
Greenhouse experiment 2	11	8	**88 x 3 = 264**
Greenhouse experiment 3	6	10	**60 x 3 = 180**

2.10.1. Harvesting

After the emergence of plants from pots on day 7 of the sowing date, plants were harvested thereafter at weeks 3, 6 and 9 of the growth stage. In the Crop Technology Unit laboratory, Compton, the following parameters were recorded on each individual plant:

(a). Plant height (cm).
(b). Number of leaves.
(c). Total fresh shoot weight (g), (includes total stem and leaf weight).
(d). Total fresh leaf weight (g), (weighed only the leaves of plant).

The wet weights were taken immediately on the same day of harvest. Plant material was then bagged in paper envelopes, labelled and oven dried at 80^0C in ventilated ovens for 4 days. The following parameters were then measured on the oven-dried plant material:

(a). Oven-dry shoot weight.
(b). Oven dry leaf weight.

Along with maize plant growth measurements, plants showing any deficiencies were identified by their physical appearance and lustre. The nutrient uptake and deficiencies by plants were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). ICP-AES uses inductively coupled plasma as an energy source to vaporize, dissociate and ionize the inorganic material in a water solution, then to detect the atomic concentration. This technique can determine the concentration, even at ultra trace levels in a solution sample.

2.10.2. Analysis of Plant Tissue for Na, K, Ca and Mg by (ICP-AES)

A dry-ashing extraction method proposed by (Allen, 1989) was used for plant tissue analysis of nutrients for all the three harvests of Glasshouse Experiments 1 and 2. Extractions were not carried out on samples of Glasshouse Experiment 3, as there were no physical symptoms of deficiency in these plants, and also this experiment focused more on leachate analysis. Plant material samples were sub-sampled to half the number for this extraction test (i.e., 5 and 4 sub-replicates of each treatment at their respective harvests, from Glasshouse Experiments 1 and 2).

Method

Maize plant shoot material that has been oven-dried was broken down in a mechanical grinder. Approximately 0.25g of ground sample was placed in an acid washed crucible, which was placed in a muffle furnace at 550°C for 4 hours. Samples were cooled before adding 5 ml of HCl. Samples were then covered with a watch glass and heated in a water bath for 15 minutes. 1 ml of HNO_3 was added to each sample and heating continued until the samples were dry then 1 ml of 50% HCl was added to dissolve the residue. Some 9 ml of distilled water was then added and warmed slightly to complete the dissolution. Samples were then filtered using Whatman No 44 paper, into 25 ml volumetric flasks and made up to the mark with distilled water. Samples were then analysed for Na, K, Ca and Mg by ICP-AES. Results were calculated and interpreted as follows:

$$\text{Na, K, Ca or Mg \%} = \frac{\text{Concentration (ppm) x vol. of solution (ml) x dilution}}{\text{Sample weight (g)}} \qquad (2.9)$$

2.11. Soil Analyses

After each individual harvest, the soil was removed from pots and separated from the roots and analysed for % water loss immediately. The remaining soil was left to dry in individual plastic trays at room temperature (air-dried).

Sample preparation

Soil samples to be analysed for pH; organic matter content; available sodium, potassium, calcium and magnesium; total nitrogen; available nitrogen; and total phosphorus were prepared in the following way: air-dry soil was passed through a 2 mm sieve. Material remaining in the sieve was then gently broken down with a pestle and mortar, until all aggregates were disrupted. This process was repeated until only stones remained on the sieve surface. **N.B.** As samples were far too many to handle at any one particular time of analysis, replicates of each treatment were sub-sampled from their original number to halve the number for all the soil analyses (i.e., 5, 4 and 5 sub-replicates of each treatment of their respective harvests, from Glasshouse Experiments 1-3).

2.11.1. Soil Moisture (Field moist water content)

Maximum maize yield can be achieved under adequate water conditions. As soil moisture plays an important role in the growth and development of maize, as discussed in Section 1.8c, it is necessary to measure moisture content of soils after each harvest. A known amount of soil was weighed into crucibles and heated overnight in a ventilated oven at 105^0C (Avery and Bascomb, 1982).

% Water content =

$$\frac{\text{Mass of moist sample taken (g)} - \text{Mass of oven-dry sample taken (g)}}{\text{Mass of moist sample taken (g)}} \times 100 \tag{2.10}$$

2.11.2. Soil pH

It is necessary to measure soil pH to evaluate the acidity of zeolite-amended soils versus fertilizer-amended soils at each harvest.

Method

A suspension of 10 g of air-dried and sieved soil and 25 ml of distilled water were stirred and left at room temperature for 10 min. The solution was stirred again and pH recorded until a stable reading was obtained with a pH probe (Allen 1989) meter, which had been calibrated using buffer solutions of pH 4 and 7. Measurements were performed for all sub-replicates. Soil pH can be standardized to allow comparison with other soil samples by measurement in a salt solution (Rowell 1994). A 2 ml aliquot of 0.125M calcium chloride solution (freshly prepared) was therefore added to the initial solution, in order to obtain consistency of pH readings in the event of a highly soluble salt content, which might affect electrode readings. The solution was left to stand for 2 minutes and pH recorded again (Avery and Bascomb, 1982).

2.11.3. Soil Organic Matter Content

Soil organic matter creates conditions that are conductive to increased crop production by improving soil structure. It can also have beneficial effects on the soil erodibility, by increasing aggregate stability and encouraging infiltration (Le Bissonnais *et al.,* 1995). Rowell (1994) proposed loss on ignition (LOI) as the most appropriate method to determine soil organic matter.

Method

Before commencing LOI, 5 g of 2 mm sieved soil samples were placed in an oven at 105°C overnight, to determine the moisture content of these air-dried soil samples. Loss of organic matter on ignition was then determined by placing the crucibles and contents from water content determination into a muffle furnace at 375°C in air for 16 hours.

$$\textbf{\% LOI} = \frac{\text{Mass of oven-dry soil (g)} - \text{Mass of ignited soil (g)}}{\text{Mass of oven-dry soil (g)}} \times 100 \qquad (2.11)$$

2.11.4. Total Nitrogen Determination by Kjeldahl Method

The Kjeldahl method is an analytical method for the determination of soil organic nitrogen (Rowell 1994). Johan Kjeldahl, a Danish chemist, developed the method in 1883.

Principle

The principle involved can be summarized in three steps: (a) The sample is first digested in strong sulphuric acid in the presence of a catalyst, which helps in conversion of the amine nitrogen to ammonium ions, (b) ammonium ions are then converted into ammonia gas, heated and distilled. The ammonia gas is led into a trapping solution where it dissolves and converts into an ammonium hydroxide ion, (c) finally the amount of trapped ammonia is determined by titration with a standard solution, and a calculation made.

Total nitrogen analysis by acid digestion:

(a). $\text{Organic N} + H_2SO_4 + \text{Heat} + \text{Catalyst} \Longrightarrow CO_2 + H_2O + NH_4HSO_4$ (2.12)

(b). $NH_4HSO_4 + 2NaOH \Longrightarrow NH_3 + Na_2SO_4 + H_2O$ (2.13)

(c). $NH_4OH + HCl\ [\text{or } H_2SO_4] \Longrightarrow NH_4Cl\ [\text{or } (NH_4)_2SO_4]$ (2.14)

Method

Five grams of sub-sampled soil samples were placed in temperature resistant 30 cm long digestion test tubes. 2 Kjeldahl tablets (3.5 g K_2SO_4, 0.4g $CuSO_4$. $5H_2O$) are added to these digestion tubes. Copper sulphate is the most commonly used catalyst. In addition, 20 ml of concentrated sulphuric acid (H_2SO_4) is added, and digested at

380^0C for 60 minutes using a Kjeldahl digestor (Plate 2.5). Organic nitrogen is converted to ammonium-N by sulphuric acid with catalyst added to accelerate the digestion. The resultant acid digest is then distilled for 4 min in the presence of 40% NaOH. Ammonium ions NH_4^+ are converted to ammonia (NH_3) by this process, which is then released from the solution by steam distillation and condensed as ammonium hydroxide (NH_4OH) and the distillate is then collected. 2% boric acid indicator is added to the distillate and titrated with 0.01/0.1 M HCl to give total organic nitrogen content.

Plate 2.5. Kjeldahl digestor along with the scrubber and titration unit.

2.11.4.1. Available Nitrogen

Plants obtain N from the soil mainly in the form of nitrate (Wild, 1998). The amount of nitrate in the soil and therefore the amount of available N, depends on the rate at which organic N mineralizes to become nitrate and the rate at which nitrate is immobilized as it becomes organic N. The purpose of measuring available N in this study was to determine differences in NO_3^- levels in the zeolite-amended soils and fertilizer-amended soils. Moist soil samples were extracted for mineralizable nitrogen as soon as the plants were harvested. The standard extractable solution used was potassium chloride (KCl), which removes soluble and exchangeable nitrate and ammonium (Rowell, 1994). Ammonium-N and nitrate-N can be analysed separately, but for Glasshouse Experiment 1 only ammonical-N was determined. However, Glasshouse Experiments 2 and 3 focused on determining all forms of nitrogen separately. This analysis gives a qualitative indication of available ammonium present in the soil rather than ammonium present in both the zeolite + soil.

Method

Pre-incubated samples were prepared by taking 5 g of soil and washing with 15 ml distilled water and 15 ml of 4M KCl. 0.5 g magnesium oxide (MgO) was added to this solution and refluxed immediately for 2 minutes in the Kjeldahl steam distillator (Plate 2.6), distillate is then collected. 2% boric acid indicator is added to the distillate and titrated with 0.01/0.1 M HCl to give available-N content.

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O \qquad (2.15)$$

Post-incubated samples were prepared by taking 5 g of soil in a test tube and washing with 15 ml distilled water. The test tubes then covered with polythene film and left in the incubator at 40^0C for 7 days. During incubation, the organic nitrogen releases ammonium by soil microbial activity. The soil-water samples were then washed with 15 ml of 4M KCl solutions and the refluxing was repeated as that for pre-incubated samples by adding 0.5 g MgO. The distillate was collected and titrated with 0.01/0.1M HCl. The ammonium-N was then calculated, by subtracting the pre-incubated sample values from the post-incubated sample values (Radojevic and Bashkin, 1999).

Plate 2.6. Kjeldahl distillation chamber for Nitrogen analysis.

2.11.5. Available Phosphorus

The most common method used for the extraction of Phosphorus is Olsen's method (Rowell, 1994). The method used here measures amount of P, which is exchangeable with bicarbonate and gives a good indication of availability of P in soil. The extractant used in this method sodium bicarbonate $NaHCO_3$ is usually used for the determination of phosphorus concentrations in alkaline to neutral soils in temperate areas. Troug's reagent is more commonly used for acid soils.

Method

Phosphorus was extracted from 5 g of air-dried and sieved soil dissolved in 100 ml of sodium bicarbonate solution adjusted to pH 8.5 (by adding drops of NaOH), and left on the rotary shaker for 30 min at 175 rpm. Samples were then filtered using Whatman No 44 papers. Ammonium molybdate was then added to 10 ml sample of aliquot in a 50 ml volumetric flask, together with ascorbic acid as a reducing agent in order to colorimetrically determine phosphorus concentration. Antimony potassium tartrate was added as a catalyst. The solution was then made up to the 50 ml mark with distilled water. The resulting blue phosphomolybdate solution was then measured at 880 nm using a spectrophotometer with respect to standards made up ranging from 0-20 ppm.

2.11.6. Soil Available Na, K, Ca and Mg Analysis by (ICP-AES)

Nutrients such as Na, K, Ca and Mg present in the soil solution are available for plant growth and can be taken up by roots. Availability of these nutrients depend on the amount in soil solution plus the exchangeable amount held in the soil by clay minerals, humus and sesquioxides. Availability also depends on the distribution of plant roots. This study considered the chemical extraction of available nutrients present in the soil as exchangeable cations. The term 'available' used here refers to the amount determined after chemical extraction by ICP-AES.

Method

Nutrients were extracted by shaking 5 g of air-dried and sieved soil with 125 ml of 1M-ammonium acetate solution buffered at pH 7 for one hour at 180 rpm. The solution was then filtered through Whatman No 44 papers. Nutrient concentrations were then measured by ICP-AES with respect to their appropriate standards (Allen, 1989).

2.11.7. Soil Total Elemental Composition Analysis by (XRF)

X-Ray fluorescence spectrometry was used for the determination of total Na, K, Ca, Mg, Cu, Mn, Zn and Fe in soil. Samples were prepared by placing ball-milled soil samples in-between the gas permeable membrane (microporous film) and 6 μm X-ray transparent film (Mylar). The sample was then analysed by XRF spectrometer. Before running the sample for XRF analysis a predetermination of organic and water loss from the sample by TGA was necessary.

2.12. Statistical Analysis of Data

All data were analysed on the computer package SPSS, version 10 for Windows. All three-glasshouse experiments were treated as separate experiments. One-way analysis of variance ANOVA within the individual harvests, and a two-way analysis of variance following general linear model was used across the harvests for all of the plant and soil measurements. Before analysis, data were tested for homogeneity of variance, to determine if they met the correct criteria for ANOVA. Data were also analysed for least significant differences (LSD) within the treatments for each experiment separately.

Least Significant Difference (LSD)

LSD tests show statistical differences between the treatments at their respective P (significance level). $P \leq 0.05$ has been mentioned as significant, $P \leq 0.01$and >0.001 as highly significant, and $P \leq 0.001$ as very highly significant. LSD is calculated by using the following formula:

$$\text{LSD} = \text{SEd} \times t \qquad (2.16)$$

Where: t = tabulated t-value for x degrees of freedom at a selected P, and SEd = Standard Error of difference, which is calculated by using the following formula:

$$\text{SEd} = \sqrt{(2 * RMS / n)} \qquad (2.17)$$

Where: n = number of replicates, and RMS = Residual Mean Square.

For example, if the calculated LSD value for a set of 10 treatment means is 0.82, the difference between any two-treatment means must be at least 0.82 or more to be significantly different from each other. The letters a, b, c, d, e have been assigned to denote the statistical difference between the treatments. If any two or more treatments share the same letter, these treatments are not significantly different from each other. In other words, if treatments do not share the common letter, these treatments are significantly different from each other.

2.13. List of Instruments

Analytical Technique	Instrument	Place Available
X-Ray Diffraction (XRD)	Phillips PW 1710 X-ray diffractometer.	**UOW**
X-Ray Fluorescence (XRF)	Fissions ARL 84 10 XRF analyser.	**UOW**
Thermo-gravimetric Analysis (TGA)	Mettler M3, TA controller TC 10A/TC15.	**UOW**
Scanning Electron Microscopy (SEM)	EVO-50 ZEISS.	**UOW**
Ion Chromatography (IC)	ICS-90 ion chromatography system.	**UOW**
Atomic Spectrometry (ICP)	Spectro ciros CCD analyser.	**UOW**
Particle Size Analysis	Mastersizer X analyser.	**UOW**
Surface Area Analysis (BET)	Beckman coulter SA3100 analyser.	**UOW**
Nitrogen Analysis (Kjeldahl method) • Kjeldahl Digestor • Distillation Unit • Automatic titrator	• Gerhardt Turbotherm • Gerhardt Vapodest 30 • Denver instrument titrator 280	**CTU**
Phosphorus Analysis (Olsen's method)	CECIL, CE 343/Grating spectrophotometer series 2.	**CTU**

Other Instruments Used

Technique	Instrument	Place Available
pH measurements	pH Checker by HANNA.	**UOW**
Reaction gel stirring	Silverson L4 RT laboratory mixer.	**UOW**
Soil extractions	EAS Shaker.	**UOW**
Soil steam sterilization	Camplex soil sterilizer.	**CTU**

UOW: University of Wolverhampton Main Campus

CTU: Crop Technology Unit, Compton Campus

2.14. Reagents and Suppliers

Reagent	**Purity**	**Supplier**
Aluminium powder	99 %	**Aldrich**
Ammonium acetate	97 %	**Scientific and Chemical Supplies**
Ammonium nitrate	98%	**Scientific and Chemical Supplies**
Ammonium molybdate	99 %	**BDH**
Antimony potassium tartrate	99 +%	**ACROS Organics**
Ascorbic acid	99 %	**Baker J.T.**
Boric acid	GPR	**Aldrich**
Calcium chloride	GPR	**Fisher chemicals**
Devadro's alloy	99 %	**Aldrich**
2,3-Diaminopropionic acid	98 +%	**Aldrich**
Hydrochloric acid (37%)	Conc.	**Aldrich**
Kheldjahl tablets	------	**Thompson and capper Ltd**
Ludox-30 (30 wt% in water)	------	**Aldrich**
Ludox AS-40 (40 wt% in water)	------	**Aldrich**
Magnesium oxide	99 +%	**Aldrich**
Potassium chloride	99.9 %	**Fisher Chemicals**
Potassium hydroxide	85 +%	**Aldrich**
Sodium aluminate	98 %	**Fisher Chemicals**
Sodium bicarbonate	99.9 %	**Fisher Chemicals**
Sodium hydroxide	97 +%	**BDH**
Sodium silicate	98 %	**Fisher Chemicals**
Sulphuric acid (98%)	Conc.	**Aldrich**
Tetra-butyl ammonium hydroxide (40%)	------	**Aldrich**
Fertilizers		
Gem Ammonium Nitrate (27-0-0)	27% N	**Garden warehouse**
Gem Super Phosphate (0-18-0)	18% P	**Garden warehouse**
Gem Potash (0-0-10)	10% K	**Garden warehouse**

Chapter 3

Synthesis and Ion Exchange

Introduction

This chapter focuses on the results and discussion based on synthesis and ion exchange of zeolites, along with their characterization, particle size and surface area techniques both before and after ion exchange. Verified synthesis of zeolites was modified accordingly, and ion exchange was carried out on zeolites in order to eliminate sodium completely, and introduce ammonium into the framework.

3.1. Synthesis

Since the successful verified synthesis of Phillipsite in a Na-K system (Hayhurst, 1977), other methods have been used to synthesize Phillipsite and have been patented. Grose and Flanigen (1978) patented the hydrothermal synthesis of Phillipsite from aqueous gels in the $[N(CH_3)_4]_2O$- Na_2O- Al_2O_3- SiO_2 system. The Phillipsite thus formed exhibited large-pore adsorption characteristics. Franco *et al.* (1990) synthesized Phillipsite hydrothermally from TEA^+, Na^+ and K^+ containing gels. No work has been reported on the synthesis of Linde type F, apart from the verified synthesis of (Warzywoda and Thompson, 1991). Verified synthesis methods of Phillipsite and Linde-type F were initially used for this work and both of these zeolites were successfully synthesized for Glasshouse Experiments 1 and 2. Later studies focused on synthesizing high-aluminium Phillipsite (Cichocki, 1991), and high-crystalline Phillipsite (Hayhurst, 1977) for Glasshouse Experiment 3. Once the zeolites were synthesized they were ion exchanged and characterized by the most commonly used techniques (XRD, XRF, TGA and SEM), both before and after ion exchange. All zeolites used were analyzed for their particle size and surface area, to study their diffusion properties.

3.2. Phillipsite

3.2.1. Synthesis

Phillipsite is a monoclinic zeolite with a two-dimensional channel system and an 8-membered ring opening. Synthesis was carried out according to the following gel molar composition: **6.95 Na_2O: 3.50 K_2O: 1 Al_2O_3: 18.5 SiO_2: 325 H_2O** (Hayhurst, 1977). As discussed earlier (Section 2.1.1), samples were taken at regular intervals from 8-24 hours and their pH measured (Figure 3.1).

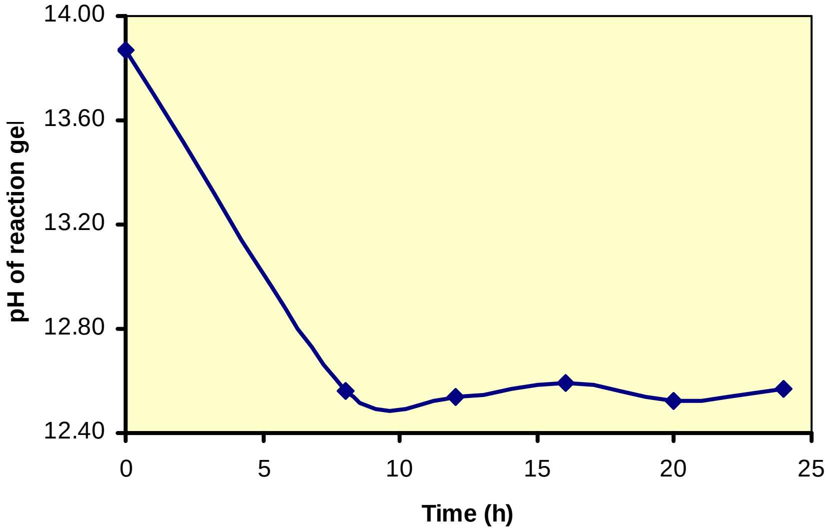


Figure 3.1. pH of zeolite formation at different time intervals.

As the original synthesis gel is highly caustic, the final as-synthesized product obtained was also basic in pH with a decrease of a unit from the starting gel composition from 13.87 to 12.52, and remained constant at each sample interval. Phillipsite is formed after 8 hours of incubation in accord with Hayhurst (1977). However, in order to obtain highly crystalline product, synthesis was carried out for 24 hours. A highly crystalline synthesized Phillipsite was obtained after 19 hours of incubation (Figure 3.2).

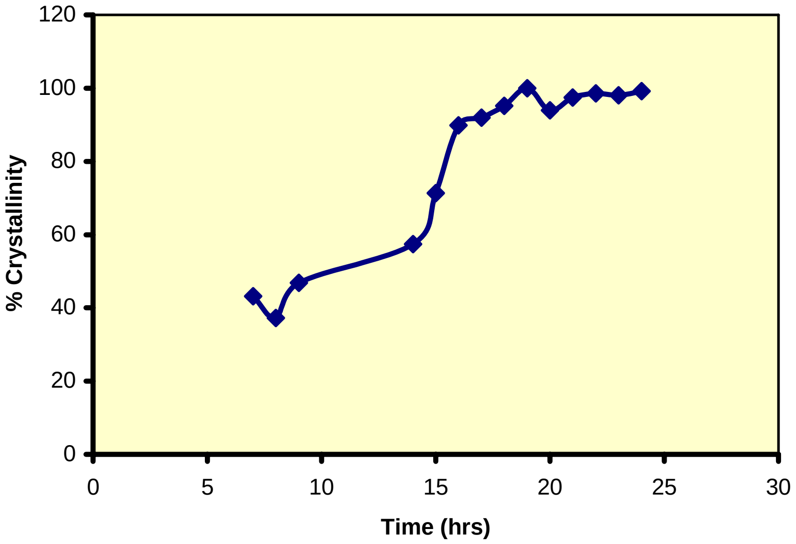


Figure 3.2. % Crystallinity of as-synthesized Phillipsite.

3.2.2. Characterization

Before commencing plant experiments, all synthesized and natural zeolites (i.e., synthetic and natural Phillipsite, Linde type F, high-aluminium Phillipsite and high-crystalline Phillipsite) were characterized by XRD, XRF, TGA and SEM, to study their crystallinity, chemical composition, loss on ignition and crystal morphology. The XRD patterns of 8-24 hour incubated samples for Phillipsite accord with the ICDD standard reference pattern 39-1375 for this zeolite, as obtained from the XRD database software, thereby confirming the synthesised zeolite to be Phillipsite. Samples were amorphous <8 hours of incubation, except for the samples with seed crystals added that were synthesized after 6 hours of incubation. The sample at 19 hours of incubation was chosen as a standard for bulk synthesis, due to its high crystallinity, as indicated by intensive peak heights at various peak angle ranges ($^{o}2\theta$) and uniform crystallites, as indicated by particle size distribution.

XRD along with SEM data proved the 19-hour sample to be highly crystalline. Synthesis was therefore carried out in bulk by scaling up the reaction gel. The synthesized oven-dried product was analysed for its chemical composition by XRF and its residual water content by TGA. In order to establish the Si:Al ratios of as-synthesised Phillipsite along with its Na and K content, XRF analysis was performed on the sample. Analysis revealed Si:Al ratio of Phillipsite to be 2.35:1 and a high K to low Na concentration in the final as-synthesized product. Trace amounts of other elements were also detected and can be associated with impurities present in reagents used for synthesizing Phillipsite. Results were obtained as individual elemental oxide form (Table 3.2). The unit cell composition of as-synthesised Phillipsite calculated from XRF data is as follows: $K_{4.15}Na_{2.02}$ $[Al_6Si_{12}O_{36}]$: $12.78H_2O$ (Appendix 1.1)

Crystallinity was calculated within a synthesis batch over a range of incubation times. Crystallinity of a zeolite can be calculated by measuring the height of the peaks at an angle $2\theta^{o}$ range (from XRD) where the most intensive peaks are produced after baseline correction. The sample that presents the largest area is considered as 100% crystalline, and areas of other samples are normalized accordingly. Table 3.1 shows that synthesized Phillipsite has its maximum crystallinity after 19 hours of incubation, as the heights of the major peaks at 4 peak angles out of the selected 5 are higher than the rest of the samples.

Table 3.1. Table showing peak heights and % crystallinity of as-synthesised Phillipsite samples at major peak angle ranges from X-ray diffraction data.

	Samples after incubation (hrs)	**Peak Angle (°2θ)**						
		12.435	**17.855**	**27.320**	**27.615**	**30.385**	**Mean Height**	**Crystallinity (%)**
Peak Height (cm)	**8**	289	328	135	433	346	1531	25.70
	10	437	296	369	967	306	2375	39.87
	12	502	259	751	1823	655	3990	66.98
	14	571	562	835	2190	686	4844	81.32
	16	566	645	876	2144	870	5101	85.63
	18	615	640	973	2181	888	5297	88.92
	19	697	692	1011	2621	936	5957	100.00
	20	724	605	949	2550	835	5663	95.06
	22	635	667	912	2294	906	5414	90.88
	24	630	625	980	2304	784	5323	89.36

Table 3.2. Elemental oxides (% wt) of as-synthesized Phillipsite before ion exchange.

Elemental Oxide	**% wt of element**
SiO_2	45.70
Al_2O_3	19.40
K_2O	15.40
Na_2O	3.98
P_2O_5	0.47
CaO	0.15
Others	0.07
Volatile Content	14.94

The volatile content referred to in Table 3.2 is the residual water content present in pores and cavities inside the zeolite framework. TGA performed on samples provides thermal behaviour data of a sample when heated from 20°C to 900°C in the presence of nitrogen/air. Weight loss from samples can be integrated according to the boiling/melting points of water and organic templates used in the synthesis of a material (zeolite). Phillipsite was synthesized without the presence of any templating agent, so a weight loss of 14.94% can be related to water loss from the sample and is shown in TGA weight loss curve (Figure 3.3).

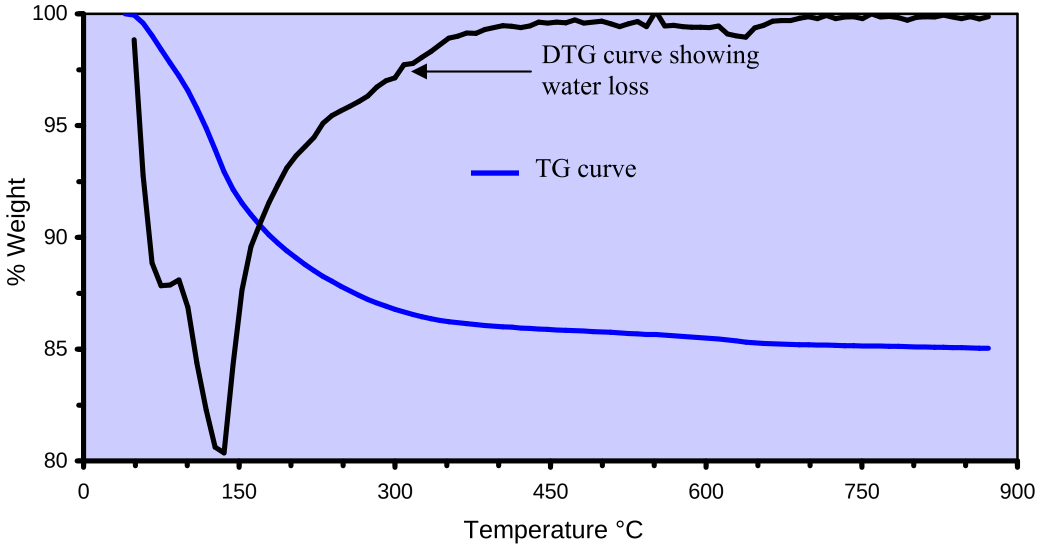
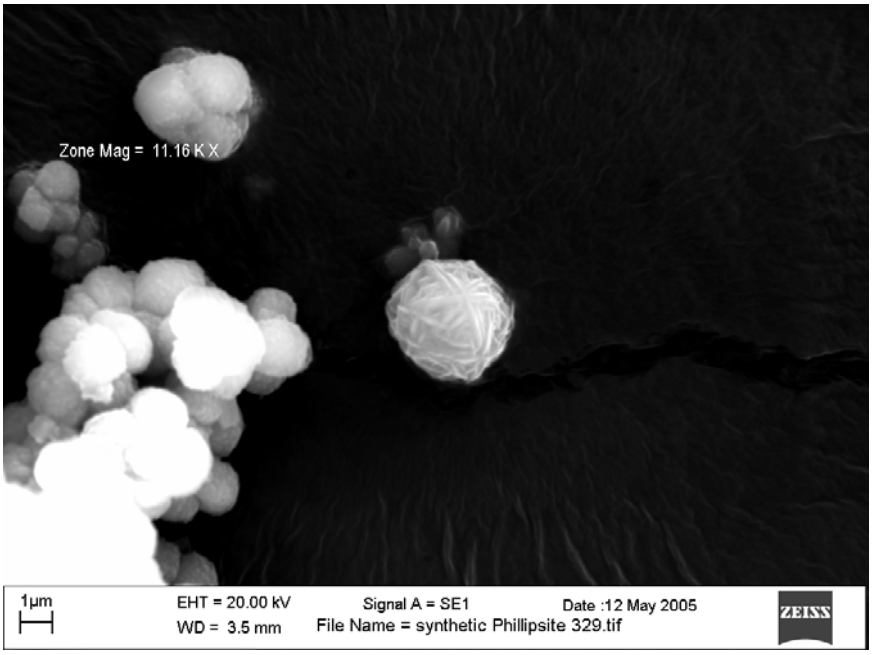
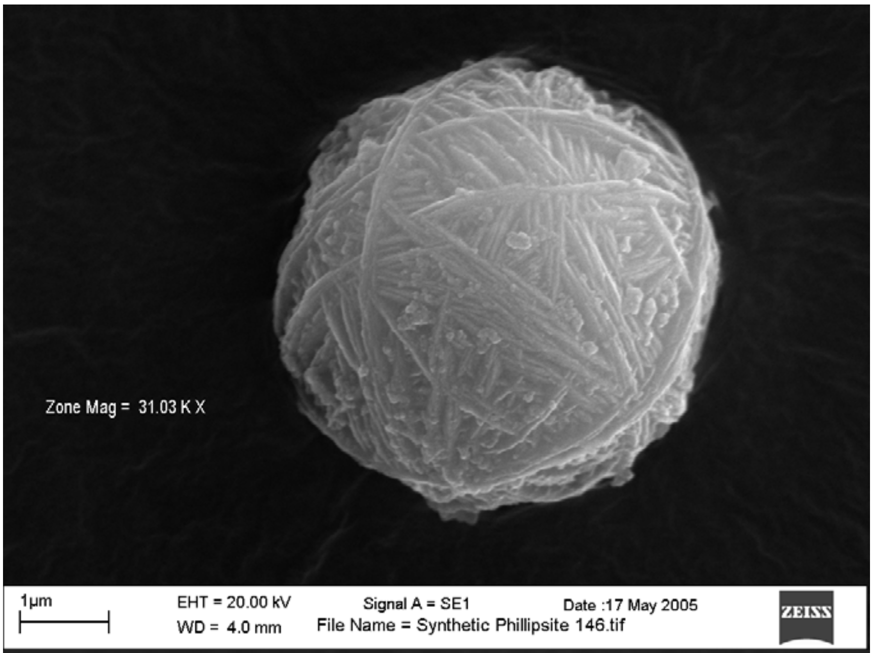


Figure 3.3. TGA % Weight loss curve of as-synthesized Phillipsite.

In order to establish crystal morphology and purity of as-synthesized Phillipsite, samples were observed under SEM. SEM image (Plate 3.1) confirmed the phase purity of Phillipsite without any amorphous phase as indicated by the XRD pattern (Figure 3.7). Crystals varied from 1-5 μm in diameter, and were spherical with fairly uniform morphology.

Plate 3.1. Scanning electron micrographs of as-synthesized Phillipsite showing varying crystal sizes.

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WD = 4.0 mm
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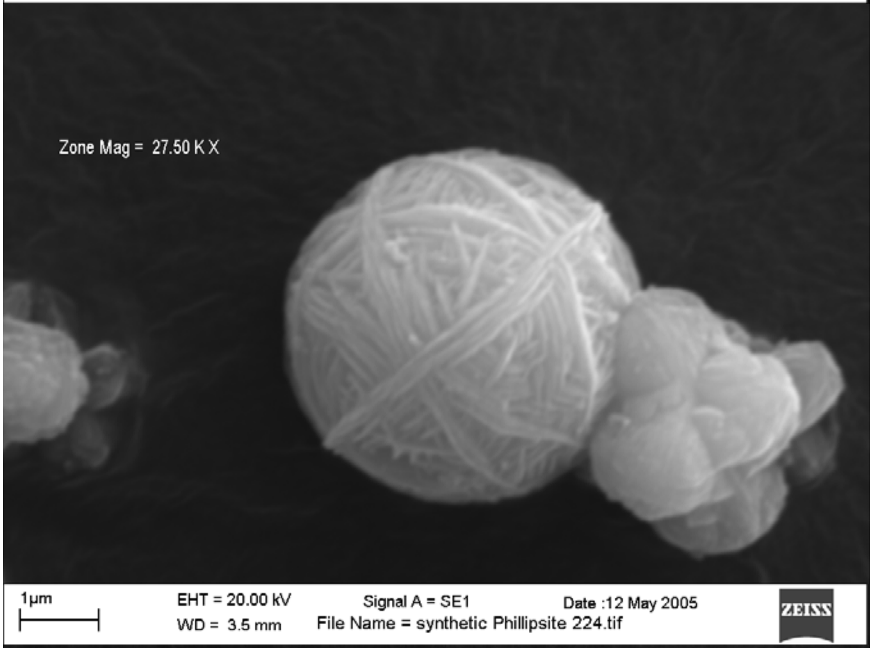
Date :17 May 2005
ZEISS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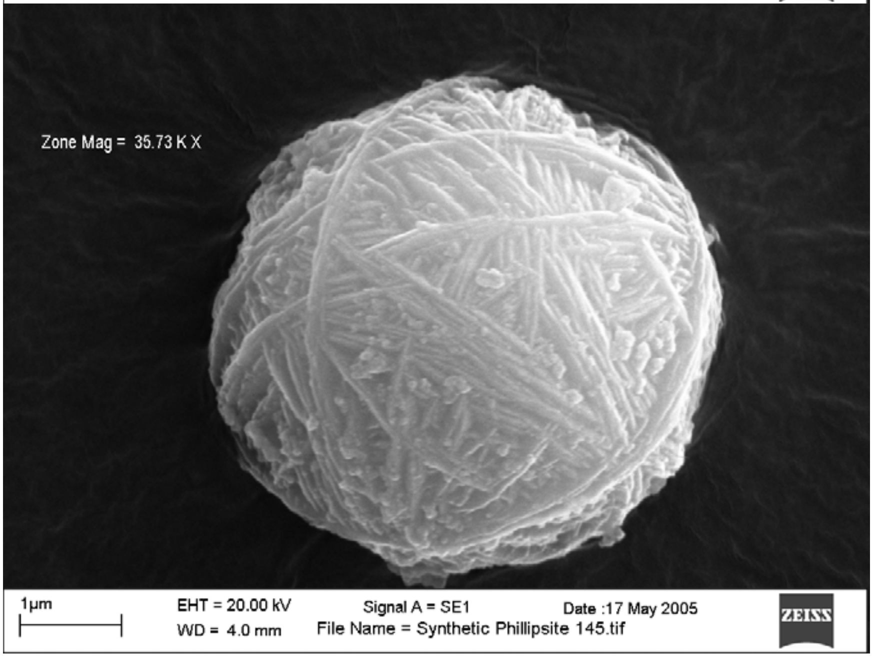
ZEISS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1µm
EHT = 20.00 kV
WD = 4.0 mm
Signal A = SE1
File Name = Synthetic Phillipsite 145.tif
Date :17 May 2005
ZEISS

3.2.3. Ion exchange

Ion exchange was carried out on as-synthesized Phillipsite, as discussed in Section 2.5.1a. Once ion exchange was established, samples were re-characterized by XRD, XRF, TGA and SEM. The structure of Phillipsite remained unaltered after ion exchange as Na and K cations are exchanged for NH_4^+ cation without altering the Si:Al ratio of zeolite (Figure 3.6). Elemental composition analysis revealed Na being completely exchanged for NH_4^+ and K partially exchanged for NH_4^+ (Table 3.3). XRF analysis cannot determine the elemental Nitrogen instead by accounting for number of moles of Na/K being replaced by equal numbers of moles of NH_4^+; the amount of NH_4^+ exchanged into the zeolite was established (Figure 3.5). The results were supported by the TGA weight loss curve for ion exchanged Phillipsite. The unit cell composition of as-synthesised ion exchanged Phillipsite calculated from XRF data is: $K_{0.88}(NH_4)_{5.44}$ $[Al_6\ Si_{12}\ O_{36}]$: $11.67H_2O$. The volatile content referred to in Table 3.3 is the residual water and NH_4^+ present in the cavities within the zeolite framework. Phillipsite was ion exchanged in the presence of ammonium nitrate as an exchange reagent, so the weight loss of 18.02% can be accounted for by water and ammonia loss from the sample and is shown in TGA weight loss curve (Figure 3.4).

Table 3.3. Elemental oxides (% wt) of as-synthesized Phillipsite after ion exchange.

Elemental Oxide	% wt of element
SiO_2	52.50
Al_2O_3	22.30
K_2O	3.02
Na_2O	0.00
P_2O_5	0.53
CaO	0.10
Others	0.17
Volatile Content	18.02

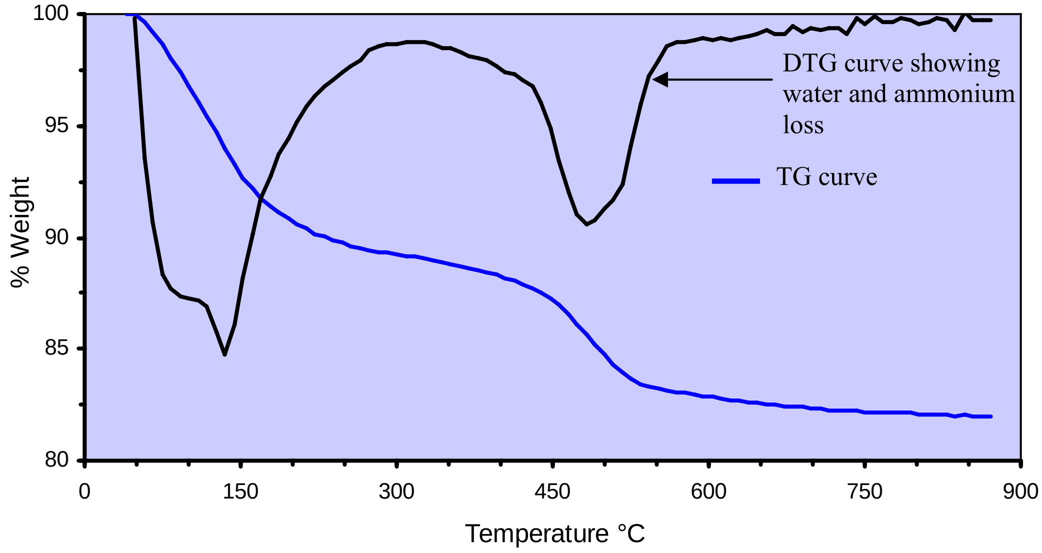


Figure 3.4. TGA % weight loss curve of ion exchanged Phillipsite.

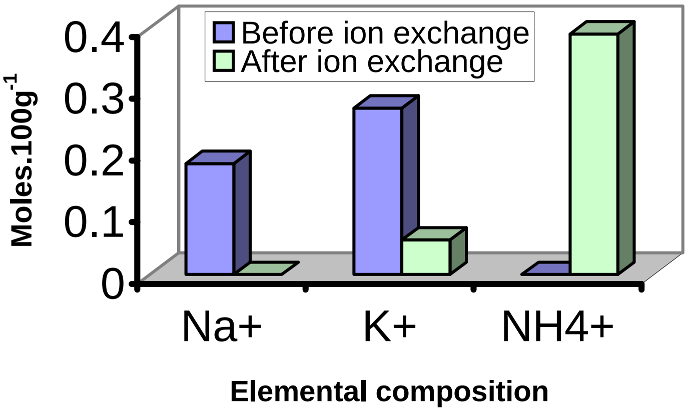


Figure 3.5. Moles/100g of Na^+, K^+ and NH_4^+ as calculated from Table 3.2 and 3.3 of pre- and post- ion exchanged synthetic Phillipsite (Appendix 1.2).

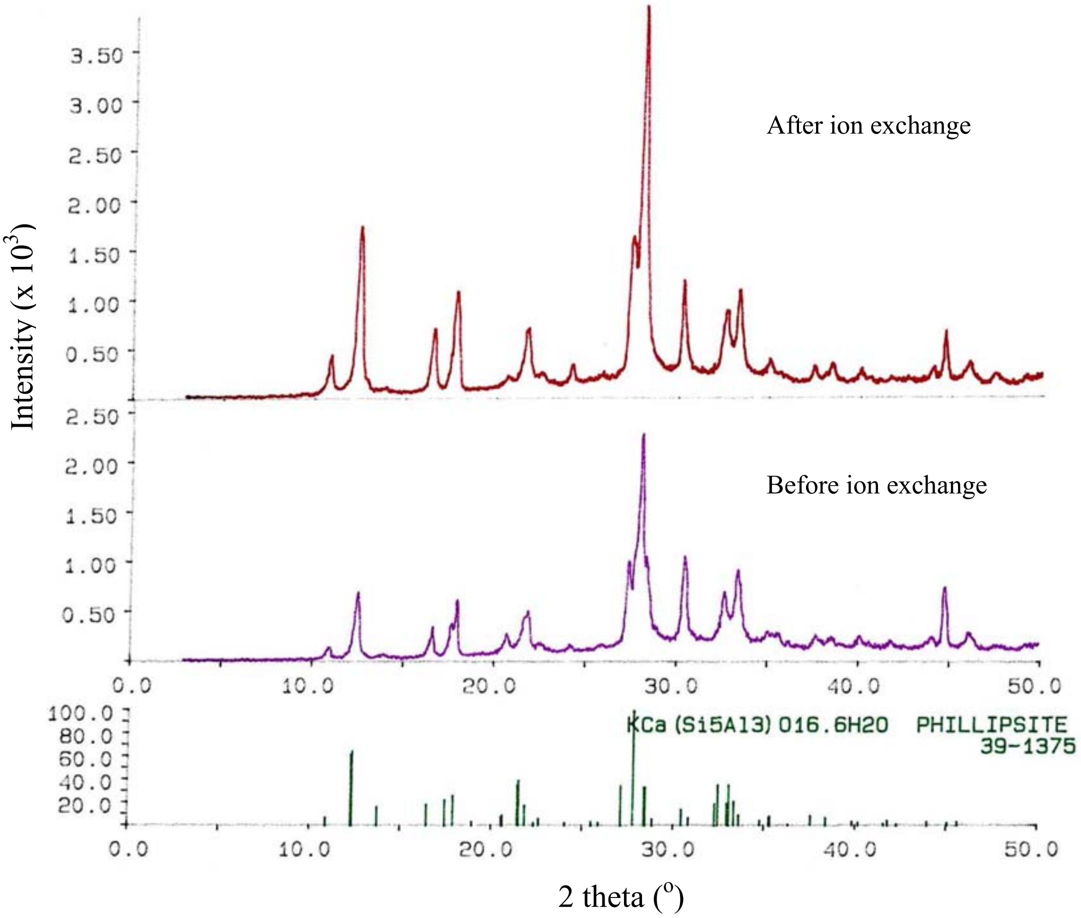


Figure 3.6. XRD patterns of as-synthesized Phillipsite before and after ion exchange along with the ICDD standard reference pattern 39-1375 for Phillipsite.

3.3. Linde type F

3.3.1. Synthesis

Linde type F (also known as Edingtonite) is a tetragonal zeolite and can also be orthorhombic, with an 8-membered ring opening. Synthesis was carried out according to the following gel molar composition:

5.26 K_2O: Al_2O_3: 3 SiO_2: 94.5 H_2O (Warzywoda and Thompson, 1991). (3.1)

As discussed Section 2.1.2, samples were taken at regular intervals from 90-100 hours and pH measured (Figure 3.7). As the original synthesis gel is highly caustic the final as-synthesised product obtained was also basic in pH with a decrease of less than a unit from the starting gel composition from 14.96 to 14.43, and remained constant at each sample interval. Linde type F is formed after 96 hours of incubation in accord with Warzywoda and Thompson (1991). A highly crystalline as-synthesized Linde type F was obtained after 96 hours of incubation (Figure 3.8).

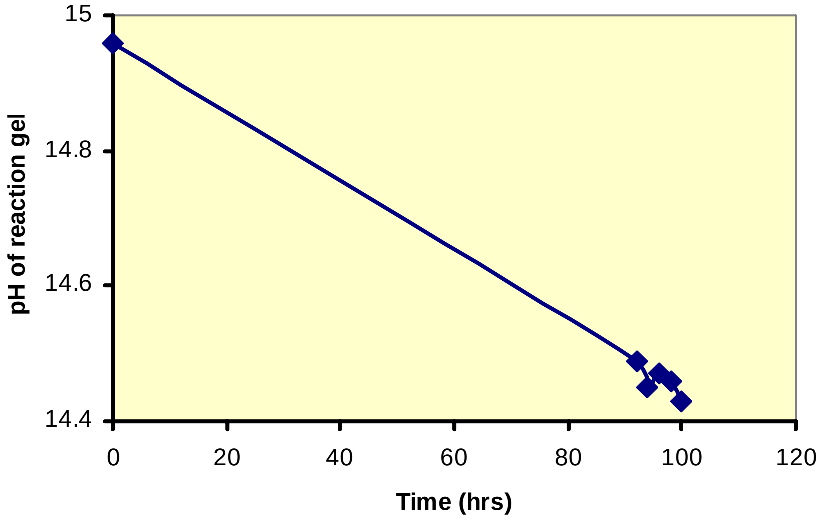


Figure 3.7. pH of zeolite formation at different time intervals.

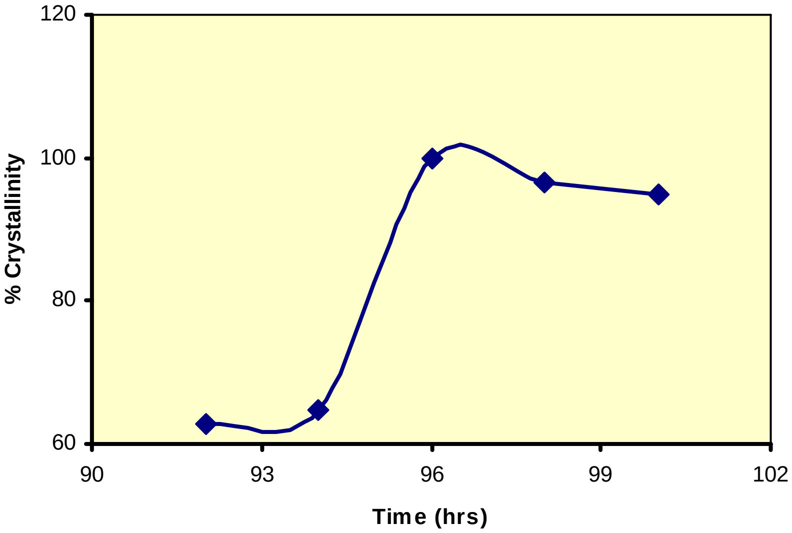


Figure 3.8. % Crystallinity of as-synthesized Linde type-F.

3.3.2. Characterization

The XRD patterns of 96-100 hour incubated samples accord with the ICDD standard reference pattern 45-123 of Edingtonite as obtained from XRD database software, thereby confirming the synthesized zeolite to be Linde type F. The sample at 96 hours of incubation was chosen as a standard for bulk synthesis, due to its high crystallinity, as indicated by intensive peak heights at various peak angle ranges ($^o2\theta$) on comparing with other samples. In order to establish the Si:Al ratios of as-synthesized Linde type F along with its K content, XRF analysis was performed on the sample. Analysis revealed Si:Al ratio of Linde type F to be 1.55:1 and a high K concentration in the final product. Trace amounts of other elements were also detected and can be associated with impurities present in reagents used for synthesizing Linde type F. Results are obtained as individual elemental oxide form (Table 3.4). The unit cell composition of as-synthesised Linde type F calculated from XRF data is: $K_{7.42}$ [$Al_{7.58}Si_{10}O_{35.16}$]: $9.58H_2O$.

Table 3.4. Elemental oxides (% wt) of as-synthesized Linde type F.

Elemental Oxide	% wt of element
SiO_2	39.60
Al_2O_3	25.50
K_2O	23.10
P_2O_5	0.29
CaO	0.17
Others	0.25
Volatile Content	13.82

The volatile content referred to in Table 3.4 is the residual water content present in pores and channels within the zeolite framework. Linde type F was synthesized without the presence of any templating agent, so the weight loss of 13.82% can be related to water loss from the sample and is shown in TGA weight loss curve (Figure 3.9).

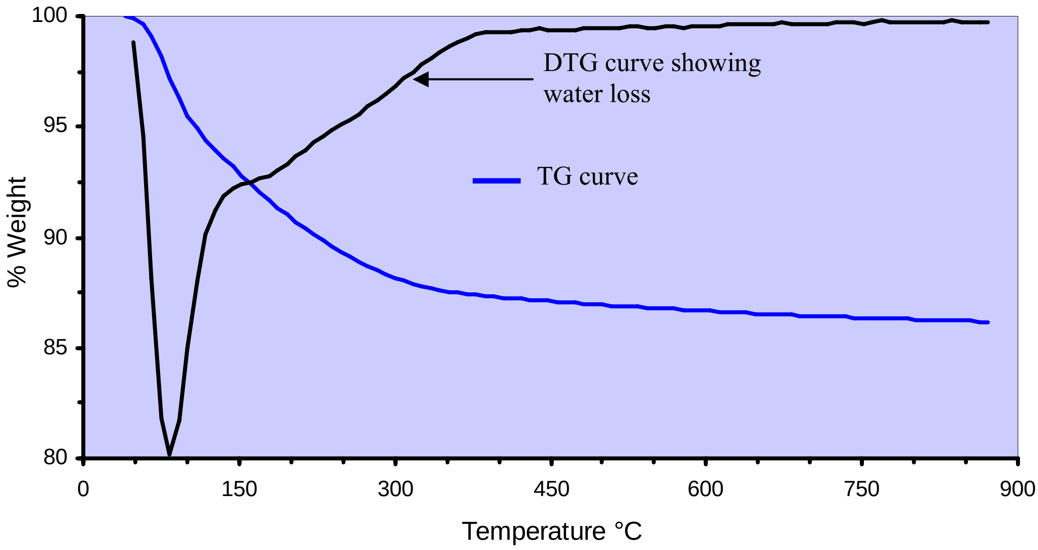


Figure 3.9. TGA % Weight loss curve of as-synthesized Linde type F.

3.3.3. Ion exchange

Ion exchange was carried out on as-synthesized Linde type F, as discussed in Section 2.5.1b. Once ion exchange was established, samples were characterized by XRD, XRF, TGA and SEM. The structure of Linde type F remained unaltered after ion exchange as K ions are exchanged for NH_4^+ ions without altering the Si:Al ratio of zeolite. Elemental composition analysis revealed K^+ ions exchanged for NH_4^+ ions significantly due to the absence of other major available cations (Table 3.5). By accounting for number of moles of K being replaced by equal number of moles of NH_4^+, the amount of NH_4^+ exchanged into the zeolite was established (Figure 3.11). The results were supported by TGA weight loss curve for ion exchanged Linde type F. The unit cell composition of as-synthesised ion exchanged Linde type F calculated from XRF data is: $K_{1.37}(NH_4)_{10.06}\,[Al_{7.40}Si_{10}O_{34.8}]$: 9.11 H_2O.

Table 3.5. Elemental oxides (% wt) of as-synthesized Linde type F after ion exchange.

Elemental Oxide	% wt of element
SiO_2	43.90
Al_2O_3	27.30
K_2O	4.78
P_2O_5	0.41
CaO	0.10
Others	0.19
Volatile Content	27.83

The volatile content referred to in Table 3.5 is the residual water and NH_4^+ present in the cavities within the zeolite framework. Linde type F was ion exchanged in the presence of ammonium nitrate as an exchange reagent, so the weight loss of 27.83% can be related to water and ammonia loss from sample and is shown in the TGA weight loss curve (Figure 3.10).

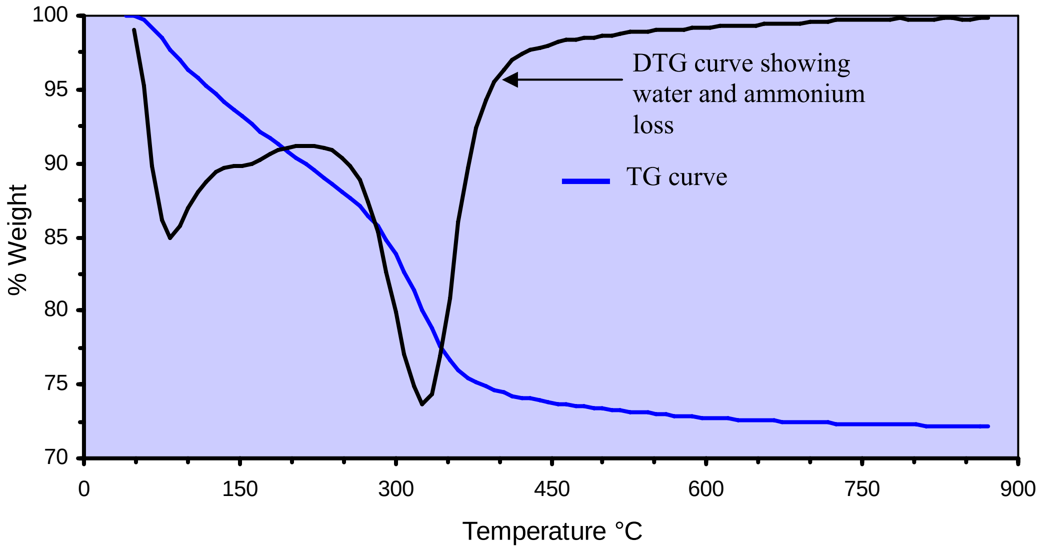


Figure 3.10. TGA % weight loss curve of ion exchanged Linde type F.

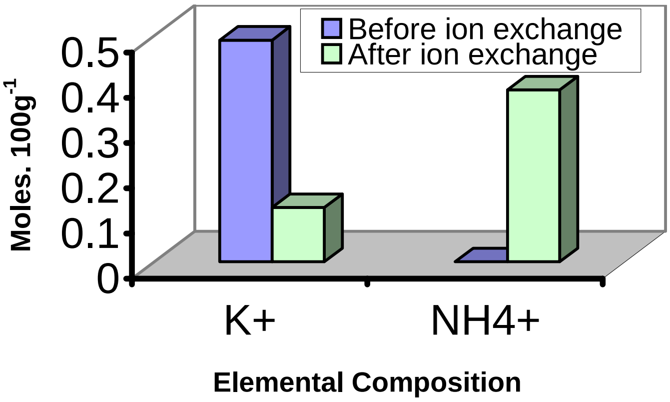


Figure 3.11. Moles/100g of K^+ and NH_4^+ before and after ion exchange as calculated from Table 3.4 and 3.5 of pre- and post- ion exchanged Linde type F.

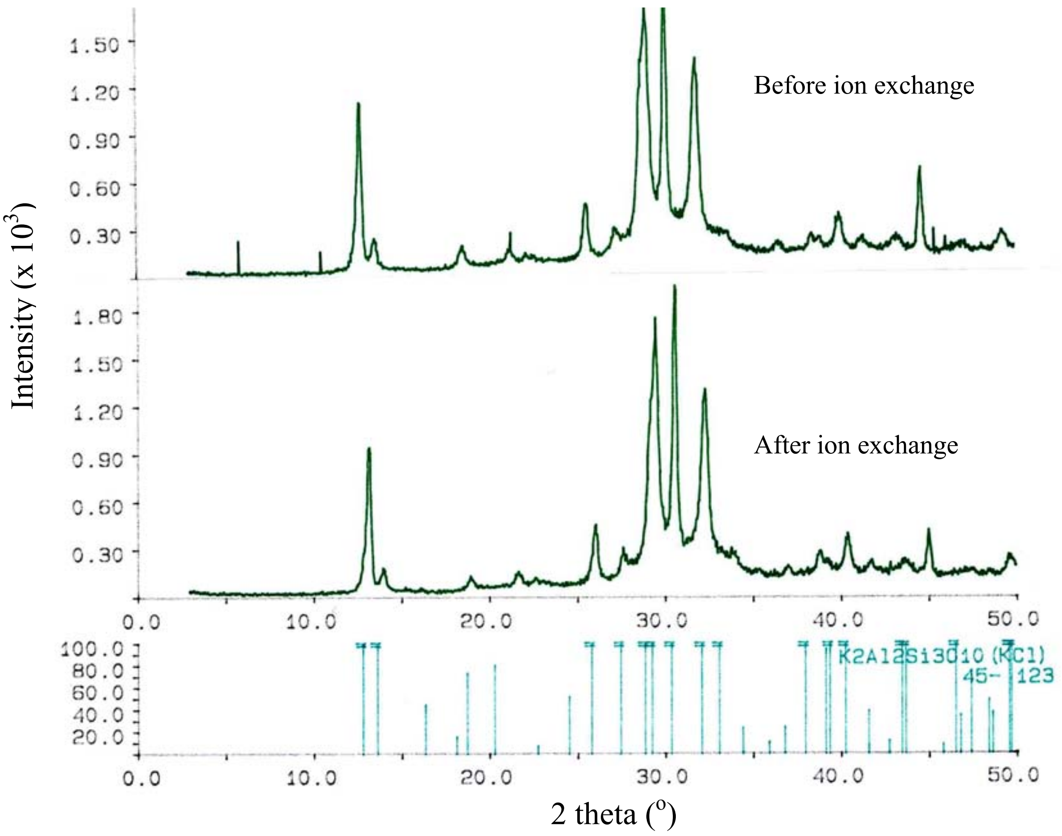


Figure 3.12. XRD patterns of as-synthesized Linde type F before and after ion exchange along with the ICDD standard reference pattern 45-123 for Edingtonite.

3.4. High-aluminium Phillipsite

3.4.1. Synthesis

Synthesis was carried out according to the following gel molar composition:

1.53 Na_2O: 0.44K_2O: Al_2O_3: 5SiO_2: 82.7H_2O (Cichocki, 1991). (3.2)

As discussed in Section 2.1.3, samples were taken at regular 24-hour intervals from 5-8 days and pH measured. The as-synthesized final product obtained was also basic in pH with a decrease of less than a unit from the starting gel composition from 12.92 to 12.43, and remained constant at each sample interval (Figure 3.13). High aluminium Phillipsite is formed after 7 days of incubation, in accordance with Cichocki (1991). Although structure appears to be formed after 5-6 days of incubation, a high crystalline sample was obtained only after 7 days of incubation (Figure 3.14).

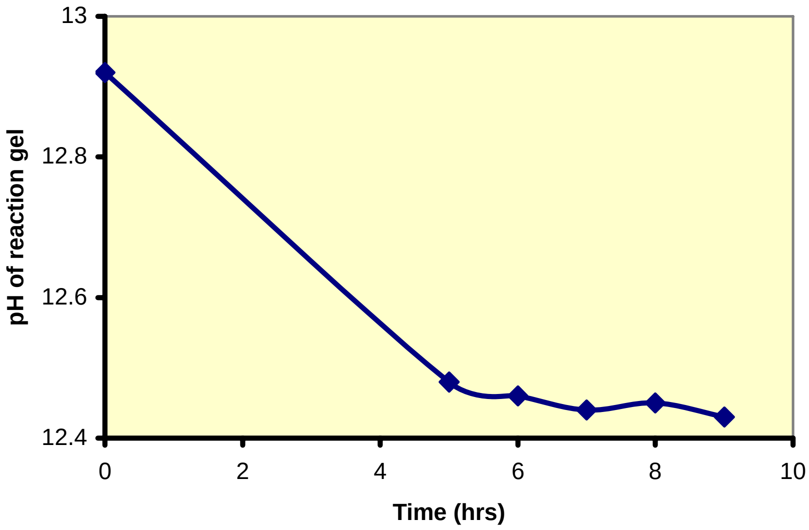


Figure 3.13. pH of zeolite formation at different time intervals.

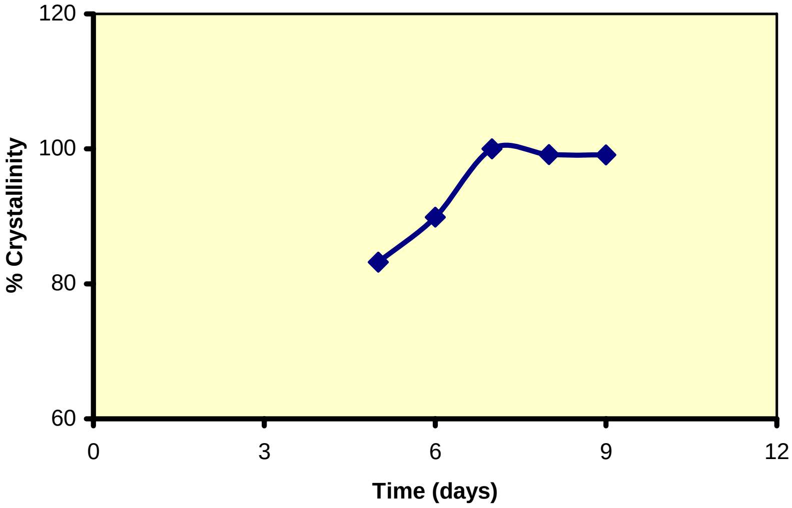


Figure 3.14. % Crystallinity of as-synthesized high-aluminium Phillipsite.

3.4.2. Characterization

As synthesized high-aluminium Phillipsite was characterized to study its structure, Si:Al ratio and crystal morphology. The XRD pattern for the 7 day incubated sample accords with ICDD standard reference pattern 39-1375, thereby confirming the synthesized zeolite to be Phillipsite (Figure. 3.18). The sample at 7 days of incubation was chosen as a standard for bulk synthesis, due to its high crystallinity, as indicated by intensive peak heights at various peak angle ranges ($^{o}2\theta$) compared with other samples. The high aluminium content of this zeolite was established by performing XRF analysis on the sample. The Si:Al ratio for high-aluminium Phillipsite was 1.95:1, and a high Na^+ and low K^+ concentration were established in the final product. Results were obtained as individual elemental oxide form (Table 3.6). The unit cell composition of as-synthesised high aluminium Phillipsite calculated from XRF data is: $K_{4.22}Na_{1.65}$ [$Al_{7.40}Si_{12}O_{38.80}$]: $13.65H_2O$.

Table 3.6. Elemental oxides (% wt) of as-synthesized high-aluminium Phillipsite before ion exchange.

Elemental Oxide	% wt of element
SiO_2	47.008
Al_2O_3	24.596
Na_2O	3.181
K_2O	12.471
P_2O_5	0.025
CaO	0.011
Others	0.008
Volatile Content	15.387

High-aluminium Phillipsite was synthesized without the presence of any templating agent, so the weight loss of 15.39% can be related to water loss from sample and is shown in TGA weight loss curve (Figure 3.15).

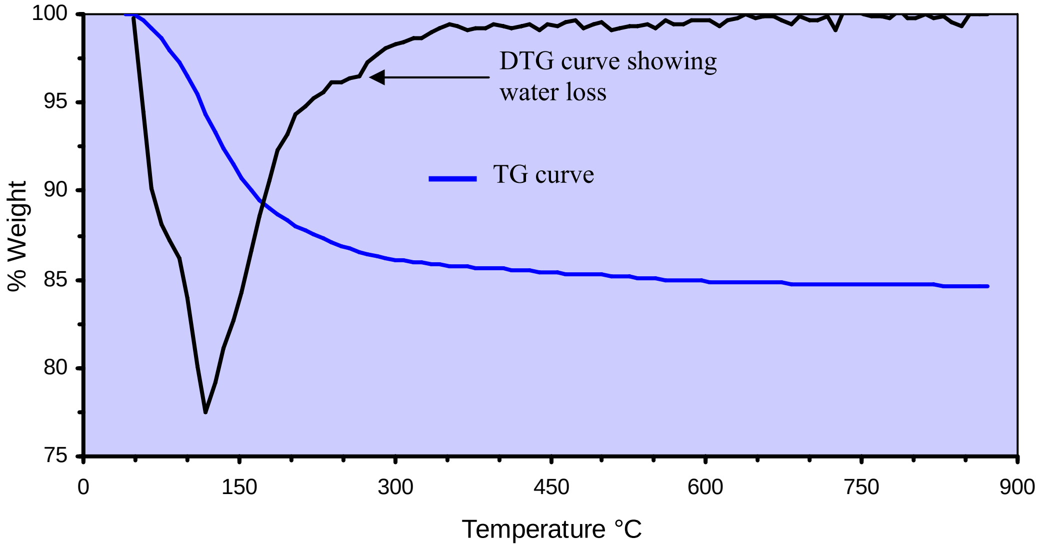


Figure 3.15. TGA % weight loss curve of as-synthesized high-aluminium Phillipsite.

There is a high negative charge on the framework of high-aluminium Phillipsite induced by Al substituting for Si in [MO_4] tetrahedral. Ion exchange with ammonium nitrate source will therefore produce a high ammonium Phillipsite to balance the negative charge.

3.4.3. Ion exchange

Ion exchange was carried out on as-synthesized high-aluminium Phillipsite, as discussed in Section 2.5.1c. Once ion exchange was established, samples were characterized by XRD, XRF, TGA and SEM. The structure of the zeolite remained unaltered after ion exchange as Na and K ions are exchanged for NH_4^+ ions without altering the zeolite Si:Al ratio. Elemental composition analysis revealed Na^+ ions exchanged for NH_4^+ ions completely and K^+ ions partially (Table 3.7). By accounting for number of moles of Na^+ and K^+ replaced by equal number of moles of NH_4^+, the amount of NH_4^+ exchanged into the zeolite was established (Figure 3.16). The results were supported by the TGA weight loss curve for ion exchanged high-aluminium Phillipsite. The unit cell composition of as-synthesized ion exchanged high-aluminium Phillipsite calculated from XRF data is: $K_{0.83}(NH_4)_{6.33}$ $[Al_{7.37}Si_{12}O_{38.74}]$: $13.15H_2O$.

Table 3.7. Elemental oxides (% wt) of as-synthesized high-aluminium Phillipsite after ion exchange.

Elemental Oxide	% wt of element
SiO_2	53.030
Al_2O_3	27.640
Na_2O	0.000
K_2O	2.890
P_2O_5	0.002
CaO	0.007
Others	0.006
Volatile Content	21.323

High-aluminium Phillipsite was ion exchanged in the presence of ammonium nitrate as an exchange reagent, so the weight loss of 21.32% can be related to water and ammonia loss from the sample and is shown in TGA weight loss curve (Figure 3.17).

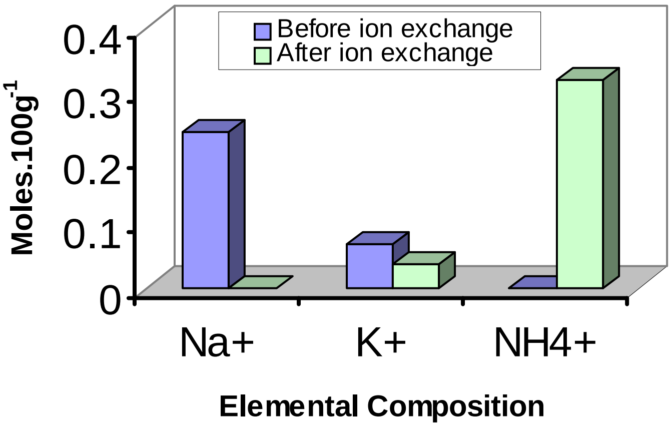


Figure 3.16. Moles/100g of K^+ and NH_4^+ before and after ion exchange as calculated from Table 3.6 and 3.7 of pre- and post- ion exchanged high-aluminium Phillipsite.

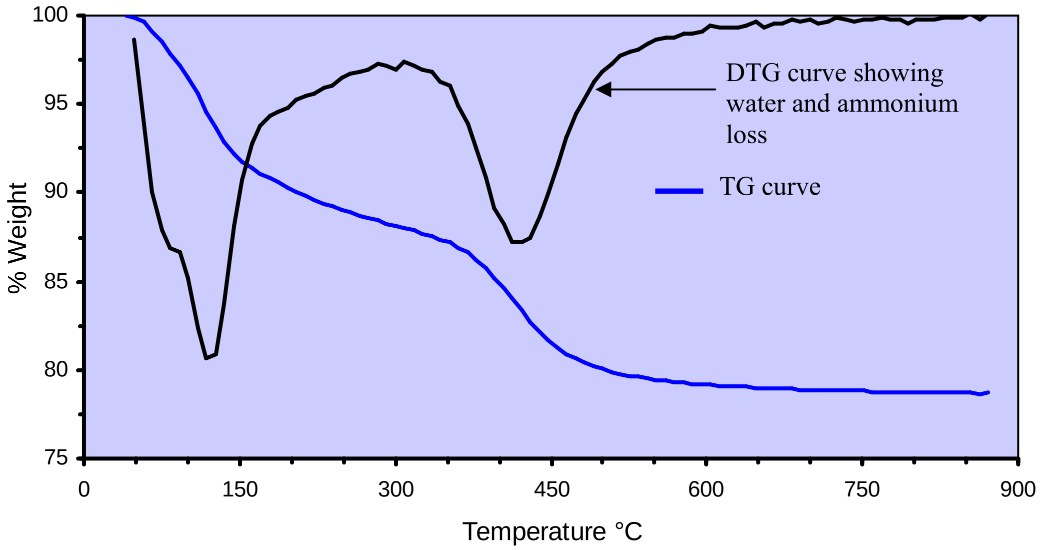


Figure 3.17. TGA % weight loss curve of ion exchanged high-aluminium Phillipsite.

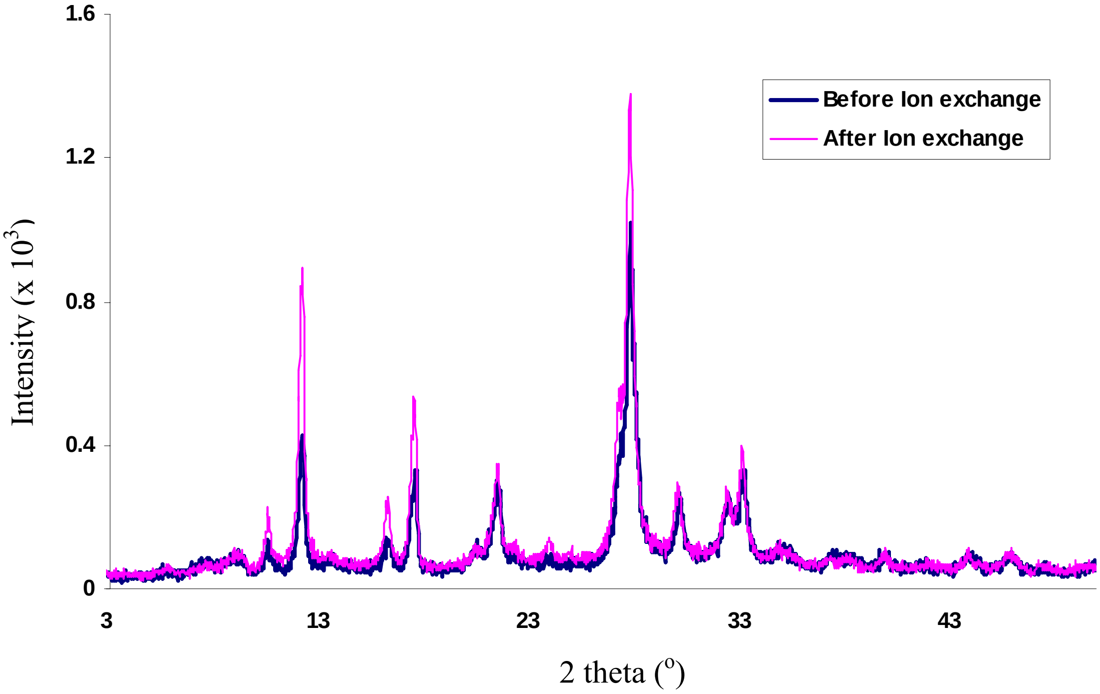


Figure 3.18. XRD patterns of as-synthesized high-aluminium Phillipsite before and after ion exchange.

3.5. High-crystalline Phillipsite

3.5.1. Synthesis

Synthesis was carried out according to the following gel molar composition:

6.95 Na_2O: 3.50 K_2O: 1 Al_2O_3: 18.5 SiO_2: 325 H_2O (Hayhurst & Sand, 1977). (3.3)

As discussed in Section 2.1.4, samples were taken at regular intervals from 8-24 hours and pH measured (Figure 3.19).

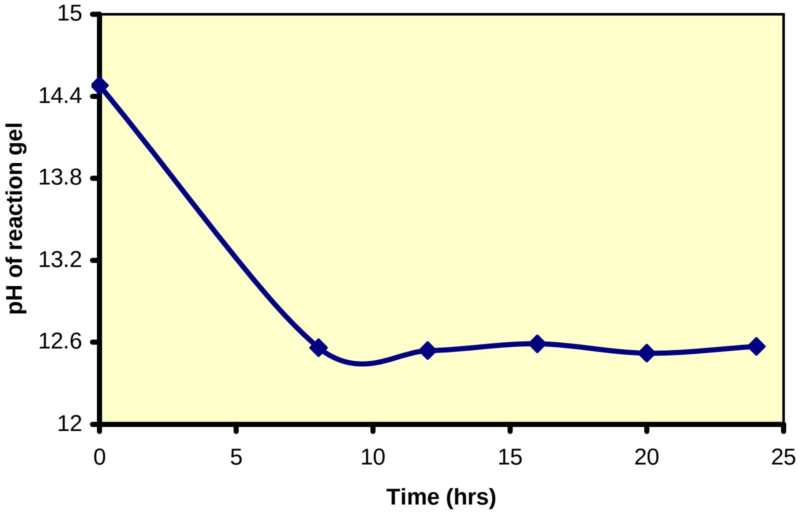


Figure 3.19. pH of zeolite formation at different time intervals.

3.5.2. Effect of ageing

High yield of zeolite Na-Y, and an increase by a factor of 1.5 in the rate of crystallization of this zeolite (aged at room temperature for 24 hours) was first reported by Breck (1974). Results showed that ageing of aluminosilicate gels, obtained by mixing alkaline solutions of Na aluminate and silicate, leads to a significant shortening of gel crystallization time. Phillipsite synthesis was carried out with the additional step of ageing the original reaction gel at room temperature for 24 hours before incubating in the oven at 100° C. A high-crystalline sample was obtained after 19 hours of incubation (Figure 3.20).

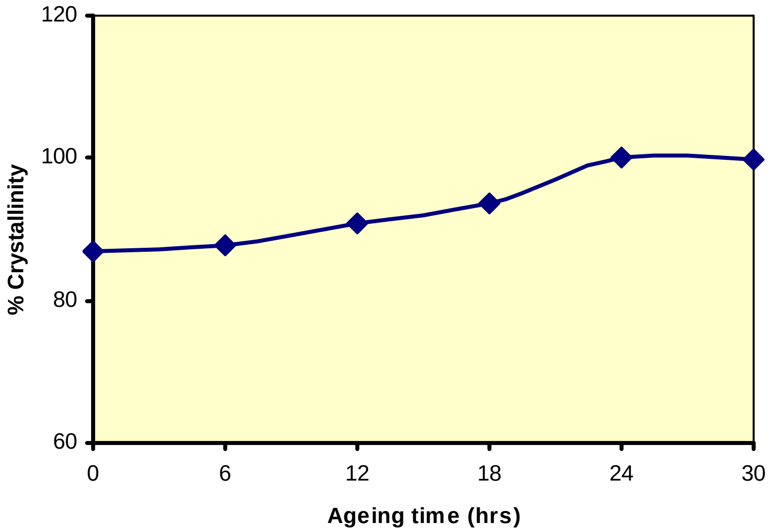


Figure 3.20. % Crystallinity of as-synthesized high-crystalline Phillipsite.

An increase ~15% was evident on ageing the original reaction gel for 24 hours at room temperature. This is considered to be the maximum ageing time. Experiments on ageing the reaction gel 24-30 hours, did not show any notable increase in crystallinity.

3.5.3. Characterization

As synthesized high-crystalline Phillipsite was characterized to examine its structure, Si:Al ratio and the crystal morphology of the zeolite. XRD and SEM data proved (24-hour aged; 19-hour synthesized sample) to be highly crystalline and matched the standard reference pattern 39-1375 for Phillipsite (Figure 3.24). Synthesis was therefore carried out in bulk for Glasshouse Experiment 3 by scaling up the reaction gel. The synthesized oven-dried product was analysed for its chemical composition by XRF and its residual water content by TGA.

XRF analysis revealed the Si:Al ratio of Phillipsite to be 2.37:1 and a high K to low Na concentration in the final product. Trace amounts of other detected elements can be associated with impurities present in the reagents used for synthesizing Phillipsite. Results were obtained as individual elemental oxide form (Table 3.8). The unit cell composition of as-synthesised high crystalline Phillipsite calculated from XRF data is: $K_{3.38}Na_{2.32}$ $[Al_6Si_{12}O_{36}]$: $11.87H_2O$.

Table 3.8. Elemental oxides (% wt) of as-synthesized high-crystalline Phillipsite.

Elemental Oxide	% wt of element
SiO_2	49.29
Al_2O_3	20.46
K_2O	10.33
Na_2O	4.62
P_2O_5	0.42
CaO	0.56
Others	0.09
Volatile Content	13.92

High-crystalline Phillipsite was synthesized without the presence of any templating agent, so the weight loss of 13.92% can be related to water loss from the sample and is shown in the TGA weight loss curve (Figure 3.22).

3.5.4. Ion exchange

Ion exchange was carried out on as-synthesized high-crystalline Phillipsite as discussed in Section 3.5.1d. Once ion exchange was established, samples were characterized by XRD, XRF, TGA and SEM. The structure of the zeolite remained unaltered after ion exchange (Figure 3.21). Elemental composition analysis revealed Na^+ ions exchanged for NH_4^+ ions completely and K^+ ions partially (Table 3.9). By accounting for number of moles of Na^+ and K^+ replaced by equal number of moles of NH_4^+, the amount of NH_4^+ exchanged into the zeolite was established. The results were supported by the TGA weight loss curve for ion exchanged high-crystalline Phillipsite (Figure 3.23). The unit cell composition of as-synthesized ion exchanged high-crystalline Phillipsite calculated from XRF data is: $K_{0.79}(NH_4)_{5.18}$ [Al_6 Si_{12} O_{36}]: $10.84H_2O$.

Table 3.9. Elemental oxides (% wt) of as-synthesized high- crystalline Phillipsite after ion exchange.

Elemental Oxide	% wt of element
SiO_2	50.86
Al_2O_3	21.65
K_2O	2.92
Na_2O	0.00
P_2O_5	0.37
CaO	0.48
Others	0.14
Volatile Content	21.87

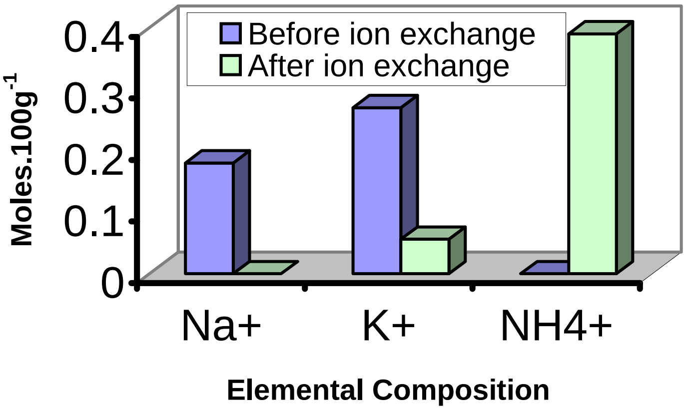


Figure 3.21. High crystalline Phillipsite before and after ion exchange, as calculated from Tables 3.4 and 3.5.

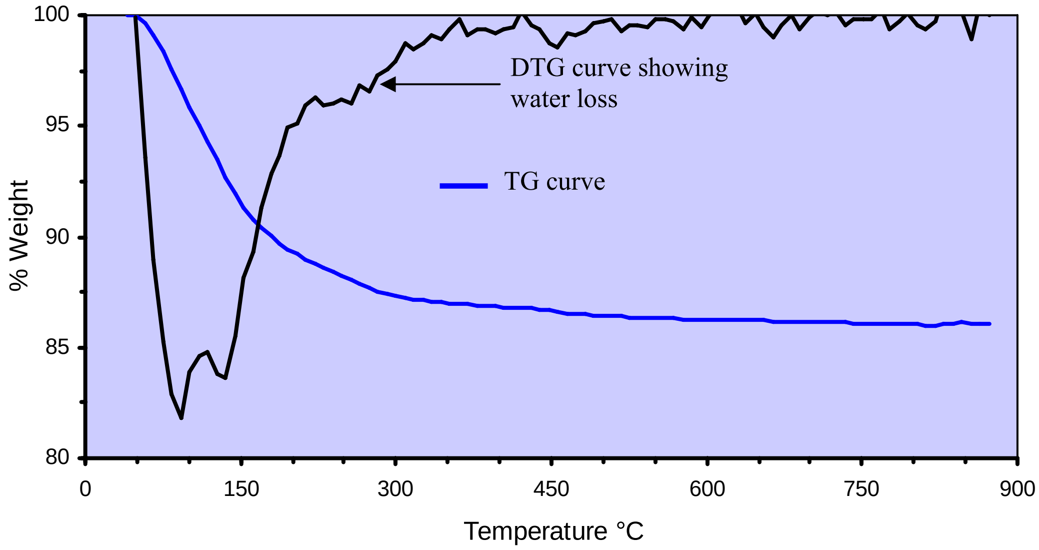


Figure 3.22. TGA % weight loss curve of as-synthesized high-crystalline Phillipsite.

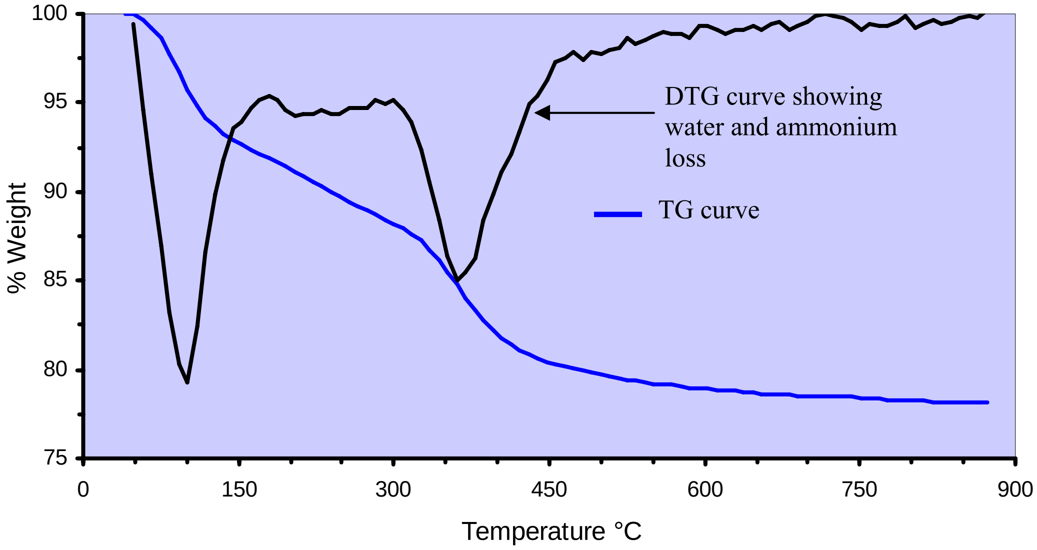


Figure 3.23. TGA % weight loss curve of ion exchanged high-crystalline Phillipsite.

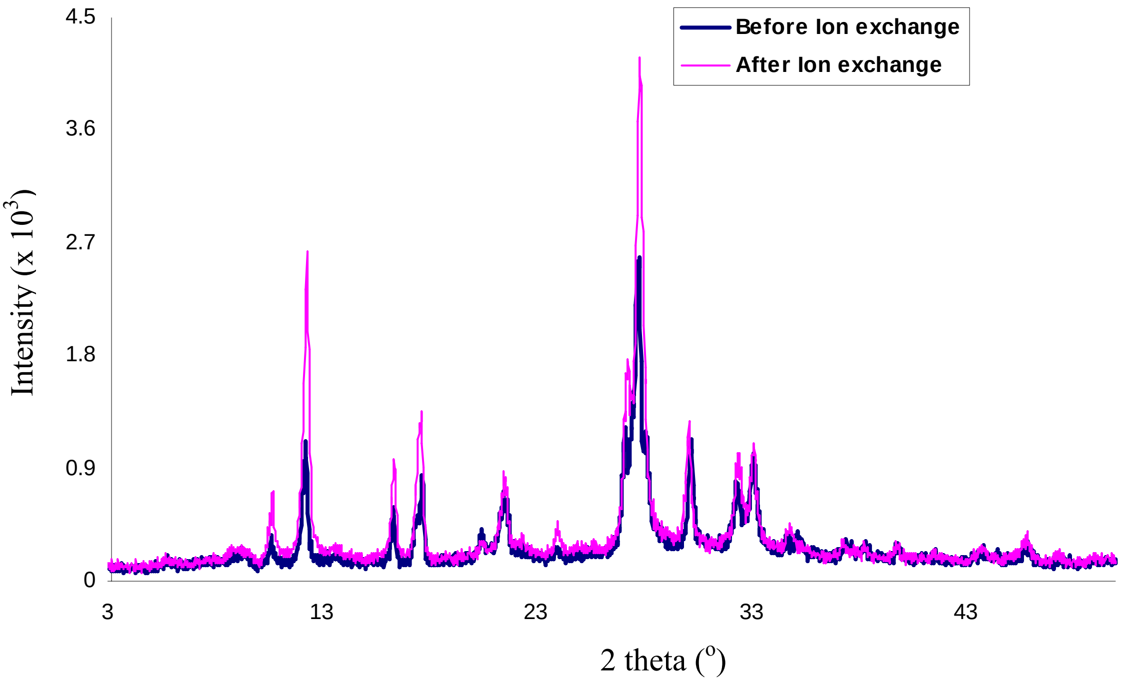


Figure 3.24. XRD patterns of as-synthesized high-crystalline Phillipsite before and after ion exchange.

3.6. Rietveld refinement of natural Phillipsite

As natural Phillipsite tuff obtained from Pine Valley, U.S.A, consists of Phillipsite and traces of Erionite, it was necessary to quantify the % of Phillipsite present in this tuff. Rietveld refinement was performed on Phillipsite tuff and the results are discussed below.

3.6.1. Rietveld Refinement

Investigations of the mineralogy, chemistry, gas adsorption and NH_4^+-exchange capacity of a suite of 40 samples of high-grade zeolitic tuffs from 23 deposits in nine western states of the U.S.A, revealed Phillipsite-rich tuff to be a mixture of Phillipsite and Erionite (Sheppard and Arthur 1982). Analysis confirmed Erionite to be present in traces. Rietveld refinement performed on Phillipsite-rich tuff (as discussed in Section 2.3) showed Phillipsite as a major dominant phase and Erionite to be present in traces (Figure 3.25).

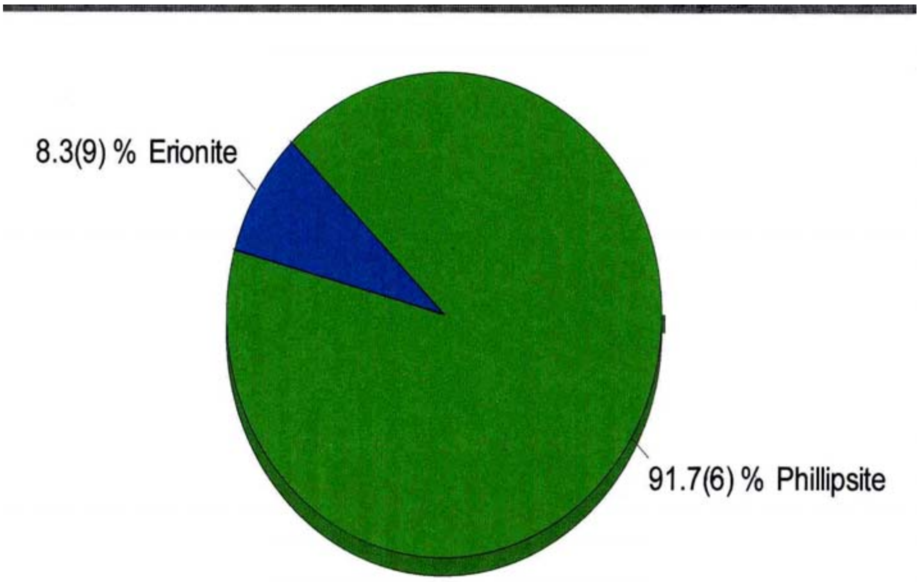


Figure 3.25. Rietveld refinement of natural Phillipsite-rich tuff.

3.6.2. Characterization

Natural Phillipsite was characterized to examine its structure, Si:Al ratio and crystal morphology. XRD matched the standard reference pattern 39-1375 for Phillipsite (Figure 3.26). The product was analysed for its chemical composition by XRF, and its residual water content by TGA. Natural Phillipsite obtained from Pine Valley is associated with impurities such as Fe (Table 3.10) in very high concentrations, thereby rendering a reddish brown colour for this zeolite-tuff (Figure 3.25a).

Figure 3.25a. Natural Phillipsite-rich tuff obtained from Pine Valley, Nevada.

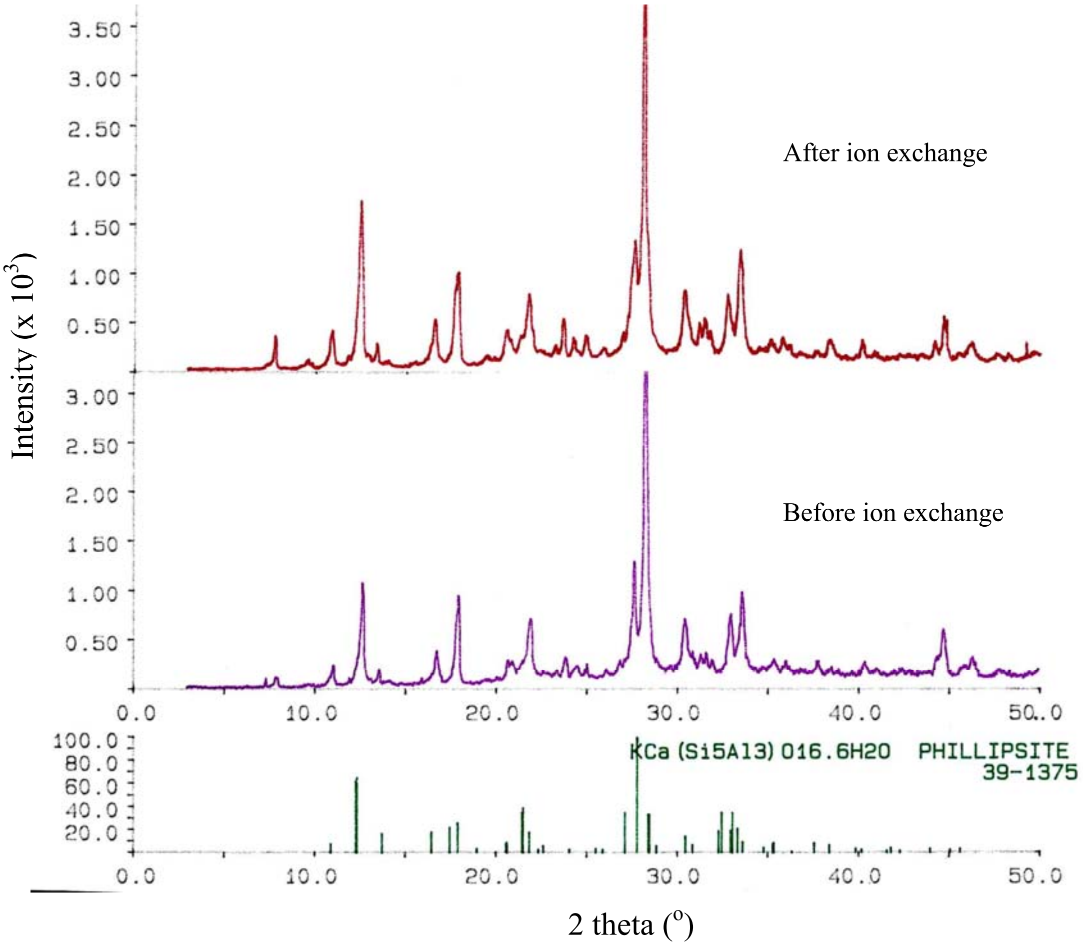


Figure 3.26. XRD patterns of natural Phillipsite-rich tuff before and after ion exchange along with the ICDD standard reference pattern 39-1375 for Phillipsite.

XRF analysis revealed the Si:Al ratio of natural Phillipsite to be 3.20:1 and a high Na to low K concentration in the final product, as reported by Sheppard and Arthur (1982). Trace amounts of other detected elements can be associated with impurities present in this zeolite-tuff. Results were obtained as individual elemental oxide form (Table 3.10). The unit cell composition of natural Phillipsite as calculated from XRF data is: $K_{1.13}Na_{4.99}Fe_{0.63}$ $[Al_{4.40}Si_{12}O_{32.8}]$: $13.99H_2O$.

Table 3.10. Elemental oxides (% wt) of natural Phillipsite.

Elemental Oxide	% Wt of element
SiO_2	44.60
Al_2O_3	13.90
K_2O	3.30
Na_2O	9.58
Fe_2O_3	3.14
P_2O_5	0.49
CaO	0.79
TiO_2	0.21
Others	0.25
Volatile Content	16.74

Weight loss of 16.74% in natural Phillipsite can be related to water loss from the sample and is shown in the TGA weight loss curve (Figure 3.27).

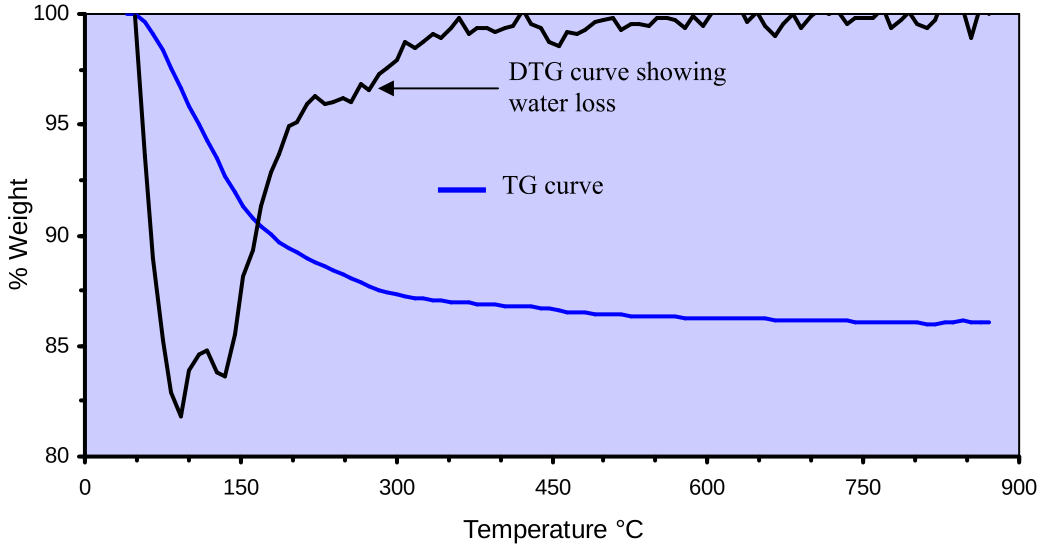


Figure 3.27. TGA % Weight loss curve of natural Phillipsite before ion exchange.

3.6.3. Ion exchange

Ion exchange was carried out on natural Phillipsite, as discussed in Section 2.5.1b. The structure of the zeolite remained unaltered after ion exchange. Elemental composition analysis revealed Na^+ ions exchanged for NH_4^+ ions completely and K^+ ions partially (Table 3.11). By accounting for number of moles of Na^+ and K^+

replaced by equal number of moles of NH_4^+, the amount of NH_4^+ exchanged into the zeolite was established (Figure 3.29). The results were supported by the TGA weight loss curve for ion exchanged natural Phillipsite (Figure 3.28).

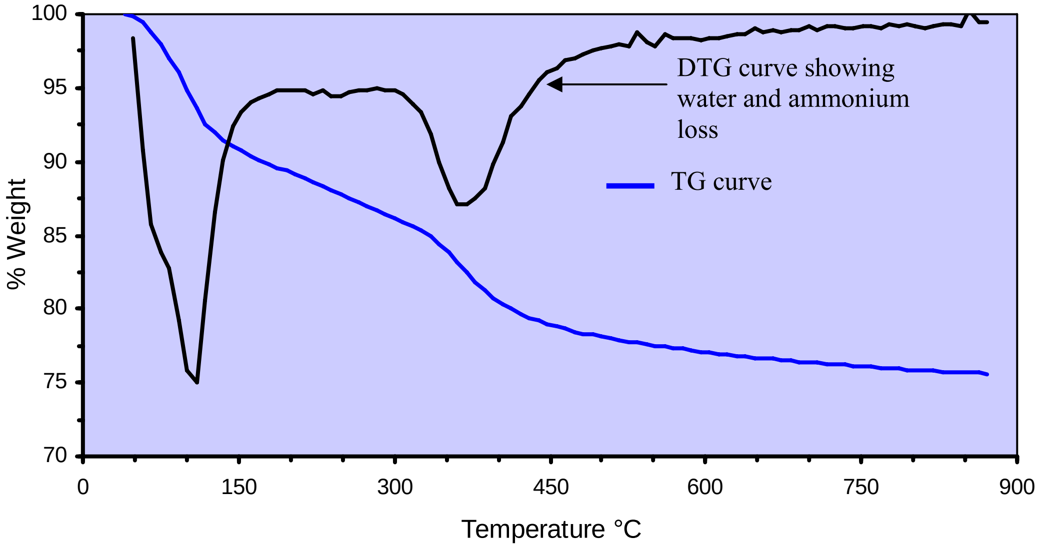


Figure 3.28. TGA % Weight loss curve of natural Phillipsite after ion exchange.

The unit cell composition of ion exchanged natural Phillipsite calculated from XRF data is: $K_{0.58}(NH_4)_{3.30}Fe_{0.47}$ $[Al_{3.61}Si_{12}O_{31.22}]$: $11.34H_2O$.

Table 3.11. Elemental oxides (% wt) of natural Phillipsite after ion exchange.

Elemental Oxide	% Wt of element
SiO_2	60.80
Al_2O_3	15.50
K_2O	2.31
Na_2O	0.00
Fe_2O_3	3.19
P_2O_5	0.62
CaO	0.48
TiO_2	0.17
Others	0.20
Volatile Content	21.35

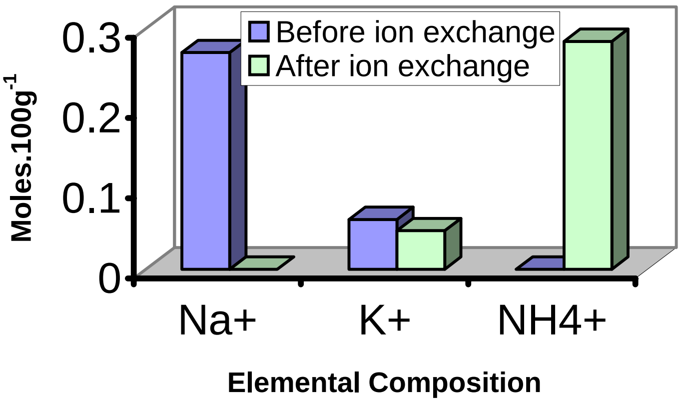


Figure 3.29. Natural Phillipsite moles/100g of Na^+, K^+ and NH_4^+ before and after ion exchange, as calculated from Tables 4.10 and 4.11.

3.7. Particle size

Particle size analysis was carried out on pre-and post-ion exchanged zeolites, as discussed in Section 2.6. As-synthesized zeolite material varied from 2-1000 µm, depending on zeolite type. Comparisons are made between pre-and post-ion exchanged zeolite samples, in order to establish particle size variation. Particle sizes along with surface area analysis of zeolites were used to construct a hypothesis to establish the diffusion and ion exchange properties of as-synthesized zeolites.

For instance, on comparing the particle size distribution of high-crystalline Phillipsite versus high-aluminium Phillipsite for Glasshouse Experiment 3, a very similar trend of particle size distribution was evident (Figure 3.30 and 3.31) before and after ion exchange. A very high (~ 90%) distribution of zeolite particles and a similar trend both before and after ion exchange (Figure 3.31) in the range of 15-125 µm for high-crystalline Phillipsite signifies uniformity of this zeolite compared to a widespread distribution of particles both before and after ion exchange for high-aluminium Phillipsite. It is evident from these histograms that the gel aged before crystallization (high crystalline Phillipsite) differs from an unaged gel (high aluminium Phillipsite) not only in narrowing the dimensional distribution of crystals in crystallization products, but also in a large percentage of larger crystals falling within a certain particle size range. Particle size analysis is also critical for comparing two different zeolites added as soil amendments in each glasshouse experiment. Although particle sizes differ between zeolites, they were introduced after ion exchange without any ball milling/sieving (Except in the case of natural Phillipsite) to study their characteristics as a soil amendment for comparison purposes and also to consider their diffusion and ion exchange properties in each glasshouse experiment. Particle size distribution of as-synthesized zeolites (pre-and post-ion exchanged) are shown below in Figures 3.30-3.35 and discussed in Section 3.9.

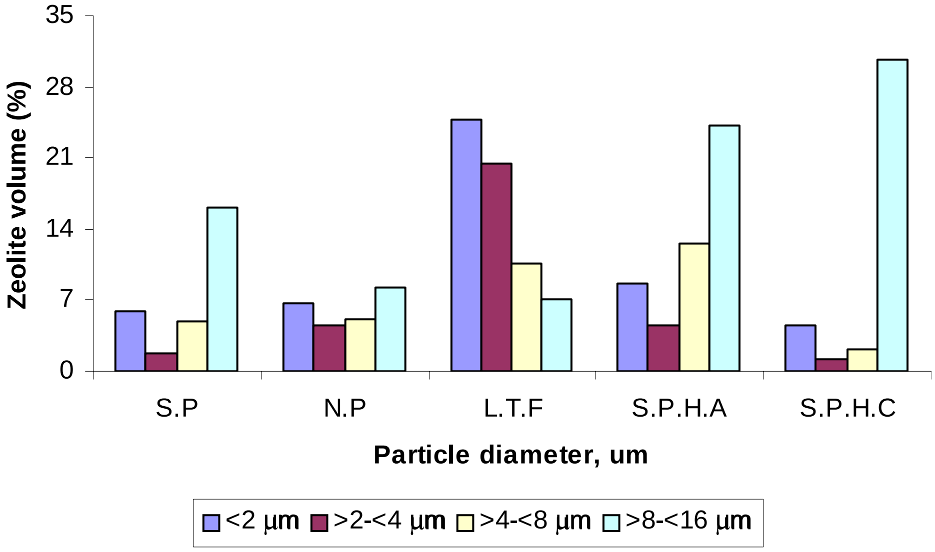


Figure 3.30. Particle size distribution from 2-16 µm of zeolites: S.P. synthetic Phillipsite; N.P. natural Phillipsite; L.T.F. Linde type F; S.P.H.A. synthetic Phillipsite high-aluminium; S.P.H.C. synthetic Phillipsite high crystalline before ion exchange.

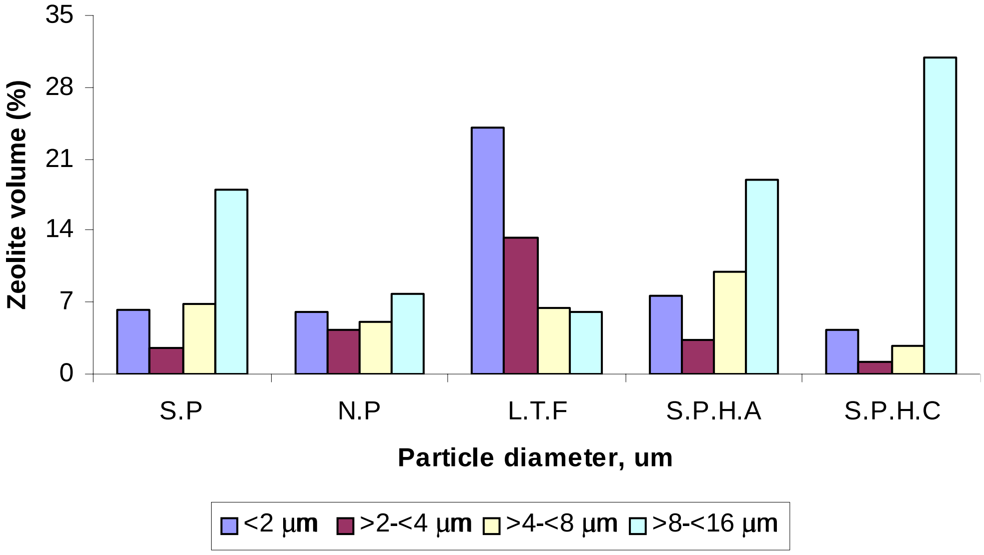


Figure 3.31. Particle size distribution from 2-16 µm of zeolites: S.P. synthetic Phillipsite; N.P. natural Phillipsite; L.T.F. Linde type F; S.P.H.A. synthetic Phillipsite high-aluminium; S.P.H.C. synthetic Phillipsite high crystalline after ion exchange.

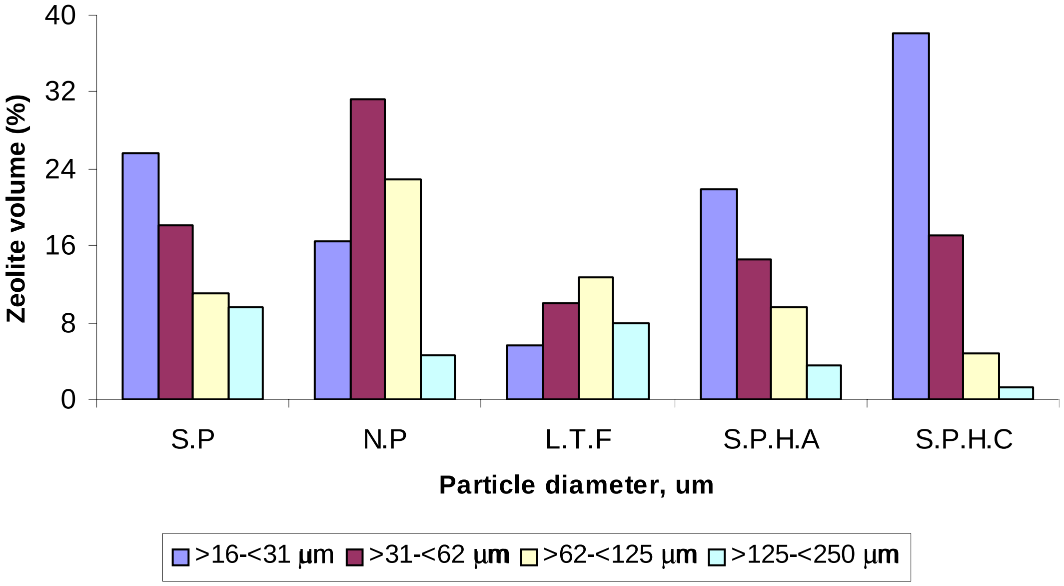


Figure 3.32. Particle size distribution from 31-250 µm of zeolites: S.P. synthetic Phillipsite; N.P. natural Phillipsite; L.T.F. Linde type F; S.P.H.A. synthetic Phillipsite high-aluminium; S.P.H.C. synthetic Phillipsite high crystalline before ion exchange.

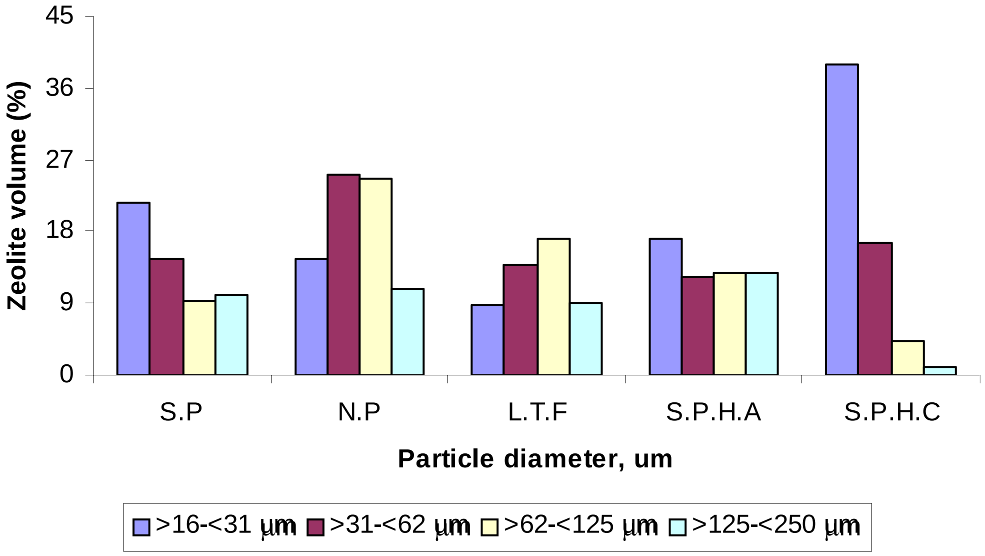


Figure 3.33. Particle size distribution from 31-250 µm of zeolites: S.P. synthetic Phillipsite; N.P. natural Phillipsite; L.T.F. Linde type F; S.P.H.A. synthetic Phillipsite high-aluminium; S.P.H.C. synthetic Phillipsite high crystalline after ion exchange.

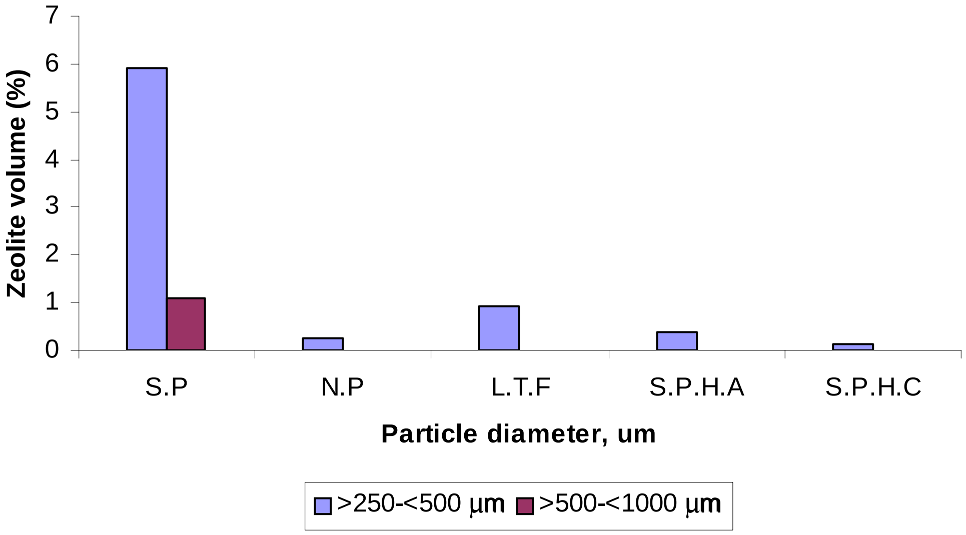


Figure 3.34. Particle size distribution from 500-1000 µm of zeolites: S.P. synthetic Phillipsite; N.P. natural Phillipsite; L.T.F. Linde type F; S.P.H.A. synthetic Phillipsite high-aluminium; S.P.H.C. synthetic Phillipsite high crystalline before ion exchange.

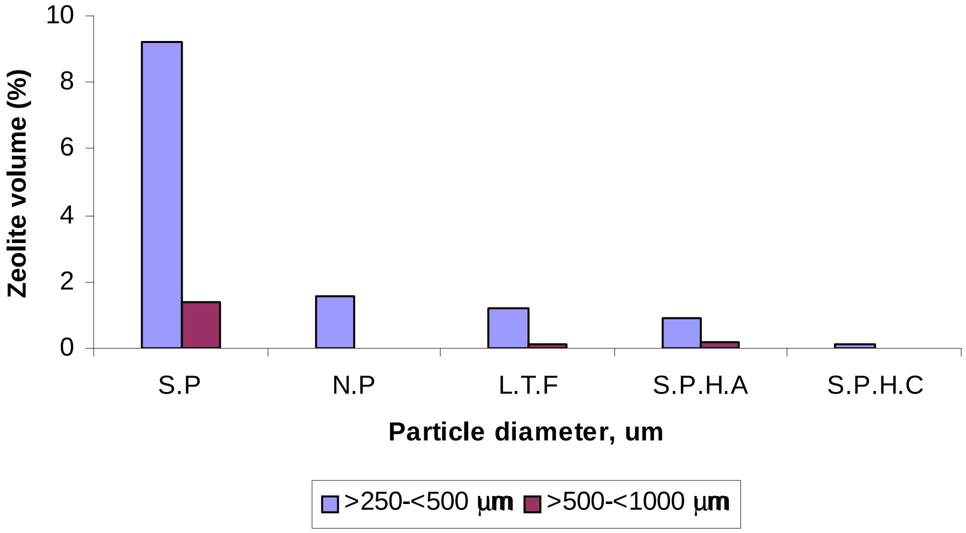


Figure 3.35. Particle size distribution from 500-1000 µm of zeolites: S.P. synthetic Phillipsite; N.P. natural Phillipsite; L.T.F. Linde type F; S.P.H.A. synthetic Phillipsite high-aluminium; S.P.H.C. synthetic Phillipsite high crystalline after ion exchange.

3.8. Surface area

Surface area analysis was carried out on all as-synthesized synthetic and natural pre- and post-ion exchanged zeolite samples using the Brunauer, Emmett and Teller (BET) model of adsorption, as discussed in Section 2.8. Most methods are based on the isothermal adsorption of Nitrogen. Either a single point or multi-point method is used to calculate surface area. Data from the multipoint determination are used to calculate matrix surface area by use of the t-plot method of Lippens and deBoer (1965).

The BET surface area of various zeolites, both before and after ion exchange are shown in Table 3.12. The relationship between surface areas, pore size and particle size distribution together will determine the diffusion and ion exchange properties of zeolites, to construct a model of cation exchange and therefore predict potential slow/controlled release of ammonium in the soil.

Table 3.12. Surface area analysis of zeolites using Beckman Coulter Analyser.

Zeolites	**BET surface area** (m^2/g)	
	Before ion exchange	*After ion exchange*
Synthetic Phillipsite	28.359	36.853
Natural Phillipsite	13.654	15.328
Linde type F	40.662	50.204
High-crystalline Phillipsite	36.324	44.189
High-aluminium Phillipsite	26.356	34.836

3.9. Discussion

The verified synthesis of Phillipsite by Hayhurst (1977) and Linde-type F by Warzywoda and Thompson (1991) were initially used for this work and both zeolites were successfully synthesized. The XRD structures of synthetic Phillipsite and synthetic Linde-type F did match their respective reference patterns both before and after ion exchange (Figures 3.7 and 3.13). Verified synthesis of high-aluminium Phillipsite by Cichocki (1991) was used for later studies and compared with high-crystalline Phillipsite to understand diffusion and ion exchange properties (Figures 3.18 and 3.24). Ion exchange was critical for exchanging NH_4^+ and eliminating Na^+ completely from these zeolites, as Na^+ in high concentrations is detrimental to maize growth (Barbarick and Pirela, 1984). TGA and XRF analysis proved vital tools in estimating the amount of NH_4^+ exchanged into the zeolite and the amount of Na^+/K^+ present in these zeolites both before and after ion exchange (Appendix 1.2). TGA provided two differential weight loss patterns both before and after ion exchange (i.e. the ion exchange samples showing a second peak of NH_3^+ loss along with the water loss peak).

All zeolites were synthesized in bulk, to carry out glasshouse experiments on maize growth (sections 2.8.1-2.8.3). Synthesized and ion exchanged zeolites were checked for reproducibility of structure and framework (Si:Al ratio) after each individual batch of synthesis and ion exchange, by performing XRD and XRF. Uniformity of the structure and composition were established by these characterization techniques, within a batch for a particular zeolite synthesis. After ion exchange a shift in the peak positions of XRD could be assigned to the size of the unit cell and the symmetry of the lattice. A shift towards a lower 2θ indicates an increase in unit cell, and a shift to a higher 2θ indicates a decrease in unit cell. Increase in peak intensities could be associated with the position of the atoms and the scattering power; higher intensity of peaks might be due to a higher X-ray scattering power.

3.9.1. Release of NH_4^+ from zeolites

All five zeolites used for this study were introduced as a soil amendment to investigate release of NH_4^+ from these zeolites and to establish ion exchange phenomena of cations present in soil with cations present in exchange sites within the channels of zeolite frameworks. Ion exchange is an intrinsic property of many zeolites, the channels and cages within zeolites are such that intracrystalline water is occluded readily and consequently cations are mobile. High aluminium zeolites, in particular Linde type F and high aluminium Phillipsite have higher NH_4^+ content (Table 3.13). When introduced as a soil amendment, exchange of NH_4^+ with cations present in soil is greatly influenced by the external surface area and internal micropore volume of that particular zeolite. Ionic radii of cations also play a vital role in ion exchange, and finally the cation exchange selectivity of a particular zeolite can inhibit or promote NH_4^+ exchange (Szostak, 1989). This phenomenon can be demonstrated in the case of Linde type F, whereby high affinity of this zeolite towards ammonium might inhibit its exchange for other cations present in soil, thereby leading to nitrogen deficiency in soils when used as an alternative N fertilizer.

Table 3.13. Zeolites with Si:Al ratios and their corresponding ammonium uptake.

Zeolites	**Cation System**	**Si:Al ratio**	**Nitrogen present before ion exchange**	**Nitrogen present as NH_4^+ (g/100g) after ion exchange**
Synthetic Phillipsite	Na, K	2.35: 1	0	6.85
Natural Phillipsite	Na, K	3.20: 1	0	5.79
Linde type F	K	1.55: 1	0	7.58
High-aluminium synthetic Phillipsite	Na, K	1.95: 1	0	7.13
High-crystalline synthetic Phillipsite	Na, K	2.41: 1	0	6.71

It is evident from its ionic radii that ammonium ions are larger than the mono or divalent exchangeable cations present in soil, therefore its release from a zeolite depends upon its cation exchange capacity along with its selectivity for monovalent cations (K^+, Na^+) over divalent cations (Ca^{2+}, Mg^{2+}). Kovanda and Ruzek (1996) showed on exchanging ammonium enriched zeolite P_c and solutions containing K^+, Na^+, Ca^{2+} and Mg^{2+}, 50% of the exchange reaction occurred within the first two hours for monovalent cations, whereas it took 12-16 hours to complete 50% of exchange reaction for divalent cations.

3.9.2. Cation exchange in Zeolites

Zeolites with a lower Si:Al ratio take up more NH_4^+ compared to zeolites with a higher Si:Al ratio (Table 3.13). High aluminium content in the zeolite framework suggests higher negative charge deficit, and to balance out this deficit more cations are incorporated into the framework during synthesis. During ion exchange, cations with a higher ionic radii (NH_4^+) occupy the sites of cations with a smaller ionic radii (Na^+) completely before occupying the sites of other cations with a slightly higher ionic radius. Gualtieri *et al.* (2002) showed that the nature of cations in the extra framework sites during ion exchange selectivity of Phillipsite is mainly ruled by ionic size. K has higher ionic radii than Na, therefore during ion exchange NH_4^+ will occupy Na sites first and then K sites, thereby eliminating Na completely and to some extent K. Ionic radii of some of the major cations are listed in Table 3.14.

Table 3.14. Ionic radii of some major cations used for synthesis and ion exchange of zeolites (Szostak, 1989).

Cations	**Symbol**	**Ionic radii (Å)**
Ammonium	NH_4	1.43
Potassium	K	1.38
Sodium	Na	1.02
Calcium	Ca	0.99
Magnesium	Mg	0.72

As K is an essential plant nutrient, ion exchange was interrupted to avoid complete elimination of this cation from the zeolite framework. Duration of ion exchange was altered for any two zeolites used for a particular glasshouse experiment in order to facilitate equal amounts of K in these zeolites for comparison as discussed in section 2.5. Once introduced as a soil amendment for all three Glasshouse experiments, NH_4^+ present in the framework of all these five zeolites (Table 3.13) was released at a rate dependent upon surface area and cation exchange capacity. Dwairi (1998) evaluated Jordanian Phillipsite tuff as a controlled release fertilizer and explained ammonium ions released by acidic deionised water is a cation exchange reaction:

NH_4^+-Phillipsite + H^+ = H^+ -Phillipsite + NH_4^+ (3.4)

The release of NH_4^+ ions from zeolite into the soil is a complicated process, strongly influenced by the kinetics of cation exchange reactions between the zeolite and the soil solution and by conditions under which a dynamic equilibrium in the soil system can be established.

3.9.3. Variation in zeolite structures

The zeolites used for this work were synthetic Phillipsite, natural Phillipsite, Linde type F, high-aluminium Phillipsite and high-crystalline Phillipsite. Based on Glasshouse Experiments 1 and 2, whereby ammonium-exchanged zeolites were used as soil amendments, Phillipsite was selected to be the best potential controlled release fertilizer compared with its natural counterpart and Linde type F. It was therefore decided to synthesize a low crystalline high-aluminium, and high-crystalline low aluminium Phillipsite for Glasshouse Experiment 3, to study ion exchange and diffusion properties of these zeolites, particularly affecting the release of NH_4^+ from their channel system. High aluminium Phillipsite incorporates more NH_4^+ due to its higher negative charge deficit and can be a useful N fertilizer amendment for low nitrogen soils. Crystallinity of these zeolites was established by XRD patterns, taking into account major peak intensities at their same respective $^{o}2\theta$ angles (Figure 3.36).

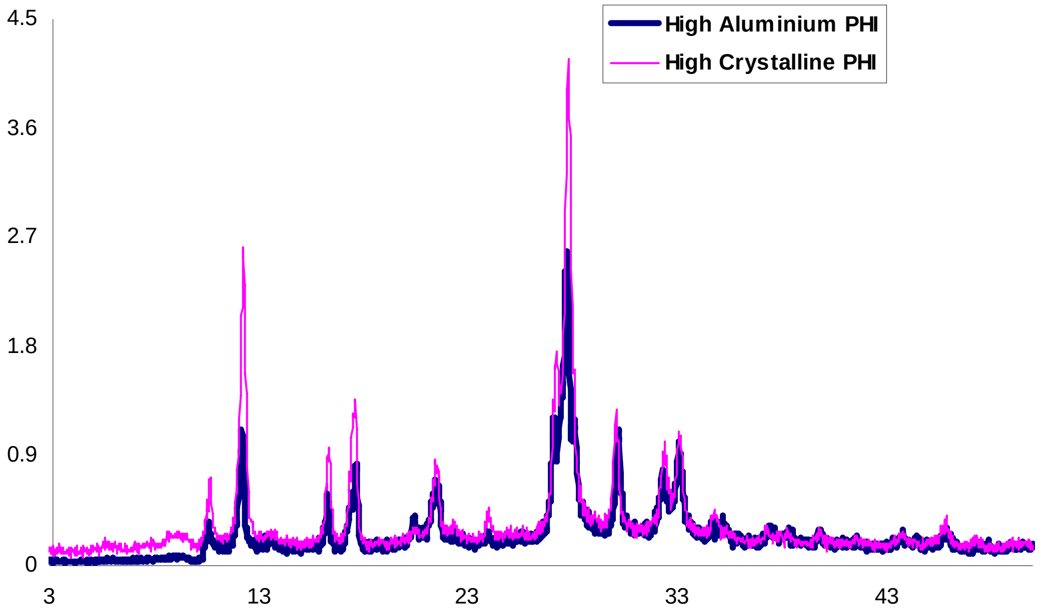


Figure 3.36. Peak intensities from XRD 3-D patterns of as-synthesized high-aluminium and high-crystalline Phillipsite after ion exchange.

High-aluminium Phillipsite shows low peak intensities compared to high-crystalline Phillipsite both before and after ion exchange (Figures 3.18 and 3.24) and also the particle size distribution for this zeolite showed a wide variation with respect to high-crystalline Phillipsite, with a much more uniform particle size distribution (Figures 3.37 and 3.38). Ageing played a vital role in the crystallization process during zeolite synthesis. On ageing an aluminosilicate gel, notable changes occurred in their colloidal structure and are evident as decrease in surface area and crystal growth with increase in ageing time. This can be associated with recondensation (i.e. with dissolution of small particles when the gels are aged, due to high solubility of these particles and also with the mass transfer of larger particles to the surfaces and into the gaps between them, (Breck, 1973). During ageing (i.e. during the time gel is held at room temperature before the start of heating), zeolite crystal nuclei can be formed in the gel. The number of nuclei formed in the gel and the rate of crystallization of gel on subsequent heating are increased with increased ageing time. Zhdanov *et al.* (1990) showed that holding the gel at room temperature for longer before crystallization leads to a decrease in the average or the maximum crystal dimensions and also significantly narrows the limits of their size distribution, thereby supporting the above result. It can therefore be assumed that acceleration of the crystallization process can be due to large number of nuclei already formed in the gels during the ageing process (i.e., up to the start of the heating process), or due to high rates of nucleation in gels subjected to ageing during crystallization itself.

Considering synthetic Phillipsite and Linde type F zeolites, a much wider particle size distribution is observed (Appendix 1.4), and can be explained by these zeolites being synthesized without any preliminary ageing of the reaction gel. The uniformity of particle size of aged reaction gel showed a highly crystalline final product compared to an unaged reaction gel (Figure 3.36), with higher peak intensities. Surface area measurements were carried out for zeolite samples to determine total surface area, total pore volume, micropore surface area and micropore volume affecting the rate of exchange and diffusion. Aged high crystalline Phillipsite has a high % of zeolite crystals within the range of 10-100 μm thereby narrowing down the particle size distribution (Figure 3.37), whereas non-aged high aluminium Phillipsite has a wider distribution of zeolite crystals from 1-1000 μm (Figure 3.38).

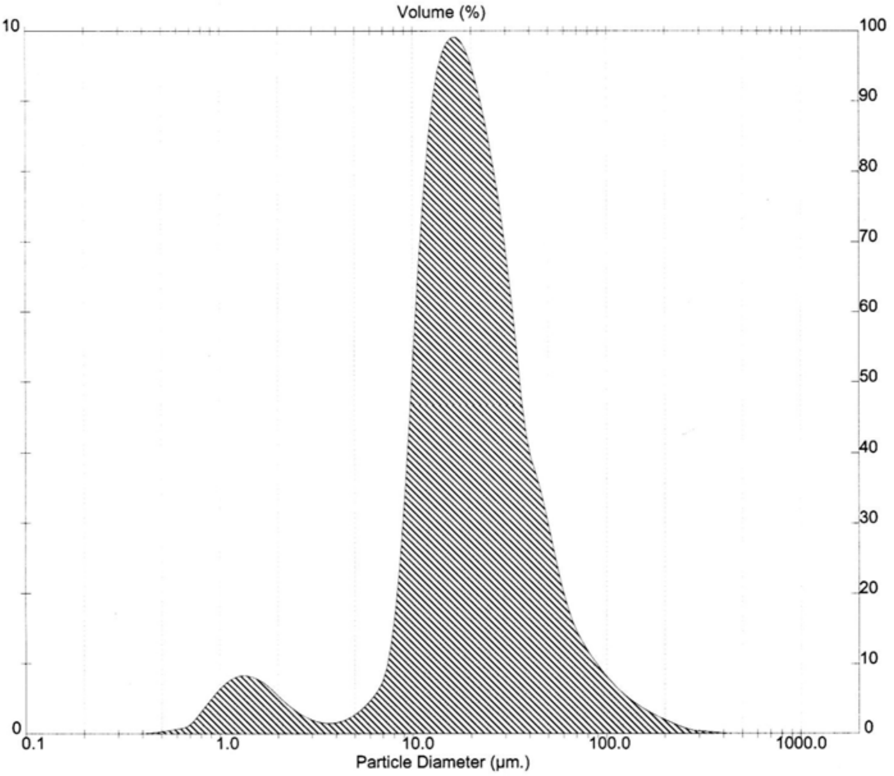


Figure 3.37. Particle size distribution of as-synthesized aged high-crystalline Phillipsite.

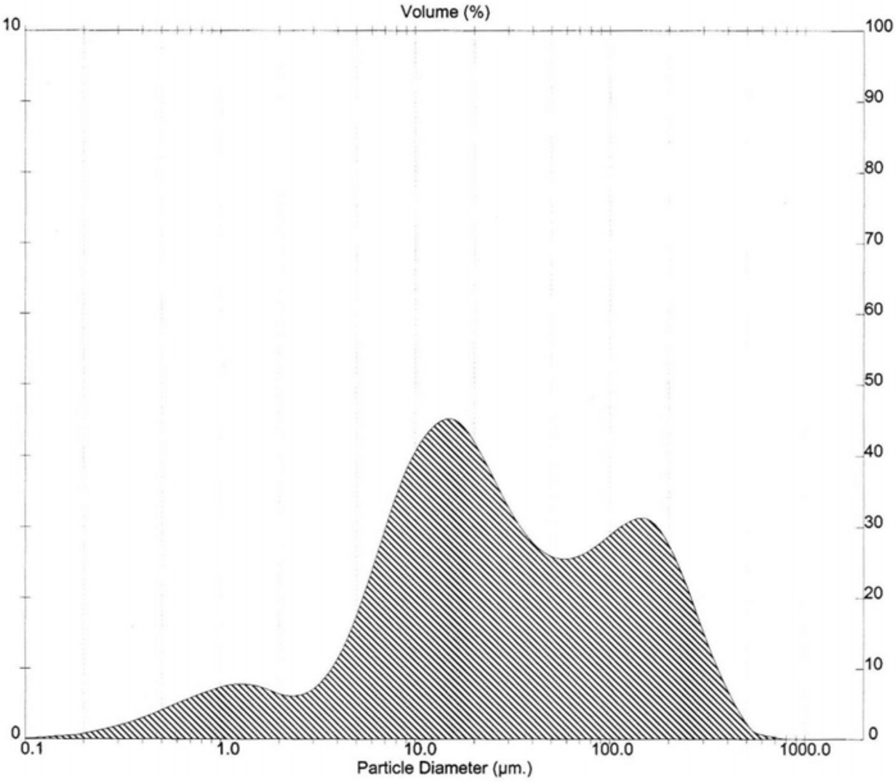


Figure 3.38. Particle size distribution of as-synthesized unaged high-aluminium Phillipsite.

A constructive hypothesis can be derived from Figures 3.37-3.38. High crystalline Phillipsite might be a potential source of increased ion exchange in soil due to its uniformity, larger crystal size and smaller particle size distribution compared to high aluminium Phillipsite with smaller crystal sizes and larger particle size distribution. Falabella *et al.* (1998) showed that zeolites with very small crystallites present low crystallinity, because the crystal sizes are below the detection limit of the technique used (X-ray diffraction). Therefore, it can be assumed that low crystallinity values obtained for small crystallite zeolites do not always indicate a decrease in crystallinity; therefore the above assumption may only be a possibility.

The most commonly used *t*-plot method developed by Lippens and deBoer (1965) was used for surface area analysis of zeolites. This method allows evaluation of external surface area and micropore volume by plotting the adsorbed volume against the statistical thickness *t* of the adsorbed N_2 layer. Under the conditions of BET measurement, N_2 molecules condense, filling the micropore volume. Thus BET area of a zeolite is really the equivalent area that would be covered by the quantity of sorbate required to fill the intracrystalline pores if molecules were arranged as a close packed monolayer. It does not correspond to internal area of the framework. Surface areas of all five zeolites used in this study are presented in Table 3.12.

Furthermore, the differences in crystallite sizes will be reflected in the values of external surface area, i.e. zeolites with smaller crystallites should exhibit considerably higher external surface areas. On comparing surface area values (Table 3.12) and particle size distribution for zeolites, it is evident that highly crystalline Phillipsite has smaller crystallites (Figure 3.37) with a larger surface area, whereas high aluminium Phillipsite has larger crystallites (Figure 3.38) with a smaller surface area. Similarly synthetic Phillipsite and natural Phillipsite have larger crystallites with a smaller surface area and Linde type F has smaller crystallites with a larger surface area.

From these results the gradual influence of adsorption on external surface of a zeolite is clear. The higher the external surface area, the stronger is the contribution to adsorbed volume, and thereby micropore volume filling of a zeolite is dependent on the external surface area. Internal micropore volume filling and external surface area also influence ion exchange (i.e. zeolites with larger surface area increase the rate of exchange process compared to zeolites with a smaller surface area) (Breck, 1973).

A model can therefore be deduced taking into consideration particle size distribution and surface area of zeolites. The larger the particle size (zeolite crystallites), the smaller is the surface area and therefore a possible decrease in ion exchange capacity, whereas the smaller the particle size the higher is the surface area and thereby there might be an increase in the ion exchange capacity of these zeolites. A model to explain the release dynamics of NH_4^+ from all five zeolites used in this study with regard to plant and soil analysis from all three-glasshouse experiments is discussed in Chapter 5.

3.10. Conclusions

Based on synthesis, ion exchange, surface area and particle size distribution the following conclusions can be derived for both synthetic and natural zeolites.

(1) All four zeolites used for this study were successfully synthesized and ion exchanged, to eliminate Na^+ completely and to introduce NH_4^+ into the framework.

(2) In both synthetic and natural Phillipsite forms, the K^+ concentrations were successfully reduced from their original concentration by ion exchange with NH_4^+, thereby enabling the zeolites to be rich in NH_4^+ and low in K^+. The same principle applied for Linde type F, high aluminium Phillipsite and high crystalline Phillipsite whereby; the original K^+ concentrations were reduced after ion exchange with NH_4^+.

(3) Analysis of surface area and particle size distribution provided an outline as to the physical properties of these materials, and might give an insight into the exchange of cations in and out of their framework, when introduced as soil amendments.

Following synthesis and ion exchange, synthetic and natural zeolites were introduced as soil amendments and studied in Glasshouse Experiments 1, 2 and 3. Comparative studies with conventional fertilizers were conducted following with, synthetic Phillipsite vs. natural Phillipsite (Glasshouse Experiment 1), synthetic Phillipsite vs. synthetic Linde type F (Glasshouse Experiment 2) and synthetic Phillipsite (high crystalline) vs. synthetic Phillipsite (high aluminium) (Glasshouse Experiment 3). Results of all three Glasshouse experiments are presented in Chapter 4.

Chapter 4

Glasshouse Experiments

Introduction

In this chapter, experimental data along with statistical analyses for all three Glasshouse Experiments are presented. Research focused on studying the effects of zeolites on vegetative growth (Glasshouse experiments 1 and 2), and both vegetative and reproductive growth until cob formation (Glasshouse Experiment 3) of potted maize plants, along with slow release of ammonium from zeolites when added as soil amendments. Previous studies showed ammonium (NH_4^+) exchanged natural Phillipsite to be a potential slow release fertilizer; all three Glasshouse experiments were therefore aimed to investigate the effectiveness of ammonium ion exchanged zeolites as soil amendments, to select the zeolitic soil amendment to both increase plant growth and decrease nitrate leaching. In order to increase crop yield, farmers have practiced multiple fertilizer application during the plant growth cycle for years. If zeolites were used as soil amendments, controlled release of ammonium from these microporous materials into the soils could be a favourable alternative in providing N to maize plants until the grain-filling phase of the growth cycle, thereby eliminating the frequent fertilizer applications. Ammonium exchanged zeolite application as an alternative fertilizer would therefore not only save labour costs, but could also aid in decreasing nitrate leaching to groundwater, which is a major global concern.

For Glasshouse Experiment 1, synthetic and natural Phillipsite were selected to study their effectiveness as soil amendments for plant growth. For Glasshouse Experiment 2, ammonium exchanged synthetic Phillipsite and synthetic Linde type F were selected as soil amendments. Linde type F was selected for this experiment due to its higher affinity towards ammonium and, synthetic Phillipsite was found to be the more effective soil amendment for plant growth from Glasshouse Experiment 1. For Glasshouse Experiment 3, two different forms of ammonium exchanged synthetic Phillipsite (high aluminium and high crystalline) were used as soil amendments to study how changes in the physico-chemical characteristics of Phillipsite affected the release of ammonium from its framework, thereby affecting maize growth along with nitrate leaching from the soil. As discussed in Sections 2.8.1-2.8.3 (different % w/w loadings of zeolite to soil) were selected for Glasshouse Experiments 1, 2 and 3 in order to examine the effectiveness of lower loaded to higher loaded zeolites in affecting plant growth and soil characteristics, as influenced by ammonium release and cation exchange in and out of zeolite frameworks.

These experiments followed a Complete Randomised Design (CRD), i.e., pots randomly arranged in the Glasshouse following randomly generated numbers using windows statistical software. Analysis took the form of one-way Analysis of Variance (ANOVA) where the variation was due to the differences in the treatments, followed by a test of Least Significant Difference (LSD) for both plant and soil data, at each individual harvest. Two-way ANOVA was used across all three harvests, where the variation was due to the differences in treatments and the time interval between the harvests. Use of LSD is explained in section 2.12.

4.1. Plant growth

A summary of plant growth stage and harvesting for all three Glasshouse Experiments is shown in Table 4.1. Plants were harvested at regular three weekly intervals from the germination date. Harvesting comprised complete destruction of plant material from the point of stem emergence from the soil, followed by measurements of plant height, number of leaves, leaf fresh weight and shoot fresh weight; subsequently oven-dried leaf and shoot dry weights were also measured. Soils from the pots were separated from roots and samples oven-dried to determine moisture content, the remaining soil was left to dry at room temperature for further macro- and micro- nutrient analysis (as discussed in Section 4.2).

Table 4.1. Plant growth and harvesting stages.

Growth stage/Harvesting	Week	Days
First signs of germination	1	7
Destructive harvest 1	4	28
Destructive harvest 2	7	49
Destructive harvest 3	10	70

The experimental study focused on effects of zeolite-amended soils on vegetative growth of maize, nutrient uptake, available nutrients in the soil (Glasshouse Experiments 1-3); ammonium, nitrite and nitrate leaching from soils in comparison with a conventional fertilizer amended soil (Glasshouse Experiments 2 and 3); along with mean cob yield with respect to available nutrients in the soil (Glasshouse Experiment 3). Results from the leaching measurements were related to plant growth, in order to construct a hypothesis of how the use of zeolites can affect nitrate leaching and plant responses to nitrogen.

The size of the pot was selected first to be suitable for the length of the growing period. The number of replicates was determined by a balance between number of treatments and available space in the glasshouse. As the primary focus of the experiment was to study vegetative growth, plants were harvested before cob formation (final harvest at 70 days) for Glasshouse Experiments 1 and 2. After harvesting for the third time (final harvest at 70 days), plants of all 6 treatments from Glasshouse experiment 3 were still left to grow in the glasshouse until cob formation. As twice the amount of soil was used in this experiment compared to Glasshouse Experiments 1 and 2, nutrient availability in soil at later stages of plant growth promoted cob formation. The restriction on number of pots that could be randomized in the glasshouse (Table 2.2), led to the use of smaller size pots for Glasshouse Experiments 1 and 2 (Plate 4.1). For Glasshouse Experiment 3, only 6 treatments were selected therefore the glasshouse could accommodate larger size pots (Plate 4.2).

One Way Analysis of Variance for each harvest followed Post Hoc tests (LSD) with plant height, number of leaves, shoot fresh weight, shoot dry weight, leaf fresh weight and leaf dry weight as the dependent factor and, treatment as the independent factor. Figures 4.1-4.9 show results from Harvests 1, 2 and 3 for all measured plant parameters of Glasshouse Experiment 1, 2 and 3. In these figures treatments with no significant differences between each other, sharing the common letters are not represented above the columns due to the space constrain. Only the treatments with significant differences are represented, with different letters above each column. Significant differences between the zeolitic treatments and controls, along with LSDs between the treatments at $P \leq 0.05$ are represented in these figures to compare treatment effects at different time intervals. The effects on different growth parameters are discussed in sequence.

Plate 4.1. Completely randomized design of pot arrangement in the Cambridge glasshouse for Glasshouse Experiments 1 and 2.

Plate 4.2. Completely randomized design of pot arrangement in the Cambridge glasshouse for Glasshouse Experiment 3.

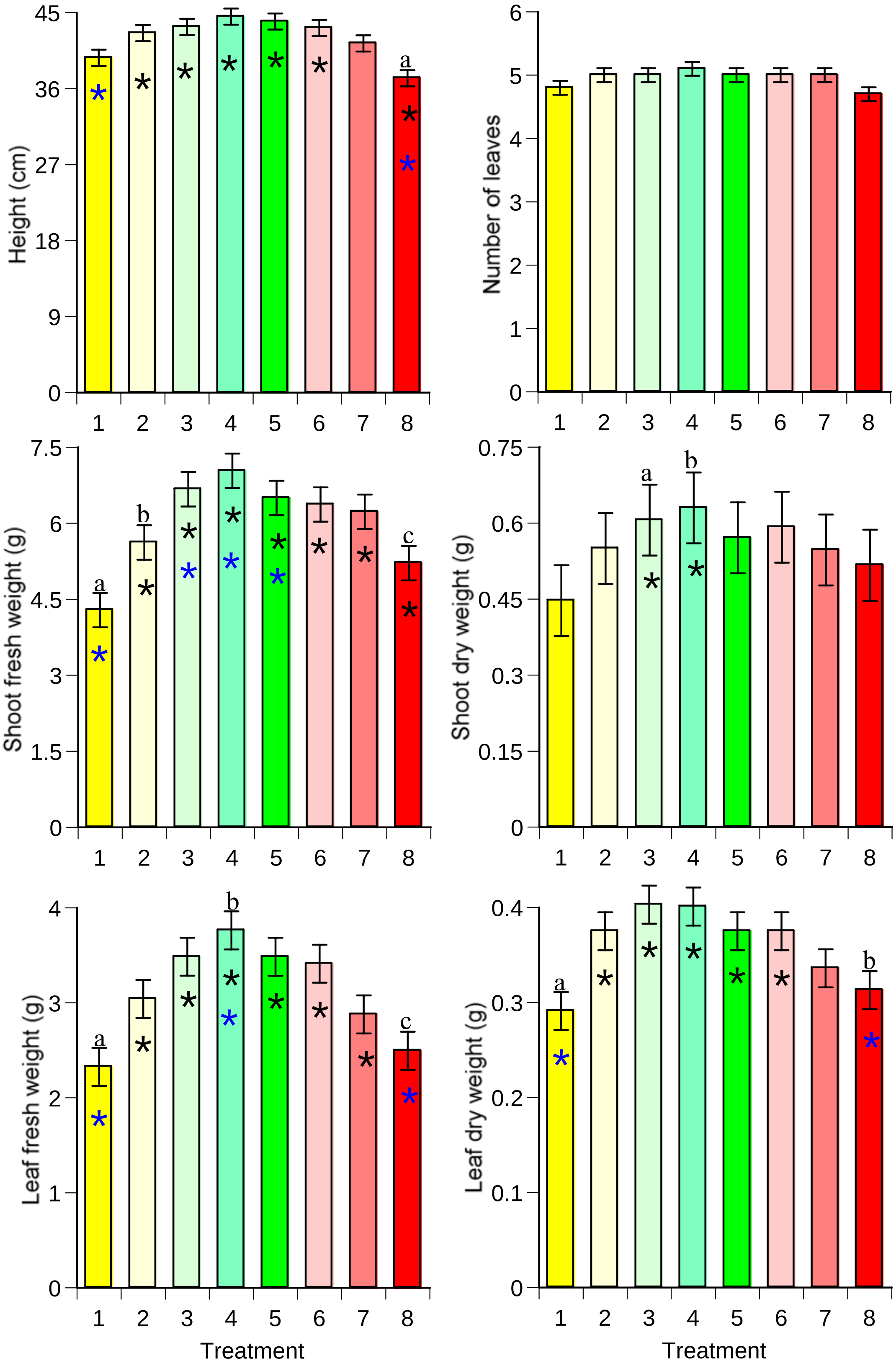


Figure 4.1. Plant growth measurements of Glasshouse Experiment 1; at Harvest 1, for treatments (1) C.High (2) C.Std (3) 2% S.Phillipsite (4) 4% S.Phillipsite (5) 8% S.Phillipsite (6) 2% N.Phillipsite (7) 4% N.Phillipsite and (8) 8% N.Phillipsite. Error bars show ± 1 standard error. ★, Significantly different from C.High and, ★ significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at $p \leq 0.05$) from each other as discussed in section 2.12.

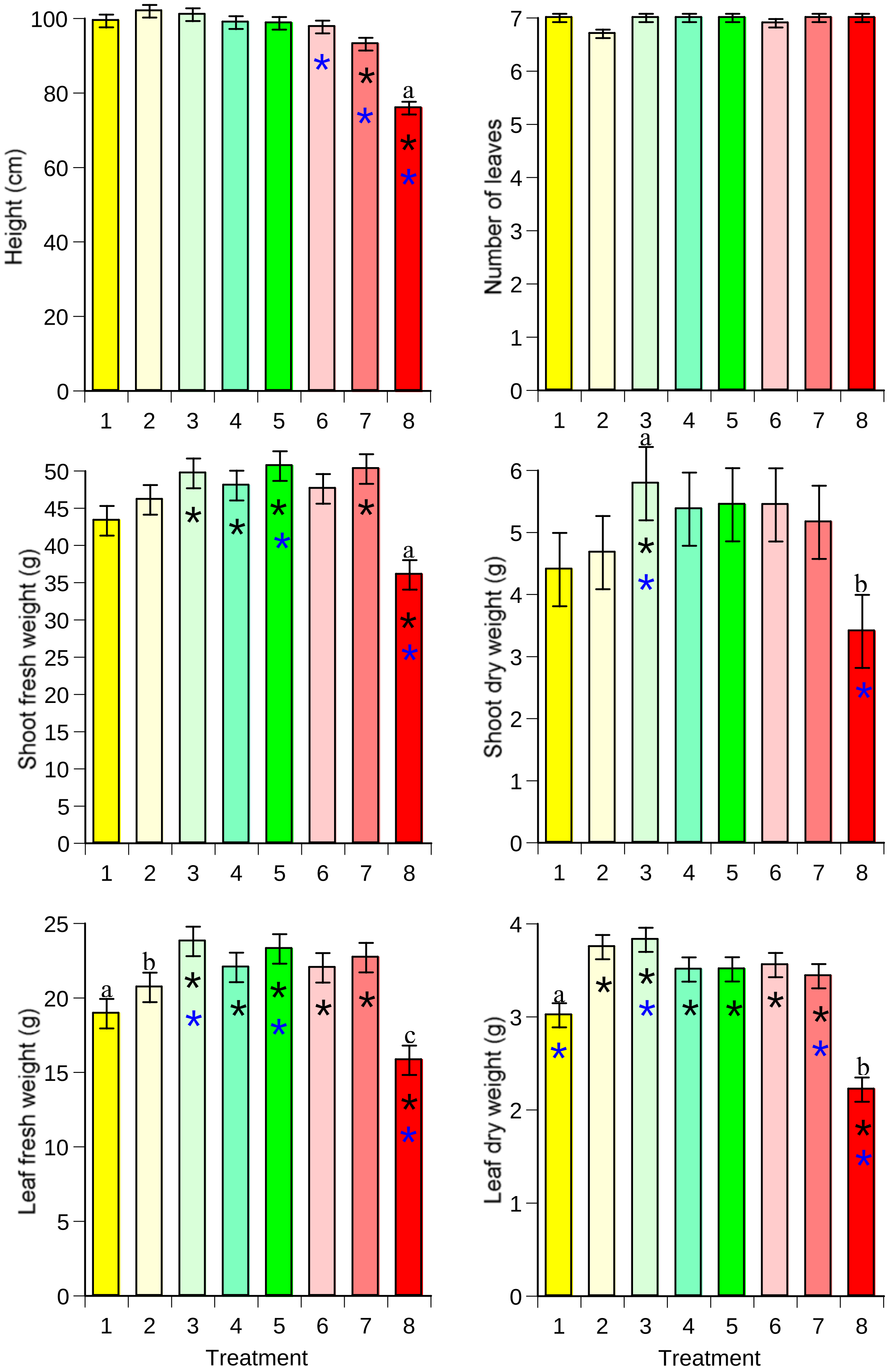


Figure 4.2. Plant growth measurements of Glasshouse Experiment 1; at Harvest 2, for treatments (1) C.High (2) C.Std (3) 2% S.Phillipsite (4) 4% S.Phillipsite (5) 8% S.Phillipsite (6) 2% N.Phillipsite (7) 4% N.Phillipsite and (8) 8% N.Phillipsite. Error bars show ± 1 standard error.★, Significantly different from C.High and, ★ significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at p ≤ 0.05) from each other as discussed in section 2.12.

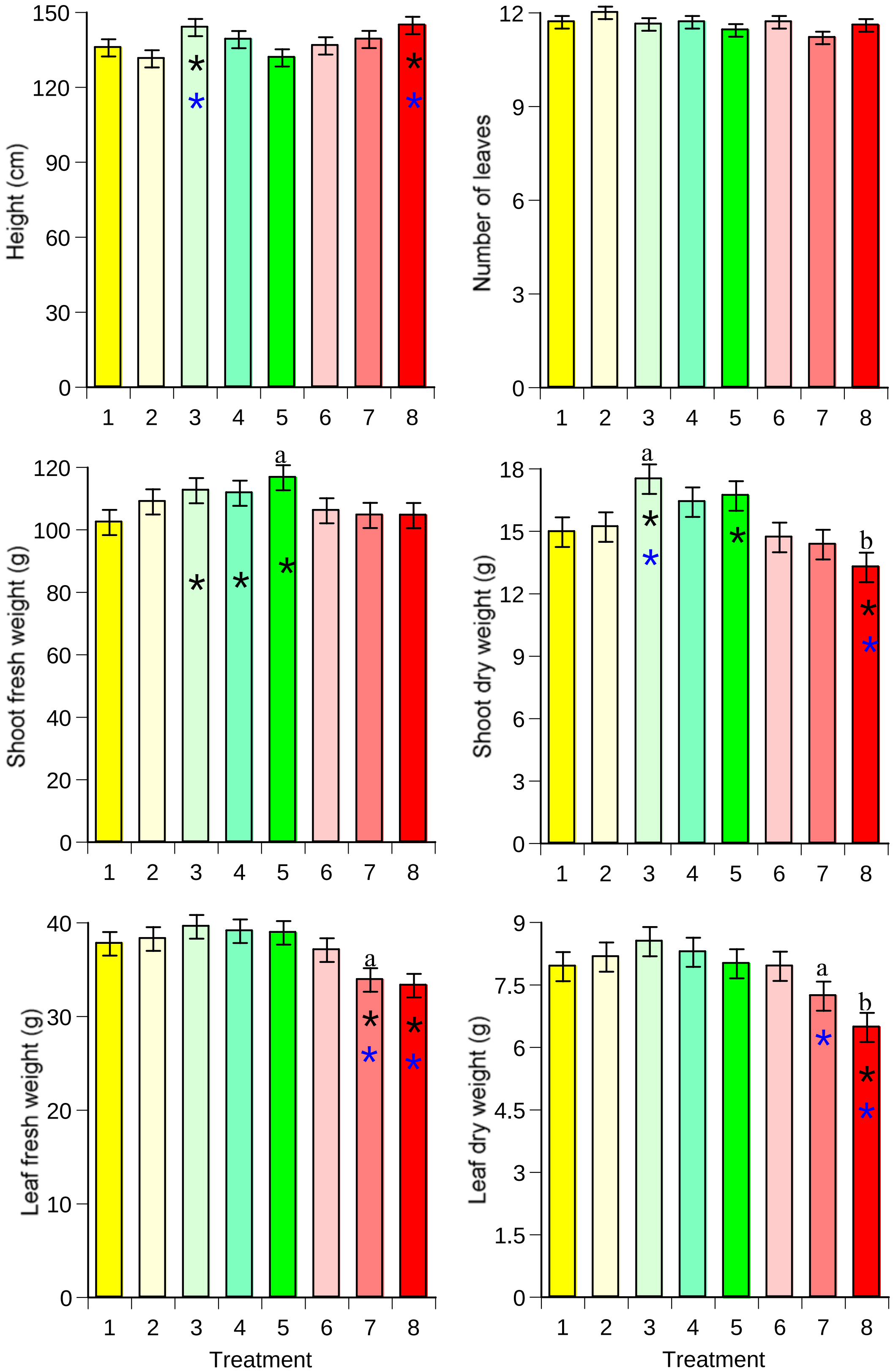


Figure 4.3. Plant growth measurements of Glasshouse Experiment 1; at Harvest 3, for treatments (1) C.High (2) C.Std (3) 2% S.Phillipsite (4) 4% S.Phillipsite (5) 8% S.Phillipsite (6) 2% N.Phillipsite (7) 4% N.Phillipsite and (8) 8% N.Phillipsite. Error bars show ± 1 standard error.★, Significantly different from C.High and ★, significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at p ≤ 0.05) from each other as discussed in section 2.12.

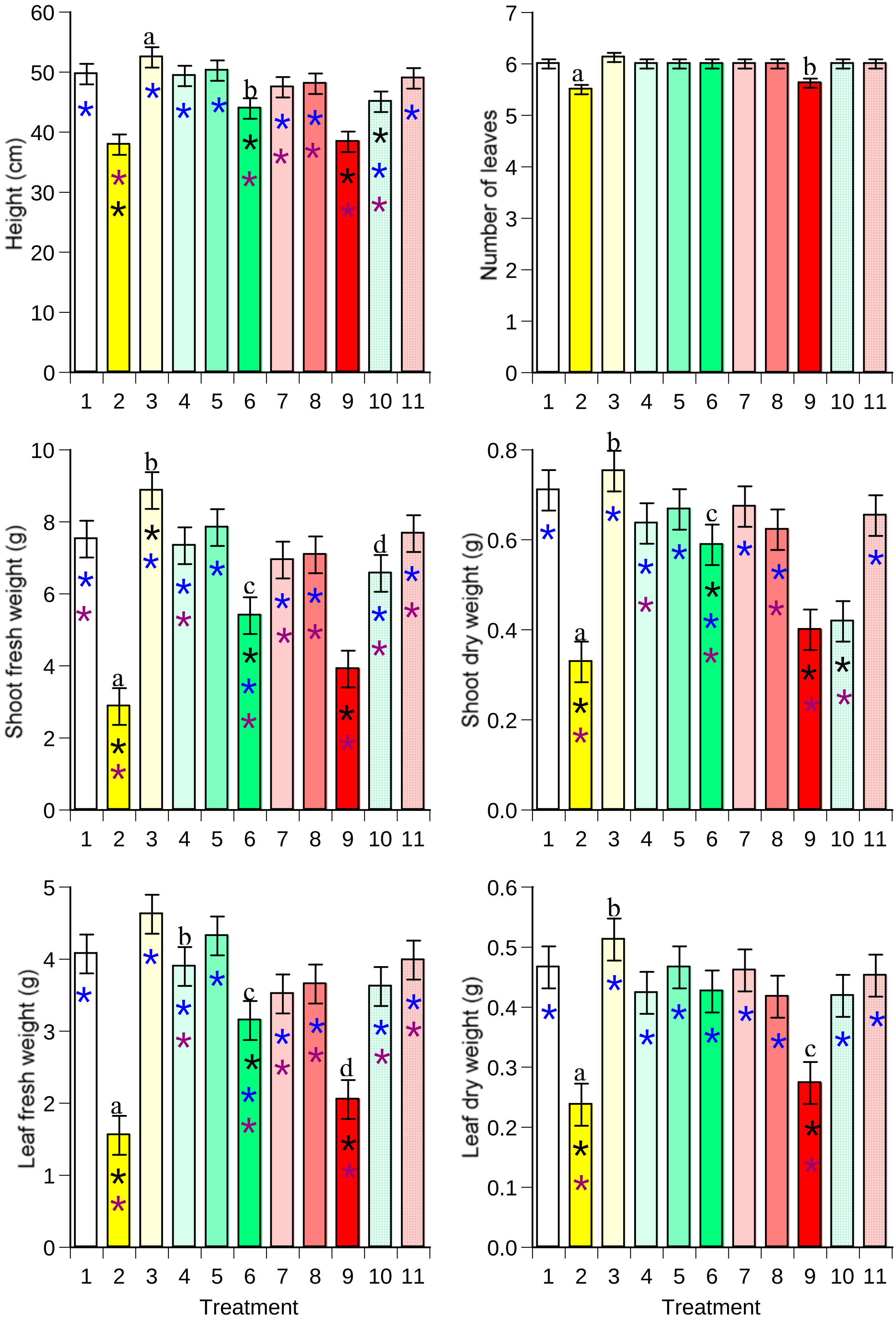


Figure 4.4. Plant growth measurements of Glasshouse Experiment 2; at Harvest 1, for treatments (1) C.Blank (2) C.High (3) C.Std (4) 1% S.Phillipsite (5) 2% S.Phillipsite (6) 4% S.Phillipsite (7) 1% Linde type F (8) 2% Linde type F (9) 4% Linde type F (10) 2% Unexchanged synthetic Phillipsite (11) 2% Unexchanged Linde type F. Error bars show ± 1 standard error.★, Significantly different from C.Blank★, significantly different from C.High and ★ significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at $p \leq 0.05$) from each other as discussed in section 2.12.

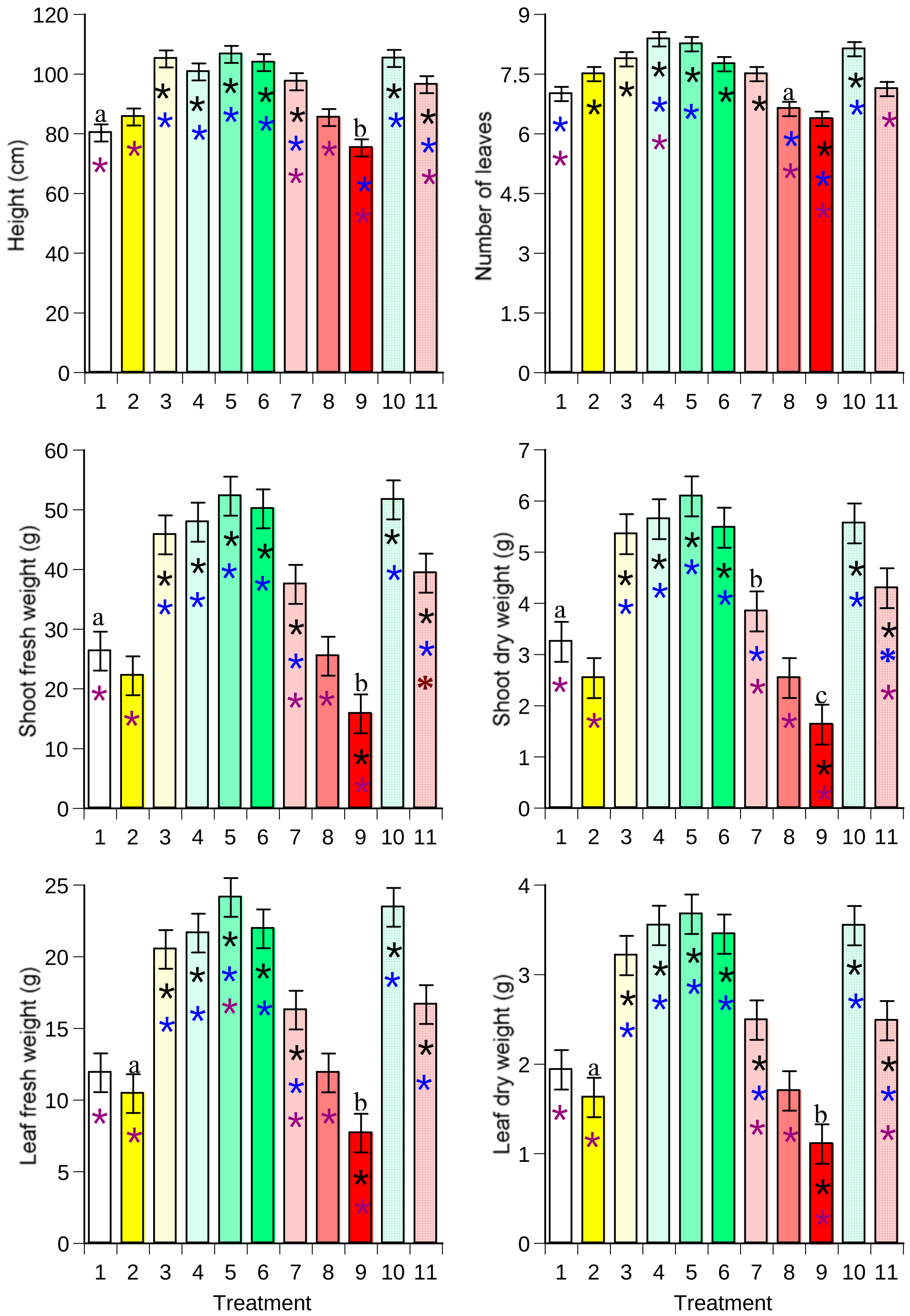


Figure 4.5. Plant growth measurements of Glasshouse Experiment 2; at Harvest 2, for treatments (1) C.Blank (2) C.High (3) C.Std (4) 1% S.Phillipsite (5) 2% S.Phillipsite (6) 4% S.Phillipsite (7) 1% Linde type F (8) 2% Linde type F (9) 4% Linde type F (10) 2% Unexchanged synthetic Phillipsite (11) 2% Unexchanged Linde type F. Error bars show ± 1 standard error.★, Significantly different from C.Blank★, significantly different from C.High and ★ significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at $p \leq 0.05$) from each other as discussed in section 2.12.

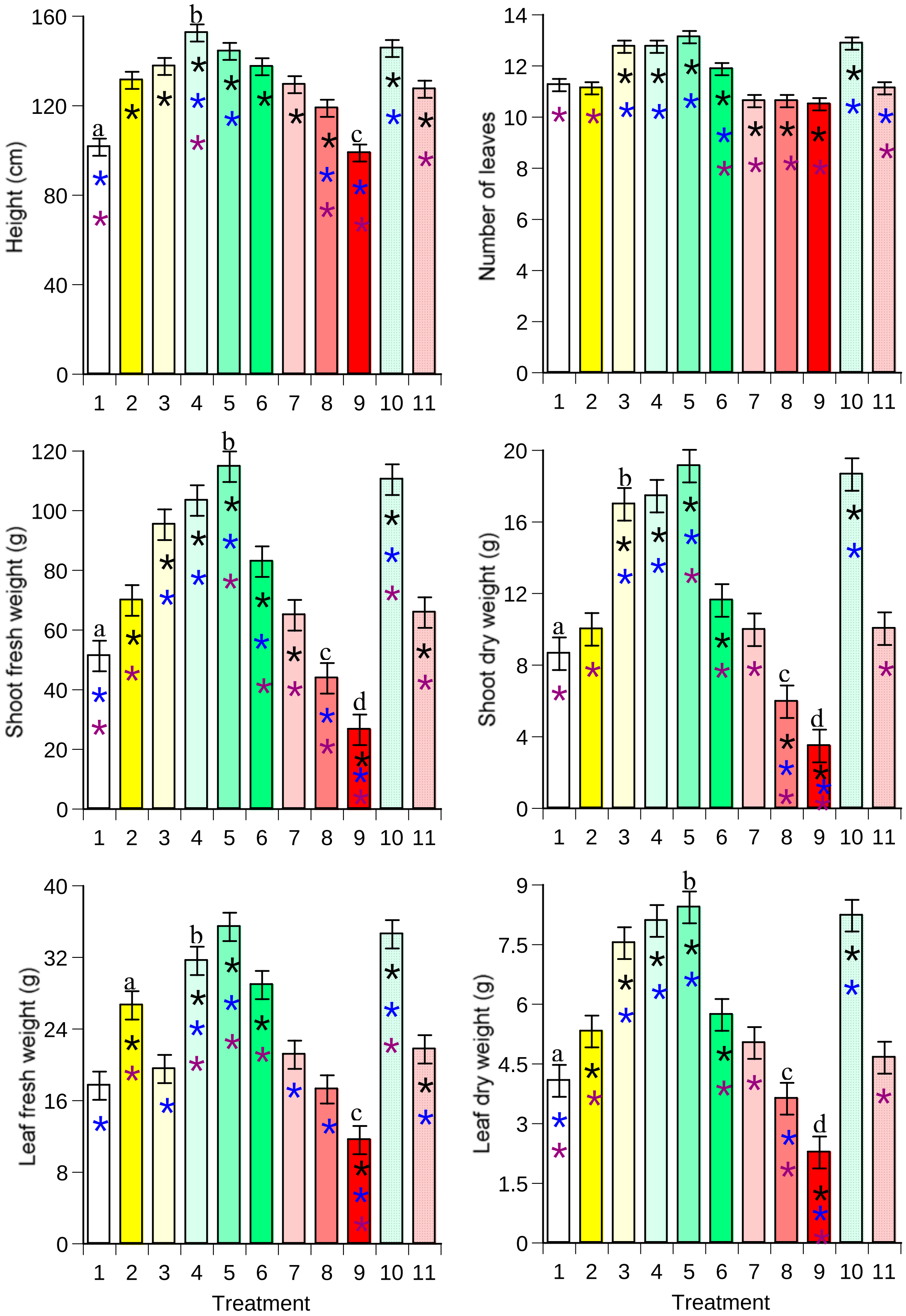


Figure 4.6. Plant growth measurements of Glasshouse Experiment 2; at Harvest 3, for treatments (1) C.Blank (2) C.High (3) C.Std (4) 1% S.Phillipsite (5) 2% S.Phillipsite (6) 4% S.Phillipsite (7) 1% Linde type F (8) 2% Linde type F (9) 4% Linde type F (10) 2% Unexchanged synthetic Phillipsite (11) 2% Unexchanged Linde type F. Error bars show ± 1 standard error.★, Significantly different from C.Blank★, significantly different from C.High and★ significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at $p \leq 0.05$) from each other as discussed in section 2.12.

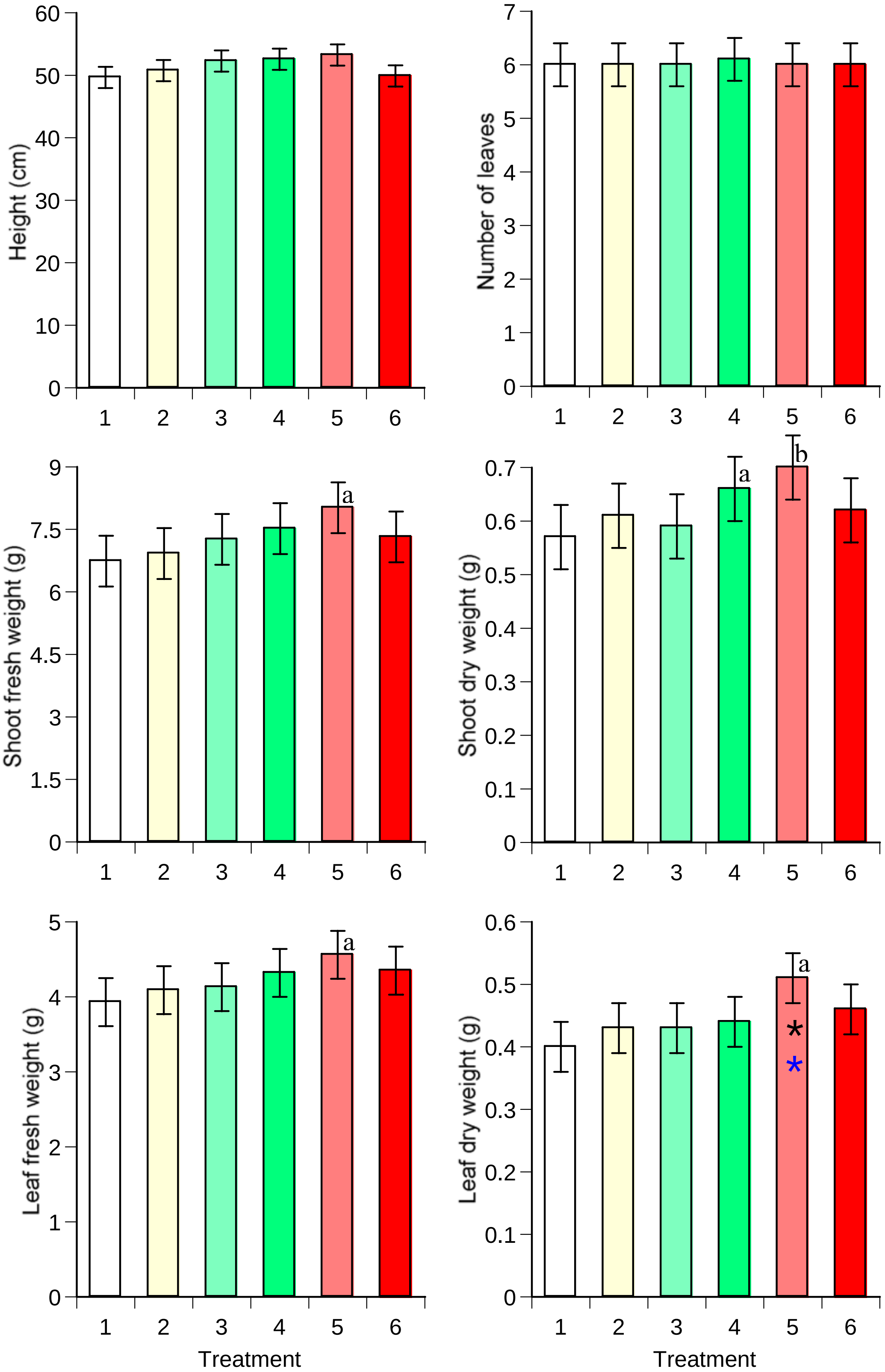


Figure 4.7. Plant growth measurements of Glasshouse Experiment 3; at Harvest 1, for treatments (1) C.Blank (2) C.Std (3) 1% High-aluminium synthetic Phillipsite (4) 2% High-aluminium synthetic Phillipsite (5) 1% High-crystalline synthetic Phillipsite (6) 2% High-crystalline synthetic Phillipsite. Error bars show ± 1 standard error.★, Significantly different from C.Blank and ★, significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at $p \leq 0.05$) from each other as discussed in section 2.12.

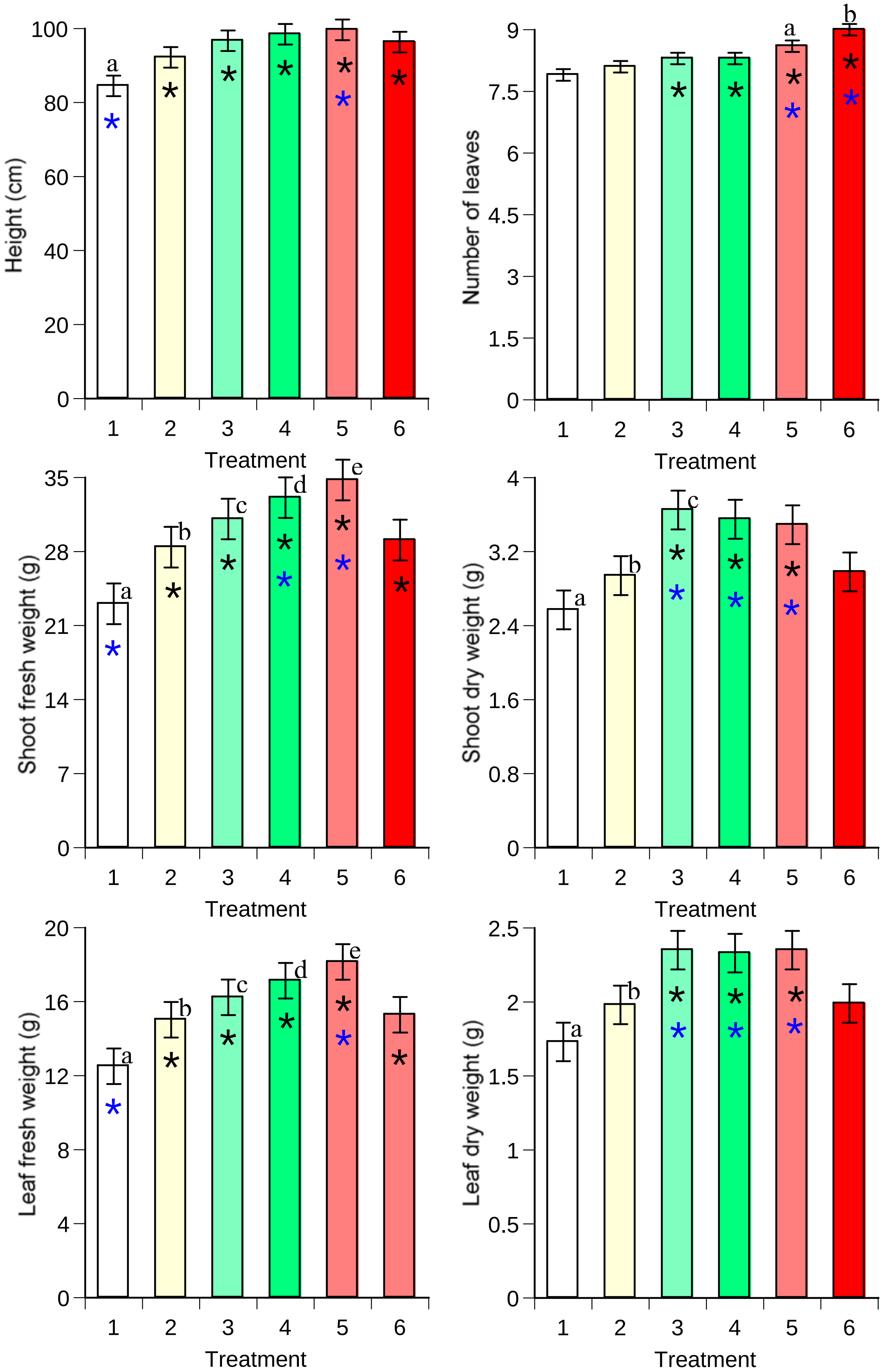


Figure 4.8. Plant growth measurements of Glasshouse Experiment 3; at Harvest 2, for treatments (1) C.Blank (2) C.Std (3) 1% High-aluminium synthetic Phillipsite (4) 2% High-aluminium synthetic Phillipsite (5) 1% High-crystalline synthetic Phillipsite (6) 2% High-crystalline synthetic Phillipsite. Error bars show ± 1 standard error. ★,significantly different from C.Blank★, significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at p ≤ 0.05) from each other as discussed in section 2.12.

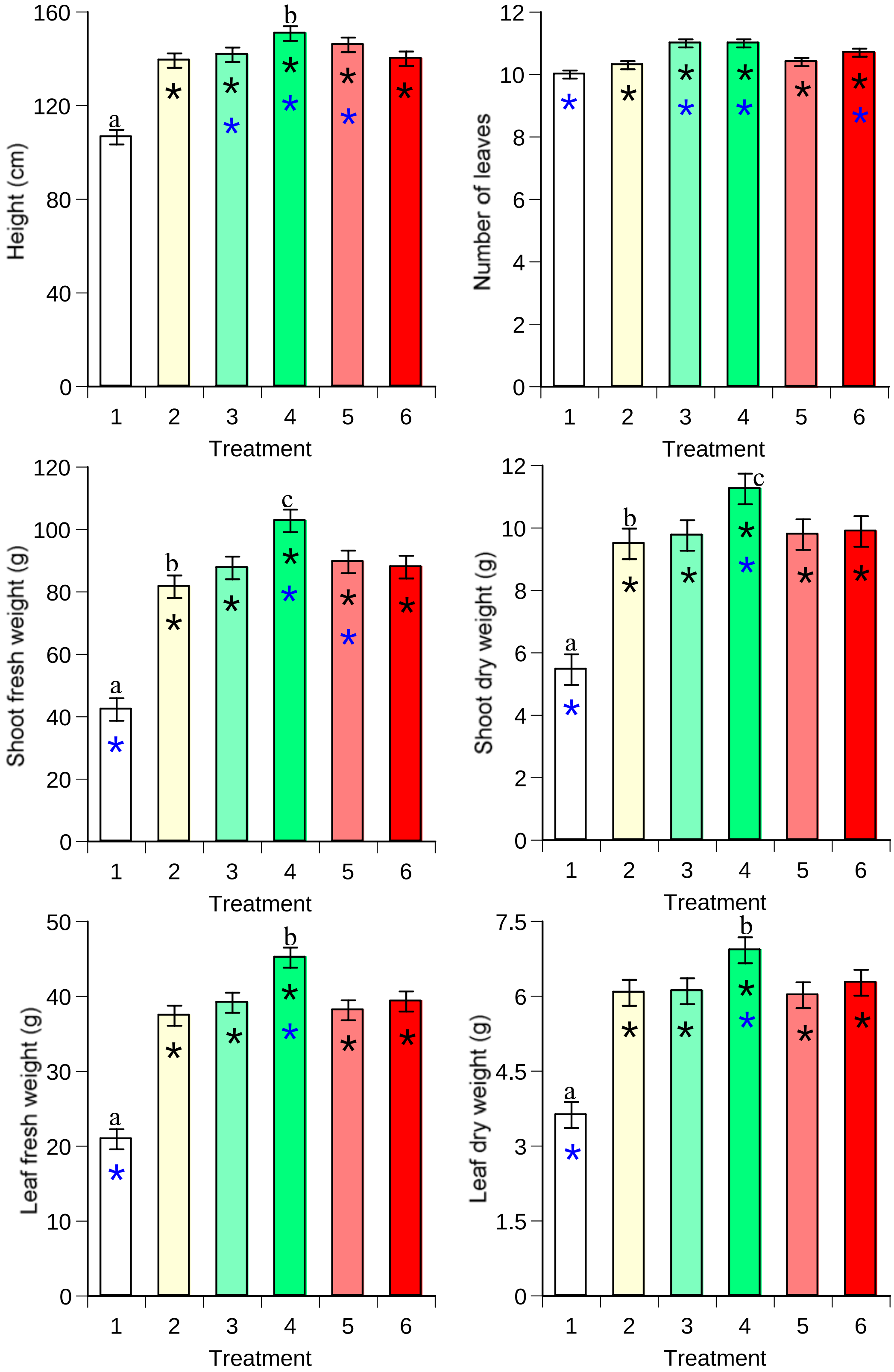


Figure 4.9. Plant growth measurements of Glasshouse Experiment 3; at Harvest 3, for treatments (1) C.Blank (2) C.Standard (3) 1% High-aluminium synthetic Phillipsite (4) 2% High-aluminium synthetic Phillipsite (5) 1% High-crystalline synthetic Phillipsite (6) 2% High-crystalline synthetic Phillipsite. Error bars show ± 1 standard error. ★, Significantly different from C.Blank ★, significantly different from C.Std. Where means have been given different letters above the columns, they are significantly different (at $p \leq 0.05$) from each other as discussed in section 2.12.

4.1.1 Plant Height

Plant height measurements were taken at each destructive harvest. Plant height was measured from the point of plant emergence to the tip of the longest leaf at any particular harvest. On comparison of plant height over time for all three Glasshouse experiments, significant differences for treatment effects were found. This was confirmed by analysis using one-way ANOVA followed by an LSD test. Significant ($p \leq 0.05$) differences were observed between the treatments at Harvests 1, 2 and 3 as represented by letters in Figures 4.1-4.9, discussed below.

For Glasshouse Experiment 1, natural Phillipsite at 8% loading showed significantly ($p \leq 0.05$) lower plant height at Harvests 1 and 2, and none of the synthetic Phillipsite loadings showed any significance at all three Harvests. Although at Harvest 3, 8% loading of natural Phillipsite showed significantly ($p \leq 0.05$) taller plants, plants lacked lustre and vigour, as evident from their leaf and shoot dry weights discussed in Sections 4.1.3 and 4.1.4. On comparison for interactions within the treatments over time (Harvest 1-3), significant ($p \leq 0.05$) differences were observed for 1% and 2% synthetic Phillipsite amended soils at Harvests 2 and 3.

For Glasshouse Experiment 2, significant differences were observed between the treatments at Harvests 1, 2 and 3. At each harvest 2% synthetic Phillipsite (both ammonium exchanged and unexchanged) showed a highly ($p \leq 0.05$) significant difference, with increase in plant height over time. At Harvest 1 (Figure 4.4), C.high, 4% synthetic Phillipsite and 4% Linde type F showed significantly ($p \leq 0.05$) lower plant height, and at Harvest 2 (Figure 4.5) C.blank and C.high along with 2% and 4% Linde type F amended soils showed significantly ($p \leq 0.05$) lower plant height. At Harvest 3 (Figure 4.6), synthetic Phillipsite amended soils showed significantly ($p \leq 0.05$) higher plant height at 1% and 2% loading, and also C.blank and 4% Linde type F showed significantly ($p \leq 0.05$) lower plant height. Treatment with 2% unexchanged synthetic Phillipsite showed a significant ($p \leq 0.05$) difference at Harvest 3.

On analysing interactions for plant height measurements between treatments over time (two way ANOVA across Harvests 1-3), results indicated that ammonium exchanged Phillipsite soils (1 and 2%) were significantly ($p \leq 0.01$) different from all other treatments at Harvests 2 and 3. Ammonium exchanged Phillipsitic soil amendments, along with its counterpart 2% unexchanged Phillipsite with added fertilizer, can therefore be considered as potential soil amendments for plant growth (as indicated by their height, shoot weight, lustre and vigour).

For Glasshouse Experiment 3, significant differences for zeolite-amended treatments were observed at Harvests 2 and 3. At Harvest 2, 1% Phillipsite (high-crystalline) showed significantly ($P \leq 0.05$) higher plant height, and at Harvest 3, 2% Phillipsite (high-aluminium) showed significantly ($P \leq 0.05$) higher plant height over time. This result can be explained by the presence of more NH_4^+ in the high aluminium Phillipsite framework at the start of the experiment, thereby providing plants with more N at all growth stages.

4.1.2. Number of leaves

For Glasshouse Experiment 1, no significant differences were observed for number of leaves on each plant irrespective of treatment. Although plants of some treatments lacked lustre and vigour they still produced the same number of leaves at each individual harvest. Leaves lacking lustre also showed interveinal chlorosis, which may be a symptom of copper deficiency. Usually natural Phillipsite amended soils showed this phenomenon (Plate 4.3).

Plate 4.3. Plants grown in ● Synthetic Phillipsite and ▬ Natural Phillipsite amended soils at 2% loading at Harvest 2.

Studies by Colella *et al*. (1998) on natural Phillipsite confirmed the high selectivity of this zeolite towards Cu and Zn. Although Cu deficiency symptoms were prominent at Harvest 2, by the end of Harvest 3 plants from natural Phillipsite amended soils did not appear to show any deficiency. Cu deficiency at Harvest 2 might therefore, have affected the overall growth of plants grown in natural Phillipsite amended soils.

For Glasshouse Experiment 2, no significant differences were observed for number of leaves on each plant at Harvest 1, irrespective of treatment. Plants of ammonium exchanged Linde type F treatments lacked lustre and vigour. Leaves lacking lustre also showed chlorosis of older leaves and thin spindly stalks, which may be explained by Nitrogen deficiency. These plants produced fewer leaves, compared to all other treatments at Harvests 2 and 3. Ammonium exchanged Synthetic Phillipsite amended soils did not show any nutrient deficiencies and leaves were healthy (Plate 4.4). From Plate 4.4 it is evident that ammonium exchanged synthetic Phillipsite amended-soils produced healthier plants with no nutritional deficiency symptoms, whereas ammonium exchanged Linde type F amended-soils produced plants with clearly visible nutritional deficiencies and are discussed in detail in Section 4.2, where the chemical analyses of plants and soils are considered.

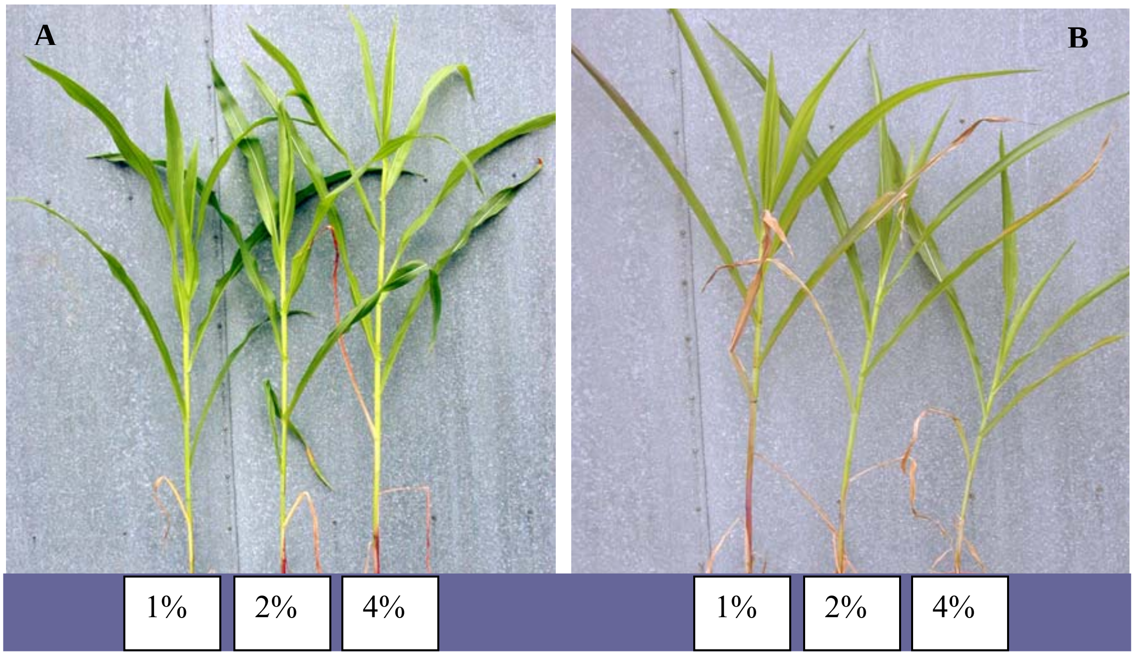


Plate 4.4. Comparison between plants grown in ammonium exchanged (A) 1, 2 and 4% synthetic Phillipsite amended soils and (B) 1, 2 and 4% Linde type F amended soils.

For Glasshouse Experiment 3, no significant differences were observed for number of leaves on each plant at Harvest 1, irrespective of treatment. At Harvest 2 plants grown in high-crystalline Phillipsite (1 and 2% loading) soils had significantly ($P \leq 0.05$) more leaves. And at Harvest 3, no significant differences were observed.

4.1.3. Leaf fresh and dry weight

For Glasshouse Experiment 1 at Harvest 1 (Figure 4.1), 4% synthetic Phillipsite showed significantly ($p \leq 0.05$) higher leaf fresh weight over all other treatments and both C.high and 8% natural Phillipsite soils showed significantly ($p \leq 0.01$) lower leaf fresh and dry weights. At Harvest 2 (Figure 4.2), both the controls and 8% natural Phillipsite showed significantly ($p \leq 0.05$) lower leaf fresh weights, and on comparing leaf dry weight measurements of zeolite added treatments both C.high and 8% natural Phillipsite amended soils showed significant ($p \leq 0.01$) differences. At Harvest 3 (Figure 4.3), 4 and 8% natural Phillipsite amended soils showed significantly ($p \leq 0.01$) lower leaf fresh and dry weights.

For Glasshouse Experiment 2 at Harvest 1 (Figure 4.4), on comparing leaf fresh weight measurements of treatment effects, LSD test ($p \leq 0.05$) confirmed C.high, 4% synthetic and 4% Linde type F treatments to have significantly ($p \leq 0.05$) lower leaf fresh weight, and C.std along with 1 and 2% synthetic Phillipsite treatments showed significantly ($p \leq 0.05$) higher leaf fresh weights. At Harvest 2 and 3 (Figures 4.5 and 4.6), 4% Linde type F treatment showed significantly ($p \leq 0.05$) lower leaf fresh weight and both 2% ammonium exchanged and unexchanged Phillipsite treatments showed significantly ($p \leq 0.05$) higher leaf fresh weight.

Leaf dry weight measurements showed C.std and 4% Linde type F treatments to be significantly ($p \leq 0.01$) different at Harvest 1; and at Harvest 2, C.blank and C.high and all three loadings of Linde type F showed significantly ($p \leq 0.05$) lower leaf dry weight. At Harvest 3 on comparing treatment effects, C.blank and 2 and 4% Linde type F treatments showed significant differences ($p \leq 0.01$), and both ammonium exchanged and unexchanged 2% Phillipsite soils showed significant differences ($p \leq 0.01$). Analysis of leaf fresh and dry weights across the harvests for interactions between the treatments showed at 1% and 2% loadings ammonium exchanged Phillipsite and at 2% loading unexchanged Phillipsite treatment to be significantly

($p \leq 0.05$) heavier. At higher loading (4%) both synthetic Phillipsite and Linde type F treatments showed significantly ($p \leq 0.05$) lower leaf fresh and dry weights.

For Glasshouse Experiment 3 at Harvest 1 (Figure 4.7), on comparing leaf fresh weight measurements of treatment effects, 1% high-crystalline Phillipsite was significantly ($P \leq 0.05$) different from all other treatments. Leaf dry weight measurements showed 1% high crystalline Phillipsite to be significantly ($P \leq 0.05$) different over all other treatments. At Harvest 2 (Figure 4.8) for leaf fresh weight, both C.blank and 1% high crystalline Phillipsite treatments were significantly ($P \leq 0.05$) different and for leaf dry weight only C.blank was significantly ($P \leq 0.05$) different over all other treatments. At Harvest 3 (Figure 4.9), leaf fresh and dry weight measurements showed C.blank and 2% high aluminium Phillipsite treatments to be significantly ($P \leq 0.05$) different. Across the harvests, interactions between the treatments over time showed significant ($P \leq 0.01$) differences for leaf fresh and dry weights of plants grown in high-aluminium Phillipsite soils.

4.1.4. Shoot fresh and dry weight

Shoot weight is the most commonly used parameter for comparing overall growth effects, and comprises of total leaf weight + total stem weight both before (fresh weight) and after oven drying (dry weight). For Glasshouse Experiment 1 at Harvest 1, on comparing shoot fresh and dry weight measurements of zeolite added treatments, both the controls (C.high and C.std) and 8% natural Phillipsite amended soils had significantly ($p \leq 0.05$) lower shoot fresh weight. Synthetic Phillipsite amended soils showed significantly ($p \leq 0.01$) greater shoot dry weights at 2 and 4% loadings. At Harvest 2, 8% natural Phillipsite amended soils showed significantly ($p \leq 0.05$) lower shoot fresh and dry weight. In contrast, 2% synthetic Phillipsite-amended soil showed significantly ($p \leq 0.01$) greater shoot dry weight. At Harvest 3, synthetic Phillipsite treatments showed highly significant ($p \leq 0.01$) differences for shoot fresh weight. In contrast, shoot dry weight measurements showed significantly ($p \leq 0.01$) greater dry weight for 2% synthetic Phillipsite loading. Natural Phillipsite loading at 8% showed significantly ($p \leq 0.01$) lower shoot dry weight. Results of leaf and shoot fresh and dry weights together with plant height measurements initially suggest that at 2% loading synthetic Phillipsite has the potential to increase plant growth (Table 4.2). On analysing plant growth measurements by two-way ANOVA for interactions within the treatments over time (Harvest 1-3), significant ($p \leq 0.01$) differences were observed for leaf and shoot weights at Harvests 2 and 3 for synthetic Phillipsite treatments. It can be concluded from these preliminary results that at 2% loading synthetic Phillipsite might be a potential soil amendment for plant growth, and higher loadings of zeolite to soil can decrease plant growth.

Table 4.2. Oven-dry shoot weights of all 8 treatments at Harvests 2 and 3 (± standard error of the mean, n = 10) at $p \leq 0.05$ for Glasshouse Experiment 1.

Treatment		Harvest 2 Mean shoot dry weight (g)	(S.E)	Harvest 3 Mean shoot dry weight (g)	(S.E)
Control high		4.40ac	(0.11)	14.96a	(0.93)
Control standard		4.68a	(0.57)	15.20ac	(0.50)
Synthetic Phillipsite	2%	5.81b	(0.14)	17.50bc	(0.50)
	4%	5.38ab	(0.29)	16.40abc	(0.84)
	8%	5.45ab	(0.22)	16.70cb	(0.55)
Natural Phillipsite	2%	5.44ab	(0.21)	14.71a	(0.97)
	4%	5.16ab	(0.33)	14.36a	(0.41)
	8%	3.41c	(0.12)	13.27a	(0.25)
LSD ($p \leq 0.05$)		1.12		1.67	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse Experiment 2; at Harvests 1, 2 and 3, on comparing shoot fresh weight measurements of treatment effects C.blank, C.high, 4% synthetic Phillipsite and 4% Linde type F soils showed significantly ($p \leq 0.05$) lower shoot fresh weights. Significantly ($p \leq 0.05$) higher fresh weights were shown by 1% synthetic Phillipsite treatment at Harvest 1, and both 2% ammonium exchanged and unexchanged synthetic Phillipsite treatments showed significant ($p \leq 0.05$) treatment effects at Harvests 2 and 3. Shoot dry weight measurements showed C.high and C.std treatments to be significantly ($p \leq 0.01$) different at Harvest 1. At Harvest 2, C.blank and C.high and all three loadings of Linde type F showed significantly ($p \leq 0.01$) lower shoot dry weight with 2% synthetic Phillipsite treatment showing significantly ($p \leq 0.01$) higher shoot dry weight. At Harvest 3 on comparing treatment effects C.blank and 2% and 4% Linde type F treatments showed significant effects ($p \leq 0.01$), and both ammonium exchanged and unexchanged 2% Phillipsite soils showed significant ($p \leq 0.01$) differences. Analysis of shoot fresh and dry weights across the harvests showed 2% ammonium exchanged Phillipsite to significantly ($p \leq 0.05$) increase shoot weight. At higher % loading (4%) of both synthetic Phillipsite and Linde type F, soils showed a significant ($p \leq 0.05$) decrease in shoot fresh and dry weights (Table 4.3). Analysis of shoot fresh and dry weights across the harvests for interactions between the treatments showed 2% ammonium exchanged Phillipsite loading along with 2% unexchanged Phillipsite to have significantly ($p \leq 0.05$) higher weights at Harvests 2 and 3. Results of leaf, shoot fresh and dry weights together with plant height measurements, suggest that at 2% loading ammonium exchanged synthetic Phillipsite might be a potential soil amendment for maize growth. Although unexchanged 2% synthetic Phillipsite loading showed significant effects for plant height and shoot dry weight, it should be taken into consideration that this treatment included an N fertilizer addition (Section 2.8.2).

Table 4.3. Oven-dry shoot weights of all 11 treatments at Harvests 2 and 3 (± standard error of the mean, n = 10) at $p \leq 0.05$ for Glasshouse Experiment 2.

Treatment		**Harvest 2 Mean shoot dry weight (g)**	**(S.E)**	**Harvest 3 Mean shoot dry weight (g)**	**(S.E)**
Control blank		3.25a	(0.18)	8.63a	(0.58)
Control standard		5.35b	(0.57)	16.98b	(0.40)
Control high		2.54a	(0.32)	9.99ad	(0.92)
Synthetic Phillipsite	1%	5.64b	(0.31)	17.43bc	(1.07)
	2%	6.08b	(0.51)	19.11c	(0.61)
	4%	5.48b	(0.32)	11.61d	(1.43)
Linde type F	1%	3.84ab	(0.39)	9.97ad	(1.18)
	2%	2.54a	(0.27)	5.95e	(0.39)
	4%	1.63a	(0.13)	3.48f	(0.45)
Unexchanged S. Phillipsite	2%	5.56b	(0.34)	18.64bc	(0.90)
Unexchanged Linde type F	2%	4.30ab	(0.61)	10.03ad	(1.23)
LSD ($p \leq 0.05$)		0.92		2.13	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse Experiment 3, at Harvest 1 on comparing shoot fresh and dry weight measurements for all 6 treatments 1% high crystalline Phillipsite showed significant ($P \leq 0.05$) difference. At Harvest 2, C.blank and 1% high crystalline Phillipsite showed significant ($P \leq 0.05$) differences for shoot fresh weight and only C.blank showed highly significant ($P \leq 0.01$) difference for shoot dry weight. At Harvest 3, highly significant ($P \leq 0.01$) differences were observed for C.blank and 2% high aluminium Phillipsite for both shoot fresh and dry weights. Across the harvests, results of leaf and shoot fresh and dry weights (Table 4.4) together with plant height measurements suggest that at 2% loading, high-aluminium Phillipsite might be a potential soil amendment to increase plant growth. However, it should be taken into consideration that this treatment has a higher NH_4^+ content than its counterpart high-crystalline Phillipsite at the same loading due to its Si:Al ratio.

Table 4.4. Oven-dry shoot weights of all 6 treatments at Harvests 2 and 3 (± standard error of the mean, n = 10) at $p \leq 0.05$ for Glasshouse Experiment 3.

Treatment		**Harvest 2 Mean shoot dry weight (g)**	**(S.E)**	**Harvest 3 Mean shoot dry weight (g)**	**(S.E)**
Control blank		2.57a	(0.18)	5.46a	(0.33)
Control standard		2.94a	(0.34)	9.49b	(0.43)
Synthetic Phillipsite	1%	3.65b	(0.19)	9.76b	(0.44)
(high-aluminium)	2%	3.55b	(0.13)	11.25c	(0.55)
Synthetic Phillipsite	1%	3.49b	(0.19)	9.79b	(0.65)
(high-crystalline)	2%	2.98a	(0.13)	9.89b	(0.48)
LSD ($p \leq 0.05$)		0.49		1.16	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

4.1.5. Cob formation

Plants of Glasshouse Experiment 3, were left to grow in the glasshouse after Harvest 3 until cob formation. Although cob formation in glasshouse conditions does not present a true representation of field conditions, results from this experiment can show the effectiveness of a controlled release fertilizer in the form of zeolite amendment on cob formation. As hypothesized, high-aluminium Phillipsite treatments showed significantly higher cob fresh and dry weights than its counterpart high-crystalline Phillipsite, and both the controls (Table 4.5). An LSD test for cob fresh and dry weights showed highly significant ($P \leq 0.01$) differences for C.blank and 1% loaded high-aluminium Phillipsite. Significant differences were also observed between C.blank and C.std soils, with lower and higher cob fresh and dry weights.

Table 4.5. Fresh and oven-dry cob weights for all 6 treatments, after 16 weeks of plant growth (± standard error of the mean, n = 5) at $p \leq 0.05$

Treatment		Mean Cob fresh weight at final destructive harvest (16 weeks)	(S.E)	Mean Cob dry weight at final destructive harvest (16 weeks)	(S.E)
C. blank		8.76a	(0.63)	1.95a	(0.29)
C. std		37.56b	(1.46)	5.75b	(0.45)
Synthetic Phillipsite	1%	51.74c	(1.79)	10.13c	(0.58)
(high-aluminium)	2%	45.98d	(1.19)	8.32d	(0.50)
Synthetic Phillipsite	1%	46.50d	(1.61)	8.60d	(0.61)
(high-crystalline)	2%	39.04b	(1.06)	6.49b	(0.16)
LSD ($p \leq 0.05$)		3.24		1.11	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

From Glasshouse Experiment 1 results (Figures 4.1-4.3), it is evident that synthetic NH_4^+- ion exchanged Phillipsite added soils showed a better plant growth response compared to natural NH_4^+ - ion exchanged Phillipsite added soils and the controls. From Glasshouse Experiment 2 (Figures 4.4-4.6) results, it is evident that NH_4^+- ion exchanged synthetic Phillipsite amended soils showed an active plant growth response with increased shoot weight compared to NH_4^+- ion exchanged Linde type F amended soils and the controls. Unexchanged synthetic Phillipsite amended soils at 2% loading also showed an increase in shoot weight. Finally, from Glasshouse Experiment 3 results (Figures 4.7-4.9), it is evident that NH_4^+- ion exchanged high aluminium Phillipsite showed a significant increase in plant growth compared to NH_4^+- ion exchanged high crystalline Phillipsite.

4.1.6. Chemical analysis of shoot material

Plant shoot material was analysed for total Potassium, Calcium, Magnesium and Sodium content and this was expressed as a percentage of dry weight for Glasshouse

Experiments 1 and 2. Typical percentage concentrations of Ca, K and Mg found in plant material are 0.5-5% for K, 0.3-2.5 % for Ca, and 0.1-0.5% for Mg (Allen, 1989). For Glasshouse Experiment 1, all eight treatments showed Ca, K, Mg and Na nutrient levels in plant material to be within required percentage concentrations at all three harvests (Tables 4.6-4.8).

Table 4.6. Mean % K, Ca, Mg and Na of dry plant shoot material at Harvest 1.

Treatment	**Mean K**		**Mean Ca**		**Mean Mg**		**Mean Na**	
	(%)	(S.E)	**(%)**	(S.E)	**(%)**	(S.E)	**(%)**	(S.E)
Control high	8.94a	(0.08)	0.24	(0.001)	0.17	(0.004)	0.04	(0.001)
Control standard	9.70a	(0.27)	0.14	(0.007)	0.16	(0.011)	0.03	(0.004)
Synthetic Phillipsite 2%	9.73a	(0.05)	0.44	(0.013)	0.25	(0.003)	0.05	(0.003)
4%	10.24b	(0.15)	0.38	(0.020)	0.25	(0.006)	0.04	(0.003)
8%	10.57b	(0.26)	0.32	(0.009)	0.19	(0.009)	0.04	(0.005)
Natural Phillipsite 2%	9.30a	(0.15)	0.59	(0.041)	0.32	(0.007)	0.06	(0.005)
4%	9.38a	(0.03)	0.57	(0.005)	0.30	(0.010)	0.04	(0.003)
8%	9.35a	(0.09)	0.50	(0.014)	0.24	(0.016)	0.04	(0.006)
LSD ($p \leq 0.05$)	0.85		NS		NS		NS	

Table 4.7. Mean % K, Ca, Mg and Na of dry plant shoot material at Harvest 2.

Treatment	**Mean K**		**Mean Ca**		**Mean Mg**		**Mean Na**	
	(%)	(S.E)	**(%)**	(S.E)	**(%)**	(S.E)	**(%)**	(S.E)
Control high	14.10a	(0.07)	1.34	(0.001)	1.66	(0.016)	0.15	(0.012)
Control standard	12.66a	(0.60)	1.32	(0.006)	1.66	(0.070)	0.14	(0.014)
Synthetic Phillipsite 2%	22.50b	(0.31)	1.15	(0.002)	0.59	(0.025)	0.13	(0.004)
4%	27.55c	(0.37)	0.82	(0.006)	0.57	(0.019)	0.11	(0.023)
8%	28.80c	(0.20)	0.62	(0.011)	0.66	(0.004)	0.10	(0.003)
Natural Phillipsite 2%	13.31a	(0.51)	1.28	(0.030)	1.02	(0.007)	0.10	(0.038)
4%	16.07a	(0.08)	1.24	(0.026)	0.89	(0.008)	0.10	(0.001)
8%	17.98a	(0.18)	1.04	(0.002)	0.72	(0.004)	0.10	(0.002)
LSD ($p \leq 0.05$)	1.99		NS		NS		NS	

Table 4.8. Mean % K, Ca, Mg and Na of dry plant shoot material at Harvest 3.

Treatment	**Mean K**		**Mean Ca**		**Mean Mg**		**Mean Na**	
	(%)	(S.E)	**(%)**	(S.E)	**(%)**	(S.E)	**(%)**	(S.E)
Control high	6.16a	(0.24)	1.28	(0.022)	1.52	(0.026)	0.17	(0.004)
Control standard	6.52a	(0.22)	1.18	(0.022)	1.34	(0.032)	0.16	(0.006)
Synthetic Phillipsite 2%	13.51b	(0.12)	1.11	(0.014)	0.59	(0.004)	0.13	(0.002)
4%	16.91cd	(0.21)	1.10	(0.031)	0.45	(0.002)	0.13	(0.003)
8%	19.04cd	(0.37)	0.94	(0.008)	0.47	(0.009)	0.12	(0.002)
Natural Phillipsite 2%	7.73ae	(0.36)	0.55	(0.008)	0.97	(0.002)	0.12	(0.001)
4%	8.99ae	(0.79)	0.44	(0.008)	0.84	(0.003)	0.11	(0.003)
8%	10.60e	(0.18)	0.93	(0.001)	0.65	(0.002)	0.10	(0.001)
LSD ($p \leq 0.05$)	2.93		NS		NS		NS	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test (± standard error of the mean, n = 5). NS represents no significance.

No significant ($p \leq 0.05$) differences were observed for % Ca and % Mg at all three harvests. Na levels in shoot material of all eight treatments were minimal at all three harvests, with a slightly higher % concentration in control soil. At Harvest 1 (Table 4.6), plants grown in 2 and 4% synthetic Phillipsite amended soils showed significant ($p \leq 0.05$) differences. Plants had a higher % K in the shoot when compared to other treatments. When followed by a LSD test, it was found that these two treatments had significantly ($p \leq 0.05$) higher K than C.high and C.std. At Harvest 2 (Table 4.7), plants grown in all three loadings of synthetic Phillipsite amended soils showed higher % K in the shoot, and both 4, and 8% soils had significantly ($p \leq 0.05$) higher K. At Harvest 3 (Table 4.8), plants grown in all three loadings of synthetic Phillipsite amended soils showed higher % K in the shoot, with 2% synthetic Phillipsite amended soils to be significantly different from other treatments at $p \leq 0.05$.

For Glasshouse Experiment 2, all 11 treatments showed Ca, K, Mg and Na nutrient levels in plant material to be within required percentage concentrations at all three harvests. Na concentration in shoot material of all treatments was minimal, with a slightly higher % concentration of Na in 2% unexchanged synthetic Phillipsite plants at all three harvests. This can be accounted for by high Na concentrations present in the original Phillipsite framework, exchanging for NH_4^+ present in soil (in the form of NH_4NO_3 fertilizer). Tables 4.9-4.11 show % concentrations of Na, K, Ca and Mg from Harvest 1-3 along with their LSDs (± standard error of the mean, n = 3) at $p \leq 0.05$.

Table 4.9. Mean % K, Ca, Mg and Na of dry plant shoot material at Harvest 1.

Treatment		**Mean Na**(%)	(S.E)	**Mean K** (%)	(S.E)	**Mean Ca** (%)	(S.E)	**Mean Mg** (%)	(S.E)
Control blank		0.04a	(0.004)	8.40a	(0.37)	0.54a	(0.019)	0.21	(0.030)
Control standard		0.03a	(0.008)	8.65a	(0.17)	0.30bc	(0.029)	0.14	(0.014)
Control high		0.05a	(0.008)	7.85a	(0.20)	0.61a	(0.004)	0.28	(0.009)
Synthetic Phillipsite	1%	0.03a	(0.003)	10.47bc	(0.56)	0.51ab	(0.017)	0.24	(0.024)
	2%	0.05a	(0.003)	9.57ab	(0.12)	0.40ab	(0.023)	0.20	(0.022)
	4%	0.04a	(0.001)	8.26a	(0.59)	0.33ab	(0.029)	0.21	(0.033)
Linde type F	1%	0.04a	(0.002)	9.40ab	(0.45)	0.44ab	(0.009)	0.20	(0.013)
	2%	0.05a	(0.001)	7.93a	(0.49)	0.28b	(0.039)	0.17	(0.011)
	4%	0.04a	(0.005)	7.52a	(0.14)	0.23b	(0.023)	0.21	(0.004)
Unexchanged S. Phillipsite	2%	0.14b	(0.065)	11.58bc	(1.03)	0.47ab	(0.067)	0.21	(0.004)
Unexchanged Linde type F	2%	0.05a	(0.014)	12.74cd	(1.17)	0.24b	(0.020)	0.16	(0.011)
LSD ($p \leq 0.05$)		0.05		1.20		0.23		NS	

Table 4.10. Mean % K, Ca, Mg and Na of dry plant shoot material at Harvest 2.

Treatment		**Mean Na** (%)	(S.E)	**Mean K** (%)	(S.E)	**Mean Ca** (%)	(S.E)	**Mean Mg** (%)	(S.E)
Control blank		0.09ab	(0.003)	8.35a	(1.07)	1.26a	(0.002)	0.83a	(0.029)
Control standard		0.09ab	(0.006)	14.94b	(0.55)	1.30a	(0.003)	1.29b	(0.041)
Control high		0.14bc	(0.027)	11.31ab	(3.45)	1.31a	(0.014)	1.01c	(0.046)
Synthetic Phillipsite	1%	0.10abc	(0.010)	18.93c	(0.06)	1.24a	(0.003)	0.88a	(0.013)
	2%	0.11abc	(0.003)	23.86d	(2.23)	1.17a	(0.033)	0.82a	(0.046)
	4%	0.11abc	(0.012)	25.01d	(0.78)	1.01b	(0.015)	0.80a	(0.074)
Linde type F	1%	0.09ab	(0.004)	30.88e	(0.95)	1.19a	(0.002)	0.52d	(0.083)
	2%	0.15cb	(0.021)	25.12d	(0.35)	1.16a	(0.003)	0.45d	(0.006)
	4%	0.13abc	(0.009)	24.57d	(0.18)	1.03b	(0.051)	0.40d	(0.052)
Unexchanged S. Phillipsite	2%	0.41d	(0.054)	31.48e	(0.79)	0.97b	(0.002)	0.79a	(0.003)
Unexchanged Linde type F	2%	0.10abc	(0.006)	37.36f	(2.05)	0.75c	(0.040)	0.42d	(0.006)
LSD ($p \leq 0.05$)		0.05		3.67		0.13		0.11	

Table 4.11. Mean % K, Ca, Mg and Na of dry plant shoot material at Harvest 3.

Treatment		**Mean Na** (%)	(S.E)	**Mean K** (%)	(S.E)	**Mean Ca** (%)	(S.E)	**Mean Mg** (%)	(S.E)
Control blank		0.11a	(0.027)	0.54a	(0.67)	1.26a	(0.001)	0.83a	(0.004)
Control standard		0.20a	(0.066)	3.88bc	(0.28)	1.32ab	(0.007)	1.16b	(0.012)
Control high		0.20a	(0.023)	2.97abc	(0.94)	1.33b	(0.010)	1.07b	(0.018)
Synthetic Phillipsite	1%	0.17a	(0.009)	4.58bcd	(0.28)	1.28ab	(0.013)	0.95a	(0.026)
	2%	0.10a	(0.003)	5.57bcd	(0.33)	1.08c	(0.060)	0.81a	(0.007)
	4%	0.09a	(0.005)	7.46cdef	(0.58)	0.83de	(0.009)	0.72a	(0.017)
Linde type F	1%	0.20a	(0.115)	9.80def	(0.58)	1.24a	(0.007)	0.40c	(0.024)
	2%	0.19a	(0.039)	9.81def	(0.43)	1.20a	(0.008)	0.34c	(0.062)
	4%	0.17a	(0.050)	11.11ef	(0.58)	0.89de	(0.015)	0.28c	(0.038)
Unexchanged S. Phillipsite	2%	0.38b	(0.013)	10.44def	(0.18)	0.82de	(0.016)	0.65a	(0.027)
Unexchanged Linde type F	2%	0.15a	(0.030)	12.98f	(0.38)	0.55e	(0.032)	0.36c	(0.031)
LSD ($p \leq 0.05$)		0.15		3.20		0.06		0.18	

NB. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test (± standard error of the mean, n = 3).

At Harvest 1, plants grown in 2% unexchanged synthetic Phillipsite and Linde type F-amended soils accumulated significantly more % K in the shoot. An LSD test showed these two treatments to be significant ($p \leq 0.05$). At Harvest 2, for K uptake by plants 1% loaded synthetic Phillipsite and Linde type F along with 2% unexchanged synthetic Phillipsite and Linde type F showed significant ($p \leq 0.05$) differences. At Harvest 3, only 2% unexchanged Linde type F showed significant ($p \leq 0.05$) differences. Analysis of data across the harvests for interactions between the treatments over time revealed significant ($p \leq 0.05$) differences. Higher Ca concentration was found in the shoot material of C.high and significantly ($p \leq 0.05$)

higher Mg concentrations were found in the shoot material of C.high. At 2% loading, unexchanged synthetic Linde type F soils showed a significantly ($p \leq 0.05$) higher K content in plant shoot material. However, the concentrations of other nutrients, such as Ca and Mg for this treatment, were significantly ($p \leq 0.05$) lower at all three harvests.

These results therefore suggest that Ca and Mg cations present in soil actively exchange for K present in Linde type F frameworks, thereby increasing the concentration of the later and decreasing the concentrations of the former in soil. Mg deficiency in plants grown in both ammonium exchanged and unexchanged Linde type F soils showed loss of healthy green colour and was evident from plant leaves (Plate 4.5). As expected, unexchanged Phillipsite soils showed higher Na content in plant shoot material. Due to the ion exchange interactions in a zeolite-soil system, NH_4^+ present in the soil as NH_4NO_3 fertilizer exchanges for Na present in the unexchanged zeolite framework. The Na released will then be available in excess in the soil for the plants to take up, thereby showing a significant ($p \leq 0.05$) increase at Harvests 2 and 3.

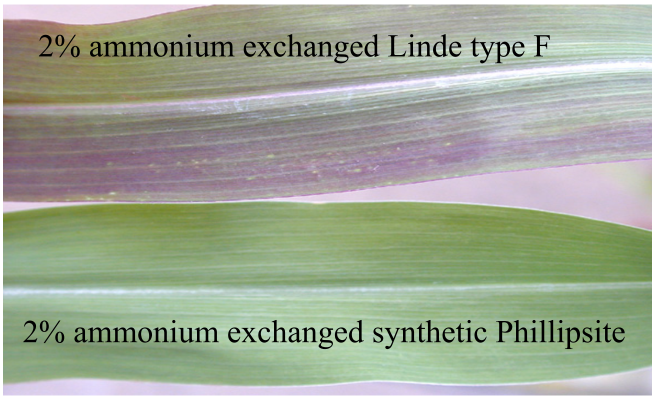


Plate 4.5. Comparison of leaves from synthetic Linde type F and Phillipsite plants, with Linde type F plant showing Mg and N deficiencies at Harvest 2.

As discussed in Section 1.11, the purple coloration of leaves might be associated with N and P deficiency. The most widespread group of pigmented flavonoids is the anthocyanins, which are responsible for most of the red, purple and blue colours observed in plant parts. Anthocyanins are glycosides that have sugars at position 3 and sometimes elsewhere (Figure 4.10). Without their sugars, anthocyanins are known as anthocyanidins. During N deficiency, there is an excess accumulation of carbohydrates, which when not used in N metabolism may be used in anthocyanin synthesis, leading to the accumulation of purple colour pigment.

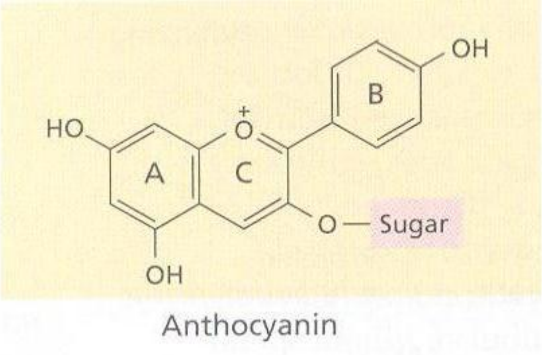


Figure 4.10. The structure of anthocyanin. Source: Taiz and Zeiger (2002)

For Glasshouse Experiment 3, chemical analyses of shoot material were omitted, as none of the zeolite treatment effects showed any visible nutrient deficiency symptoms during the entire plant growth stage and due to time constraints. With the exception of C.blank treatment, plants grown in all other treatments showed lustre and vigour (Plate 4.6).

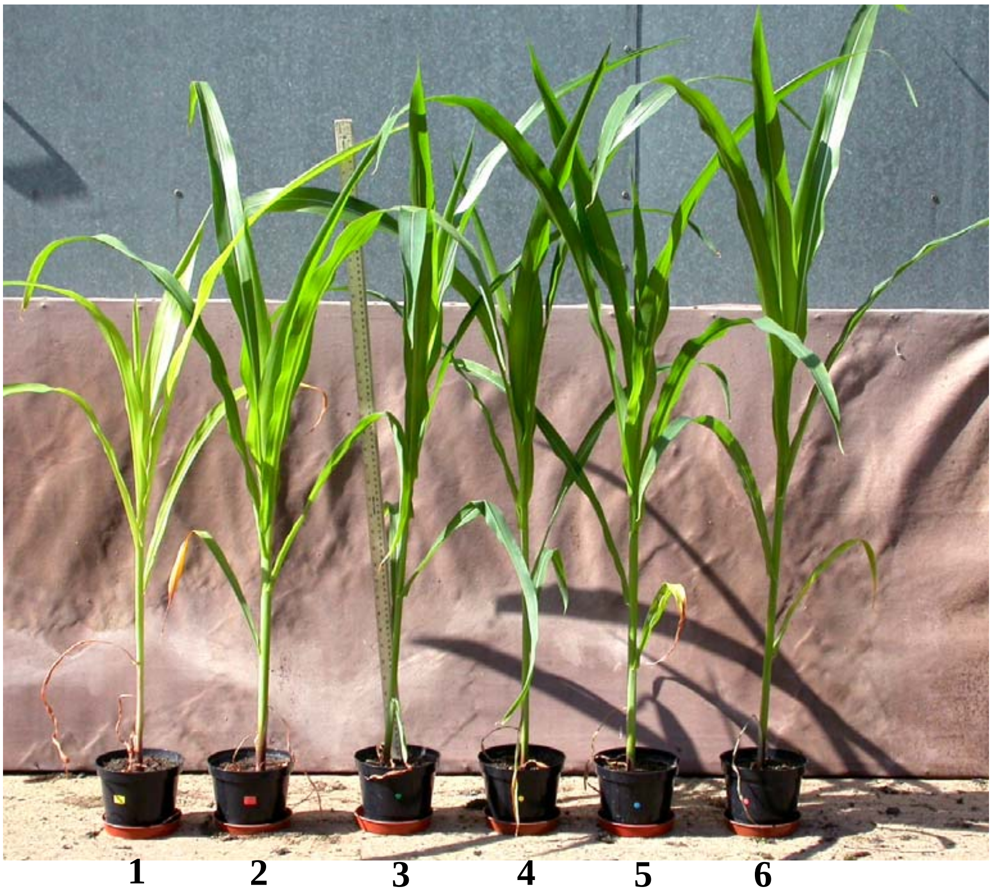


Plate 4.6. Plant growth at Harvest 3 for treatments: (1) C.blank, (2) C.standard, (3) 1% High-crystalline synthetic Phillipsite, (4) 2% High-crystalline synthetic Phillipsite, (5) 1% High-aluminium synthetic Phillipsite and (6) 2% High-aluminium synthetic Phillipsite.

4.2. Chemical analyses of soil samples

Plant growth might be directly influenced by the amount of N present in soil and available for the plants to complete its life cycle. In order to predict a potential controlled release fertilizer in the form of ammonium exchanged zeolite, plant growth results had to be related to soil analysis results to construct a model of N release and conversion in soil; and uptake by plants for their metabolism. Soil analyses for total nitrogen and available NH_4^+ and NO_3^- were therefore carried out on all replicate sample treatments. Along with N other major nutrients, which directly or indirectly influence plant growth are P, K, Ca and Mg. Following Olsen's method for P extraction and ammonium acetate extraction for the essential nutrients, and by relating these results with plant uptake of nutrients, a theory was constructed to show exchange of cations in and out of zeolite framework affecting nutrient uptake from soil and thereby influencing plant growth. Soil moisture, soil pH, organic matter, and total/available N, P, K, Ca, Mg were measured after each individual harvest for Glasshouse Experiments 1, 2 and 3. Leachate measurements were carried out for Glasshouse Experiments 2 and 3 by analysing soil leachates on ion chromatography (IC) for NH_4^+, NO_3^- and NO_2^-.

4.2.1. Soil Moisture

As plants were given equal amounts of water at any particular day, irrespective of their treatment, no significant differences were observed between the treatments at all three harvests. Following one-way ANOVA, none of the soils showed any differences in their moisture levels. Considering high and low w/w loadings of zeolite to soil used for all three Glasshouse Experiments, results are indicative that zeolite-amended soils did not have any direct effect on changing soil moisture content.

4.2.2. Soil pH

The soil used for this experiment was taken from the Compton Campus, and had a pH of 6.5-6.8 for all three Glasshouse Experiments before addition of any zeolite or fertilizer. Soil pH measurements were recorded in both H_2O and $CaCl_2$ solution. Measurements taken in $CaCl_2$ can stabilize pH readings and reduce the dependency of the reading on solution concentration (Landon, 1991). In $CaCl_2$ solution, pH values are generally lower than those in water by ~0.5-1 unit, with the difference being greater for neutral soils. For Glasshouse Experiment 1, Tables 4.12a and b show mean soil pH of all 8 treatments in H_2O and $CaCl_2$, at all three harvests along with the outcome of LSD tests carried out for treatment effects versus harvesting time. Significant treatment effects for synthetic and natural Phillipsite was found on soil pH at all three harvests. On comparing treatment effects at Harvest 1, all three loadings of synthetic Phillipsite amended soils showed significantly ($p \leq 0.05$) greater pH. At Harvest 2, 2 and 4% synthetic Phillipsite amended soils along with 8% natural Phillipsite amended soil were significantly ($p \leq 0.05$) different. At Harvest 3, 2 and 8% loadings of both natural and synthetic Phillipsite were significantly different ($p \leq 0.05$).

Table 4.12a. Mean soil pH in H_2O at all three harvests (± standard error of the mean, n = 5) at $p \leq 0.05$

Treatment	**Harvest 1**	(S.E)	**Harvest 2**	(S.E)	**Harvest 3**	(S.E)
Control high	6.22a	(0.017)	6.08a	(0.015)	6.38a	(0.037)
Control standard	6.20a	(0.049)	6.04a	(0.073)	6.38a	(0.029)
Synthetic Phillipsite 2%	6.57b	(0.032)	5.69b	(0.021)	5.35b	(0.031)
4%	6.70c	(0.021)	5.96c	(0.028)	4.89c	(0.049)
8%	6.91d	(0.011)	6.01a	(0.033)	4.72d	(0.066)
Natural Phillipsite 2%	6.26a	(0.015)	5.32d	(0.012)	5.24e	(0.021)
4%	6.41e	(0.023)	5.28d	(0.016)	4.97c	(0.013)
8%	6.47e	(0.029)	5.40e	(0.030)	4.60f	(0.026)
LSD ($p \leq 0.05$)	0.07		0.07		0.09	

Table 4.12b. Mean soil pH in $CaCl_2$ at all three harvests (± standard error of the mean, n = 5) at $p \leq 0.05$

Treatment	**Harvest 1**	(S.E)	**Harvest 2**	(S.E)	**Harvest 3**	(S.E)
Control high	5.94a	(0.029)	5.52a	(0.018)	5.73a	(0.073)
Control standard	5.84b	(0.032)	5.65a	(0.013)	5.64a	(0.041)
Synthetic Phillipsite 2%	5.76c	(0.029)	4.74b	(0.014)	4.55b	(0.013)
4%	5.84b	(0.014)	4.94c	(0.036)	4.30c	(0.033)
8%	5.96ab	(0.014)	5.31d	(0.038)	4.39c	(0.046)
Natural Phillipsite 2%	5.53d	(0.023)	4.34e	(0.015)	4.31c	(0.017)
4%	5.67e	(0.024)	4.38e	(0.051)	4.05d	(0.028)
8%	5.68e	(0.030)	4.37e	(0.027)	3.88d	(0.021)
LSD ($p \leq 0.05$)	0.06		0.07		0.09	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

On comparing pH of all 8 treatments across Harvests 1-3, synthetic Phillipsite amended soils showed a higher pH at all three loadings when compared to natural Phillipsite amended soils when measured in both H_2O and $CaCl_2$. On analysing interactions within the treatments over time (Harvests 1-3) two-way ANOVA, 8% synthetic Phillipsite had a significantly ($p \leq 0.01$) higher pH, which decreased during the growth period with a final pH of 4.72 at the end of Harvest 3. All other treatments showed decreased pH during the growth period by > 1 unit when measured in both H_2O and $CaCl_2$, except for the control soils for which pH remained consistent at all three harvests. Soil pH values of synthetic Phillipsite loaded soils were 1.25-2 units lower from Harvest 1 to Harvest 3 in H_2O, and 1.25-1.5 units lower in $CaCl_2$. For natural Phillipsite loaded soils, pH values were 1.25-1.75 units lower from Harvest 1 to Harvest 3 in H_2O and $CaCl_2$.

For Glasshouse Experiment 2, Table's 4.13a and b show mean soil pH of all 11 treatments in H_2O and $CaCl_2$ at all three harvests. At Harvest 1 significant ($p \leq 0.05$) differences were found for 4% ammonium exchanged Linde type F and 2% unexchanged Linde type F. At Harvest 2, 4% ammonium exchanged Linde type F along with 2% unexchanged Linde type F showed significant effects. At Harvest 3, 1% ammonium exchanged synthetic Phillipsite and 2% unexchanged Linde type F treatments showed significant ($p \leq 0.05$) differences. Across the harvests both exchanged and unexchanged synthetic Phillipsite and Linde type F treatments showed significant differences, with 2% unexchanged Linde type F treatment having significantly ($p \leq 0.01$) higher pH. As the amount of hydrogen ions present in the soil is inversely related to pH (McKenzie *et al.* 2002), from (Table 4.13a) it is evident that ammonium exchanged synthetic Linde type F soils have a slightly higher pH than the ammonium exchanged Phillipsite soils. This can be explained by the fact that NH_4^+ exchange from Linde type F framework with cations present in the soil might be slower due the high affinity of this zeolite towards NH_4^+, therefore retaining it in the framework.

Table 4.13a. Mean soil pH in H_2O at all three harvests (± standard error of the mean, n = 5) at $p \leq 0.05$

Treatment		Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control blank		6.23a	(0.024)	5.78a	(0.012)	5.92a	(0.018)
Control standard		6.00b	(0.076)	5.92ac	(0.074)	5.93a	(0.021)
Control High		5.87b	(0.054)	5.58abe	(0.013)	5.77ab	(0.029)
Synthetic Phillipsite	1%	5.17ab	(0.053)	5.36eb	(0.185)	5.46d	(0.061)
	2%	6.36a	(0.067)	5.56abe	(0.129)	5.11ef	(0.116)
	4%	6.64c	(0.034)	5.71ab	(0.145)	5.00ef	(0.052)
Linde type F	1%	6.67c	(0.034)	5.41be	(0.052)	5.60b	(0.035)
	2%	6.79c	(0.027)	6.08c	(0.067)	5.13ac	(0.063)
	4%	7.06d	(0.014)	6.51d	(0.080)	6.28c	(0.230)
Unexchanged S. Phillipsite	2%	6.63c	(0.012)	6.31cd	(0.042)	6.29c	(0.038)
Unexchanged Linde type F	2%	7.30e	(0.025)	7.46f	(0.057)	7.59f	(0.051)
LSD ($p \leq 0.05$)		0.22		0.24		0.21	

Table 4.13b. Mean soil pH in $CaCl_2$ at all three harvests (± standard error of the mean, n = 5) at $p \leq 0.05$

Treatment		Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control blank		5.63a	(0.025)	5.10a	(0.017)	5.14a	(0.064)
Control standard		5.45ad	(0.062)	5.15a	(0.045)	5.07a	(0.017)
Control High		5.52ad	(0.039)	5.17a	(0.134)	4.98b	(0.023)
Synthetic Phillipsite	1%	5.32d	(0.035)	4.50c	(0.127)	4.57e	(0.034)
	2%	5.39d	(0.035)	4.48c	(0.141)	4.27f	(0.075)
	4%	5.60a	(0.032)	4.51c	(0.082)	4.21f	(0.080)
Linde type F	1%	5.88b	(0.027)	5.02a	(0.042)	5.05ab	(0.028)
	2%	5.91b	(0.016)	5.28a	(0.049)	4.78c	(0.056)
	4%	6.22c	(0.022)	5.81b	(0.058)	5.71d	(0.123)
Unexchanged S. Phillipsite	2%	5.82ab	(0.048)	5.08a	(0.038)	5.05ab	(0.011)
Unexchanged Linde type F	2%	6.31c	(0.016)	6.31d	(0.086)	6.37g	(0.059)
LSD ($p \leq 0.05$)		0.20		0.20		0.14	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse experiment 3, Table's 4.14a and b show mean soil pH of all 6 treatments in H_2O and $CaCl_2$, at all three harvests. An LSD test showed significant ($P \leq 0.01$) differences for all 6-treatments at Harvest 3. No significant differences were observed between the treatments at Harvest 1 and 2. No relationship between (%) loading to soil pH was observed in H_2O. However analysis of pH measurements across the harvests in $CaCl_2$ showed all treatments had a significant ($P \leq 0.05$) decrease in pH from Harvest 1 to 2 and then a subsequent increase in pH.

Table 4.14a. Mean soil pH in H_2O (± standard error of the mean, n = 5) at all three harvests.

Treatment		Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control blank		5.94a	(0.017)	5.84a	(0.048)	5.87a	(0.027)
Control standard		5.62b	(0.015)	5.11b	(0.043)	5.66b	(0.030)
Synthetic Phillipsite	1%	5.73c	(0.019)	4.85b	(0.587)	4.62c	(0.038)
(high-aluminium)	2%	5.99a	(0.072)	4.76b	(0.032)	4.74d	(0.030)
Synthetic Phillipsite	1%	5.70bc	(0.041)	5.41a	(0.041)	5.18e	(0.027)
(high-crystalline)	2%	5.93a	(0.063)	4.79b	(0.011)	4.89f	(0.104)
LSD ($p \leq 0.05$)		0.11		0.58		0.12	

Table 4.14b. Mean soil pH in $CaCl_2$ (± standard error of the mean, n = 5) at all three harvests.

Treatment		Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control blank		5.18a	(0.014)	4.81a	(0.013)	5.17a	(0.012)
Control standard		5.04b	(0.025)	4.55b	(0.011)	4.89b	(0.023)
Synthetic Phillipsite	1%	5.31c	(0.018)	4.06c	(0.023)	4.07c	(0.025)
(high-aluminium)	2%	5.41d	(0.051)	4.01c	(0.016)	4.04c	(0.025)
Synthetic Phillipsite	1%	5.17a	(0.043)	4.19d	(0.025)	4.63d	(0.092)
(high-crystalline)	2%	5.35cd	(0.036)	4.20d	(0.018)	4.41e	(0.012)
LSD ($p \leq 0.05$)		0.08		0.05		0.05	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

4.2.3. Soil organic matter

The soil organic matter can be rated in terms of availability (Table 4.15).

Table 4.15. Soil organic matter content ratings in (g) of oven dry soil weight.

Organic matter content, (mg/g)	Rating
>200	Very high
100-200	High
40-100	Medium
20-40	Low
<20	Very low

Source: Landon (1991)

The organic matter content for soils of all 8 treatments used in Glasshouse Experiment 1 is shown in Figure 4.11.

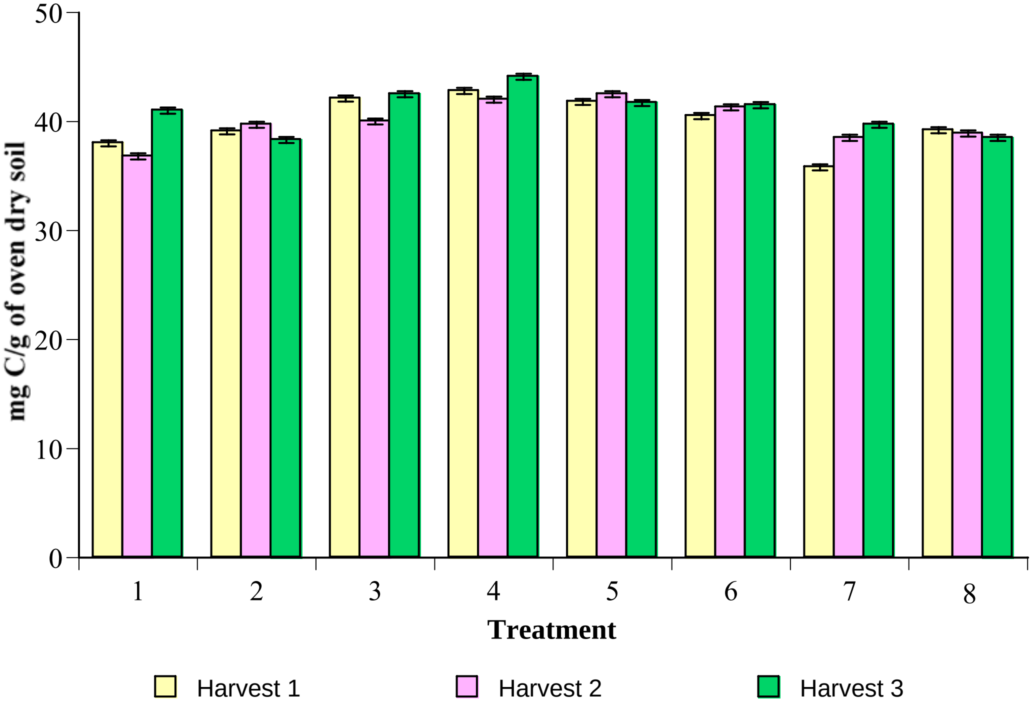


Figure 4.11. Mean organic matter (± standard error of the mean, n = 5) at all three harvests, for treatments (1) C.high (2) C.std (3) 2% S.Phillipsite (4) 4% S.Phillipsite (5) 8% S.Phillipsite (6) 2% N.Phillipsite (7) 4% N.Phillipsite and (8) 8% N.Phillipsite.

From Figure 4.11, it is evident that synthetic Phillipsite amended soils fall in the range of 40-50 mg/g of oven-dry soil, therefore these soils can be classified as medium organic matter soils, whereas the natural Phillipsite amended soils fall in the range of 25-40 mg/g and can be classified as low organic matter soils. For control soils organic matter content was significantly ($p \leq 0.05$) lower than synthetic Phillipsite amended soils, but in the same range as 2 and 4% natural amended soils, and can therefore be classified as low organic matter content soils. Following one-way ANOVA and LSD test for all 8 treatments at all three harvests, C.blank, 4 and 8% natural Phillipsite amended soils showed significant effects ($p \leq 0.01$) at Harvest 1 and 2; At Harvest 3, 4% synthetic Phillipsite loading showed significantly ($p \leq 0.01$) higher organic matter with 4 and 8% natural Phillipsite amended soils showing significantly ($p \leq 0.01$) less organic matter (Figure 4.11).

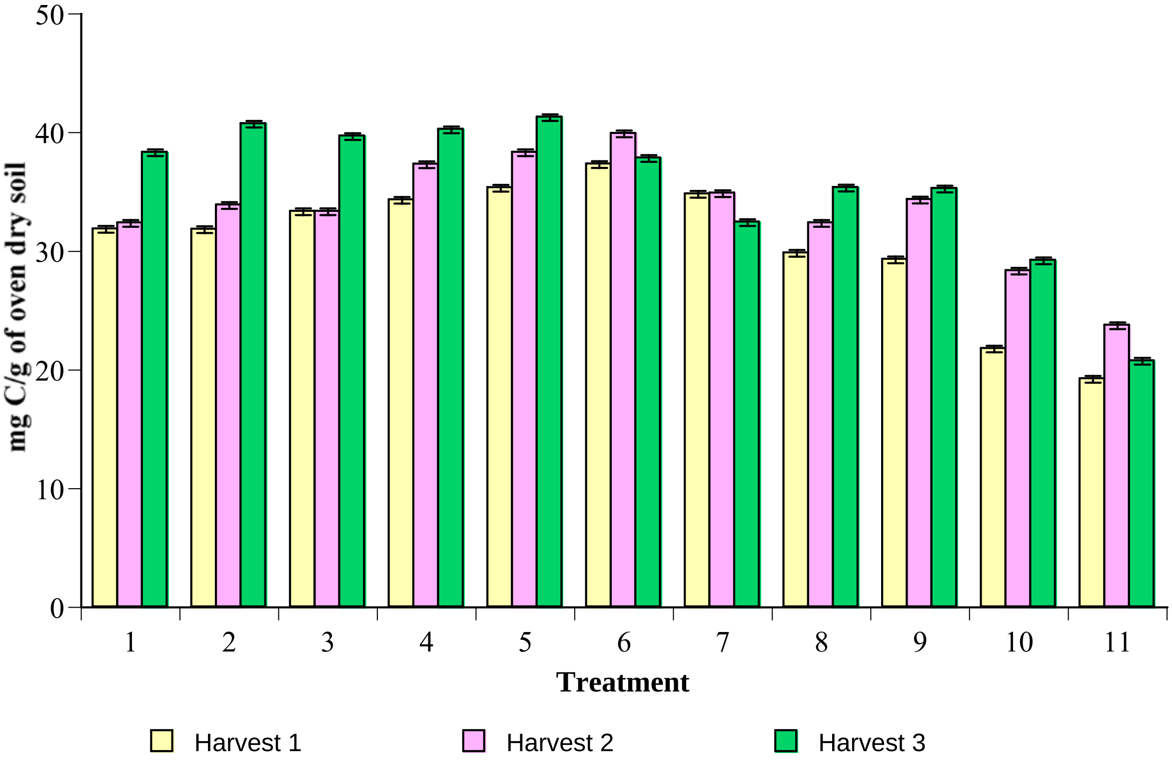


Figure 4.12. Mean organic matter (± standard error of the mean, n = 5) at all three harvests, for treatments (1) C.blank (2) C.high (3) C.std (4) 1% S.Phillipsite (5) 2% S.Phillipsite (6) 4% S.Phillipsite (7) 1% Linde type F (8) 2% Linde type F (9) 4% Linde type F (10) 2% unexchanged synthetic Phillipsite and (11) 2% unexchanged Linde type F.

For Glasshouse Experiment 2, the soil organic matter content for unexchanged synthetic Phillipsite and Linde type F soils was significantly ($p \leq 0.05$) lower at all three harvests (Figure 4.12). The organic matter content for all three loadings of exchanged Linde type F soils was significantly ($p \leq 0.01$) lower than exchanged Phillipsite soils across the harvests. An LSD test for all 11 treatments revealed 2% unexchanged Linde type F amended soils had significantly ($p \leq 0.01$) less organic matter compared with all other treatments, at all three harvests.

For Glasshouse Experiment 3, the soil organic matter content for C.blank and C.standard soils was significantly ($P \leq 0.05$) less than exchanged zeolite amended treatments at all three harvests. Following one-way ANOVA and LSD test for all 6 treatments, 2% high-aluminium Phillipsite amended soils had significantly ($P \leq 0.01$) higher organic matter, at Harvests 2 and 3 (Figure 4.13).

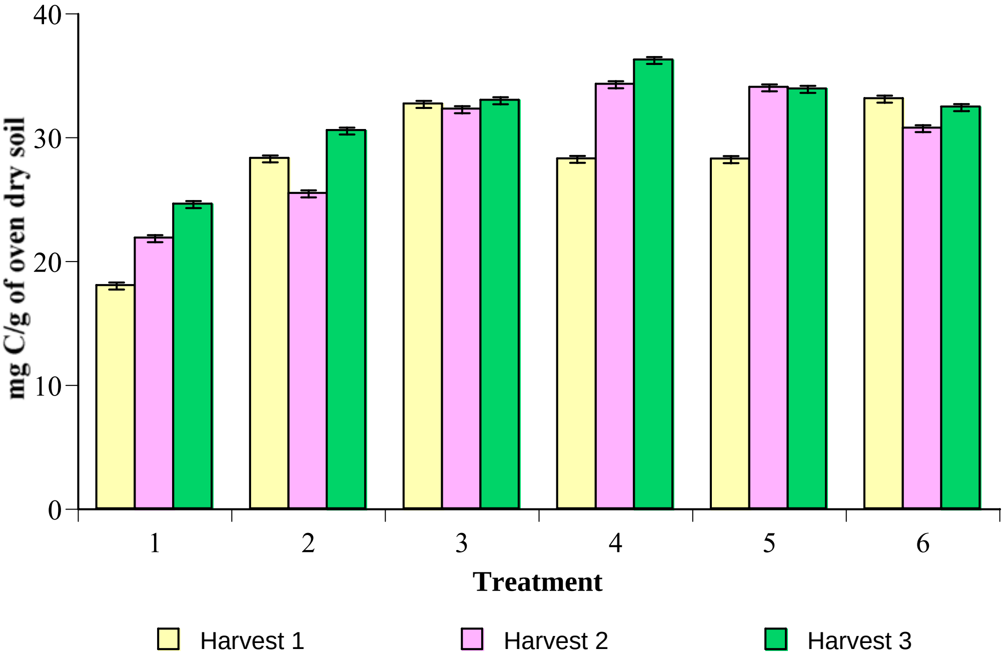


Figure 4.13. Mean organic matter (± standard error of the mean, n = 5) at all three harvests, for treatments (1) C.blank (2) C.standard (3) 1% High-aluminium synthetic Phillipsite (4) 2% High-aluminium synthetic Phillipsite (5) 1% high-crystalline synthetic Phillipsite (6) 2% High-crystalline synthetic Phillipsite.

4.2.4. Soil total nitrogen

Soil total nitrogen was measured by the standard Kjeldahl method, as proposed by Johan Kjeldahl, a Danish chemist, in 1883 (Section 2.11.4). As zeolites have ammonium in their framework, this test may not hold a true representation of total N present in soil alone, but total N taking into consideration ammonium, nitrate and nitrite N present in soil + ammonical N present in the zeolite itself. With control soils, a true representation of total N can be expected, as fertilizer addition comprised of N in the form of ammonium nitrate (27% N).

For Glasshouse Experiment 1, total N measurements were made at all three harvests and the results are presented in Table 4.16. At all three harvests, it is evident that synthetic Phillipsite-amended soils had higher total N compared to natural Phillipsite-amended soils. There is a direct association between % zeolite loading to total N present in soil i.e., higher the % zeolite (synthetic Phillipsite) loading to soil;

the higher is the final amount of total N at each individual harvest. A similar trend was found for natural Phillipsite amended soils.

Table 4.16. Mean soil total Nitrogen mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment	Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control high	10.87a	(0.80)	12.60a	(1.36)	14.24a	(0.83)
Control standard	12.88a	(0.61)	15.58a	(1.84)	12.35a	(3.82)
Synthetic Phillipsite 2%	20.55b	(1.27)	23.78b	(0.56)	17.79b	(0.88)
4%	25.07bd	(0.89)	30.46c	(3.37)	27.63c	(2.15)
8%	40.08c	(1.39)	53.80d	(2.32)	39.62d	(1.23)
Natural Phillipsite 2%	15.35ab	(1.29)	17.55a	(0.36)	13.82a	(1.08)
4%	21.84bc	(1.66)	25.66bc	(1.99)	14.14a	(0.84)
8%	30.51d	(1.54)	38.18e	(4.81)	20.44b	(0.67)
LSD ($p \leq 0.05$)	5.07		5.93		2.67	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

At Harvest 1, synthetic and natural Phillipsite-amended soils showed significant differences. An LSD test revealed 8% synthetic Phillipsite-amended soils to have significantly ($p \leq 0.05$) higher total N at all three Harvests. On analysing for interactions between treatments over time (Harvest 1-3) using two-way ANOVA, significant differences were observed for both 8% synthetic and 8% natural Phillipsite at $p \leq 0.01$ showing significantly ($p \leq 0.01$) high total N.

For Glasshouse Experiment 2; at all three harvests, it was evident that ammonium exchanged Linde type F soils had higher amounts of total N than ammonium exchanged synthetic Phillipsite soils (Table 4.17). The original amount of NH_4^+ present in Linde type F framework was higher than Phillipsite due to its Si:Al ratio. Secondly, due to the higher affinity of LTF towards NH_4^+ it might be retained in the framework and is unavailable in the soil for nitrification processes, contrary to synthetic Phillipsite amended soils, whereby NH_4^+ is released from the zeolite upon ion exchange and converted to NO_3^- and utilized by plants. It can therefore be assumed that total N in Linde type F loaded soils will be higher at all three harvests in relation to Phillipsite loadings.

Table 4.17. Mean soil total Nitrogen mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment		**Harvest 1** (S.E)	**Harvest 2** (S.E)	**Harvest 3** (S.E)
Control blank		11.60a (1.26)	11.86a (0.27)	7.85a (0.24)
Control standard		13.10ac (0.83)	11.54a (0.75)	9.92b (0.52)
Control High		18.53b (0.89)	12.61a (0.71)	12.60cd (0.20)
Synthetic Phillipsite	1%	14.03c (0.37)	13.11a (0.31)	8.30a (1.67)
	2%	18.44b (0.83)	17.47b (0.17)	13.25cd (1.00)
	4%	27.64d (0.21)	25.52c (0.84)	18.15e (0.35)
Linde type F	1%	24.83e (0.84)	20.68d (0.48)	18.70e (0.39)
	2%	32.92f (0.87)	26.89c (1.29)	22.76f (0.35)
	4%	39.53g (1.85)	33.26f (1.59)	28.76g (0.26)
Unexchanged S. Phillipsite	2%	13.84c (0.32)	12.48a (0.58)	10.77b (0.42)
Unexchanged Linde type F	2%	15.30c (0.29)	12.66a (0.35)	7.22a (0.52)
LSD ($p \leq 0.05$)		1.96	1.89	1.62

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

At Harvest 1, an LSD test showed 4% synthetic Phillipsite, and 1, 2 and 4% Linde type F treatments to have significantly ($p \leq 0.05$) higher N concentrations. At Harvest 2, significant ($p \leq 0.05$) differences were observed for 2% synthetic Phillipsite and 1 and 4% Linde type F treatments. At Harvest 3, Linde type F treatment was significantly different ($p \leq 0.05$) at 2 and 4% loadings. Analysis for interactions between treatments over time showed significant differences ($p \leq 0.01$). Unexchanged synthetic Phillipsite and Linde type F soils at 2% loading had similar amounts of total N, with no significant differences. Significant ($p \leq 0.05$) differences were, however, observed for 2 and 4% ammonium exchanged Phillipsite and Linde type F soils.

For Glasshouse Experiment 3, at all three harvests it was evident that ammonium exchanged high-aluminium Phillipsite soils had higher concentrations of total N than ammonium exchanged high-crystalline Phillipsite soils (Table 4.18). As the original amount of NH_4^+ present in high-aluminium Phillipsite framework was higher than high-crystalline Phillipsite, due to its Si:Al ratio, it can be postulated that total N in these soils will be higher at all three harvests in relation to loadings.

Table 4.18. Mean soil total Nitrogen mg/100g (± standard error of the mean, n = 5) at all three harvests.

Treatment		**Harvest 1** (S.E)		**Harvest 2** (S.E)		**Harvest 3** (S.E)	
Control blank		11.75a	(0.53)	12.11a	(0.35)	8.99a	(1.48)
Control standard		11.40a	(0.80)	13.03ac	(1.06)	12.00a	(0.55)
Synthetic Phillipsite	1%	21.30b	(1.89)	15.79abc	(0.25)	12.38a	(2.15)
(high-aluminium)	2%	29.84c	(0.59)	23.27bc	(0.31)	10.01a	(1.08)
Synthetic Phillipsite	1%	18.22ab	(0.29)	16.54abc	(0.79)	12.48a	(0.75)
(high-crystalline)	2%	24.17bc	(0.25)	20.60cb	(1.19)	12.74a	(0.97)
LSD ($p \leq 0.05$)		7.98		8.34		3.79	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

An LSD test following one-way ANOVA showed no significant differences between treatments at all three harvests. On comparison across the harvests for interactions between treatments over time (Harvests 1-3) using two-way ANOVA, both high aluminium and high crystalline Phillipsite treatments at 1 and 2% loadings showed significant ($P \leq 0.05$) differences.

4.2.5. Soil available ammonium

Soil available ammonium can be referred to as ammonium present in the soil available for conversion to nitrate by nitrification process, and thereby taken up by plants for their biochemical functions. The steam distillation method (Rowell, 1994) for ammonium-N was used to determine available ammonium (Section 2.11.4.1) after each individual harvest and the results are presented in Tables 4.19-4.21 for all three Glasshouse Experiments. There was a direct association between zeolite loading to available ammonium in these soils (i.e., higher the % zeolite loading to soil the higher is the availability of ammonium in soil).

For Glasshouse Experiment 1, at all three harvests there is a direct association between percent zeolite loading to available ammonium present in the soil (Table 4.19). An LSD test revealed 8% synthetic and natural Phillipsite amended soils to have significantly ($p \leq 0.05$) higher ammonium than both the controls at all three harvests. At Harvests 1-3 for this loading, synthetic Phillipsite soils had significantly

($p \leq 0.05$) higher ammonium levels than natural Phillipsite soils. Significant ($p \leq 0.05$) differences were observed for 2, 4 and 8% loadings of both natural and synthetic Phillipsite when analysed for interactions of treatments over time (Harvest 1-3), and control soils did not show any significant differences compared with each other at all three harvests.

Table 4.19. Mean soil available ammonium mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment	Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control high	4.73a	(0.68)	4.03a	(1.68)	2.38a	(0.22)
Control standard	5.71a	(1.01)	2.50a	(0.63)	1.90a	(0.09)
Synthetic Phillipsite 2%	3.99a	(0.78)	6.50a	(0.69)	1.39a	(0.17)
4%	7.22a	(0.32)	18.27b	(2.94)	7.87b	(0.56)
8%	16.69b	(1.92)	33.94c	(4.43)	10.11c	(1.21)
Natural Phillipsite 2%	3.61a	(0.23)	5.94a	(0.43)	2.09a	(0.13)
4%	6.37a	(1.13)	17.92b	(2.87)	2.44a	(0.71)
8%	13.59b	(1.34)	31.30c	(4.60)	5.56d	(1.01)
LSD ($p \leq 0.05$)	4.71		9.01		1.55	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse Experiment 2; at all three harvests, the amount of NH_4^+ present in ammonium exchanged Linde type F amended soils is considerably less than ammonium exchanged Phillipsite amended soils, irrespective of loadings (Table 4.20). Although no significant differences were observed at each individual harvest, analysis for interactions between treatments across the harvests revealed, ammonium exchanged Linde type F amended soils had significantly ($p \leq 0.05$) less ammonium in the soils at all three harvests, and can be accounted for ammonium not being released rapidly from Linde type F frameworks. Ammonium exchanged Phillipsite amended soils had significantly ($p \leq 0.05$) higher available ammonium at all three harvests. High amounts of ammonium in unexchanged 2% synthetic Phillipsite soils at Harvests 2 and 3 might be accounted for NH_4^+ exchanging in and out of the framework from this zeolite more easily than its counterpart Linde type F at the same loading.

Table 4.20. Mean soil available ammonium mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment		**Harvest 1**	(S.E)	**Harvest 2**	(S.E)	**Harvest 3**	(S.E)
Control blank		3.69a	(0.74)	1.76a	(0.61)	1.78a	(0.59)
Control standard		5.18a	(0.24)	3.29ab	(0.36)	3.50bd	(0.18)
Control High		5.11a	(1.03)	3.50ab	(0.43)	4.20bd	(0.20)
Synthetic Phillipsite	1%	5.60a	(0.86)	4.27b	(0.71)	3.66bd	(0.18)
	2%	5.36a	(0.74)	4.20b	(0.69)	3.71bd	(0.24)
	4%	5.74a	(0.57)	4.34b	(0.18)	5.11c	(0.21)
Linde type F	1%	1.50b	(1.02)	1.59a	(0.11)	0.94d	(0.23)
	2%	1.32b	(1.83)	1.44a	(0.13)	0.83d	(0.11)
	4%	1.06b	(1.01)	1.21a	(2.83)	0.80d	(0.71)
Unexchanged S. Phillipsite	2%	1.61ab	(0.34)	3.55b	(0.18)	2.44b	(0.13)
Unexchanged Linde type F	2%	1.68ab	(0.31)	1.82a	(0.40)	0.89d	(0.18)
LSD ($p \leq 0.05$)		2.15		2.24		0.78	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse Experiment 3; at all three harvests, the amount of NH_4^+ present in ammonium exchanged high-crystalline Phillipsite amended soils is lower than ammonium exchanged high-aluminium Phillipsite amended soils, irrespective of loadings (Table 4.21).

Table 4.21. Mean soil available ammonium mg/100g (± standard error of the mean, n = 5) at all three harvests.

Treatment		**Harvest 1**	(S.E)	**Harvest 2**	(S.E)	**Harvest 3**	(S.E)
Control blank		6.77a	(0.40)	3.58a	(0.30)	2.18a	(0.10)
Control standard		13.21b	(0.74)	10.19b	(0.56)	7.78b	(0.69)
Synthetic Phillipsite	1%	8.91ac	(0.59)	7.78c	(0.44)	6.21c	(0.45)
(high-aluminium)	2%	18.70e	(0.76)	14.39d	(0.45)	15.79d	(0.38)
Synthetic Phillipsite	1%	9.74c	(0.78)	6.94c	(0.45)	5.32e	(0.28)
(high-crystalline)	2%	22.40d	(1.72)	11.98e	(0.40)	10.24f	(0.39)
LSD ($p \leq 0.05$)		2.24		1.06		1.01	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

Following one-way ANOVA, an LSD test revealed at Harvest 1, ammonium exchanged (1 and 2%) high-aluminium Phillipsite and 2% high crystalline Phillipsite to be significantly ($P \leq 0.05$) different. At Harvest 2, both the controls and 2% high aluminium and high crystalline Phillipsite are significantly ($P \leq 0.05$) different. Finally, at Harvest 3 all treatments are significantly ($P \leq 0.05$) different from each other. On comparison across the harvests for interactions between treatments over time, both high aluminium and high crystalline Phillipsite treatments at 1 and 2% loadings showed significant ($P \leq 0.05$) differences.

4.2.6. Soil available nitrate

Soil available nitrate can be referred to as the remaining nitrate present in the soil after conversion from ammonium to nitrite and nitrate by nitrification process to be taken up by plants for their biochemical functions. The steam distillation method (Rowell, 1994) with an additional step of adding Devarda's alloy was used to determine available nitrate after each individual harvest (Tables 4.22-4.23) for Glasshouse Experiments 2 and 3. At all three harvests there is a direct association between percent zeolite loading to available nitrate present in soil (i.e., the higher the % zeolite (synthetic Phillipsite) loading to soil the higher the final nitrate content at each individual harvest).

Table 4.22. Mean soil available nitrate mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment		Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control blank		3.74a	(0.57)	3.62a	(0.18)	3.58a	(0.21)
Control standard		5.74bd	(0.29)	5.11b	(0.17)	6.93bc	(0.67)
Control High		7.63c	(0.31)	7.95c	(0.31)	7.77bc	(0.27)
Synthetic Phillipsite	1%	7.07c	(0.27)	3.99a	(0.37)	6.65b	(0.24)
	2%	7.35c	(0.24)	5.60b	(0.20)	6.30b	(0.18)
	4%	8.40c	(0.49)	7.07e	(0.24)	8.54c	(0.40)
Linde type F	1%	1.07d	(0.68)	1.04e	(0.38)	0.68d	(0.74)
	2%	2.10d	(0.24)	0.95e	(0.43)	0.81d	(0.29)
	4%	2.53a	(1.39)	0.68e	(0.11)	1.35d	(0.13)
Unexchanged S. Phillipsite	2%	6.33bcd	(0.30)	6.09f	(0.07)	4.83e	(0.21)
Unexchanged Linde type F	2%	5.32d	(0.13)	4.55b	(0.40)	4.41e	(0.13)
LSD ($p \leq 0.05$)		1.33		0.68		0.89	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse Experiment 2, an LSD test revealed 2% unexchanged synthetic Phillipsite amended soil to be significantly ($p \leq 0.05$) different at Harvest 2 (Table 4.22). On analysing nitrate levels across the harvests, interactions between the treatments over time showed Linde type F soils to have significantly ($p \leq 0.01$) less nitrate in soils, and can be accounted for by ammonium not being released rapidly from the Linde type F framework. Ammonium exchanged Phillipsite amended soils (at all three loadings) had significantly ($p \leq 0.01$) higher available nitrate content in soil at all three harvests, and at Harvest 3, 4% loaded synthetic Phillipsite soils had significantly ($p \leq 0.01$) more nitrate. Lower amounts of available nitrate in 2% loaded unexchanged Linde type F soils on comparison with unexchanged Phillipsite soils might be accounted for by ammonium (present in soil as added NH_4NO_3 fertilizer) exchanging into the zeolite framework, but not exchanging out into the soil effectively to be converted to nitrate, due to its high affinity towards this cation.

For Glasshouse Experiment 3, across the harvests significant ($P \leq 0.05$) differences were observed for 2% loaded high aluminium and high crystalline Phillipsite treatments when analysed for interaction between treatments (Table 4.23).

Table 4.23. Mean soil available nitrate mg/100g (± standard error of the mean, n = 5) at all three harvests.

Treatment		**Harvest 1**	(S.E)	**Harvest 2**	(S.E)	**Harvest 3**	(S.E)
Control blank		4.98a	(0.45)	5.04a	(0.78)	3.92a	(0.20)
Control standard		7.39b	(0.39)	6.44a	(0.25)	4.64ac	(0.26)
Synthetic Phillipsite	1%	7.28b	(0.82)	6.33a	(0.17)	5.93b	(0.62)
(high-aluminium)	2%	8.96c	(0.43)	8.91bc	(0.23)	6.84b	(0.34)
Synthetic Phillipsite	1%	8.06bcd	(0.23)	6.32a	(0.19)	4.92c	(0.19)
(high-crystalline)	2%	9.18d	(0.45)	8.12bc	(1.17)	6.21b	(0.52)
LSD ($p \leq 0.05$)		1.19		1.44		0.94	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

Ammonium exchanged high-aluminium Phillipsite amended soils had significantly lower nitrate in the soils at Harvests 1, which can be accounted for ammonium being released at a slower rate from this zeolite, compared to its counterpart high-crystalline Phillipsite, with a rapid release of NH_4^+ at this stage of plant growth. At Harvest 2, available nitrate levels in the soil were similar in both the zeolites at 1% loading, but higher in high-aluminium Phillipsite at 2% loading. At Harvest 3 the excess NH_4^+ present in high-aluminium Phillipsite framework exchanges more uniformly, in contrast to high-crystalline Phillipsite, whereby most of the NH_4^+ has been exchanged out from the framework to be converted to nitrate by nitrification process. Therefore, available nitrate levels are slightly higher in the former soils. Available nitrate concentrations in C.blank soils were significantly ($P \leq 0.05$) lower than C.standard and zeolite amended soils at all three harvests.

4.2.7. Soil available Phosphorus

As phosphate is an essential macronutrient, an equal amount of super phosphate (18% P) was added to soils, irrespective of their treatment, in order to facilitate plants with energy storage reactions and to maintain structural integrity. Available P levels were established after each individual harvest following Olsen's method (Section 2.11.5). As soils received equal amounts of P fertilizer at the start of the experiment, any significant differences between the treatment effects can be accounted for by preferential uptake of P over other nutrients, based on their availability (Figures 4.14-4.16). For Glasshouse Experiment 1 (Figure 4.14); one-way ANOVA followed by an LSD test showed at Harvest 1; 4% natural Phillipsite had significantly ($p \leq 0.05$) higher P content in soil and C.std had significantly ($p \leq 0.05$) less P. At Harvest 2, 8% synthetic Phillipsite showed significant differences, and at Harvest 3; 2 and 4% loadings of both synthetic and natural Phillipsite showed significant ($p \leq 0.05$) differences. Maize plants did not show P deficiency during their growth period; thereby assuming that plants actively up took P. As shown in Figure 4.14, whereby available P concentration in soils decreased from Harvest 1 to 3 for most treatments, indicates that plants have taken up P actively without any interference from other nutrients. Analysis for interactions between treatments over time showed significant differences for 4 and 8% loadings of both synthetic and natural Phillipsite. At Harvest 3, both 4 and 8% loadings for synthetic and natural Phillipsite amended soils showed significant reductions in available P, suggesting that plants may have taken up more P. This may be associated with lower availability of other major nutrients in the soil at this stage of plant growth prone to leaching and ion exchange into the zeolite framework.

Glasshouse experiment 1

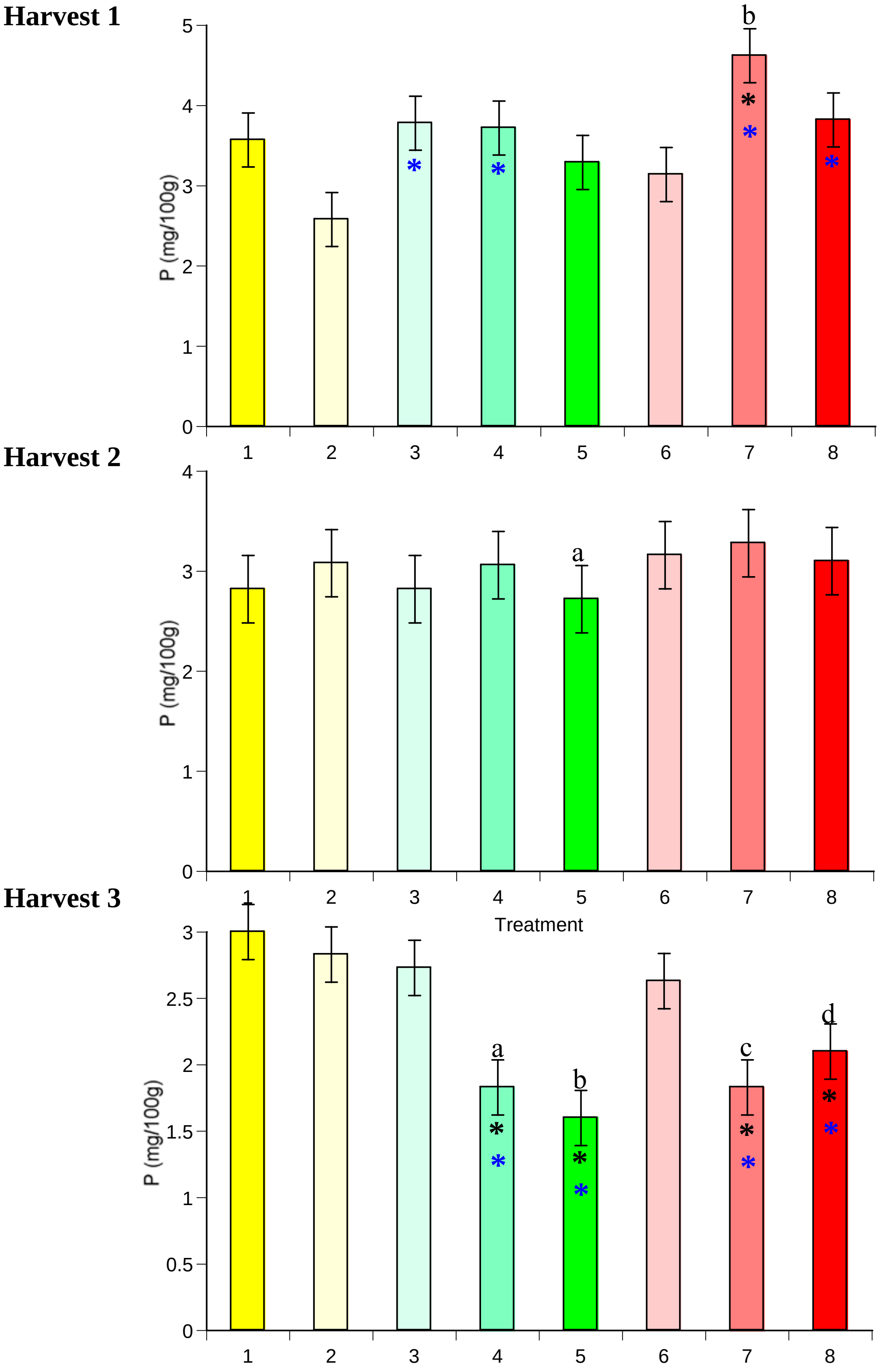


Figure 4.14. Mean soil available phosphorus (± standard error of the mean, n = 5) for treatments (1) C.High (2) C.Std (3) 2% S.Phillipsite (4) 4% S.Phillipsite (5) 8% S.Phillipsite (6) 2% N.Phillipsite (7) 4% N.Phillipsite and (8) 8% N.Phillipsite.★, Significantly different from control (1) and★, significantly different from control (2) and, where means have been given different letters above the columns, they are significantly different (at p ≤ 0.05) from each other as discussed in section 2.12.

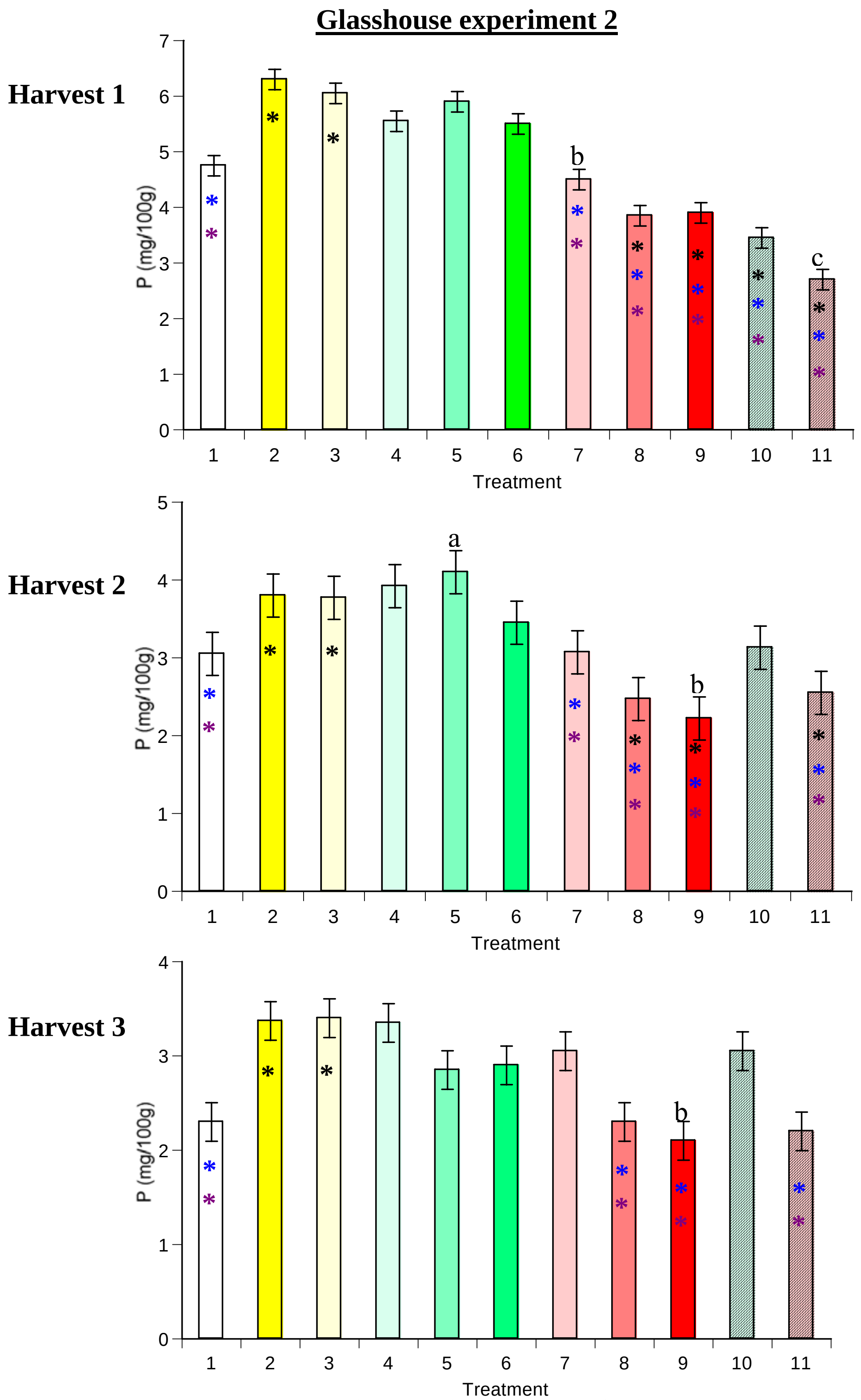
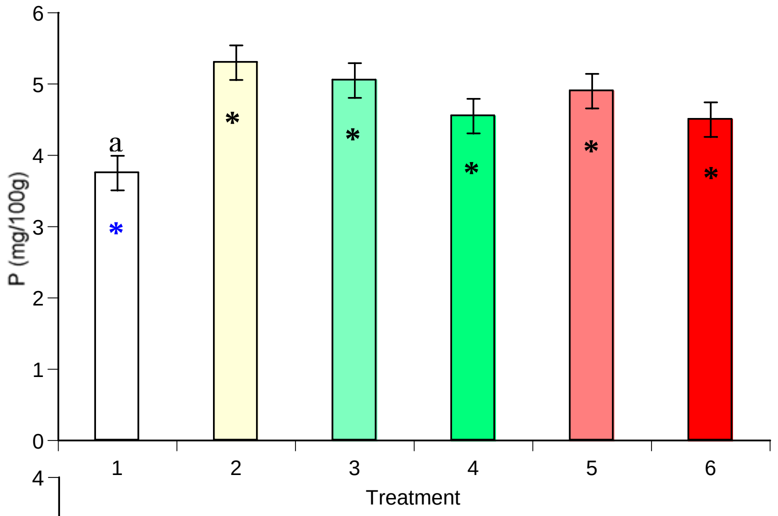

Glasshouse experiment 2

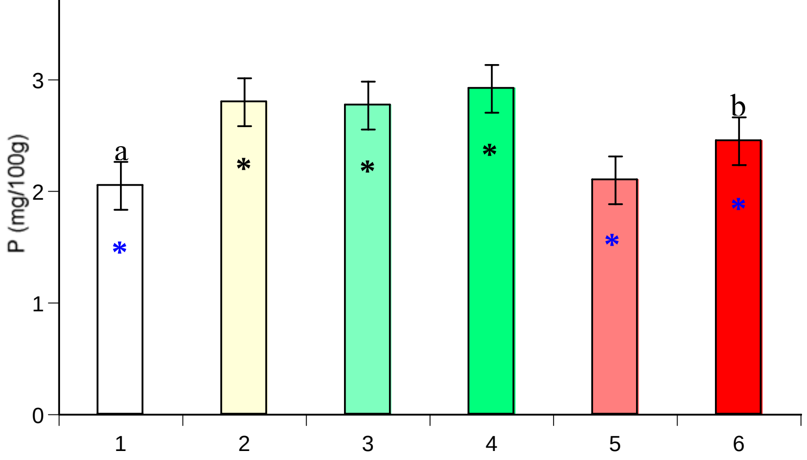
Figure 4.15. Mean soil available Phosphorus (± standard error of the mean, n = 5) for treatments (1) C.blank (2) C.high (3) C.std (4) 1% S.Phillipsite (5) 2% S.Phillipsite (6) 4% S.Phillipsite (7) 1% Linde type F (8) 2% Linde type F (9) 4% Linde type F (10) 2% Unexchanged synthetic Phillipsite (11) 2% Unexchanged Linde type F. ★, Significantly different from control (1)★, significantly different from control (2) and ★ significantly different from control (3) and, where means have been given different letters above the columns, they are significantly different (at p ≤ 0.05) from each other.

Glasshouse experiment 3

Harvest 1



Harvest 2



Harvest 3

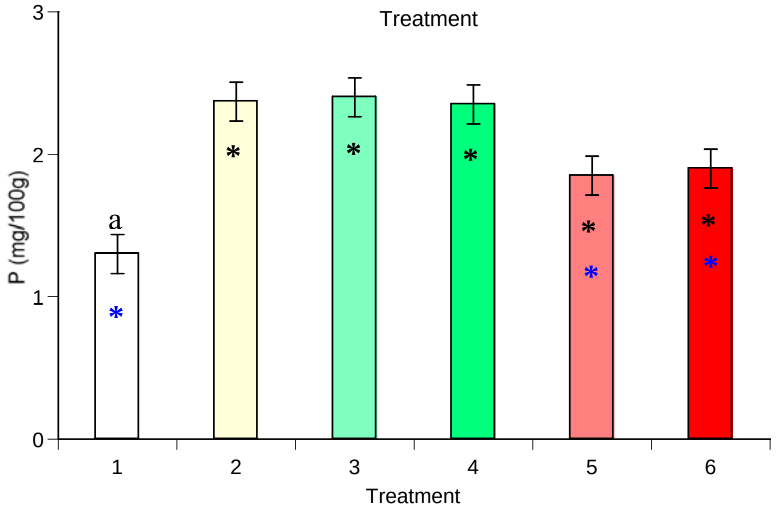


Figure 4.16. Mean soil available Phosphorus (± standard error of the mean, n = 5) for treatments (1) C.blank, (2) C.standard, (3) 1% High-aluminium synthetic Phillipsite, (4) 2% High-aluminium synthetic Phillipsite, (5) 1% High-crystalline synthetic Phillipsite and (6) 2% High-crystalline synthetic Phillipsite.★, Significantly different from control (1)★, significantly different from Control (2) and, where means have been given different letters above the columns, they are significantly different (at $p \leq 0.05$) from each other.

For Glasshouse Experiment 2, results of soil available P demonstrates C.blank and Linde type F amended soils have less P than synthetic Phillipsite amended soils (Figure 4.15). As ammonium exchanged Linde type F released NH_4^+ into the soils at a much slower rate than ammonium exchanged Phillipsite, N deficiency in these soils might lead to plants taking up P over N (due to its low-availability) at all three harvests. In unexchanged Phillipsite and Linde type F amended soils P uptake by plants was higher at Harvest 1; at Harvests 2 and 3 unexchanged Linde type F soils showed a higher uptake of P than unexchanged Phillipsite soils, this can be accounted for by synthetic Phillipsite exchanging NH_4^+ out of the framework, whereas Linde type F held on to NH_4^+ due to its higher affinity for this cation. Synthetic Phillipsite soils had available N at all stages of plant growth, thereby allowing plants to uptake both N and P more uniformly. Significantly ($p \leq 0.05$) lower P concentrations in the soil were observed for C.blank and all three loadings of ammonium exchanged Linde type F soils across all three Harvests.

For Glasshouse Experiment 3, one-way ANOVA followed by an LSD test showed C.blank soils to have significantly ($P \leq 0.05$) lower P at all three harvests, and both 1 and 2% high-crystalline Phillipsite amended soils showed significantly ($P \leq 0.05$) lower P levels in the soils at Harvests 2 and 3 (Figure 4.16). At Harvests 2 and 3 high crystalline Phillipsite soils had significantly lower available P concentrations in the soil. This may be accounted for by lower N availability in high crystalline Phillipsite amended soils, due to the rapid release of NH_4^+ at Harvest 1, and therefore enabling the plants to take up more P from these soils. As higher availability of N in high aluminium Phillipsite soils at all three harvests encourages the plants grown in these soils to take up P more uniformly. Thus, there is no evidence of significant decreases in available P from these soils.

4.2.8. Soil available Potassium

Available K was measured at all three harvests and is expressed as mg/100g of oven-dry soil. Available K decreased during the plant growth period for all three-glasshouse experiments. For Glasshouse Experiment 1 (Table 4.24), available K was greatest at Harvest 1; followed by Harvest 2; then Harvest 3 for both synthetic and natural Phillipsite-amended soils at all three loadings. However, for control soils available K was highest at Harvest 1, followed by Harvest 3 and then Harvest 2.

Synthetic Phillipsite-amended soils had a slightly higher available K than the natural Phillipsite amended soils at all three harvests.

An LSD test revealed 2 and 4% synthetic and natural Phillipsite soils to have significantly ($p \leq 0.05$) higher available K at Harvest 1. At Harvest 2, 8% synthetic Phillipsite was significantly ($p \leq 0.05$) different, and at Harvest 3; 4 and 8% synthetic Phillipsite along with 8% natural Phillipsite had significantly ($p \leq 0.05$) higher K concentrations. Analysis for interactions within the treatments over time (Harvests 1-3) showed significant ($p \leq 0.05$) differences for synthetic and natural Phillipsite treatments at all three loadings.

Table 4.24. Mean soil available potassium mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment	Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control high	17.89a	(0.71)	5.70a	(0.21)	9.02a	(0.35)
Control standard	17.38a	(0.45)	5.53a	(0.17)	7.18a	(0.26)
Synthetic Phillipsite 2%	57.58b	(0.50)	38.90be	(2.93)	26.46be	(2.11)
4%	115.75c	(5.10)	106.89c	(7.46)	65.83c	(4.77)
8%	179.06d	(3.34)	176.36d	(2.17)	130.53d	(3.15)
Natural Phillipsite 2%	37.48e	(2.64)	31.43be	(0.41)	27.14be	(1.48)
4%	75.15f	(2.02)	62.53e	(1.08)	45.11e	(4.51)
8%	111.70c	(1.73)	109.24c	(6.81)	89.17f	(6.16)
LSD ($p \leq 0.05$)	4.41		21.98		17.25	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse Experiment 2 (Table 4.25), available K was greatest at Harvest 1; followed by Harvest 2; then Harvest 3 for both ammonium exchanged/unexchanged synthetic Phillipsite and Linde type F treatments at all three loadings. Similar trends were observed for all control soils. High available K in unexchanged Linde type F-amended soils compared with unexchanged synthetic Phillipsite soils can be accounted for their synthesis in a K, and Na-K system, respectively. Upon ion exchange with NH_4^+ (present as NH_4NO_3 fertilizer in soil) Linde type F takes up NH_4^+ for K, and Phillipsite takes up NH_4^+ for K and Na, thereby increasing K concentrations in soil. An LSD test revealed significant ($p < 0.05$) differences for 2% unexchanged Linde type F at Harvest 1, significant effects ($p < 0.05$) for all of the exchanged and unexchanged synthetic Phillipsite and Linde type F treatment at Harvest 2 and significant effects ($p < 0.05$) for 4% Linde type F and both the 2% unexchanged zeolites at Harvest 3. Across the harvests, significant ($p < 0.05$) differences were observed for both 2 and 4% loadings of ammonium exchanged Phillipsite and Linde type F, and also unexchanged 2% Phillipsite and Linde type F showed significant ($p < 0.05$) differences. Unexchanged Linde type F soils had high K content due to its synthesis in K form, whereby K is the major counter balancing cation in the framework.

Table 4.25. Mean soil available Potassium mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment		**Harvest 1** (S.E)		**Harvest 2** (S.E)		**Harvest 3** (S.E)	
Control blank		12.38a	(0.98)	4.00a	(1.09)	4.38a	(0.18)
Control standard		12.98a	(0.63)	6.03a	(0.65)	5.12a	(0.30)
Control High		18.81a	(0.99)	6.49a	(0.80)	5.55a	(0.39)
Synthetic Phillipsite	1%	35.08b	(0.50)	14.55b	(2.27)	13.33ab	(0.24)
	2%	53.45ce	(0.21)	26.74c	(1.54)	21.63b	(3.13)
	4%	102.34d	(1.37)	72.43d	(1.53)	46.64c	(8.15)
Linde type F	1%	53.28e	(0.93)	39.03e	(3.58)	21.05b	(4.53)
	2%	102.46d	(1.02)	84.07f	(2.71)	53.15c	(1.44)
	4%	197.65f	(3.07)	177.61g	(5.53)	138.73d	(4.81)
Unexchanged S. Phillipsite	2%	192.00f	(2.01)	151.77h	(4.10)	114.79e	(5.12)
Unexchanged Linde type F	2%	277.34g	(2.86)	215.04i	(5.98)	190.74f	(8.82)
LSD ($p \leq 0.05$)		13.78		10.51		11.05	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse Experiment 3, low available K in 1 and 2% high-aluminium Phillipsite amended soils at Harvest 1 can be accounted for release of this cation slowly at the start of the experiment, and thereafter more uniformly at Harvests 2 and 3 probably due to its low crystallinity and coarser particle size distribution (Table 4.26). As the original amount of K concentration in high-aluminium Phillipsite is higher than high-crystalline Phillipsite, a slightly higher concentration of K is observed in the soils of this zeolite. An LSD test revealed all 6 treatments to be significantly ($P \leq 0.05$) different from each other at Harvest 1, 2% high aluminium Phillipsite to be significantly different ($P \leq 0.05$) at Harvest 2 and 2% high aluminium Phillipsite along with 1% high crystalline Phillipsite to be significantly ($P \leq 0.05$)

different at Harvest 3. Interactions between the treatments across the harvests showed significant ($P \leq 0.05$) differences for both 2% loaded high aluminium and high crystalline Phillipsite treatments.

Table 4.26. Mean soil available potassium mg/100g (± standard error of the mean, n = 5) at all three harvests.

Treatment		Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control blank		13.77a	(0.42)	5.26a	(0.30)	4.01a	(0.18)
Control standard		16.07b	(0.32)	5.93a	(0.55)	3.75a	(0.25)
Synthetic Phillipsite	1%	28.78c	(0.60)	22.28b	(0.95)	15.29b	(0.75)
(high-aluminium)	2%	40.87d	(1.02)	33.15c	(0.61)	22.14c	(0.99)
Synthetic Phillipsite	1%	32.64e	(0.67)	19.53b	(0.76)	11.55d	(0.17)
(high-crystalline)	2%	49.36f	(1.78)	27.03b	(0.97)	15.01b	(0.55)
LSD ($p \leq 0.05$)		2.26		5.72		1.38	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

4.2.9. Soil available Calcium

Control soils were fertilized with calcium ammonium nitrate, also known as 'nitrate chalk' at the start of Glasshouse Experiment 1. Calcium ammonium nitrate was applied to both control soils as a fertilizer source. For Glasshouse Experiment 1, it is evident from Table 4.27 a higher Ca content was present in both the control soils.

Table 4.27. Mean soil available calcium mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment		Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control high		122.60a	(0.55)	126.42a	(0.25)	124.94a	(0.36)
Control standard		122.95a	(0.89)	126.65a	(0.33)	124.07a	(0.59)
Synthetic Phillipsite	2%	114.28b	(0.61)	112.02b	(0.66)	115.26bc	(0.40)
	4%	113.17b	(1.29)	108.75b	(2.16)	111.71c	(1.25)
	8%	108.21b	(1.07)	111.19b	(3.17)	108.71c	(1.55)
Natural Phillipsite	2%	113.49b	(2.13)	113.58b	(0.54)	117.50b	(1.57)
	4%	118.48ab	(1.17)	110.22b	(0.84)	112.82bc	(2.78)
	8%	115.70ab	(0.93)	109.47b	(2.23)	109.65c	(1.81)
LSD ($p \leq 0.05$)		7.18		6.94		3.58	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

Significant decreases in available Ca were observed with increasing zeolite at each Harvest. Control soils have significantly ($p \leq 0.05$) higher available Ca than synthetic and natural Phillipsite amended soils at all three harvests. There is an association between zeolite loadings to available Ca in soil and Ca levels remained consistent at each individual harvest within the treatments with no significant differences. Analysis for interactions within treatments across the harvests showed significant ($p \leq 0.05$) differences for the controls, 2 and 4% synthetic Phillipsite soils and 4 and 8% natural Phillipsite soils. None of the plants grown in control or zeolite-amended soils showed any Ca deficiency.

For Glasshouse Experiment 2, all treatments were subject to equal amounts of Ca as originally present in the soil at the start of the experiment. Therefore, significant differences between zeolite added treatment effects with controls could be subject to ion exchange reactions between the Ca cation present in soil with cations in the zeolite framework. From the results, it can be assumed that ammonium exchanged synthetic Phillipsite soils had a lower selectivity towards Ca than ammonium exchanged Linde type F soils at all three loadings. With respect to unexchanged Phillipsite and Linde type F soils at 2% loading similar trends were observed (Table 4.28).

Table 4.28. Mean soil available calcium mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment		**Harvest 1** (S.E)	**Harvest 2** (S.E)	**Harvest 3** (S.E)
Control blank		127.74a (1.11)	123.92a (8.51)	125.48a (0.66)
Control standard		129.87a (0.11)	126.90a (0.72)	128.54bc (0.40)
Control High		128.98a (0.86)	126.35a (1.08)	122.46a (1.71)
Synthetic Phillipsite	1%	133.04bc (0.26)	131.47b (1.61)	130.69bc (0.29)
	2%	134.21bc (2.61)	132.14b (1.35)	128.81b (2.13)
	4%	134.10bc (2.33)	132.75b (5.04)	132.17c (2.61)
Linde type F	1%	127.40a (0.46)	125.89ab (4.88)	130.02bc (0.47)
	2%	115.51c (0.16)	118.82a (0.44)	124.99a (1.25)
	4%	120.93d (0.13)	120.11a (0.29)	110.71d (0.13)
Unexchanged S. Phillipsite	2%	133.01bc (0.61)	132.11b (1.11)	132.88c (1.06)
Unexchanged Linde type F	2%	125.17a (0.17)	119.70a (0.43)	125.27a (0.19)
LSD ($p \leq 0.05$)		2.78	5.15	3.04

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

An LSD test revealed 4% ammonium exchanged Linde type F to be significantly (p <0.05) different at Harvests 1 and 3. These results are in relation with Ca levels in dry plant shoot material (Tables 4.10, 4.11). Analysis across the harvests for interactions between treatments over time showed significant (p <0.05) differences.

For Glasshouse Experiment 3, an LSD test revealed no significant differences between treatments at all three harvests (Table 4.29). Across the harvests, significant ($P \leq 0.05$) differences were observed for both 2% high aluminium and high crystalline Phillipsite treatments.

Table 4.29. Mean soil available Calcium mg/100g (± standard error of the mean, n = 5) at all three harvests.

Treatment		Harvest 1 (S.E)		Harvest 2 (S.E)		Harvest 3 (S.E)	
Control blank		156.33a	(2.82)	153.91a	(0.62)	149.41a	(2.21)
Control standard		160.40a	(1.90)	157.44a	(1.85)	150.94a	(1.08)
Synthetic Phillipsite	1%	169.55bc	(0.34)	162.68b	(2.06)	154.89ab	(1.68)
(high-aluminium)	2%	171.67bc	(2.14)	165.43b	(1.79)	155.97b	(2.17)
Synthetic Phillipsite	1%	175.40c	(1.68)	161.88b	(1.35)	155.80b	(1.15)
(high-crystalline)	2%	171.85bc	(1.47)	165.92b	(1.68)	157.02b	(1.73)
LSD ($p \leq 0.05$)		4.52		3.91		4.16	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

4.2.10. Soil available Magnesium

Soil available Mg was measured along with K and Ca following ammonium acetate extractions (Section 2.11.6). Mg is an important constituent of the chlorophyll molecule, and is particularly important for maize growth. Quite often, tropical maize suffers from Mg deficiency (Kayode, 1985). The cation exchange selectivity of zeolite influences the amount of available Mg in soil. For Glasshouse Experiment 1, it is evident from Table 4.30 that natural Phillipsite soils had higher available Mg than synthetic Phillipsite-amended soils at Harvests 1 and 2. Due to lower concentrations of Mg in synthetic Phillipsite-amended soils at Harvest 1, lower older leaves of the maize plants turned brown (Plate 4.3). These deficiency symptoms disappeared at Harvest 2 and 3, as Mg from Phillipsite exchanged back into soil for other cations present in soil. Mg content at Harvest 3 was consistent in all 8 treatments due to plant uptake of Mg without any interference from other cations during its growth stage from Harvests 1- 3.

Table 4.30. Mean soil available magnesium mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment	Harvest 1	(S.E)	Harvest 2	(S.E)	Harvest 3	(S.E)
Control high	10.72a	(0.13)	9.88a	(0.07)	9.73a	(0.65)
Control standard	8.91b	(0.39)	6.74b	(0.09)	8.27ab	(0.71)
Synthetic Phillipsite 2%	6.99c	(0.03)	7.54ab	(0.76)	7.14b	(0.38)
4%	6.73c	(0.06)	8.26ab	(2.26)	8.43ab	(0.46)
8%	6.55c	(0.05)	10.55a	(0.77)	7.26b	(0.41)
Natural Phillipsite 2%	7.92d	(0.48)	6.12b	(0.11)	7.77b	(0.88)
4%	8.01d	(0.25)	6.83b	(0.08)	8.02b	(0.80)
8%	8.18d	(0.22)	10.01a	(1.79)	8.29ab	(1.07)
LSD ($p \leq 0.05$)	0.61		2.61		1.69	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

Significant treatment differences were observed for zeolite amended soils and control soils. Control soils had significantly ($p \leq 0.05$) higher available Mg than synthetic and natural Phillipsite-amended soils at Harvest 1. At Harvest 2 control high and 8% loadings of both synthetic and natural Phillipsite amended soils showed significantly ($p \leq 0.05$) higher available Mg. An association between zeolite loadings to available Mg was observed at Harvest 2, (i.e. the higher the loading of Phillipsite (synthetic/natural) to soil the higher the amount of available Mg in soil). At Harvest 3, control high showed significantly ($p \leq 0.05$) higher available Mg in the soil. Although significant differences were observed at individual harvests, on analysing for interactions within the treatments over time, no significant effects were observed.

For Glasshouse Experiment 2, it is evident from Table 4.31 that ammonium exchanged Phillipsite soils had higher available Mg than ammonium exchanged Linde type F-amended soils at Harvest 1. However, at Harvests 2 and 3 the trend was reversed with Linde type F soils having higher available Mg at all three loadings. Once again, the high selectivity of Phillipsite towards Mg is demonstrated with exchange of this cation in and out of ammonium exchanged zeolite frameworks.

Available Mg concentrations in ammonium exchanged synthetic Phillipsite soils decreased from Harvest 1 to Harvest 3 for all three loadings (Table 4.31). As the plants did not show any Mg deficiency at all three harvests, it can be assumed that plants have taken up Mg from soil. In the case of Linde type F soils as Mg levels in soils remained constant at each harvest and as plants showed Mg deficiencies (Tables 4.10-4.11) it can be assumed that plants have not taken up Mg. This behaviour may be linked to plants not synthesizing Mg uptake due to N deficiency (Bunt, 1976).

Table 4.31. Mean soil available magnesium mg/100g at all three harvests (± standard error of the mean, n = 5).

Treatment		**Harvest 1**	(S.E)	**Harvest 2**	(S.E)	**Harvest 3**	(S.E)
Control blank		8.61a	(0.12)	5.34a	(1.20)	4.18a	(0.12)
Control standard		8.17a	(0.16)	5.63a	(0.22)	3.61b	(0.17)
Control High		7.96b	(0.22)	5.16a	(0.32)	4.76c	(0.03)
Synthetic Phillipsite	1%	7.36c	(0.33)	5.97a	(1.47)	3.98b	(0.16)
	2%	7.19c	(0.17)	5.65a	(0.70)	3.07d	(0.29)
	4%	6.77a	(0.27)	5.47a	(1.47)	2.96d	(0.20)
Linde type F	1%	6.70a	(0.35)	5.13a	(2.76)	5.06e	(0.25)
	2%	6.73a	(0.18)	6.20a	(0.44)	5.57f	(0.14)
	4%	6.72a	(0.18)	5.17a	(0.28)	5.72f	(0.09)
Unexchanged S. Phillipsite	2%	6.38a	(0.32)	5.90a	(0.68)	5.55f	(0.06)
Unexchanged Linde type F	2%	6.33a	(0.29)	5.72a	(1.31)	5.43ef	(0.06)
LSD ($p \leq 0.05$)		0.59		1.07		0.39	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

An LSD test across the harvests revealed ammonium exchanged Phillipsite soils at 1, 2 and 4% loadings and all three controls to be significantly ($p < 0.05$) different, a decrease in Mg concentrations from Harvest 1 to 3 was observed in these soils. Ammonium exchanged Linde type F soils had significantly lower available Mg at Harvest 1 and significantly higher available Mg at Harvest 3. Analysis across the harvests for interactions between the treatments over time revealed significant ($p < 0.05$) differences for control and ammonium exchanged synthetic Phillipsite soils.

For Glasshouse Experiment 3, it is evident from Table 4.32 that ammonium exchanged high-aluminium Phillipsite soils had more available Mg than ammonium exchanged high-crystalline Phillipsite amended soils at Harvest 1. From Table 4.32 it is also evident that available Mg concentrations in ammonium exchanged synthetic Phillipsite soils decreased from Harvest 1 to Harvest 3 for both loadings and, as the plants did not show any Mg deficiency at all three harvests, it can be assumed that plants have taken up Mg from soil. An LSD test revealed ammonium exchanged high-crystalline Phillipsite to be significantly ($P \leq 0.05$) different at Harvest 3. Analysis across the harvests showed highly significant ($P \leq 0.01$) decreases in Mg concentrations for both controls.

Table 4.32. Mean soil available Magnesium mg/100g (± standard error of the mean, n = 5) at all three harvests.

Treatment		**Harvest 1**	(S.E)	**Harvest 2**	(S.E)	**Harvest 3**	(S.E)
Control blank		7.10a	(0.17)	5.41a	(0.09)	3.41a	(0.09)
Control standard		7.62a	(0.13)	5.38a	(0.13)	3.94bc	(0.09)
Synthetic Phillipsite	1%	7.18a	(0.46)	5.43a	(0.04)	4.16c	(0.15)
(high-aluminium)	2%	6.89a	(0.14)	5.16a	(0.09)	4.28c	(0.11)
Synthetic Phillipsite	1%	6.56a	(0.06)	5.38a	(0.07)	4.30c	(0.05)
(high-crystalline)	2%	5.99a	(0.09)	5.45a	(0.09)	4.73d	(0.01)
LSD ($p \leq 0.05$)		2.52		0.32		0.23	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

4.3. Total elemental analyses of soil samples by XRF

Soil analyses comprised of measuring available K, Ca and Mg, it was therefore important to known the total % concentrations of these elements in soil for Glasshouse experiment 1 (Tables 4.33-4.35). As it is difficult to separate zeolite material from soil, X-Ray fluorescence spectrometry was used for the determination of total K, Ca and Mg in zeolite-amended and fertilizer-amended soils after each harvest (Section 2.12.7).

As evident in Tables 4.33-4.35, no significant differences were observed for any of the treatments when analysed by one-way ANOVA followed by an LSD test ($p \leq 0.05$). There was no association between available K, Ca and Mg to their totals present in soil as analysed by XRF. This analysis was thereby discarded for later glasshouse experiments, due to the insensitivity of this technique.

Table 4.33. Mean total elemental (%) of K, Ca and Mg in soil at Harvest 1 (± standard error of the mean, n = 5).

Treatment		Mean K	(S.E)	Mean Ca	(S.E)	Mean Mg	(S.E)
Control high		2.78	(0.063)	0.53	(0.020)	0.78	(0.042)
Control standard		2.61	(0.038)	0.53	(0.023)	0.75	(0.031)
Synthetic Phillipsite	2%	2.73	(0.021)	0.53	(0.015)	0.78	(0.036)
	4%	2.66	(0.033)	0.49	(0.019)	0.64	(0.022)
	8%	2.72	(0.054)	0.50	(0.013)	0.52	(0.040)
Natural Phillipsite	2%	2.77	(0.035)	0.52	(0.017)	0.80	(0.049)
	4%	2.65	(0.052)	0.52	(0.019)	0.59	(0.058)
	8%	2.73	(0.017)	0.53	(0.019)	0.68	(0.038)
LSD ($p \leq 0.05$)		NS		NS		NS	

Table 4.34. Mean total elemental (%) of K, Ca and Mg in soil at Harvest 2 (± standard error of the mean, n = 5).

Treatment		Mean K	(S.E)	Mean Ca	(S.E)	Mean Mg	(S.E)
Control high		2.71	(0.018)	0.50	(0.016)	0.87	(0.032)
Control standard		2.59	(0.058)	0.51	(0.087)	0.85	(0.035)
Synthetic Phillipsite	2%	2.64	(0.043)	0.53	(0.012)	0.80	(0.060)
	4%	2.92	(0.066)	0.58	(0.016)	0.87	(0.077)
	8%	2.67	(0.056)	0.53	(0.023)	0.60	(0.027)
Natural Phillipsite	2%	2.73	(0.014)	0.50	(0.095)	0.84	(0.058)
	4%	2.80	(0.046)	0.55	(0.015)	0.89	(0.089)
	8%	2.59	(0.053)	0.51	(0.023)	0.82	(0.099)
LSD ($p \leq 0.05$)		NS		NS		NS	

Table 4.35. Mean total elemental (%) of K, Ca and Mg in soil at Harvest 3 (± standard error of the mean, n = 5).

Treatment		Mean K	(S.E)	Mean Ca	(S.E)	Mean Mg	(S.E)
Control high		2.78	(0.076)	0.58	(0.086)	0.87	(0.060)
Control standard		2.53	(0.032)	0.49	(0.018)	0.71	(0.042)
Synthetic Phillipsite	2%	2.78	(0.054)	0.60	(0.026)	0.97	(0.069)
	4%	2.37	(0.036)	0.50	(0.021)	0.77	(0.063)
	8%	2.51	(0.041)	0.47	(0.013)	0.59	(0.067)
Natural Phillipsite	2%	2.76	(0.096)	0.54	(0.023)	0.96	(0.077)
	4%	2.41	(0.061)	0.48	(0.014)	0.80	(0.035)
	8%	2.48	(0.032)	0.50	(0.080)	0.67	(0.045)
LSD ($p \leq 0.05$)		NS		NS		NS	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

4.4. Leachate measurements

For Glasshouse Experiment 2, leachate measurements were carried out, as described in Section 2.9.1. Leachate from two pots of a particular treatment effect was collected into a container in weeks 1, 3, 6 and 9 and analysed for nitrate and nitrite levels, using an IC column. Leaching of nitrate and nitrite from control and ammonium exchanged and unexchanged zeolite soils showed significantly higher amounts of nitrate and nitrite being leached out from control high soils followed by control standard and ammonium exchanged Phillipsite amended soils. Linde type F soils had significantly ($p < 0.01$) less nitrate and nitrite leaching throughout the plant growth stage. Both the unexchanged zeolite amended soils at 2% loading showed lower nitrate and nitrite leaching than their exchanged counterparts at the same loading. Tables 4.36-4.39 show nitrate and nitrite leaching from soils of all 11-treatment at weeks 1, 3, 6 and 9, respectively (± standard error of the mean, $n = 2$) at $p \leq 0.05$. Where means have been given the same common letter they do not differ at ($p \leq 0.05$), following an LSD test.

Analysis for interactions between the treatments over time following an LSD test ($p < 0.05$) revealed that control blank soils leached less nitrate and nitrite, due to non-availability of N fertilizer in these soils. As N fertilizer in the form of NH_4NO_3 was added to Control standard and Control high soils, high amounts of nitrate and nitrite leached from these soils. Significantly ($p < 0.01$) greater differences were observed between C. high and 4% ammonium exchanged Phillipsite and Linde type F treatments. C. Standard soils leached out significantly ($p \leq 0.01$) more nitrate than ammonium exchanged Phillipsite and Linde type F soils at 1 and 2% loadings. Finally, all ammonium exchanged Linde type F treatments leached out significantly ($p \leq 0.01$) less nitrate and nitrite at all three harvests compared with the three controls and ammonium exchanged Phillipsite soils. Leachate analysis also revealed unexchanged Phillipsite and Linde type F soils at 2% loading to leach less nitrate and nitrite than the C.standard and C.high soils. Although equal amounts of N fertilizer was added to these treatments, unexchanged Linde type F soils leached significantly less nitrate and nitrite than Phillipsite soils (Tables 4.36-4.39). This is probably due to the high selectivity and affinity of this zeolite towards NH_4^+.

Table 4.36. Mean nitrate (NO_3^-) & nitrite (NO_2^-) leaching from soil (mg/l) at week 1.

Treatment		NO_3^- Leaching	(S.E)	NO_2^- Leaching	(S.E)
Control blank		0.25a	(0.050)	13.90a	(0.015)
Control standard		0.66b	(0.025)	41.86b	(0.010)
Control high		1.07c	(0.025)	58.66c	(0.030)
Synthetic Phillipsite	1%	0.21ag	(0.010)	24.40d	(0.200)
	2%	0.35d	(0.015)	31.28e	(0.590)
	4%	0.74e	(0.015)	33.68f	(0.260)
Linde type F	1%	0.09f	(0.010)	1.71g	(0.180)
	2%	0.16g	(0.030)	3.42h	(0.410)
	4%	0.21ag	(0.015)	4.59i	(0.160)
Unexchanged S. Phillipsite	2%	0.44h	(0.030)	20.38j	(0.150)
Unexchanged Linde type F	2%	0.36d	(0.020)	17.90k	(0.750)
LSD ($p \leq 0.05$)		0.05		0.60	

Table 4.37. Mean nitrate (NO_3^-) & nitrite (NO_2^-) leaching from soil (mg/l) at week 3.

Treatment		NO_3^- Leaching	(S.E)	NO_2^- Leaching	(S.E)
Control blank		8.58a	(0.76)	4.60a	(0.11)
Control standard		195.12b	(3.76)	28.69b	(0.70)
Control high		284.83c	(3.05)	84.48c	(3.44)
Synthetic Phillipsite	1%	65.31d	(0.58)	21.51d	(0.95)
	2%	92.44e	(1.01)	38.69e	(1.20)
	4%	128.06f	(0.38)	65.33f	(2.15)
Linde type F	1%	3.01g	(0.65)	9.70g	(2.55)
	2%	8.65h	(1.17)	12.71g	(8.04)
	4%	11.87i	(1.68)	18.13d	(0.79)
Unexchanged S. Phillipsite	2%	55.47d	(3.76)	35.94e	(1.25)
Unexchanged Linde type F	2%	43.06j	(2.66)	26.58b	(0.77)
LSD ($p \leq 0.05$)		5.23		3.45	

Table 4.38. Mean nitrate (NO_3^-) & nitrite (NO_2^-) leaching from soil (mg/l) at week 6.

Treatment		NO_3^- Leaching	(S.E)	NO_2^- Leaching	(S.E)
Control blank		5.67a	(0.29)	5.72a	(0.06)
Control standard		72.27b	(0.28)	12.23b	(0.22)
Control high		85.68c	(2.09)	33.54c	(0.64)
Synthetic Phillipsite	1%	24.01d	(0.95)	7.48d	(0.33)
	2%	38.84e	(0.38)	8.73e	(0.28)
	4%	53.81f	(0.86)	13.01b	(0.11)
Linde type F	1%	8.64g	(1.11)	2.61f	(0.06)
	2%	11.36h	(0.37)	4.78a	(0.07)
	4%	14.05i	(0.48)	6.69g	(0.24)
Unexchanged S. Phillipsite	2%	25.15d	(1.58)	7.41d	(0.04)
Unexchanged Linde type F	2%	13.86i	(0.76)	8.48e	(0.27)
LSD ($p \leq 0.05$)		2.44		0.66	

Table 4.39. Mean nitrate (NO_3^-) & nitrite (NO_2^-) leaching from soil (mg/l) at week 9.

Treatment		**NO_3^- Leaching**	(S.E)	**NO_2^- Leaching**	(S.E)
Control blank		3.33a	(0.15)	0.70a	(0.03)
Control standard		38.47b	(0.54)	3.36b	(0.09)
Control high		75.25c	(1.23)	8.57c	(0.15)
Synthetic Phillipsite	1%	22.31d	(0.48)	2.49d	(0.49)
	2%	33.15e	(1.44)	5.53e	(0.30)
	4%	49.12f	(0.34)	7.87f	(0.12)
Linde type F	1%	3.85a	(0.12)	0.95a	(0.05)
	2%	4.74a	(0.02)	1.13ag	(0.15)
	4%	6.61g	(0.15)	1.34g	(0.24)
Unexchanged S. Phillipsite	2%	29.10h	(0.61)	6.43h	(0.06)
Unexchanged Linde type F	2%	8.42i	(0.03)	2.29d	(0.19)
LSD ($p \leq 0.05$)		1.58		0.52	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

For Glasshouse Experiment 3, leachate measurements were carried out, as described in Section 2.9.2. Leachates from 5 individual pots of a particular treatment effect were collected into a container at weeks 3, 4, 5, 6, 7 and 8 and analysed by Ion Chromatography for ammonium and nitrate levels. Control standard soils leached out significantly ($P \leq 0.01$) more ammonium and nitrate than 1% loaded synthetic Phillipsite (high-aluminium and high-crystalline) soils from weeks 3-7. Compared with 2% loaded synthetic Phillipsite (high-aluminium and high-crystalline) soils, leaching of NO_3^- was higher only at weeks 3 and 4 (Tables 4.40, 4.41). Control blank soils leached out significantly ($P \leq 0.05$) less NH_4^+ and NO_3^- throughout the plant growth stage and 2% high aluminium Phillipsite leached out significantly ($P \leq 0.01$) more NH_4^+ throughout the plant growth stage.

Table 4.40. Mean ammonium (NH_4^+) and nitrate (NO_3^-) leaching from soil mg/l (± standard error of the mean, n = 5) at week 3.

Treatment		NH_4^+ Leaching	(S.E)	NO_3^- Leaching	(S.E)
Control blank		1.78a	(0.29)	27.73a	(1.07)
Control standard		22.70b	(1.01)	144.64b	(3.25)
Synthetic Phillipsite	1%	7.64c	(0.47)	58.29c	(1.71)
(high-aluminium)	2%	13.90d	(0.82)	89.21d	(3.41)
Synthetic Phillipsite	1%	3.99e	(0.09)	68.50e	(1.64)
(high-crystalline)	2%	8.97f	(0.51)	100.01f	(2.75)
LSD ($p \leq 0.05$)		1.52		5.98	

Table 4.41. Mean ammonium (NH_4^+) and nitrate (NO_3^-) leaching from soil mg/l (± standard error of the mean, n = 5) at week 4.

Treatment		NH_4^+ Leaching	(S.E)	NO_3^- Leaching	(S.E)
Control blank		4.43a	(0.08)	21.51a	(2.57)
Control standard		44.87b	(1.46)	395.62b	(9.73)
Synthetic Phillipsite	1%	13.66c	(0.99)	84.93c	(3.18)
(high-aluminium)	2%	28.89d	(0.21)	209.62d	(2.18)
Synthetic Phillipsite	1%	10.88e	(1.13)	126.27e	(4.78)
(high-crystalline)	2%	21.19f	(0.62)	237.65d	(5.31)
LSD ($p \leq 0.05$)		2.21		32.52	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

As high-aluminium Phillipsite soils are expected to have higher ammonium content than high-crystalline Phillipsite soils, it would be expected that more nitrate would leach out from these soils. An LSD test revealed significantly ($P \leq 0.01$) more nitrate leaching from high-crystalline soils at weeks 3 and 4. This could be accounted for by rapid release of NH_4^+ into the soil from the zeolite at weeks 1 and 2, due to its uniform crystal phase boundary, smaller particle size and high crystallinity, thereby enabling leaching of NO_3^- rapidly from these soils after nitrification. At weeks 5-8 high-aluminium Phillipsite soils leached out significantly ($P \leq 0.01$) more nitrate than high-crystalline Phillipsite soils at both 1 and 2% loadings (Tables 4.42-4.45).

Table 4.42. Mean ammonium (NH_4^+) and nitrate (NO_3^-) leaching from soil mg/l (± standard error of the mean, n = 5) at week 5.

Treatment		NH_4^+ Leaching	(S.E)	NO_3^- Leaching	(S.E)
Control blank		0.57a	(0.25)	13.50a	(1.13)
Control standard		36.81b	(1.46)	96.58b	(3.93)
Synthetic Phillipsite	1%	14.24c	(0.56)	84.11c	(2.86)
(high-aluminium)	2%	29.36d	(0.84)	147.38d	(2.47)
Synthetic Phillipsite	1%	9.66e	(0.36)	67.30e	(2.05)
(high-crystalline)	2%	21.13f	(0.58)	122.38f	(3.74)
LSD ($p \leq 0.05$)		1.93		6.94	

Table 4.43. Mean ammonium (NH_4^+) and nitrate (NO_3^-) leaching from soil mg/l (± standard error of the mean, n = 5) at week 6.

Treatment		NH_4^+ Leaching	(S.E)	NO_3^- Leaching	(S.E)
Control blank		0.43a	(0.02)	9.26a	(0.70)
Control standard		23.69b	(0.97)	69.03b	(1.81)
Synthetic Phillipsite	1%	10.80c	(0.46)	45.77c	(1.40)
(high-aluminium)	2%	25.19d	(0.26)	82.06d	(1.99)
Synthetic Phillipsite	1%	7.13e	(0.29)	31.46e	(1.67)
(high-crystalline)	2%	18.98f	(0.55)	69.71b	(2.55)
LSD ($p \leq 0.05$)		1.27		4.31	

Table 4.44. Mean ammonium (NH_4^+) and nitrate (NO_3^-) leaching from soil mg/l (± standard error of the mean, n = 5) at week 7.

Treatment		NH_4^+ Leaching	(S.E)	NO_3^- Leaching	(S.E)
Control blank		0.30a	(0.04)	5.63a	(0.56)
Control standard		4.82b	(0.31)	40.63b	(1.23)
Synthetic Phillipsite	1%	7.28c	(0.07)	27.46c	(0.48)
(high-aluminium)	2%	16.76d	(0.50)	47.43d	(0.71)
Synthetic Phillipsite	1%	6.64c	(0.55)	20.47e	(1.40)
(high-crystalline)	2%	11.20e	(0.49)	38.52b	(1.23)
LSD ($p \leq 0.05$)		0.89		2.43	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

Table 4.45. Mean ammonium (NH_4^+) and nitrate (NO_3^-) leaching from soil mg/l (± standard error of the mean, n = 5) at week 8.

Treatment		**NH_4^+ Leaching**	(S.E)	**NO_3^- Leaching**	(S.E)
Control blank		0.10a	(0.07)	0.44a	(0.08)
Control standard		1.66b	(0.29)	13.47b	(0.47)
Synthetic Phillipsite	1%	7.73c	(0.44)	13.96bc	(1.85)
(high-aluminium)	2%	10.01d	(0.31)	16.57c	(1.77)
Synthetic Phillipsite	1%	4.68e	(0.33)	9.93d	(1.80)
(high-crystalline)	2%	6.21f	(0.35)	10.02d	(0.97)
LSD ($p \leq 0.05$)		0.73		3.03	

N.B. Where means have been given the same common letter they do not differ at $p \leq 0.05$, following an LSD test.

The leaching phenomenon from these soils can be explained by the higher amounts of ammonium present in high-aluminium Phillipsite frameworks, which will enable ammonium to be released and subsequently be converted to nitrate and leach out when it is present in excess in the soil at any particular stage of plant growth. As high-crystalline Phillipsite initially releases ammonium rapidly, the less available ammonium in this zeolite framework will not enable excessive ammonium to be present in the soil at any particular stage of plant growth, thereby leaching significantly ($P \leq 0.01$) less ammonium and nitrate from week 5-8. However, these soils may have leached out more NH_4^+ at weeks 1 and 2.

Interactions of treatments over time across the harvests (Harvests 1-3) showed significant ($P \leq 0.01$) differences. Nitrate leaching was significantly ($P \leq 0.01$) decreased from high crystalline Phillipsite soils at both 1 and 2% loadings, although NH_4^+ leaching from these soils significantly ($P \leq 0.01$) increased at the start of the experiment. At 1% loading both forms of Phillipsite showed a significant ($P \leq 0.01$) decrease in nitrate leaching. C.standard soils showed significant ($P \leq 0.01$) increases in leaching of both ammonium and nitrate.

4.5. Discussion

The discussion will focus on investigating how different forms of zeolites can affect the growth of maize-as measured in pot experiments and the cation exchange capacity of zeolites for cations present in soil, and their influence on plant nutrient uptake along with plant nutrient deficiencies if any, for zeolite amended soils in all three-glasshouse experiments. Initial discussion will focus on plant growth and nutrient uptake followed by the soil physico-chemical characteristics. The influence of CEC of zeolites on leaching of ammonium, nitrite and nitrate from soils, as influenced by particle size, surface area and crystallinity of zeolites will also be discussed. Finally conclusions will be drawn as to the release of cations from zeolites to select a potential zeolite treatment, as means of supplying adequate plant nutrients over growing season while minimizing possible N losses through leaching, in the form of controlled slow release fertilizer.

4.4.1. Plant growth

Zeolites can be saturated with N and K, which can then be added as a fertilizer amendment for plant growth (Notario del Pino *et al.* 1995; Notario *et al.* 1995). For this study, only P was added to soils in the form of phosphate fertilizer for all three-glasshouse experiments, as zeolites contained ammonium and potassium within their framework. By taking into account the total plant shoot dry weight at all three harvests a direct comparison can be made for plant growth between treatments. In all three-glasshouse experiments there was evidence that zeolite additions improved plant growth, and lower loadings of zeolite to soil were quite beneficial over higher loadings of zeolite to soil with regard to plant growth.

Investigations by Leggo (2000) showed a similar trend, with lower loaded (16%) zeolitic (Clinoptilolite) soil amendment showing a greater plant dry weight and grain yield compared with a higher loaded (33%) zeolitic (Clinoptilolite) soil amendment. Both these zeolite loadings had no fertilizer addition. Furthermore, studies by Burriesci *et al.* (1984) on *Prunus persica* (peaches) have shown using NH_4^+ exchanged synthetic zeolites at 25-wt % loading in soil significantly increased fruit size and average yield per tree, whereas higher zeolite content in soil (~50-wt%) showed a decline in fruit size and overall yield.

4.4.2. Nutrient uptake by plants

In a soil-zeolite system, nutrients present in soil are susceptible to ion exchange with cations present in the zeolite (Leggo, 2000). Therefore, on addition to soils in the presence of water, both natural and synthetic zeolites that have readily available NH_4^+ and K as major cations exchange with Ca, Mg, Na and K present in the soil. Nutrient uptake can be determined by relating the availability of nutrients in the soil with the status of plant material. The greater dry matter production in zeolite treated soils was enhanced by, the increased shoot weight in these soils compared to lower shoot weight in control soils.

For Glasshouse Experiment 1, nutrient (N, P, K) availability in soil might influence plant growth in all eight treatments. None of the plants showed any macronutrient deficiencies at all three harvests. As a result of ion exchange phenomena in zeolite-soil systems, it is expected that a high amount of K (present in both natural and synthetic Phillipsite) will exchange for other cations present in soil. The higher presence of K in soil might have an influence on its uptake. The original amount of K was slightly higher in as-synthesized Phillipsite framework; plants grown in these soils therefore had a higher K content in their dry matter than plants grown in natural Phillipsite-amended soils and also the controls (Table 4.24). The concentrations of K in the shoot material at Harvest 1 show a positive gain for zeolite-amended soils when compared to control soils (Table 4.6). This increase is most probably related to slight decrease in soil pH.

At Harvests 2 and 3 (Table 4.7 and 4.8) shoot material of plants grown in zeolite-amended soils showed a loss of Ca, Mg and Na compared with control soils. This might be due to synthetic and natural Phillipsite amended soil acting as a sink for Mg, Ca and Na cations, which are exchanged for NH_4^+. The decreasing values of these cations are still within the acceptable range of nutrient requirements for maize (Bedi and Sekhon, 1977). Studies by Ibrahim *et al.* (1996) showed similar observations when Jordanian Chabazite-Phillipsite tuff amended soil was used to study nutrient uptake by strawberry plants. It is well known that an increase in N supply produces morphological changes, which increases the root to shoot ratio in both perennial and annual plants (Marschner 1995). It is therefore to be expected that, plants grown in soils rich in available N might show this feature, as demonstrated by zeolite amended soils.

For Glasshouse Experiment 2, on investigating the nutrient levels in both soil and plants after each individual harvest, it was evident that the availability of nutrients (N, P, K) in soil might have influenced plant growth in all 11 treatments. All Linde type F treatments showed nutrient deficiencies. The higher amounts of K and NH_4^+ present in synthetic Phillipsite and Linde type F might exchange for cations present in soil. It was observed that K from Linde type F framework exchanges more freely than NH_4^+, thereby influencing higher uptake of K^+ by plants and depleting the NH_4^+ levels in these soils, and causing N deficiency in plants. For Phillipsite amended soils, both K and NH_4^+ might exchange out from its framework into the soil more freely, and plants therefore did not show any N deficiency. As the original amount of K was slightly higher in as-synthesized Linde type F, plants grown in these soils showed an increase in K uptake and was evident with higher K content in their shoot dry matter than plants grown in synthetic Phillipsite amended soils. An increased plant density in pots enhanced the greater dry matter in Phillipsite treated soils with stems supporting on average three to four tillers whereas, Linde type F soils had lower plant densities and long slender stems supporting fewer leaves and a single tiller per plant (Plate 4.4).

Many authors have suggested the use of zeolite application in soils improves plant N nutrition (Pirela *et al*., 1984; Allen *et al*., 1995). In studies involving Linde type F zeolite it was found the high affinity of this zeolite towards NH_4^+ might have restricted the exchange of this cation, thereby retaining it in the framework and consequently hindering plant growth, due to N deficiency in the soil. Alternatively, high concentrations of calcium nitrate and K fertilizers can be added to soil in an attempt to exchange NH_4^+ from LTF framework, due to the zeolite's selectivity towards these cations (Jakkula *et al.,* 2006). As N was deficient in Linde type F amended soils at all stages of plant growth, it might be possible that plants took up more P to compensate for the lack of N in soils at Harvests 1 and 2, thereby available P concentrations were lower in Linde type F soils (Figure 4.14).

Plants grown in unexchanged synthetic Phillipsite soils showed a high Na content and plants grown in unexchanged Linde type F soils showed a high K content in their dry shoot material at Harvests 2 and 3. This can be accounted for by Phillipsite being synthesized in a (Na, K) system and Linde type F in a (K) system, thereby releasing these cations upon exchange with NH_4^+ present in soil as N fertilizer. In both the unexchanged Phillipsite and Linde type F treatments, available P in soil was constantly taken up by plants at all three harvests, with a higher uptake of P by plants grown in Linde type F soils. This might be accounted for by NH_4^+ deficiency in Linde type F soils. From these sets of results, it is evident that synthetic Phillipsite amended soils provided plants with all the essential major nutrients (N, P and K) compared to its counterpart Linde type F.

None of the previous studies on zeolites in soil considered the physical characteristics of these materials affecting ion exchange and cation exchange. Glasshouse Experiment 3 therefore studied the crystal morphology and particle size of zeolites influencing these properties. The two different forms of zeolites used for the study, did not show any N deficiency and can be accounted for by NH_4^+ exchanging out from their framework into the soil without any affinity towards this cation. Plants grown in zeolite-amended and C.standard soils did not show any nutrient deficiency, as indicated by their physical and morphological appearance. However, plants grown in C.blank soils exhibited NPK deficiencies (Plate 4.6). The greater shoot dry matter in both forms of Phillipsite treated soils was enhanced by an increased plant density in these soils with stems supporting on average three to four tillers, and an increase in cob dry weight. These results relate to the availability of NH_4^+ in soil. Cob dry weight for C.blank treated soils was low, as expected, due to the non-availability of N/P/K in these soils (Table 4.5).

Available P concentrations in soil for all zeolite treated soils and C.standard were similar at Harvest 1, except for C.blank soils that had lower P concentrations. In contrast at Harvests 2 and 3 along with C.blank, high-crystalline Phillipsite soils (1% and 2%) showed lower available P in soil, thereby indicating a higher P uptake by plants grown in these soils. This phenomenon can be linked to slightly lower NH_4^+ availability in high-crystalline Phillipsite soils at these two harvest stages, which leads to increased P uptake. From these sets of results, it is evident that both high crystalline and high Al forms of synthetic Phillipsite amended soils provide plants with all the essential macro-nutrients (N, P and K), and can therefore be potential soil amendments, enabling nutrient uptake for plant growth.

4.4.3. Soil physical and chemical characteristics

Zeolites have been added to soils to investigate their effects on plant growth and in attempts to improve soil physico-chemical properties. Because zeolites have high CEC, ion selectivity, unique physical characteristics and chemical stability they may be effective as soil conditioners. The addition of zeolite to soil will increase CEC. Soil physical properties such as water availability; water holding capacity and aeration can also be improved by zeolite additions (Mumpton, 1999).

The uptake of nutrients in maize varies not only with the stages of plant growth, but also with soil moisture stress. Nandanam and Morachan (1974) showed with a decrease in soil moisture content maize plants uptake more N and P from soil. When maize is affected by moisture stress, the lower parts of the plant wilt and suffer damage proportionally more than the upper parts. As zeolite amended soils were given sufficient water on a daily basis during all three-glasshouse experiments, they did not have any direct influence on soil moisture content, even at higher loadings. Plant uptake of nutrients is strongly influenced by soil pH (Barbaric *et al.*, 1990). It is also an indication that decreased pH may have caused an increase in nutrient solubility. On the other hand, if soils are slightly alkaline or acidic, then by adding non NH_4^+-saturated zeolites, their pH can be increased. The increase in soil pH by zeolite addition can be accounted for the release of basic cations retained by zeolites.

For Glasshouse Experiment 1, all of the soils showed decreased pH from Harvest 1 to Harvest 3 (Table 4.12a). This decrease can be accounted for nitrification of released NH_4^+ from the zeolite in soil. Previous studies have shown that increased nitrification might decrease soil pH. The higher availability of hydrogen ions in soils prone to continuous ion exchange of NH_4^+ from zeolites can be linked to an increase in nitrification in soil (Filcheva and Tsadilas, 2002).

For Glasshouse Experiment 2, soil pH values (Table 4.13a) were higher for Linde type F soils than Phillipsite soils at all three harvests. Unexchanged Linde type F treatment showed significantly higher pH than unexchanged synthetic Phillipsite soils, and can be accounted for by NH_4^+ present in the soil, in the form of ammonium nitrate fertilizer exchanging for cations present in Linde type F zeolite. Due to the zeolite's high selectivity for NH_4^+ there might be a decrease in the nitrification process and subsequently leading to higher soil pH. Synthetic Phillipsite amended soils showed lower pH than Linde type F amended soils and might be associated with the increased nitrification in these soils due to the available NH_4^+ exchanging out from the zeolite's framework being converted to NO_3^- after nitrification processes.

For Glasshouse Experiment 3, soil pH was higher for high-aluminium Phillipsite soils at Harvest 1, followed by high-crystalline Phillipsite soils at Harvests 2 and 3 (Table 4.14a). At Harvest 1 due to the higher availability of NH_4^+ in the high crystalline Phillipsite amended soils, an increase in nitrification process might lead to a decrease in soil pH. The high crystallinity of this zeolite might enable a quicker initial rate of NH_4^+ release, compared with its counterpart high-aluminium Phillipsite with a lower crystallinity. However, at later stages of plant growth, as the NH_4^+ released from high-crystalline Phillipisite framework is lower than high-aluminium Phillipsite (based on its original composition with respect to Si:Al ratio), a decrease in nitrification processes in these soils leads to increased soil pH.

4.4.4. Cation exchange capacity of zeolites influencing release of ammonium into soil

For Glasshouse Experiment 1, soil was amended with NH_4^+ ion-exchanged synthetic Phillipsite that contains K, NH_4^+ and traces of Ca and Mg and NH_4^+ ion-exchanged natural Phillipsite that contains K, NH_4^+ along with other available cations, such as Ca, Mg and Fe in higher concentrations than the synthetic Phillipsite. Both natural and synthetic Phillipsite amended soils released ammonium (Table 4.19) as a result of cation exchange in soil. Released ammonium is converted to nitrite and then nitrate by nitrification processes in the soil. As NH_4^+ is released into the soil, it is quickly taken up by the non-infecting rhizosphere microorganisms, which play an important nutritional role of converting it to NO_3^- by nitrification processes. The plant as an N source then utilizes this NO_3^-. Andronikashvili *et al.* (1995) demonstrated that the introduction of organo-zeolitic fertilizer into a soil substrate promotes a sharp increase in microorganism's populations. Therefore, it can be assumed that although NH_4^+ is released rapidly into the soil, it is converted to NO_3^- quite rapidly and the chance of leaching is minimized by plant uptake, as shown in Glasshouse Experiment 1. However, there will be some NO_3^- leached out and this may be minimal when compared to a fertilizer addition, whereby ammonium nitrate is used, and there is a high risk of converted NO_3^- along with already present NO_3^- in the soil leaching out.

Cation exchange studies have shown rapid ion exchange reactions between NH_4^+ ions present in the NH_4^+-enriched Phillipsite and cations (especially K^+, Ca^{2+}, Mg^{2+} and Na^+) present in the soil solution (Kovanda *et al.*, 1996; Dwairi, 1998). These studies also demonstrated exchange between Na and Mg ions to be very low. Gualtieri *et al.* (2002) showed that the nature of cations in the extra framework sites during ion exchange selectivity of Phillipsite is mainly ruled by ionic size. Therefore, in Glasshouse Experiment 1, both natural and synthetic Phillipsite amended soils should follow exchange for cations present in the soil in the following sequence: $Mg < Ca < Na < K < NH_4$ based upon their ionic radii in ascending order. From Tables 4.11 and 4.12, it is evident that both natural and synthetic Phillipsite soils had similar amounts of available Ca levels in soil at all three harvests, and natural Phillipsite had slightly more available Mg than synthetic Phillipsite at Harvest 2. These results predict that both K and NH_4 are released from these zeolites in exchange for Ca and Mg, and are evident with the availability of these nutrients in the soil in high amounts at Harvests 1 and 2 (Tables 4.19 and 4.24).

Cation exchange phenomena of zeolites in the soil can be explained as follows. Firstly, NH_4^+ and K is released by both zeolites at a rapid rate into the soil in exchange for Mg, thereby lowering Mg levels in soil. At Harvest 2, Mg levels in zeolite treated soils are quite high, thereby assuming that a reverse exchange of this cation is taking place for K present in excess in the soil, and possibly with NH_4^+ (available in soil before nitrification process) to some extent. At both these stages Ca levels are constant, thereby confirming that Phillipsite has preferential selection for other cations over Ca. Ion exchange reactions did not involve Na, as only traces of available Na were found at each harvest. At Harvest 3, NH_4^+ and K levels in zeolite-amended soils were still higher than the control soils. Kovanda and Ruzek (1996) showed similar results on study of NH_4^+ release when added to soil.

For Glasshouse Experiment 2, synthetic Phillipsite released NH_4^+ into the soil in exchange for available cations present in the soil. In contrast, even with the presence of similar cationic concentrations in Linde type F amended soils to that of Phillipsite amended soils, the possible stronger affinity of this zeolite towards NH_4^+ did not aid in NH_4^+ release (Table 4.20). Cation exchange studies on Linde type F zeolite have not been reported previously. The present study therefore gives insights on the selectivity and affinity of this zeolite towards selected cations.

Studies by Gualtieri *et al.* (2002) on Phillipsite demonstrated the zeolite exhibits a stronger selectivity towards K^+. Unexchanged Phillipsite treatment might therefore release Na completely before releasing K from its framework for NH_4^+ present in the soil as N fertilizer. Tables 4.9-4.11 show higher deposition of Na in the shoot material for this treatment. On the contrary, unexchanged Linde type F might take up NH_4^+ completely from the soil due to its high selectivity for this cation in exchange for K from the framework. A higher uptake of K can therefore be observed in the shoot material for this treatment (Tables 4.9-4.11). Finally, available NH_4^+ in both unexchanged Phillipsite and Linde type F treatment soils confirms the ion exchange behaviour of these two zeolites towards the cation (Table 4.20).

For Glasshouse Experiment 3, ammonium exchanged high crystalline and high aluminium synthetic Phillipsite amended soils were examined for exchange of NH_4^+ in and out of the framework of these zeolites. Studies by Chen and Gabelman (1990) showed zeolites to have a higher adsorption capacity ≤ 30% of their dry weight, and most of the surface areas are found within the inner surface of dehydrated channels and cavities of the molecular structures. Other studies by Sousa-Aguiar *et al.* (1998) showed that zeolites with smaller crystallites exhibit a considerably higher external surface area, and therefore their contribution to the adsorbed volume is greater, even at relatively lower pressures. This property of zeolites does influence ion exchange phenomena, especially rates of exchange processes. As discussed earlier, high crystalline Phillipsite has smaller crystallites with larger surface area, and high Al Phillipsite larger crystallites with smaller surface area. It can therefore be assumed that high crystalline Phillipsite might release NH_4^+ at quicker rates than its counterpart, high Al Phillipsite.

Results from soil available NH_4^+ and NO_3^- indicates, even with lower concentrations of NH_4^+ in the framework of high-crystalline Phillipsite than its counterpart, there is a higher availability of NH_4^+ (thereby NO_3^- after nitrification) in these soils at Harvest 1 (Tables 4.21 and 4.23). This behaviour might be linked to the uniform crystal phase boundary of small crystallites and a larger surface area of high crystalline Phillipsite, which acts as a source for increased ion exchange between cations present in soil and within zeolite framework. On the contrary, high Al Phillipsite, with its large crystallites and low crystallinity, might decrease the rate of exchange process and thereby release NH_4^+ at a slower rate.

Phillipsite has selectivity towards various cations (especially K^+, Na^+ and Ca^{2+}); therefore NH_4^+ exchange from both forms of this zeolite was highly influenced by the presence of these cations in soil. Higher available K in high crystalline Phillipsite soils at Harvest 1 illustrates K might be released from its framework at a faster rate due to its zeolite's higher crystallinity. Based on plant growth results and soil available nutrient concentrations, zeolite amended soils showed positive ion exchange phenomenon between NH_4^+ present in the framework and cations present in soil. This phenomenon was higher for high crystalline Phillipsite amended soils, whereby NH_4^+ was released quite rapidly upon addition to soil.

4.4.5. Leaching of ammonium, nitrite and nitrate from soil

Leaching of N occurs when soils have more incoming water (rain or irrigation) than the soil can hold. As water moves through the soil, nitrate (NO_3^-) that is in soil solution moves along with water. Ammonium (NH_4^+) forms of N have a positive charge and are held by the negatively charged sites on the clay in the soil, therefore NH_4^+ forms of N leach very little (Rowell, 1994). From initial results of Glasshouse Experiment 1, the relatively high concentrations of NH_4^+-N present in soil in the initial period of the experiment (first few weeks) testifies to a rapid release of NH_4^+ from both the zeolites, due to ion exchange reactions with cations present in the soil. Then probably nitrification of the released NH_4^+-N occurred and consequent uptake by plants resulted in lowering the NH_4^+ content in soil. However, at this stage ion exchange is still taking place between zeolites and cations present in soil, therefore at 4 and 8% loadings there will be excessive NH_4^+ available for nitrification, as shown in Table 4.19 (Harvest 2 soils). This may or may not result in leaching, depending upon plant N uptake and zeolite exchange behaviour. Ion exchange in a zeolite-soil system is therefore promising for both synthetic and natural Phillipsite-amended soils. Glasshouse Experiment 1 did not investigate the leaching aspects of nitrate and ammonium from soils, as the original study focused only on plant growth and plant nutrient uptake. However, following success in these two areas, study was expanded to examine leaching of nutrients along with plant growth and nutrient uptake for Glasshouse Experiments 2 and 3.

For Glasshouse Experiment 2, measurements of nitrate concentrations in leachates for all 11 treatments gives an insight into ammonium exchange and release from zeolite into the soil. As C.standard and C.high soils had NH_4NO_3 as a fertilizer addition, NO_3^- released throughout the plant growth stage can be accounted for by ammonium-converted nitrate along with the fertilizer NO_3^- being leached out from these soils when present in excess. From Table 4.20, although ammonium exchanged Phillipsite amended soils have relatively higher concentrations of NH_4^+-N in the soil initially; lower amounts of NO_3^- leached out can be accounted for by plant uptake of converted nitrate subject to nitrification processes in soil. In Linde type F amended soils, there was low NH_4^+ originally present at all three harvests. The high affinity of this zeolite towards NH_4^+ might lead to lower availability of NO_3^- in soil after nitrification (Table 4.22), and consequently low amounts of nitrate are leached out from these soils (Figure 4.17). Unexchanged Phillipsite treated soils (at 2% loading) showed lower amounts of nitrate leaching throughout plant growth compared with its exchanged counterpart at the same loading and the control. This can be explained by NH_4^+ present in the soil originally exchanging into the zeolite framework and then out of the framework, thereby delaying the possibility of nitrification. Leached NO_3^- can be accounted for NO_3^- present in the form of fertilizer. As nitrification is a chemical conversion of ammonium to nitrite to nitrate (Section 1.12), lower concentrations of NO_3^- in soils should correspond to lower concentrations of NO_2^- and vice versa. Figure 4.18 shows that NH_4^+ exchanged Linde type F soils leached out less NO_2^- than NH_4^+ exchanged synthetic Phillipsite soils.

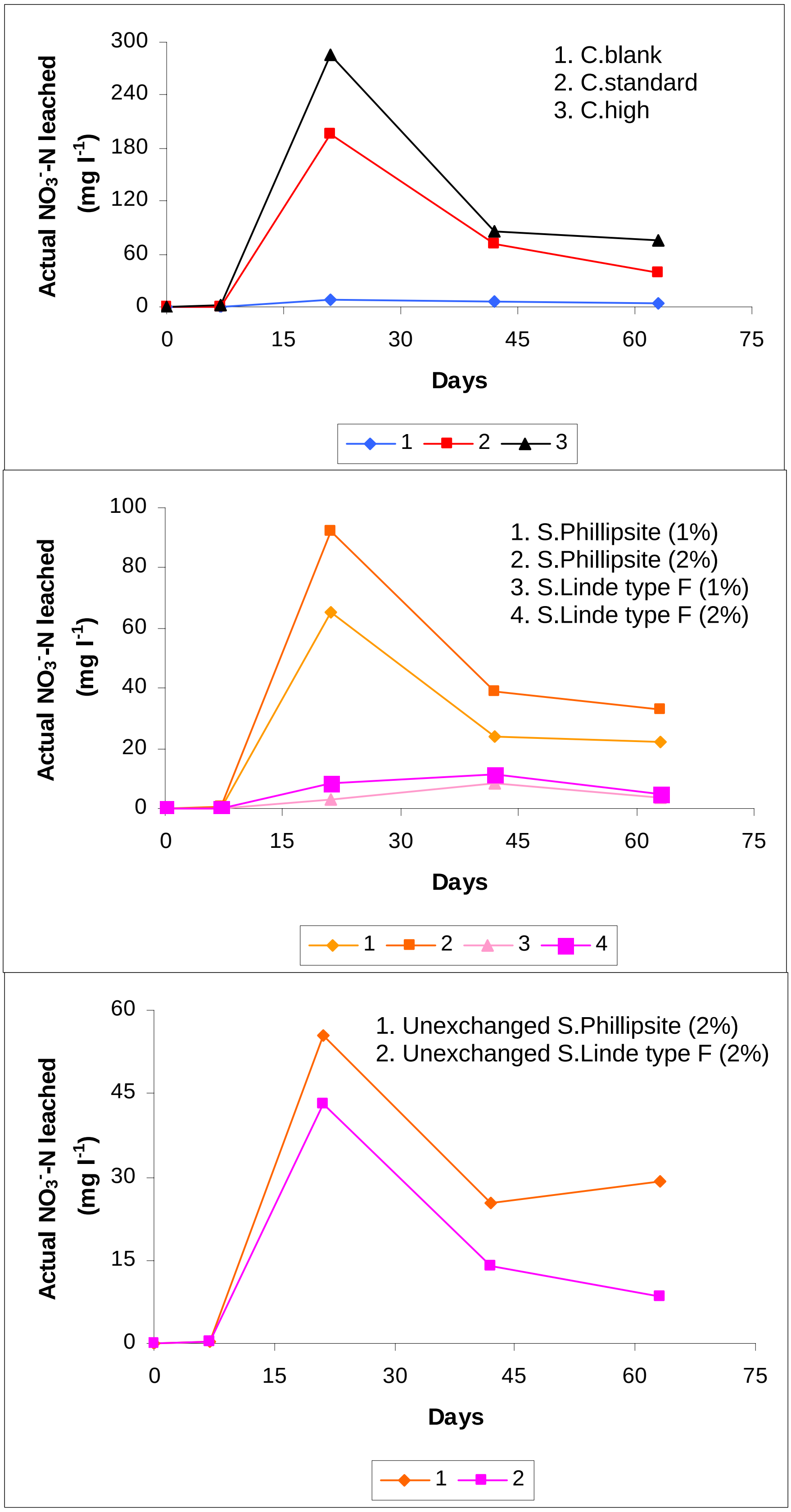


Figure 4.17. Nitrate (NO_3^-) leaching from fertilizer and zeolite treated soils as determined in the leachates collected at weeks 1, 3, 6 and 9.

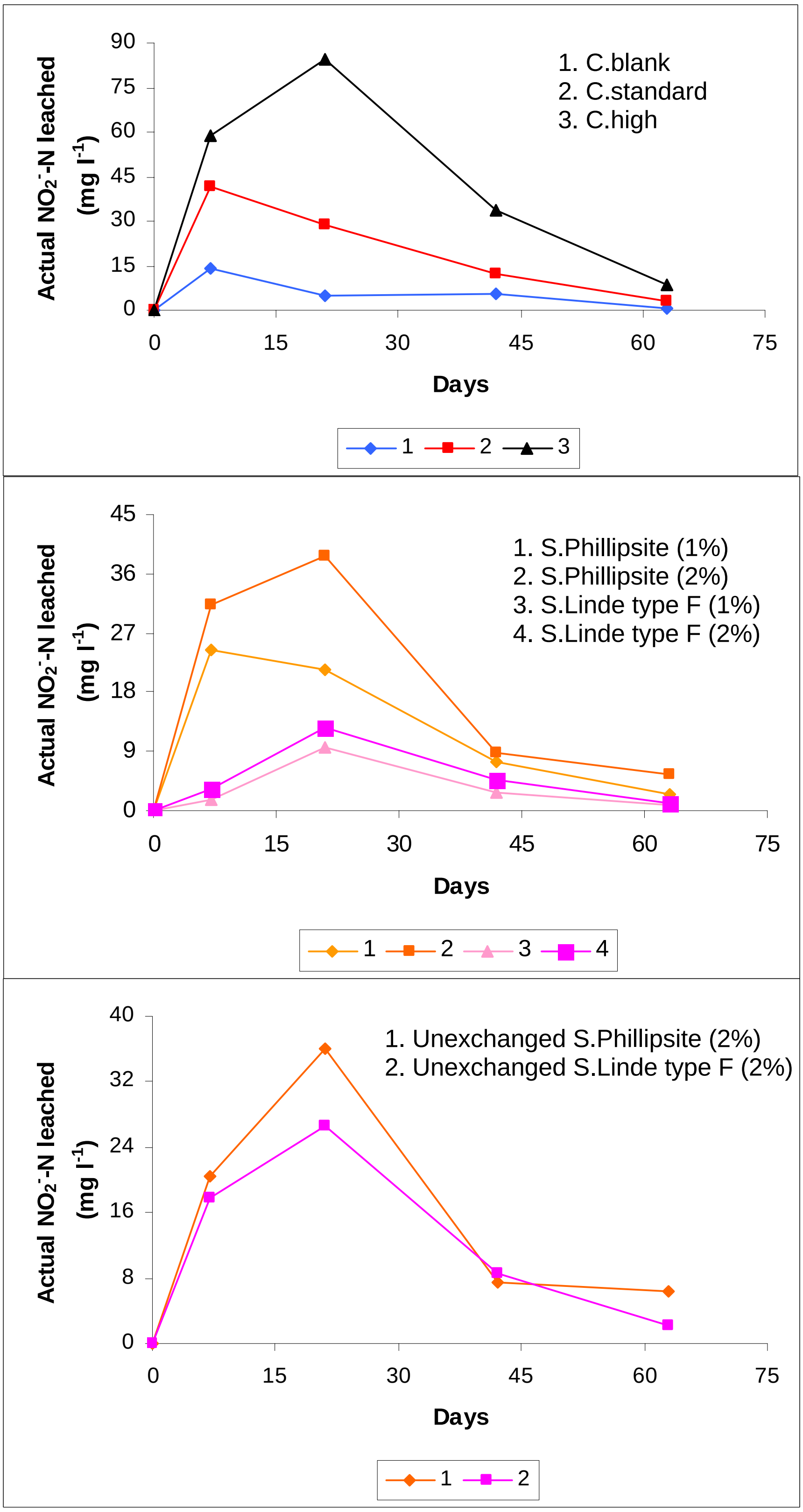


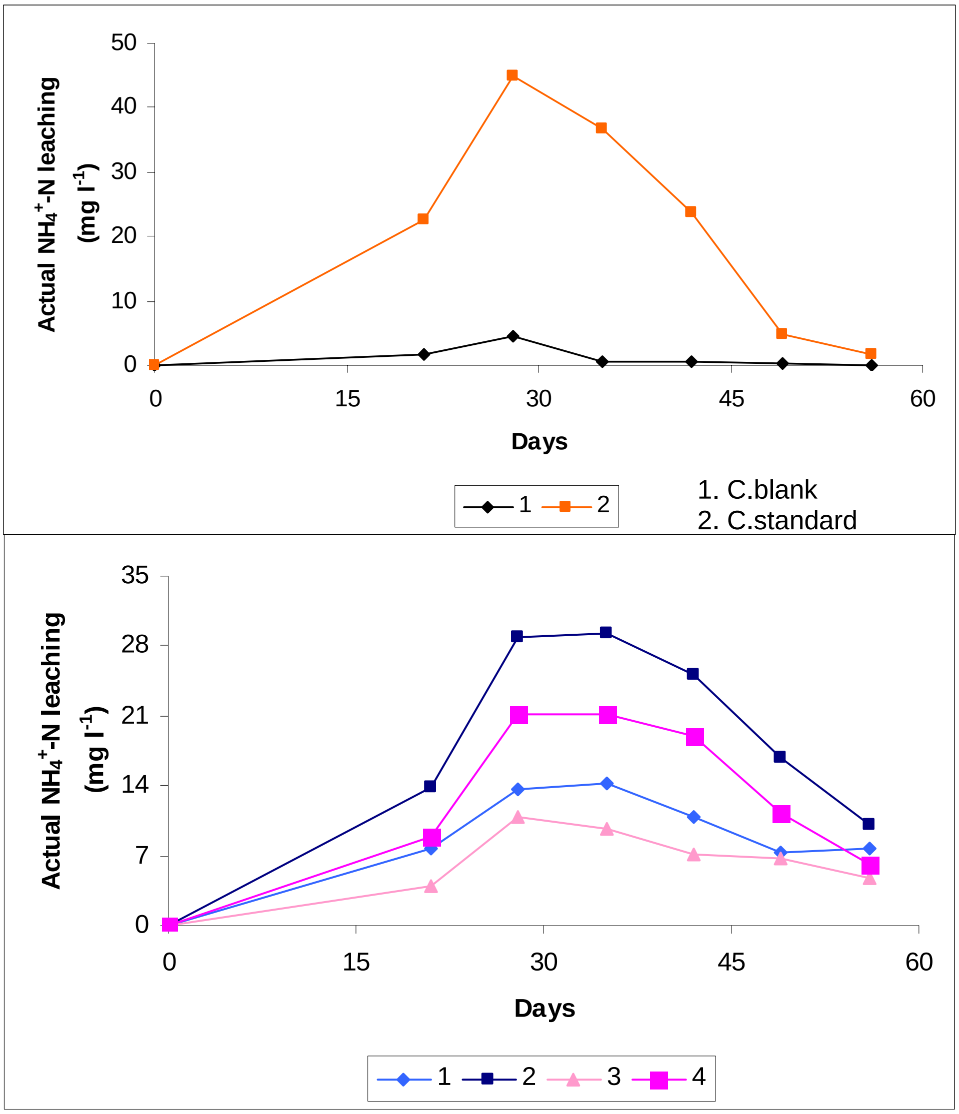
Figure 4.18. Nitrite (NO_2^-) leaching from fertilizer and zeolite treated soils as determined in the leachates collected at weeks 1, 3, 6 and 9.

Unexchanged Linde type F treated soils (at 2% loading) showed lower amounts of nitrate leaching throughout plant growth compared with its unexchanged synthetic Phillipsite counterpart at the same loading. The leaching phenomenon might be accounted for by NH_4^+ present in the soil slowly exchanging into the zeolite framework with time, and thereby terminating the possibility of nitrification due to the high affinity of Linde type F towards ammonium. Leached NO_3^- can therefore be accounted for by NO_3^- present in the form of fertilizer. Although Linde type F could act as a slow release fertilizer, the high affinity of ammonium exchanged Linde type F might hold onto the ammonium cation too strongly and therefore is not beneficial for plant growth when applied as a soil amendment.

For Glasshouse Experiment 3, leachates from all six treatments were collected and their NH_4^+ and NO_3^- concentrations determined from week 3-8 of plant growth. These results gave an insight into release phenomena of NH_4^+ from zeolite and nitrification processes in soil, to construct a hypothesis on a potential controlled-release fertilizer. Following from Glasshouse Experiment 2, whereby nitrite and nitrate concentrations in the leachates were measured, Glasshouse Experiment 3 focused on measuring ammonium and nitrate concentrations in leachates collected in weekly intervals from weeks 3-8 of plant growth.

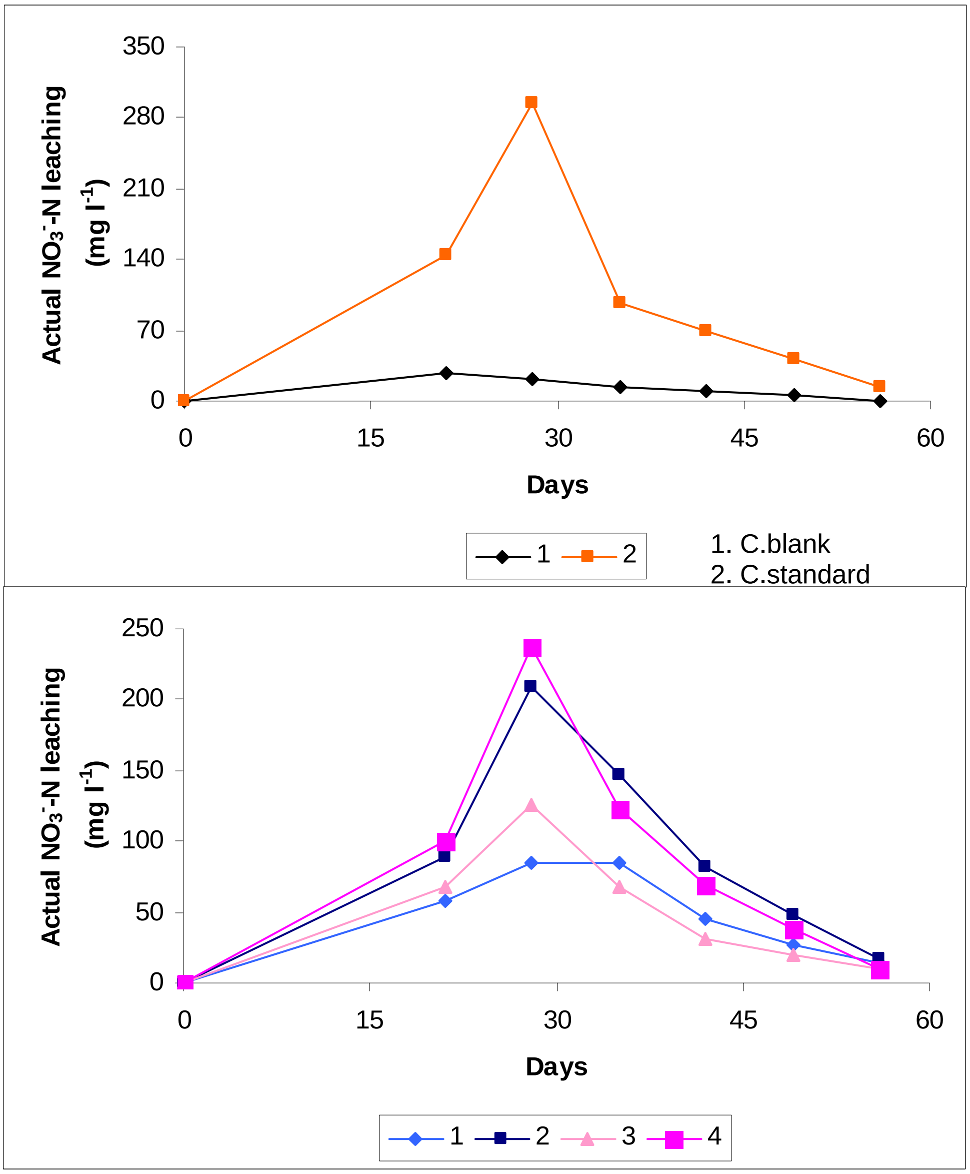
From Tables 4.40 and 4.41, it is evident that high-crystalline Phillipsite leaches out more NO_3^- initially compared to its counterpart high-aluminium Phillipsite, irrespective of loading. This initial insurgence of NO_3^- leaching at weeks 3 and 4 can be linked to excessive release of NH_4^+ from high crystalline Phillipsite, due to its high crystallinity and smaller crystallite (particle size distribution) compared to low crystallinity and larger crystallite distribution of high aluminium Phillipsite. Perrin *et al*. (1998) hypothesized that smaller zeolite particles would release NH_4^+ faster than larger particles, therefore resulting in higher N leaching. Their study demonstrated higher accumulation of N by maize when NH_4^+ loaded Phillipsite particle size decreased. This suggests that smaller zeolite particles more readily release N, most likely due to a decrease in diffusion path length.

Both forms of Phillipsite amended soils at 1% loading significantly decreased NH_4^+ and NO_3^- leaching (Figures 4.19 and 4.20) and provided sufficient N for normal maize growth with higher N use efficiency compared to soils amended with fertilizer (C.standard). The high amount of N leached from C.standard soils can be largely due to the high solubility of NH_4NO_3 and low soil CEC. In contrast, the slow release of N from ammonium exchanged Phillipsite was probably due to diffusion and cation exchange (Semmens, 1984; Allen *et al.*, 1995).



1. High aluminium S.Phillipsite (1%) 2. High aluminium S.Phillipsite (2%)
3. High crystalline S.Phillipsite (1%) 4. High crystalline S.Phillipsite (2%)

Figure 4.19. Ammonium (NH_4^+) leaching from fertilizer and zeolite treated soils as determined in the leachates collected at weeks 3, 4, 5, 6, 7 and 8.



1. High aluminium S.Phillipsite (1%) 2. High aluminium S.Phillipsite (2%)
3. High crystalline S.Phillipsite (1%) 4. High crystalline S.Phillipsite (2%)

Figure 4.20. Nitrate (NO_3^-) leaching from fertilizer and zeolite treated soils as determined in the leachates collected at weeks 3, 4, 5, 6, 7 and 8.

4.5. Conclusions

Based on plant growth, nutrient uptake and cation exchange properties of zeolites in soil, the following conclusions can be derived from all three-glasshouse experiments:

Plant growth

Comparisons with conventional NPK fertilizers revealed ammonium (NH_4^+)-ion exchanged synthetic Phillipsite amended soils at 2% loading, along with both high crystalline and high aluminium forms of NH_4^+-ion exchanged synthetic Phillipsite at 1% loading to be potential plant growth amendments, with a significant increase in plant biomass. Higher loadings (4 and 8%) did not show a greater increase in plant growth but resulted in higher available NH_4^+ in soils. For natural Phillipsite amended soils higher loadings (4 and 8%) did show a significant decrease in plant growth with higher Cu and Mg deficiencies in these soils. Comparisons with controls showed both ammonium exchanged and unexchanged synthetic Phillipsite (with added N fertilizer) amended soils at 2% loading to be potential plant growth amendments with a significant increase in plant biomass. Linde type F amended soils showed poor plant growth response due to the possible high-selectivity and affinity of this zeolite towards NH_4^+, thereby restricting its exchange into the soil and subsequently causing N deficiency in soils.

Nutrient uptake

None of the plants grown in synthetic NH_4^+-ion exchanged Phillipsite-amended soils showed any nutrient deficiencies in all three-glasshouse experiments. Plants were provided with N, P and K, without restricting the availability of these nutrients at all stages of plant growth. However, plants grown in natural NH_4^+-ion exchanged Phillipsite amended soils showed Cu and Mg deficiencies at Harvest 2, thereby hindering the overall plant growth, as evident from leaf and shoot weights. Linde type F amended soils showed N deficiency, furthermore it can be concluded that the nutrient status availability in synthetic Phillipsite soils was enriched in contrast to Linde type F soils, in which nutrient availability was depleted

Cation exchange capacity of zeolites affecting nitrate leaching

Both synthetic and natural NH_4^+-ion exchanged Phillipsite-amended soils showed promising results for NH_4^+ exchange from these zeolites. Results are indicative that NH_4^+ from natural Phillipsite might exchange out of the framework at a faster rate than its synthetic counterpart. This behaviour might be accounted for by the non-uniform structural phase boundary and the cationic impurities associated with natural Phillipsite. Studies also established Linde type F zeolite's higher affinity towards NH_4^+, whereby the soils leached out lesser nitrate due to the low-availability of ammonium in these soils. Nitrate leaching from unexchanged synthetic Phillipsite soils was lower when compared with its exchanged counterpart at the same loading.

NH_4^+-ion exchanged high aluminium Phillipsite amended soils showed promising results for NH_4^+ exchange in soil on comparison with its counterpart NH_4^+-ion exchanged high crystalline Phillipsite. The former minimizes the risk of excess nitrate leaching. Furthermore, the small particle size of high crystalline Phillipsite might have aided in increased NH_4^+ release from its framework at the early stages of plant growth.

Based on the results it can be predicted that synthetic Phillipsite, if synthesized with a coarser particle size distribution, higher Si:Al ratio and lower crystallinity; with its more regular structural phase boundary, high purity and uniform crystal size, may be an active soil amendment to increase plant growth. Synthesized in this form, Phillipsite might even be a potential slow/controlled release fertilizer for controlling nitrate pollution of groundwater in areas of multiple fertilizer application.

Chapter 5

Overall Discussion and Conclusions

Introduction

In this chapter results from all three Glasshouse experiments along with zeolite synthesis and ion exchange are discussed in terms of the aims and objectives, as outlined in Section 1.14. For this study the hypothesis, aims and objectives and methodology applied were innovative, utilizing the unique properties of microporous materials in agricultural applications, such as controlled release fertilizers and plant growth promoters. Conclusions are drawn on the potential of zeolitic materials for controlled release of plant nutrients and their special cation exchange properties influencing slow/controlled release of ammonium from their framework.

Discussion will primarily focus on the use of synthetic Phillipsite as an alternative for natural Phillipsite, and later discussion leads to selecting the best potential synthetic zeolite that can be used as a controlled release fertilizer. Finally, based on the cation exchange properties, particle size distribution, surface area and diffusion, the selected and refined zeolite will be discussed in detail as to the effectiveness of this zeolite in both increasing crop yield and decreasing nitrate leaching from soils. This Chapter will therefore give an insight as to the potential slow/controlled release fertilizer in the form of NH_4^+ exchanged zeolite, which can then be used as an alternative source of fertilizer amendment to control nitrate pollution of waters; as nitrate pollution is a major concern, especially in regions where large doses of agricultural fertilizers are applied (Hecnar, 1995).

If N in applied fertilizers is in an anionic form (nitrate), due to the net repulsion between the anions and the soil surfaces, it will be excluded/leached out. This is because negatively charged nitrate normally has little affinity for soil particle surfaces. Zeolites can therefore be used as an alternative in this situation, whereby the surfactant modified zeolites (SMZ) have been used which can reverse the surface charge, resulting in a higher affinity for negatively charged anionic contaminants, such as chromate, nitrate and sulphate if present in excess in the soil. The sorption and retention of anions by SMZ zeolites contributes to surface anion exchange (Zhang, 2003).

The most common approach widely used for zeolites as a soil amendment corresponds to negatively charged zeolite frameworks with counter balancing K and NH_4^+ present in their framework. These exchange for cations present in the soil, due to their cation exchange capacity. Released NH_4^+ is converted to NO_3^- by bacterial nitrification processes in the soil; and is then taken up by plants for their biochemical function. Synthesis of zeolites followed the most common approach of heating a mixture of (Si and Al source) in the presence of counter balancing cations, such as Na and K (hydroxide form), in a closed vessel under pressure at high temperatures. With the exception of high crystalline Phillipsite, which was synthesized following ageing of the reaction gel at room temperature, none of the other zeolites used for this project were aged prior to synthesis. Natural zeolite was used only for Glasshouse Experiment 1 for comparison with its synthetic counterpart.

5.1. Synthetic versus Natural Phillipsite

Previous studies have shown natural zeolites, when loaded with NH_4^+ and applied as a soil amendment, can act as a slow release N fertilizer (Dwairi 1998; Perrin, et al. 1998). Studies showed that along with ammonium, phosphorus and potassium can also be released from natural Phillipsite and Clinoptilolite based slow-release fertilizers (Allen *et al.,* 1993, 1996; Notario del Pino *et al.,* 1995).

For Glasshouse Experiment 1 under glasshouse conditions, growth was restricted to 9 weeks to observe plant growth and nutrient uptake. Results were promising for synthetic Phillipsite amended soils at lower loadings. Synthetic Phillipsite amended soils did not show any nutrient deficiencies, which can be accounted for a more uniform cation exchange reaction in soil due to its uniform crystal phase boundary and a single phase (non-impurity associated form) of Phillipsite (Plate 5.1).

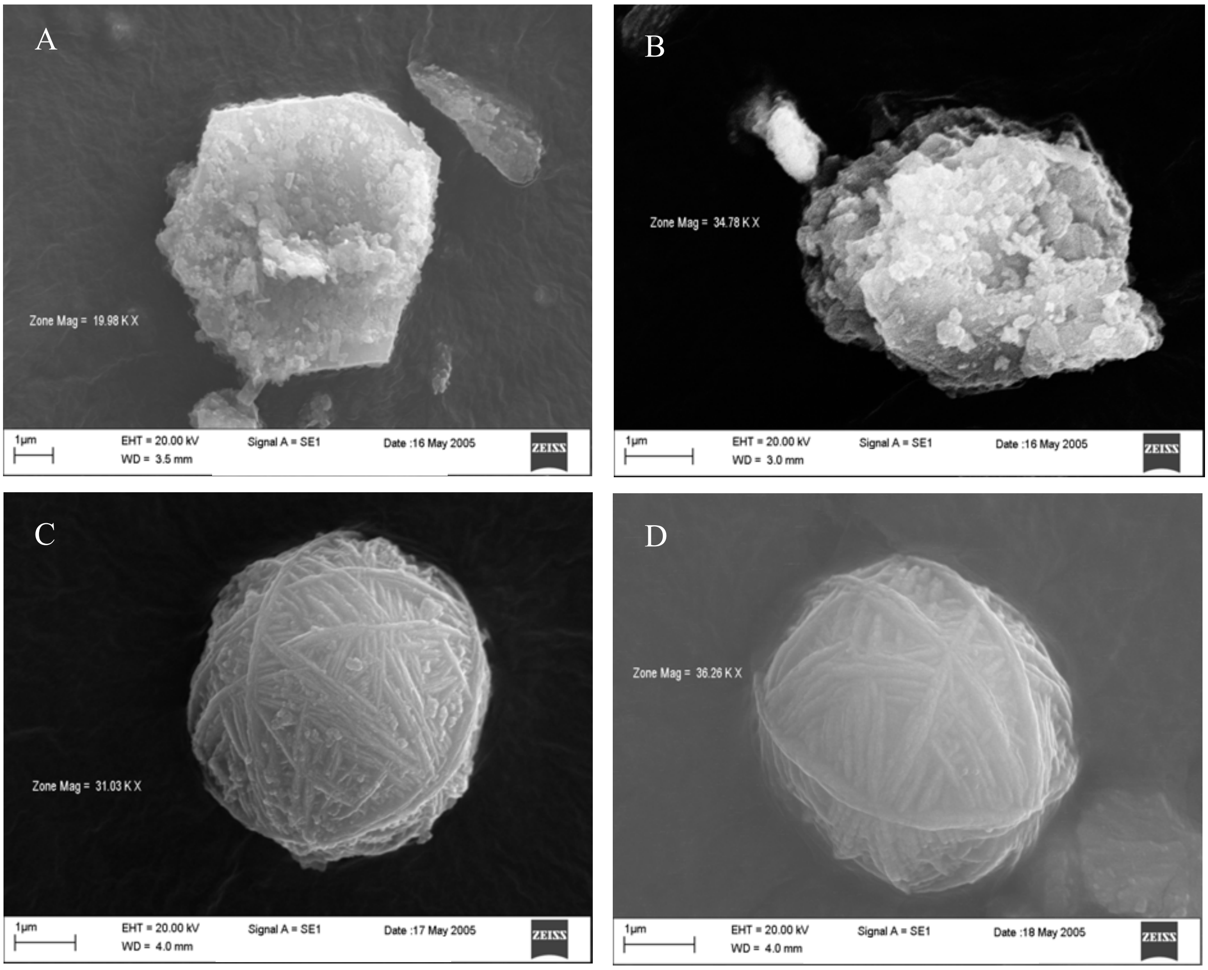


Plate 5.1. Scanning electron micrographs of A, B) Natural Phillipsite and C, D) Synthetic Phillipsite, showing a more regular crystal phase boundary for as-synthesized Phillipsite.

Natural Phillipsite obtained from Pine Valley, Nevada, USA was associated with a secondary zeolite phase Erionite. Although Erionite phase was a minor component of this zeolite, as determined by Rietveld refinement, natural Phillipsite is associated with other cationic impurities, such as Fe, Zn and Ti. These metallic cations can influence Phillipsite’s cation exchange capacity by exchanging for available cations present in the soil, thereby decreasing their concentrations and causing nutrient deficiency in plants. For synthetic Phillipsite amended soils, cation exchange is greatly influenced by K and NH_4^+ present in its framework. Although natural Phillipsite amended soils showed a good plant growth response, nutrient deficiencies were distinctly visible for plants grown in these soils at Harvest 2.

Ammonium released by both forms of Phillipsite would most likely be nitrified before taken up by plants. Nutritionally, the proportion of NH_4^+ and NO_3^- in soil solution can affect optimum growth for some plants. Studies have demonstrated the use of NH_4^+ and NO_3^- in combination to be a potential N source for maize growth (Below and Gentry, 1988; Barber *et al.,* 1994). For this study, N fertilizer in the form of calcium ammonium nitrate was added to soils, which yielded a good plant growth response, but might have incurred more nitrate leaching. Understanding the processes affecting NH_4^+ release from Phillipsite (e.g. diffusion, cation exchange and nitrification) may therefore allow the agronomist or horticulturist to manipulate proportions of NH_4^+ and NO_3^- in soil solution. In general, most zeolites can be saturated/exchanged with NH_4^+ to be used as an N fertilizer amendment. Although natural Phillipsite has been used as a soil amendment for studies on slow release fertilization (Dwairi, 1998; Allen and Braun, 2003), its effectiveness compared with its synthetic counterpart has not been investigated.

This study therefore, gave an insight as to the capability of synthetic Phillipsite as a potential controlled release fertilizer based on the availability of NH_4^+ in the soil. Synthetic Phillipsite amended soils had significantly higher total N than natural Phillipsite amended soils at all three harvests (Table 4.16). As total N corresponds to nitrogen present in the form of NH_4^+ (present in soil + zeolite) and NO_3^- and NO_2^- (present in soil) after leaching, it might be presumed that synthetic Phillipsite releases NH_4^+ at a slower rate than natural Phillipsite based on the N availability. Although synthetic Phillipsite had a slightly higher NH_4^+ content in its framework, the availability of N in the soil suggests that it might be releasing N at a slower rate.

On comparing the available NH_4^+ concentrations in zeolite-amended soils (Table 4.19), synthetic Phillipsite soils had significantly higher ammonium concentrations than natural Phillipsite soils at Harvest 3. No significant differences between treatment effects were found at Harvests 1 and 2. These results support the slow release fertilizer aspect of synthetic Phillipsite, in association with the original NH_4^+ present in both natural and synthetic Phillipsite frameworks before introducing it as a soil amendment. As leachates were not collected for this experiment, the efficiency of synthetic Phillipsite as a potential controlled release fertilizer, when compared to a standard fertilizer addition, could not be evaluated. However, based on plant growth results and available NH_4^+ results, synthetic Phillipsite was chosen to be a potential zeolite for further controlled release studies.

5.2. Synthetic Phillipsite versus Synthetic Linde type F

Previous studies on synthetic Phillipsite examined the release of NH_4^+ into a soil solution containing a mixture of cations (Kovanda *et al.*, 1996), and as a means of decreasing ammonium ion concentrations in wastewaters (Kovanda *et al.*, 1994). Glasshouse Experiment 2 was therefore designed to examine slow release fertilizer properties of high and low Si:Al ammonium exchanged synthetic zeolites. Zeolites Phillipsite and Linde type F were used as soil amendments to study maize growth. Results were potentially promising for synthetic Phillipsite amended soils at lower loadings. Linde type F soils showed poor plant growth response and this may be accounted for by its higher affinity towards NH_4^+. From these studies, it can be assumed that ammonium exchanged synthetic Phillipsite can be a cheap source of N, if this zeolite can be saturated with ammonium ions (e.g. in waste water purification processes). Although Linde type F does not act as a controlled release fertilizer, the high selectivity of this zeolite towards NH_4^+, coupled with attrition resistance, may supersede other zeolites in removal of ammonium from freshwater effluent.

The main focus of this study with respect to NO_3^- and NO_2^- leaching from soils showed a significant decrease of both these forms of N from soils amended with Phillipsite and Linde type F, compared with controls (standard and high) soils (Figures 4.16 and 4.17). Results indicate that zeolites might release NH_4^+ according to its selectivity and affinity. The non-affinity of Phillipsite towards NH_4^+ might promote ion exchange more freely with cations present in the soil, thereby replenishing soil with NO_3^--N after nitrification processes. However, the high selectivity and affinity of Linde type F towards NH_4^+ might restrict the release of NH_4^+ from its framework, thereby inhibiting plant growth, as soils were deficient in both NO_3^- and NO_2^-.

Unexchanged synthetic Phillipsite and Linde type F with added fertilizer were also used in this study, and the results were promising for both these forms of zeolite with respect to leaching of NH_4^+ and NO_3^-. As patented by Marchello *et al.* (2002), urea (diamide of carbonic acid) when coated with natural zeolites (comprising a mixture of Analcime, Phillipsite and Chabazite) showed a delay in the hydrolysis of urea to ammonia by virtue of the CEC of zeolites. The same principle applies to unexchanged synthetic zeolites with added NH_4NO_3 fertilizer introduced into the soils as a fertilizer amended treatment, to explore the possibilities for slow release fertilization and consequent plant responses. The NH_4^+ present in the fertilizer exchanging for cations present in both synthetic Phillipsite and Linde type F frameworks may lead to minimal leaching of NO_3^-. Leaching of NO_3^- from both the unexchanged zeolites can be associated with NH_4^+-N being converted to NO_3^- together with NO_3^--N present in the fertilizer.

Unexchanged Linde type F exchanges K present in its framework for NH_4^+ present as an N source in the fertilizer, thereby limiting its availability to be converted to NO_3^- and leached out. A significant decrease in NO_3^- and NO_2^- leaching can therefore be observed from these soils. Although unexchanged Phillipsite exchanges K and Na present in its framework for NH_4^+, its selectivity towards NH_4^+ might be lower, thereby increasing the overall NO_3^- concentrations in the soil after nitrification processes and consequently leaching more NO_3^- and NO_2^- compared with its counterpart Linde type F (Figures 4.16 and 4.17). Based on the results from Glasshouse Experiments 1 and 2, the research was further expanded to study two different forms of synthetic Phillipsite, which had a maximum and minimum loading of NH_4^+, in order to examine the efficiency of these zeolites as both plant growth promoters and controlled release fertilizers.

5.3. Synthetic high-aluminium Phillipsite versus synthetic high-crystalline Phillipsite

Based on the positive results from Glasshouse Experiments 1 and 2, whereby synthetic Phillipsite amended soils increased plant growth and decreased nitrate leaching, Glasshouse Experiment 3 studied Phillipsite's potential as a soil amendment when introduced in an high crystalline and high Al form. The experiment focused on two different forms of Phillipsite, in an attempt to predict the effect of increased NH_4^+ concentration in the framework, and increased crystallinity of individual zeolite crystals on leaching processes. Results predicted low crystalline ammonium exchanged Phillipsite might be a potential fertilizer treatment, to enable crop production at the same amounts to that of a conventional fertilizer with a less environmental impact. Studies by Perrin *et al.* (1998) examined application of various crushed fractions of ammonium loaded natural Phillipsite (small, medium and large particle sizes) to evaluate the release pattern of NH_4^+ when applied as a soil amendment for maize growth. Results suggested that smaller particles more readily release NH_4^+ than larger particles. Particle sizes of zeolite crystals for high crystalline Phillipsite are smaller than high Al Phillipsite (Figures 3.31-3.36). Furthermore, particle size distribution is more uniform for high crystalline Phillipsite than high-Al Phillipsite (Figures 3.38 and 3.39). These results suggest, that high crystalline Phillipsite might release NH_4^+ at a more rapid rate than high aluminium Phillipsite. Leaching of NH_4^+ does not correspond to NH_4^+ release from both forms of Phillipsite, as a lower Si:Al ratio is expected to have higher ammonium in the framework and vice versa. However, leaching of NO_3^- can be associated with NH_4^+ release and its conversion to NO_2^- and then NO_3^- by nitrification processes in the soil. Plants will utilise NO_3^- as an N source, and when present in excess in the soil, will leach out with water.

From Figure 4.18, it is evident that high aluminium Phillipsite with a Si:Al ratio (1.95:1) leached more NH_4^+ compared to high crystalline Phillipsite with a higher Si:Al ratio (2.35:1). However, as the leachates were not collected at weeks 1 and 2, the release pattern of NH_4^+ from these zeolites cannot be predicted. Released NH_4^+ is converted to NO_3^- and taken up by plants for growth. Leaching of NO_3^- from all six treatments is shown in Figure 4.19, from which a release pattern and conversion after nitrification can be deduced. As high Al Phillipsite has a higher NH_4^+ content in its framework, it is expected to release more NH_4^+ than its counterpart. However, higher leaching of NO_3^- from high crystalline Phillipsite treated soils at the beginning indicates more NH_4^+ in these soils initially.

From Figure 4.19, it is evident that high crystalline Phillipsite leached out more NO_3^- at weeks 3 and 4. The leaching pattern may be associated with the release of NH_4^+ from zeolite frameworks into soil and its conversion to NO_3^- at a faster rate initially from week 1 to 3. This indicates the impact of crystallinity on release of cations from zeolite frameworks (i.e. the higher the crystallinity of zeolites, the greater might be the release rate). As high Al Phillipsite had larger particles, it led to slower release of NH_4^+ at the beginning, but as the amount of NH_4^+ was present in excess in its framework (due to the Si:Al ratio). This led to an increase in NH_4^+ concentration in soil and consequently more leaching (Figure 4.18). This led to an increase in NO_3^- concentrations in the leachates collected from weeks 5 to 8. The pattern of leaching can therefore be associated with NH_4^+ originally present in both the zeolite frameworks and its release upon exchange with cations present in the soil.

Following from results of Glasshouse Experiments 1, 2 and 3 the overall action of Phillipsite's ability as N source and it's potential, as a controlled release fertilizer will be evaluated taking into consideration nitrate contamination of groundwater (Section 5.4). This section will also consider the most effective synthesis method for Phillipsite as a fertilizer source after ion exchange with NH_4^+, to study its effectiveness for both plant growth and nitrate leaching.

5.4. Overall hypothesis

Various methods were used to study the crystallization of negatively charged zeolite frameworks. Phillipsite was successfully synthesized in (Na, K) system and Linde type F in a (K) system. Synthesis of zeolites used for this study followed verified synthesis protocols (Robson 2001). The main aim of the study, to introduce zeolites as an N fertilizer soil amendment, was established by introducing NH_4^+ into the framework as a counter balancing cation after ion exchange.

As Na^+ is detrimental to maize growth (Barbarick and Pirela 1984), ion exchange was successfully carried out on zeolites to eliminate Na completely in Phillipsite and to minimize K in both Phillipsite and Linde type F. High sodium (Na^+) concentrations in soils are toxic to higher plants. Over 40% of irrigated lands worldwide show increased salt levels (Gupta and Sharma, 1989). Studies have shown that under saline conditions, Na^+ influx into root cells occurs via Na^+ permeable transporters (Roberts and Tester, 1997), which in turn elevates the cytoplasmic Na concentration and causes toxicity (Kingsbury and Epstein, 1986). Zeolites, especially Phillipsite, can therefore act as a sink by exchanging Na when present in excess in the soil for cations present in its framework, thereby decreasing Na concentrations in soil. Addition of K fertilizer to soils caused a significant increase in the dry matter yield of maize (Bedi and Sekhon, 1977). The same principle will hold true for K-Phillipsite and Linde type F. A higher K presence will lead to Mg deficiency symptoms, as observed in the initial harvests of all three Glasshouse Experiments due to the extractable K: Mg ratio in the zeolite amended soils being ≥ 4:1 (Bunt, 1976) as the plant prefers K for Mg, if K is in excess. However, K- zeolites can be applied to soils deficient in K (Minato, 1968).

Much work has been completed on natural Phillipsite as a slow-release fertilizer (Dwairi, 1997, 1998; Komarneni and Park, 1998). More recently, Marchello *et al.* (2002) investigated a urea-based fertilizer coated with natural zeolite to potentially act as a slow release fertilizer. Little work has been performed on synthetic zeolites as slow release fertilizers, thereby suggesting the importance of further work to provide a basis for understanding the properties and principles of ammonium exchanged synthetic zeolites to potentially act as controlled release-fertilizers when applied as a soil amendment. Glasshouse Experiment 1 addressed this by comparing both natural and synthetic zeolites, and the results were quite promising for synthetic Phillipsite amended soils. On considering the physiological measurements of maize growth for natural and synthetic Phillipsite treatments, significant differences were observed for both plant height and shoot weight. A significant increase in shoot dry weight for synthetic Phillipsite treatments might have a bearing on the final maize yield. Although a significant increase in plant height for natural Phillipsite treatments was observed, plants lacked lustre and strength and showed interveinal chlorosis (Plate 4.3).

Glasshouse Experiment 2 showed no symptoms of Nitrogen deficiency for plants grown in Phillipsite amended soils, indicating that NH_4^+ is released from Phillipsite and converted to nitrate by nitrification processes, to be taken up by plants as a NO_3^- source. However, Linde type F amended soils showed N deficiency for plants, which might be accounted for by NH_4^+ not exchanging out of its framework. As growth of maize depends on nutrient uptake from soil, in relation to NH_4^+ release from the zeolite into soil, any depletion of nutrients in the soil due to cation exchange interactions between zeolite-soil may lead to reduced growth and plant nutrient deficiency symptoms. On considering the physiological measurements of maize growth for synthetic Phillipsite and synthetic Linde type F treatments, significant differences were observed for both plant height and plant shoot weight. A significant increase in plant height and shoot dry weight for Phillipsite treatments might be associated with the available nitrate in the soil, and vice versa for Linde type F treatments. Plants grown in Linde type F treated soils showed visible nutrient deficiencies, as shown in Plate 4.4. Glasshouse Experiment 2 therefore addressed the issue as to the best potential synthetic zeolite that can be used for further studies, on applications for slow release fertilization and increased vegetative plant growth.

Based on past studies on natural Phillipsite (Perrin *et al.,* 1998), whereby smaller particle sizes of zeolites influenced higher release of NH_4^+, it was decided to use synthetic Phillipsite with different crystallinity and particle size distribution to study their influence on the release pattern of NH_4^+. As hypothesized in this study, smaller particles released N faster than larger particles. Glasshouse Experiment 3 was designed to study two different forms of synthetic Phillipsite (low crystalline and high crystalline) and assess the impact of NO_3^- leaching from these zeolite-amended soils.

Results were promising for high aluminium Phillipsite with a low crystallinity, leaching less NH_4^+ and NO_3^- initially, in contrast to high crystalline Phillipsite leaching excessive NH_4^+ and NO_3^-. A trend as to the exchange of NH_4^+ from Phillipsite framework was therefore established from this experiment (i.e. the higher the crystallinity and smaller the particle size the greater might be NH_4^+ release, and consequently the greater the NO_3^- leaching). The study therefore helped in constructing a model to evaluate release of N over a period of time for fertilizer, synthetic and natural zeolite amended soils. The model evolves around simple ion exchange interactions in a zeolite-soil system affecting nitrification processes and consequently nitrate leaching from soil (Figure 5.1).

Soil particles (both organic and inorganic) have predominantly negative charges on their surface. Many inorganic soil particles are crystal lattices that are tetrahedral arrangements of the cation form of aluminium Al^{3+} and silicon Si^{4+}, thus forming aluminates and silicates. When cations of smaller charge replace Al^{3+} and Si^{4+}, inorganic soil particles become negatively charged. The negative charge on organic soil particles is a result of the dissociation of hydrogen ions from the carboxylic acid and phenolic groups present (Sene *et al*. 1985).

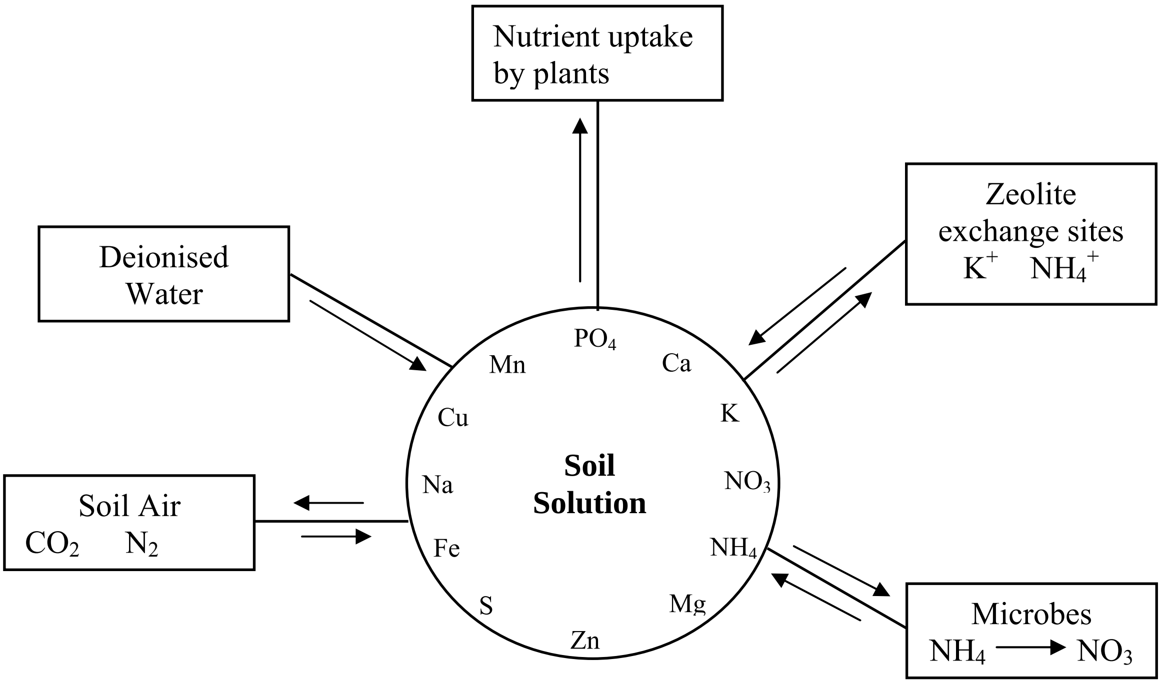


Figure 5.1. Dynamic ion-exchange interactions in a soil-zeolite system. The ions in soil solution are driven towards the root-shoot interface by the uptake of nutrients by the plant.

In a soil-zeolite system nutrients present in soil are susceptible to ion exchange with cations present in the zeolite. Mineral cations, such as NH_4^+ and K^+, adsorb to the negative charges of inorganic and organic soil particles. These cations are not easily lost when the soil is leached with water and thereby provide nutrition reserve available to plant roots. However, mineral nutrients adsorbed in this way can be replaced by other cations by the process of cation exchange capacity (CEC). Mineral anions, such as NO_3^- and Cl^-, tend to be repelled by the negative charge on the surface of soil particles and thereby remain dissolved in the soil solution and susceptible to leaching by water moving through the soil.

On addition of zeolites to soils, in the presence of water both natural (Phillipsite) and synthetic (Phillipsite, Linde type F) zeolites, which have readily available NH_4^+ and K as major cations exchange with Ca, Mg, Na and K present in the soil. The ion exchange selectivity for Phillipsite is: K > NH_4 > Ca > Na > Mg and for Linde type F is NH_4 > K > Ca > Mg. Once exchange is established in the soil, released NH_4 is converted to NO_3^- by nitrification processes and utilized by plants as an N source. Both NH_4^+ and K will exchange in and out of the zeolite framework whenever they are available in excess in the soil solution. Therefore, this system is an ideal solution for soils, which are low in K and N and, may potentially lead for further refinement of zeolites, in particular synthetic Phillipsite, as slow/controlled-release fertilizers, therefore accomplishing the aim of this study.

5.5. Overall Conclusions

The aim of this study was to determine if synthetic zeolites are better than natural zeolites at increasing plant growth and soil nutrient status. As modern agricultural practices are probably the most common sources of groundwater nitrate contamination caused by excessive fertilizer application, the research work was expanded to select the best potential synthetic zeolite, which can enhance plant growth and also provide a basis for alternative N fertilization in the form of ammonium loaded zeolites to diminish nitrate pollution of groundwater. Conclusions are derived from all three Glasshouse Experiments based on plant growth parameters, available NH_4^+ and NO_3^- concentrations in soils and NH_4^+ and NO_3^- leaching from soils.

Plant growth and soil nutrient status

The following conclusions can be derived from maize growth experiments:

(1) Glasshouse experiments on pot grown maize (*Zea mays*) plants demonstrated that zeolitic soil amendments could be effective alternatives to conventional fertilizers, providing plants with both the essential macronutrients N, P, K and all the essential micronutrients.

(2) None of the plants grown in synthetic Phillipsite-amended soils showed any visible nutrient deficiency symptoms in all three Glasshouse Experiments. However, plants grown in natural Phillipsite amended soils showed micronutrient deficiencies and plants grown in Linde type F amended soils exhibited both micro- and macro-nutrient deficiencies.

(3) Comparisons of plant growth with controls showed synthetic Phillipsite amended soils at lower loadings, to be a potential source of providing plants with all the essential nutrients during all stages of growth cycle, thereby increasing plant biomass. In soils amended with higher loadings of both synthetic and natural Phillipsite, plant growth was significantly decreased. Higher available NH_4^+ present

in the soil may be a possible cause, as high ammonium levels in soil may cause plant toxicity.

(4) Unexchanged synthetic Phillipsite and unexchanged Linde type F showed promising results by increasing plant growth due to added N fertilizer to these treatments, along with higher K in their framework. Although ammonium exchanged Linde type F amended soils provided plants with K, these soils lacked N due to the high affinity of Linde type F towards NH_4^+.

(5) Both high crystalline and high Al Phillipsite, soils provided plants with all essential micro- and macronutrients. Although high crystalline and high Al Phillipsite amended soils showed an increase in plant growth at 1% loading, high Al Phillipsite at 2% loading was a potential source for supplying more N, due to the high NH_4^+ content in its framework. The presence of more N in these soils did increase plant growth significantly and is evident from the plant shoot dry weights.

Results from all three Glasshouse Experiments confirmed ammonium exchanged synthetic Phillipsite at lower loadings (1 and 2%) to be potential fertilizer amendments when applied to soils, with respect to supporting vegetative plant growth. Overall assessment of zeolite added soils revealed a similar nutritional provision to that of a control NPK added soil, with the exception of Linde type F zeolite, which did not provide plants with sufficient N for normal plant growth.

Nitrate leaching

One of the major foci of the research study was to assess the capacity of ammonium-exchanged zeolites as potential controlled release fertilizers. Leachates were collected for Glasshouse Experiments 2 and 3. The main conclusions are:

(1) Natural Phillipsite-amended soils might exchange out more NH_4^+ due to their non-uniform crystal phase boundary. As a result it might be possible that higher NO_3^- would leach out from natural Phillipsite soils compared to synthetic Phillipsite soils after nitrification processes.

(2) The high-affinity of Linde type F zeolite towards NH_4^+ restricts its exchange and therefore its availability in soil and consequently lowers NO_3^- leaching. Although less nitrate was leached from these soils plant growth response was poor due to N deficiency, thereby ruling out Linde type F as a potential controlled release fertilizer.

(3) Synthetic Phillipsite amended soils showed promising results for NH_4^+ exchange in soil. A comparison with its counterpart natural Phillipsite and synthetic Linde type F showed synthetic Phillipsite with low crystalline and coarser particle size and uniform crystal phase boundary might promote controlled NH_4^+ exchange into the soil.

(4) High Al Phillipsite amended soils showed promising results for NH_4^+ exchange in soil. On comparison with its counterpart high crystalline Phillipsite, the former might exchange NH_4^+ slowly from its framework, as evident from the available NH_4^+ in soil at Harvest 1 (Table 4.21).

(5) With respect to leaching of NO_3^- it can be confirmed that Phillipsite with a lower crystallinity and NH_4^+ content might be an alternative form of controlled release fertilizer, thereby minimizing the risk of excess nitrate leaching, as evident from Control standard and Control high soils.

By integrating these results from pot-grown maize plants, it can be concluded that low crystalline synthetic Phillipsite might be a potential fertilizer supplement that can be used for future work to assess its potential. Based on soil N availability and N leaching from soil, it can be concluded that low crystalline and low Al synthetic Phillipsite might be the most active controlled release fertilizer. Synthetic Phillipsite is therefore singled out as a plant growth promoter over natural Phillipsite, synthetic Linde type F and most importantly over control (conventional NPK fertilizer) soil amendments.

5.6. Limitations for this study

Firstly, due to the problems associated with synthesis of zeolites in bulk under laboratory conditions, the amount of soil used for Glasshouse Experiments 1 and 2 had to be restricted. As zeolite was added as a % loading to soil, an increase in the amount of soil will lead to an increase in zeolite synthesis. On average only 60-80 g of zeolite can be synthesized in a single large reaction vessel. For Glasshouse Experiments 1 and 2, with respect to higher % loadings of zeolite (i.e., 2, 4 and 8/1, 2 and 4%) to soil nearly 3-4 kg of both Phillipsite and Linde type F were synthesized. The enormity of the plant experiment with respect to number of treatments meant handling fewer leachate replicates. Finally, the amount of soil analysis to be carried out within a limited time frame meant decreasing sub-sampling soils from 10 replicates to 5. Therefore, all soil analysis results are presented as ± standard error of the mean, $n = 5$.

5.7. Suggestions for further work

This study covered a broad range of issues, many of which merit further investigation. Listed below are some recommendations for further investigation.

(1) As all the experiments were carried out under controlled glasshouse conditions on pot-grown plants, it would be beneficial to compare the effects of zeolite addition to soil under field conditions to evaluate the effectiveness of plant growth, and a leachate experiment would evaluate the findings of Phillipsite as a controlled release fertilizer. A block design model would be the best choice for this experiment, whereby the treatments can be blocked according to the zeolite loadings and fertilizer additions.

(2) More recently, natural Phillipsite has been used as coating materials for urea (N fertilizer), to phase the release of N from these materials when applied as soil amendments. Results are promising and the work has been patented. The same principle can be applied for synthetic zeolites, in particular Phillipsite, which may aid in further decreases in N-release.

(3) The major hurdle in using synthetic zeolites as fertilizer amendments is their cost. Calculating the cost for producing zeolites on a laboratory scale it was valued to be three times an expensive product than its natural counterpart. However, based on the effectiveness of Phillipsite, in particular as a controlled release soil amendment, it would be worth exploring the possibilities of manufacturing zeolites on a large commercial scale under pilot conditions.

(4) An alternative would be to synthesize Phillipsite by using NH_4^+ as a counter balancing cation instead of Na/K. This will not only make the zeolite more effective in controlling NH_4^+ release from the framework, but it will also reduce the cost of ion exchange, whereby Na/K is replaced by NH_4^+.

(5) The small particle sizes of zeolites (similar to clays), makes them impossible to separate from soil. Therefore, a stronger basis to support the release rate of NH_4^+ as determined by Kjeldahl cannot be postulated. As the amount of NH_4^+ present in the zeolite is estimated before addition to soil, it would be beneficial to estimate the

NH_4^+ content in the zeolite after each harvest, respectively, rather than to study the available NH_4^+ in the soil and zeolite together.

(6) Some of the alternatives to the above problem would be to use isotopes, whereby zeolites can be labelled and identified at each individual harvest. The other alternative would be to use zeolite pellets, i.e. by pressing zeolite particles together as small coagulates. These zeolite pellets can then be recovered from the soil and examined for NH_4^+ content, as they would not disintegrate over time. This would somewhat contradict the release rate of NH_4^+ from zeolites, due to their size and morphology.

(7) Although Linde type F had a negative impact on plant growth, positive impacts can be derived from this study. Linde type F if tailored in the right fashion can be used in the wastewater remediation process, whereby the high selectivity and affinity of this zeolite can be channelled to separate NH_4^+. Jakkula *et al.* (2006) recently stated the possibilities of using Linde type F for wastewater treatment.

This research work therefore fulfilled all the aims and objectives as outlined in Chapter 1 and contributed to original knowledge by comparing synthetic zeolites with natural zeolites and studying Linde type F. These applications have been reported in the literature for agricultural/controlled release scenarios. Results from this work will therefore be a useful tool in the further understanding and development of zeolites as N carriers, as alternative N applications in those areas where leaching may be a potential problem due to excessive fertilizer application. Research will also be useful in removal of N from groundwater systems contaminated with excessive NH_4^+ and NO_3^-, which can result in blue baby syndrome (methemoglobinemia) in infants upon ingestion, and to diminish algal bloom in water bodies contaminated with nitrate, resulting in damage to aquatic ecosystems.

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Appendices

Appendix 1: General calculations, SEM images and Particle size distribution graphs.

1.1: Unit cell calculations

Synthetic Phillipsite before and after ion exchange as calculated from TGA and XRF results.

Before I.E.

From XRF results moles/100g of elemental composition is calculated, as follows:

Si : 0.760
Al : 0.380
K : 0.326
Na : 0.128
H_2O : 0.823

Relative molecular mass is calculated (RMM) for these elements from the starting gel molar composition of the initial reaction gel, as follows:

Si : 337.08
Al : 161.88
K : 201.37
Na : 46.43
O : 576

Therefore, total RMM = 1322.755

From the total RMM and original moles /100g, unit cell formula for synthetic Phillipsite before ion exchange is deduced as follows:

$K_{4.15}Na_{2.02}$ $[Al_6Si_{12}O_{36}]$: 12.78H_2O

After I.E.

To evaluate NH_4^+ exchanged into the framework, moles/100g of elemental composition is calculated from total RMMs after ion exchange as follows:

Si : 337.08
Al : 161.88
K : 34.408
Na : 0
O : 576.00
NH_4 : 98.148 (From TGA)

Therefore, total RMM = 1207.516

From the total RMM and final moles /100g of NH_3 lost (subtracting TGA value before ion exchange from after ion exchange), the NH_4^+ exchanged into the framework and the subsequent unit cell composition is deduced as follows:

$K_{0.88}(NH_4)_{5.44}$ $[Al_6\ Si_{12}\ O_{36}]$: 11.67H_2O

Natural Phillipsite before and after ion exchange as calculated from TGA and XRF results.

Before I.E.

From XRF results moles/100g of elemental composition is calculated, as follows:
SiO : 0.742
Al : 0.272
K : 0.070
Na : 0.309
Fe : 0.039
H_2O : 0.928

Relative molecular mass is calculated (RMM) for these elements from the starting gel molar composition of the initial reaction gel, as follows:
Si : 337.08
Al : 118.712
K : 44.183
Na : 195.50
Fe : 35.185
O : 524.80

Therefore, total RMM = 1255.461

From the total RMM and original moles /100g unit cell formula for synthetic Phillipsite before ion exchange is deduced as follows:

$K_{1.13}Na_{4.99}Fe_{0.63}\ [Al_{4.40}Si_{12}O_{32.8}]: 13.99H_2O$

After I.E.

To evaluate NH_4^+ exchanged into the framework, moles/100g of elemental composition is calculated from total RMMs after ion exchange as follows:
Si : 337.08
Al : 97.397
K : 22.678
Na : 0
O : 499.52
NH_4 : 59.534 (From TGA)

Therefore, total RMM = 1016.214

From the total RMM and final moles /100g of NH_3 lost (subtracting TGA value before ion exchange from after ion exchange), the NH_4^+ exchanged into the framework and the subsequent unit cell composition is deduced as follows:

$K_{0.58}(NH_4)_{3.30}Fe_{0.47}\ [Al_{3.61}Si_{12}O_{31.22}]: 11.34H_2O$

Linde type F before and after ion exchange as calculated from TGA and XRF results.

Before I.E.

From XRF results moles/100g of elemental composition is calculated, as follows:
Si : 0.66
Al : 0.50
K : 0.49
H_2O : 0.634

Relative molecular mass is calculated (RMM) for these elements from the starting gel molar composition of the initial reaction gel, as follows:

Si : 280.90
Al : 204.39
K : 290.29
O : 562.4

Therefore, total RMM = 1337.98

From the total RMM and original moles /100g unit cell formula for synthetic Phillipsite before ion exchange is deduced as follows:

$K_{7.42}$ [$Al_{7.58}Si_{10}O_{35.16}$]: 9.58$H_2O$

After I.E.

To evaluate NH_4^+ exchanged into the framework, moles/100g of elemental composition is calculated from total RMMs after ion exchange as follows:

Si : 280.90
Al : 199.65
K : 53.57
O : 556.8
NH_4: 181.502 (From TGA)

Therefore, total RMM = 1272.42

From the total RMM and final moles /100g of NH_3 lost (subtracting TGA value before ion exchange from after ion exchange), the NH_4^+ exchanged into the framework and the subsequent unit cell composition is deduced as follows:

$K_{1.37}(NH_4)_{10.06}$ [$Al_{7.40}Si_{10}O_{34.8}$]: 9.11 H_2O

High aluminium Phillipsite before and after ion exchange as calculated from TGA and XRF results.

Before I.E.

From XRF results moles/100g of elemental composition is calculated, as follows:

Si : 0.782
Al : 0.482
K : 0.264
Na : 0.103
H_2O : 0.854

Relative molecular mass is calculated (RMM) for these elements from the starting gel molar composition of the initial reaction gel, as follows:

Si : 337.08
Al : 199.65
K : 158.36
Na: 26.32
O : 620.80

Therefore, total RMM = 1322.755

From the total RMM and original moles /100g unit cell formula for synthetic Phillipsite before ion exchange is deduced as follows:

$K_{4.22}Na_{1.65}$ [$Al_{7.40}Si_{12}O_{38.80}$]: 13.65$H_2O$

After I.E.

To evaluate NH_4^+ exchanged into the framework, moles/100g of elemental composition is calculated from total RMM's after ion exchange as follows:

Si : 337.08
Al : 198.84
K : 32.45
Na : 0
O : 619.84
NH_4 : 114.21 (From TGA)

Therefore, total RMM = 1207.516

From the total RMM and final moles /100g of NH_3 lost (subtracting TGA value before ion exchange from after ion exchange), the NH_4^+ exchanged into the framework and the subsequent unit cell composition is deduced as follows:

$K_{0.83}(NH_4)_{6.33}[Al_{7.37}Si_{12}O_{38.74}]$: 13.15$H_2O$

High crystalline Phillipsite before and after ion exchange as calculated from TGA and XRF results.

Before I.E.

From XRF results moles/100g of elemental composition is calculated, as follows:

Si : 0.82
Al : 0.40
K : 0.22
Na : 0.15
H_2O : 0.823

Relative molecular mass is calculated (RMM) for these elements from the starting gel molar composition of the initial reaction gel, as follows:

Si : 337.08
Al : 161.88
K : 201.37
Na : 46.43
O : 576

Therefore, total RMM = 1322.755

From the total RMM and original moles /100g unit cell formula for synthetic Phillipsite before ion exchange is deduced as follows:

$K_{3.38}Na_{2.32}[Al_6Si_{12}O_{36}]$: 11.87$H_2O$

After I.E.

To evaluate NH_4^+ exchanged into the framework, moles/100g of elemental composition is calculated from total RMMs after ion exchange as follows:

Si : 337.08
Al : 161.88
K : 34.408
Na : 0
O : 576.00
NH_4 : 98.148 (From TGA)

Therefore, total RMM = 1207.516

From the total RMM and final moles /100g of NH_3 lost (subtracting TGA value before ion exchange from after ion exchange), the NH_4^+ exchanged into the framework and the subsequent unit cell composition is deduced as follows:

$K_{0.79}(NH_4)_{5.18}[Al_6Si_{12}O_{36}]$: 10.84$H_2O$

1.2: TGA calculations

Calculations for NH_4^+ exchanged into synthetic Phillipsite framework

No of moles of Na^+ present in 100 g before ion exchange = 3.98 / 61.98 X 2 = 0.12

No of moles of Na^+ present in 100 g after ion exchange = 0

No of moles of K^+ present in 100 g before ion exchange = 15.4 / 94.2 = 0.32

No of moles of K^+ present in 100 g after ion exchange = 3.02 / 94.2 X 2 = 0.064

Therefore, Total loss of Na^+ = 0.12 – 0 = 0.12 moles

Total loss of K^+ = 0.32 – 0.064 = 0.26 moles

Total loss of Na^+ and K^+ = 0.12 + 0.26 = 0.38 moles.

Theoretically, 0.38 moles of NH_4^+ are exchanged into the zeolite to compensate the loss of Na^+ and K^+.

The TGA curves of synthetic Phillipsite does support this assumption (Figures 3.4 and 3.5, before and after ion exchange)

Considering, 0.38 moles of NH_3 (g) lost under TGA; it corresponds to: 0.38 moles X 17.0304 g mol^{-1} (RMM of NH_3) = 6.6 g of NH_3 (g) lost.

And is in accordance with the LOI of synthetic Phillipsite i.e., LOI after ion exchange (Figure 3.5) – LOI before ion exchange (Figure 3.4)

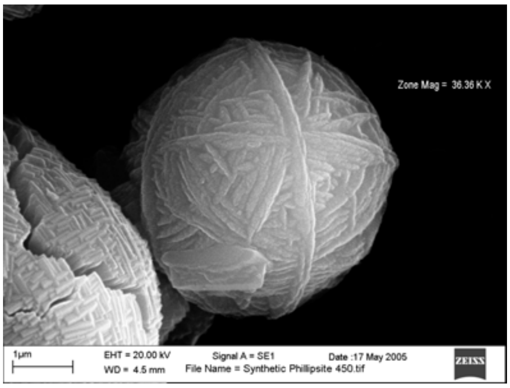
= 21.468 – 14.766 = 6.702g of NH_3 (g) lost.

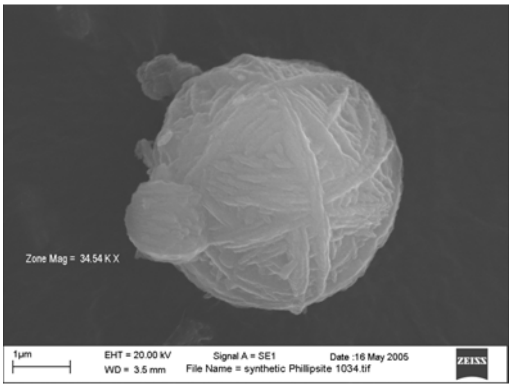
Therefore, for NH_4^+ calculation: 0.38 moles X 18.0383 g mol^{-1} (RMM of NH_4^+) = 6.85 g of NH_4^+ present in 100 g (Table 3.13).

In the similar fashion, amount of NH_4^+ exchanged into natural Phillipsite, synthetic Linde type F, synthetic high crystalline Phillipsite and synthetic high aluminium Phillipsite are calculated (Table 3.13).

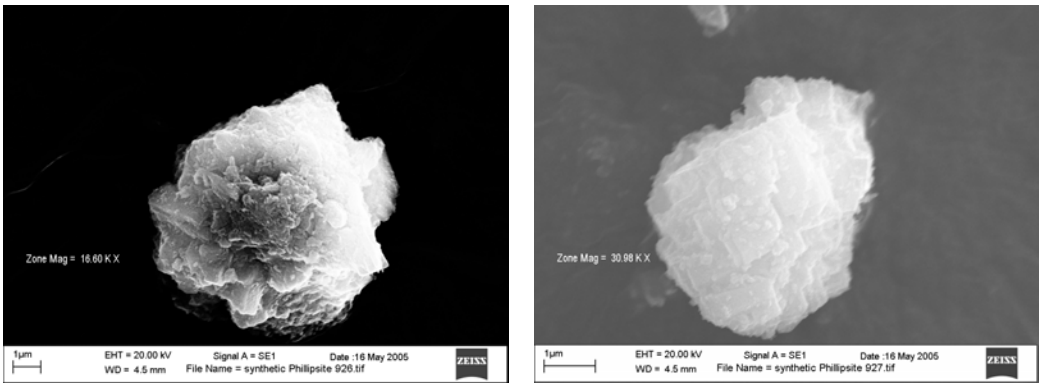
1.3: SEM images

Synthetic Phillipsite

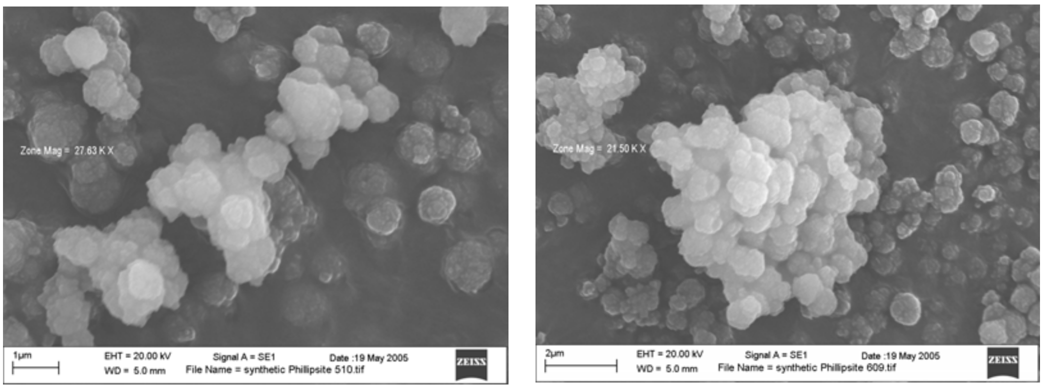




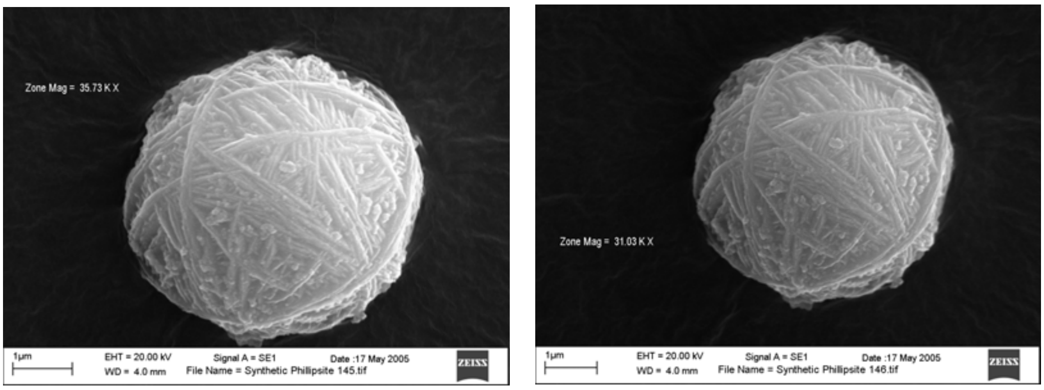
Natural Phillipsite



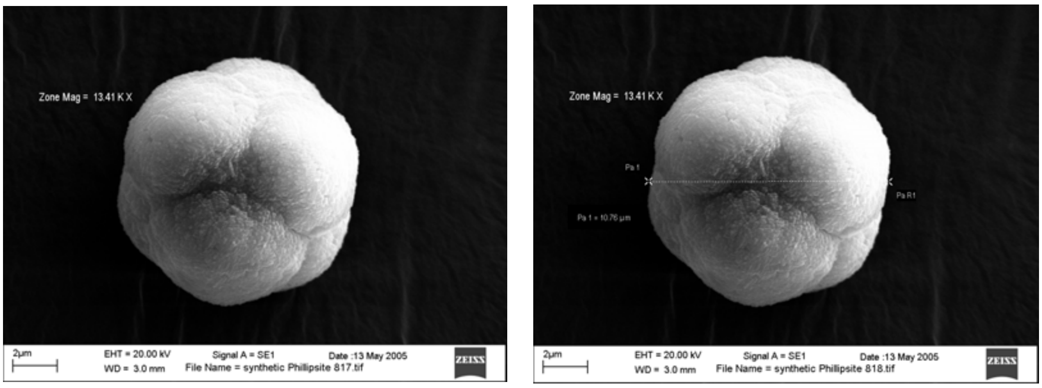
Synthetic Linde type F



Synthetic high crystalline Phillipsite

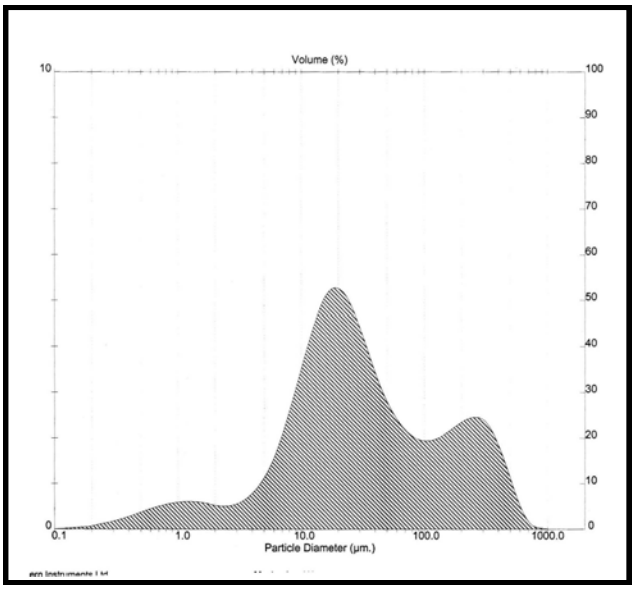


Synthetic high aluminium Phillipsite

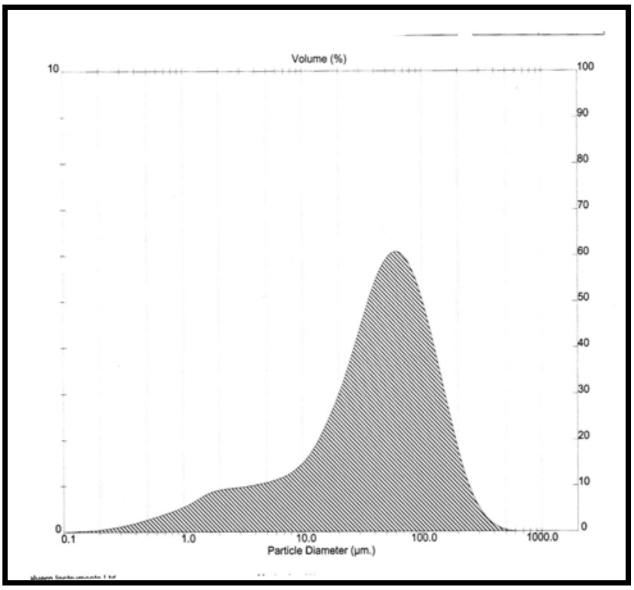


1.4: Particle size distribution curves

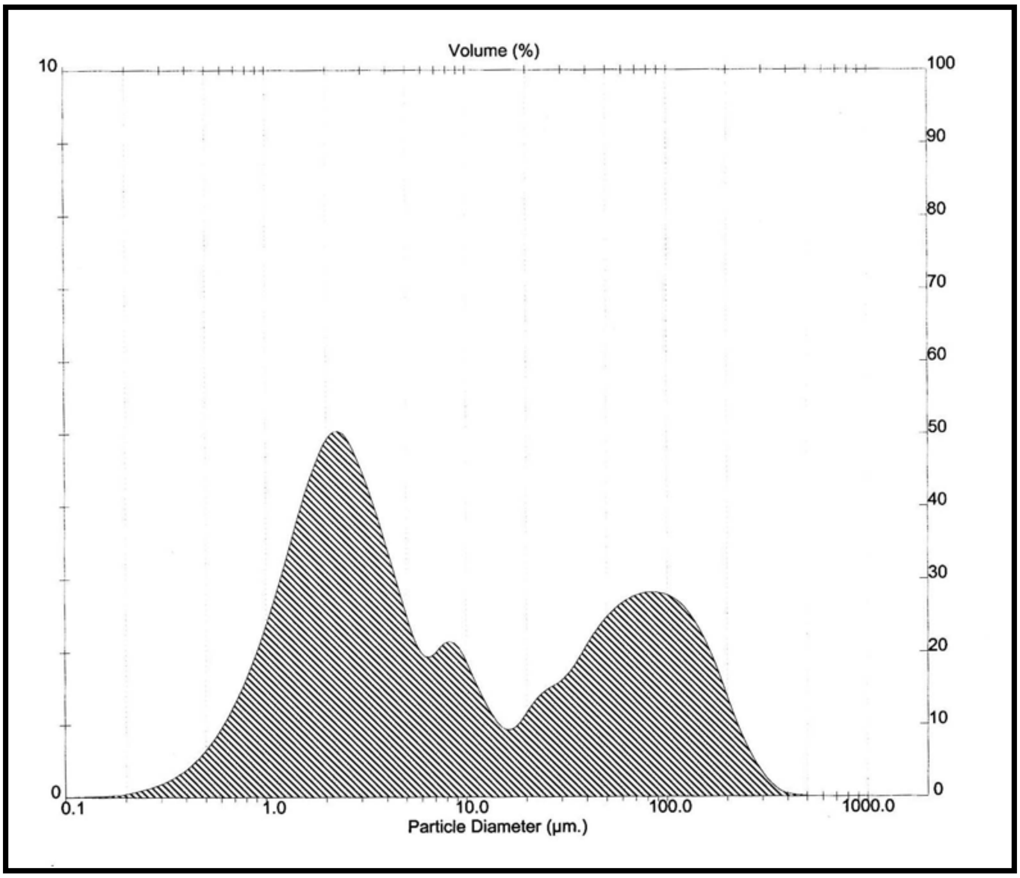
Synthetic Phillipsite



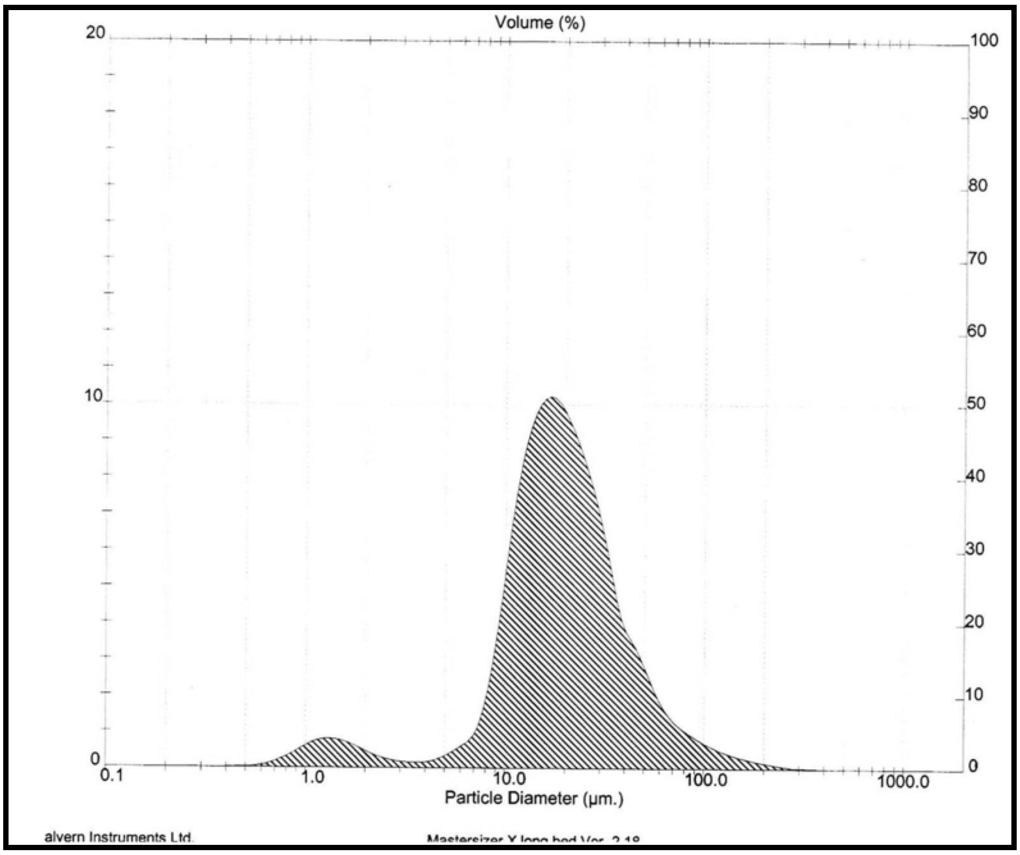
Natural Phillipsite



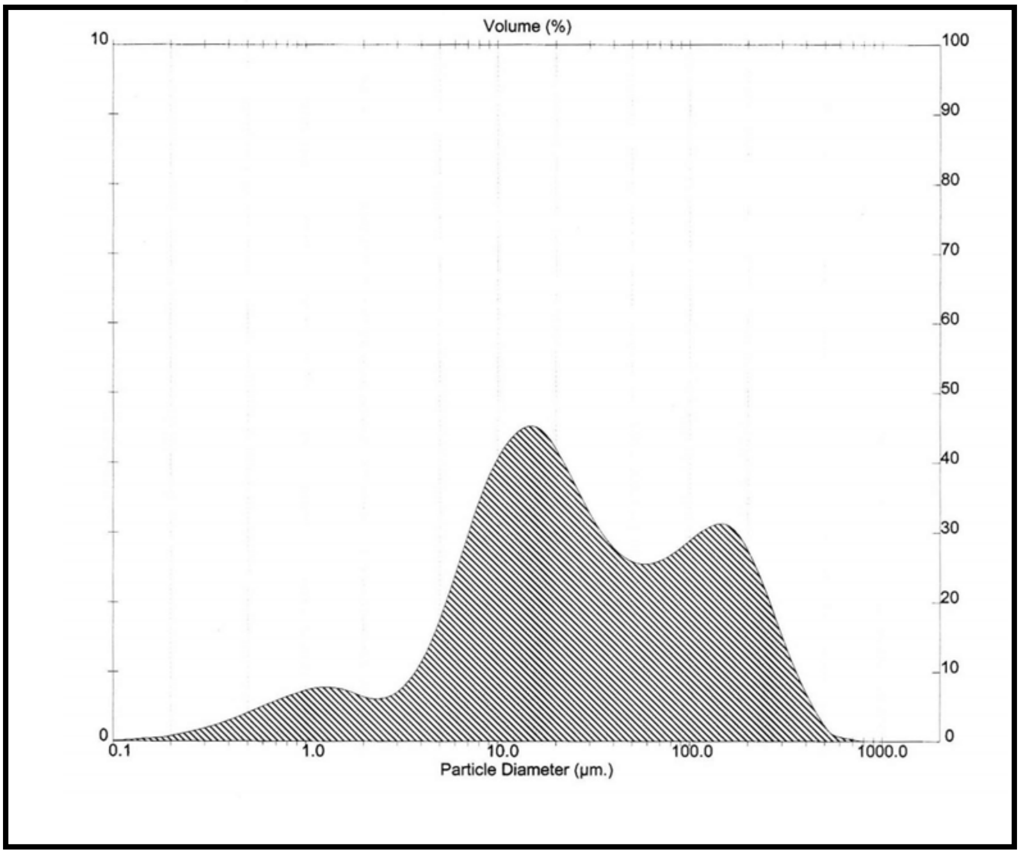
Synthetic Linde type F



Synthetic high crystalline Phillipsite



Synthetic high aluminium Phillipsite



1.5: Fertilizer addition calculations

Amount of fertilizer required depends upon surface area of pots. Diameter 10 cm, area of circle πr^2. r = 5 cm = 0.05 m

No: Pots	No Pots x πr^2
1	0.00785m^2

Soils taken from middle section field of Compton and top-soil from British sugars as determined by ADAS (Rapide nutrient analysis test showed):

	Compton		British sugars
pH	6.5-7		6.5-7
N 15mg/l	1		1
P 10mg/l	1		1
K 180-220mg/l	2	220-260 mg/l	3
Mg 12mg/l	0		0

SOIL INDEX	0	1	2	3+
Nutrient		(kg/hectare)		
N	180	165	150	120
P	100	75	55	40
K	200	180	170	120

(From Pioneer Agronomic Guide for Foriage Maize, 1995)

Example:

Nutrients Rqd	Product 50 kg bags give	Bags per hectare	Total Wt	Plot Size
125kg/hectare (x)	34.5N	17.25N	7.25	362kg

Method:

Divide nutrient required by N provided in a 50 kg bag, i.e.

$\frac{125}{17.25}$ = 7.25 bags (x 50kg) = 362 kg per hectare

Gives total weight fertilizer required.

$\underline{362}$ = *y* kg per *x*

For Glasshouse Experiment 1

Using independent N 27%, P 18% and K 10%

Nutrients Rqd	Product 50kg bags give		Bags/hectare	Total Wt	Plot Size
165kg/hectare	27N	13.5N	12.22	611.11kg	0.0078 m^2
75kg/hectare	18P	9P	8.33	416.67.7kg	0.0078 m^2
35kg/hectare	10K	5K	7.00	350.00 kg	0.0078 m^2

$\frac{165}{13.5}$ = 12.22 bags (x 50kg) = 611.11 kg per hectare for N

$\frac{75}{9}$ = 8.33 bags (x 50kg) = 416.67 kg per hectare for P

$\frac{35}{5}$ = 7.00 bags (x 50kg) = 350 kg per hectare for K

$\frac{100 \times 100}{0.0078}$ = 1282051.28 m^2 in 1 hectare for N, P and K

$\frac{611.11}{1282051.28}$ = 0.00047 kg in plot size for N

= 0.47 g total amount of N fertilizer required/pot

$\frac{416.67}{1282051.28}$ = 0.00032 kg in plot size for P

= 0.32 g total amount of P fertilizer required/pot

$\frac{350.00}{1282051.28}$ = 0.00027 kg in plot size for K

= 0.27 g total amount of K fertilizer required/pot

Similarly, calculations were carried out for Glasshouse Experiments 2 and 3, whereby knowing the pot size and independent N and P fertilizer concentrations, the amount of fertilizer to be added to each pot was calculated accordingly.

1.6: Equations applied for calculating mineralizable Nitrogen, total Nitrogen and extractable Phosphorus.

A) Mineralizable Nitrogen (g/g) =

Titre value of the Incubated sample – Non incubated sample = y (ml)

$$\text{Mineralizable Nitrogen (g/g)} = \frac{\text{y (ml)} \times \text{Acid Concentration (M)} \times \text{RMM of N}}{1000}$$

Where: RMM of Nitrogen = 14.00674; Acid Concentration = 0.01M

Mineralizable Nitrogen (mgN/100g) = g/g X 100000

B) Total Nitrogen (g/g) =

$$\frac{\text{Titre value (ml) X Acid Concentration (M) X RMM of N}}{1000} \text{ X } \frac{1}{\text{Mass of the soil}}$$

Where: RMM of Nitrogen = 14.00674

Mass of soil = 5g; Acid concentration = 0.1 M

Total Nitrogen (mgN/100g) = g/g X 100000

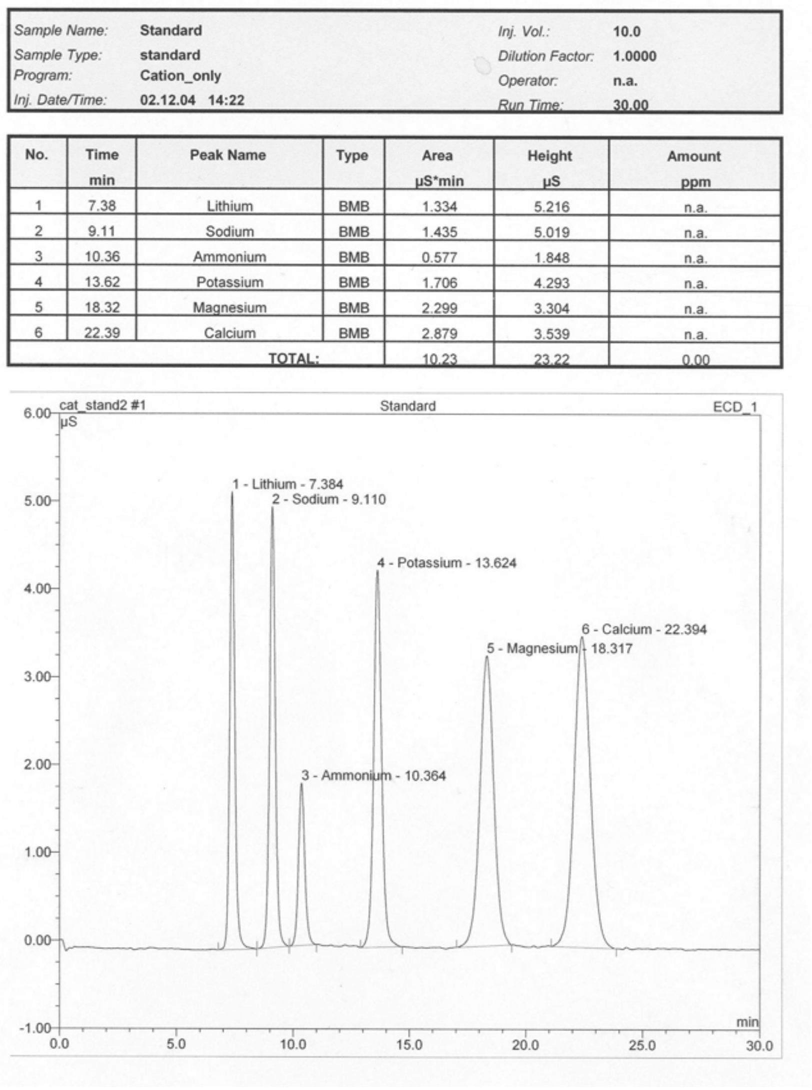
C) Extractable Phosphorus:

$$\text{Extractable P (mgP. Kg}^{-1}\text{)} = \frac{\text{Cm (}\mu\text{gP.100ml) X 100 (ml) X 100 (g)}}{\text{V aliquot (5ml) X M Soil (5g)}}$$

Where: Cm = Concentration measured from calibration curve.

1.7: Ion Chromatography standards and Calibration curves

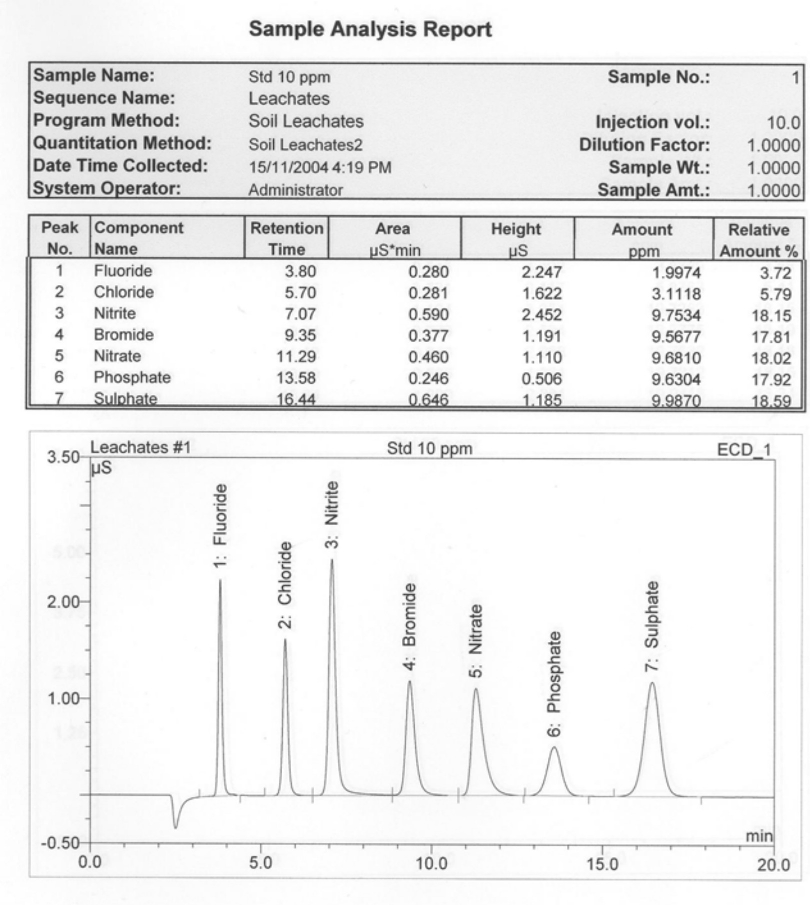
Cation standards



Sample Name: Standard
Sample Type: standard
Program: Cation_only
Inj. Date/Time: 02.12.04 14:22
Inj. Vol.: 10.0
Dilution Factor: 1.0000
Operator: n.a.
Run Time: 30.00

No.	Time min	Peak Name	Type	Area µS*min	Height µS	Amount ppm
1	7.38	Lithium	BMB	1.334	5.216	n.a.
2	9.11	Sodium	BMB	1.435	5.019	n.a.
3	10.36	Ammonium	BMB	0.577	1.848	n.a.
4	13.62	Potassium	BMB	1.706	4.293	n.a.
5	18.32	Magnesium	BMB	2.299	3.304	n.a.
6	22.39	Calcium	BMB	2.879	3.539	n.a.
		TOTAL:		10.23	23.22	0.00

Anion standards

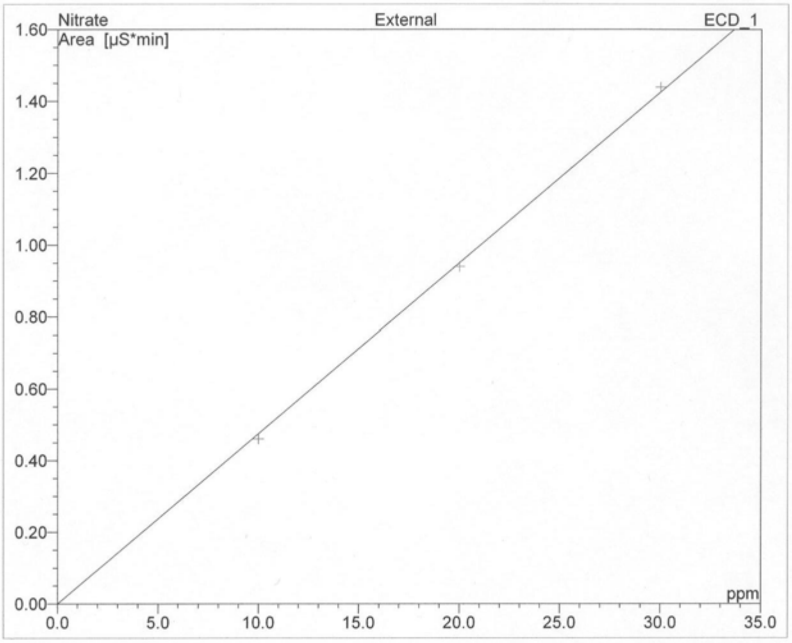


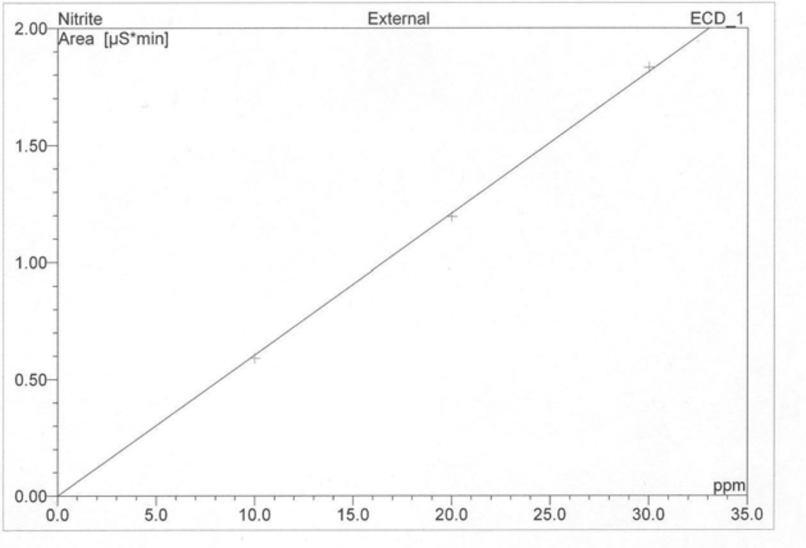
Sample Analysis Report

Sample Name:	Std 10 ppm	**Sample No.:**	1
Sequence Name:	Leachates		
Program Method:	Soil Leachates	**Injection vol.:**	10.0
Quantitation Method:	Soil Leachates2	**Dilution Factor:**	1.0000
Date Time Collected:	15/11/2004 4:19 PM	**Sample Wt.:**	1.0000
System Operator:	Administrator	**Sample Amt.:**	1.0000

Peak No.	Component Name	Retention Time	Area µS*min	Height µS	Amount ppm	Relative Amount %
1	Fluoride	3.80	0.280	2.247	1.9974	3.72
2	Chloride	5.70	0.281	1.622	3.1118	5.79
3	Nitrite	7.07	0.590	2.452	9.7534	18.15
4	Bromide	9.35	0.377	1.191	9.5677	17.81
5	Nitrate	11.29	0.460	1.110	9.6810	18.02
6	Phosphate	13.58	0.246	0.506	9.6304	17.92
7	Sulphate	16.44	0.646	1.185	9.9870	18.59

Calibration Curves





Appendix 2: Plant growth raw data

Glasshouse Experiment 1

Harvest 1

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	0% High	1	37.5	79	5	3.26	0.38	1.82	0.26
1	0% High	2	37.5	92	5	3.40	0.41	2.02	0.28
1	0% High	3	38.4	89	5	3.62	0.43	2.07	0.29
1	0% High	4	39.0	94	5	3.90	0.40	2.08	0.27
1	0% High	5	43.6	117	5	5.25	0.52	2.77	0.29
1	0% High	6	42.5	114	5	5.09	0.53	2.87	0.33
1	0% High	7	38.3	91	4	4.06	0.42	2.12	0.27
1	0% High	8	37.5	92	4	4.12	0.43	2.17	0.29
1	0% High	9	38.1	105	5	4.80	0.45	2.45	0.31
1	0% High	10	44.0	123	5	5.37	0.50	2.88	0.32
2	0% Low	1	43.8	116	5	4.90	0.53	2.63	0.33
2	0% Low	2	43.8	96	5	5.31	0.52	2.57	0.35
2	0% Low	3	43.8	96	5	5.31	0.52	2.57	0.35
2	0% Low	4	39.6	92	5	3.85	0.38	2.18	0.25
2	0% Low	5	33.0	80	5	3.94	0.36	2.24	0.25
2	0% Low	6	44.4	144	5	6.70	0.67	3.87	0.49
2	0% Low	7	45.3	147	5	7.32	0.72	3.93	0.50
2	0% Low	8	42.2	127	5	5.50	0.53	2.94	0.36
2	0% Low	9	46.8	135	5	7.24	0.69	3.93	0.45
2	0% Low	10	43.0	139	5	6.15	0.58	3.55	0.42
3	2% S.Phil	1	41.0	95	5	4.34	0.44	2.46	0.34
3	2% S.Phil	2	41.0	158	5	8.06	0.76	4.28	0.52
3	2% S.Phil	3	48.6	134	6	7.78	0.72	4.2	0.45
3	2% S.Phil	4	47.6	159	5	8.34	0.72	4.58	0.49
3	2% S.Phil	5	45.8	149	5	6.48	0.59	3.56	0.40
3	2% S.Phil	6	44.4	132	5	6.58	0.62	3.60	0.41
3	2% S.Phil	7	39.7	86	4	4.37	0.40	2.41	0.27
3	2% S.Phil	8	44.0	118	5	6.57	0.61	3.50	0.39
3	2% S.Phil	9	42.1	124	5	6.37	0.60	3.46	0.41
3	2% S.Phil	10	38.8	111	5	4.82	0.46	2.80	0.35

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
4	4% S.Phil	1	43.8	121	5	5.36	0.46	3.15	0.32
4	4% S.Phil	2	43.8	164	6	9.26	0.81	4.70	0.53
4	4% S.Phil	3	46.8	155	5	7.96	0.69	3.96	0.36
4	4% S.Phil	4	48.0	151	5	7.36	0.64	3.82	0.40
4	4% S.Phil	5	43.5	121	5	5.91	0.53	3.18	0.32
4	4% S.Phil	6	44.2	125	5	6.90	0.61	3.80	0.41
4	4% S.Phil	7	40.8	116	5	6.48	0.58	3.26	0.34
4	4% S.Phil	8	43.5	127	5	6.66	0.66	3.92	0.44
4	4% S.Phil	9	46.0	142	5	7.35	0.69	4.08	0.48
4	4% S.Phil	10	44.8	131	5	7.11	0.63	3.75	0.41
5	8% S.Phil	1	44.4	128	5	5.68	0.48	3.02	0.35
5	8% S.Phil	2	44.4	139	5	6.90	0.61	3.54	0.40
5	8% S.Phil	3	47.5	148	5	7.67	0.72	4.23	0.48
5	8% S.Phil	4	47.0	131	5	7.91	0.76	4.06	0.47
5	8% S.Phil	5	46.0	145	5	7.11	0.61	3.74	0.42
5	8% S.Phil	6	42.3	118	5	5.74	0.54	3.24	0.36
5	8% S.Phil	7	37.0	94	5	4.43	0.33	2.32	0.20
5	8% S.Phil	8	42.0	141	5	6.47	0.55	3.50	0.36
5	8% S.Phil	9	45.8	135	5	7.03	0.58	3.81	0.37
5	8% S.Phil	10	43.0	129	5	6.05	0.53	3.38	0.34
6	2% N.Phil	1	47.0	134	5	8.20	0.72	4.16	0.45
6	2% N.Phil	2	47.0	132	5	6.74	0.62	3.39	0.39
6	2% N.Phil	3	37.2	104	5	5.64	0.48	2.74	0.28
6	2% N.Phil	4	40.8	88	5	4.9	0.47	2.50	0.29
6	2% N.Phil	5	46.0	147	5	7.11	0.65	3.65	0.42
6	2% N.Phil	6	46.5	127	5	7.66	0.72	3.91	0.42
6	2% N.Phil	7	41.8	123	5	6.72	0.62	3.46	0.40
6	2% N.Phil	8	42.5	122	5	6.27	0.54	3.22	0.32
6	2% N.Phil	9	40.5	119	5	6.55	0.59	3.44	0.39
6	2% N.Phil	10	42.5	125	5	6.94	0.65	3.64	0.39
7	4% N.Phil	1	46.5	150	6	8.18	0.75	3.90	0.42
7	4% N.Phil	2	46.5	122	5	5.35	0.50	2.79	0.33
7	4% N.Phil	3	39.0	116	5	5.32	0.50	3.02	0.34
7	4% N.Phil	4	36.8	87	5	5.90	0.38	2.09	0.24
7	4% N.Phil	5	39.0	118	5	5.90	0.54	2.96	0.33
7	4% N.Phil	6	42.5	134	5	7.45	0.69	3.50	0.39
7	4% N.Phil	7	40.0	109	5	5.78	0.50	3.12	0.31
7	4% N.Phil	8	39.8	120	5	6.26	0.59	3.34	0.34
7	4% N.Phil	9	38.4	91	4	4.51	2.32	0.40	0.24
7	4% N.Phil	10	45.0	138	5	7.61	0.70	3.65	0.42
8	8% N.Phil	1	39.0	110	5	5.64	0.53	2.70	0.32
8	8% N.Phil	2	39.0	104	5	5.47	0.53	2.56	0.31
8	8% N.Phil	3	38.9	105	5	5.98	0.62	2.73	0.39
8	8% N.Phil	4	37.2	113	5	5.96	0.60	2.77	0.35
8	8% N.Phil	5	37.5	98	5	5.75	0.57	2.56	0.33
8	8% N.Phil	6	34.6	92	4	4.12	0.44	2.27	0.29
8	8% N.Phil	7	33.4	66	4	3.77	0.38	1.96	0.23
8	8% N.Phil	8	39.0	93	5	6.01	0.59	2.78	0.34
8	8% N.Phil	9	36.4	99	5	5.14	0.49	2.66	0.31
8	8% N.Phil	10	37.2	70	4	4.29	0.42	1.96	0.26

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
plant height	Between Groups	423.520	7	60.503	6.548	.000
	Within Groups	665.242	72	9.239		
	Total	1088.762	79			
leaf area	Between Groups	14221.988	7	2031.713	5.704	.000
	Within Groups	25643.500	72	356.160		
	Total	39865.488	79			
no. of leaf	Between Groups	1.200	7	.171	1.435	.205
	Within Groups	8.600	72	.119		
	Total	9.800	79			
FSW	Between Groups	56.578	7	8.083	6.801	.000
	Within Groups	85.566	72	1.188		
	Total	142.144	79			
DSW	Between Groups	.538	7	7.685E-02	1.580	.155
	Within Groups	3.503	72	4.866E-02		
	Total	4.041	79			
FLW	Between Groups	18.497	7	2.642	6.820	.000
	Within Groups	27.896	72	.387		
	Total	46.393	79			
DLW	Between Groups	.117	7	1.677E-02	3.919	.001
	Within Groups	.308	72	4.278E-03		
	Total	.425	79			

N.B. **FSW** represents Fresh shoot weight
DSW represents dry shoot weight
FLW represents fresh leaf weight
DLW represents dry leaf weight

Harvest 2

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	0% High	1	97.0	835	7	40.44	4.63	18.28	2.92
1	0% High	2	98.5	792	7	38.88	4.29	16.22	2.60
1	0% High	3	109.0	959	8	46.45	5.15	20.86	3.24
1	0% High	4	101.2	812	7	42.75	4.64	18.44	2.76
1	0% High	5	108.0	895	7	47.09	5.12	18.72	3.06
1	0% High	6	100.4	919	7	45.6	5.27	19.71	3.18
1	0% High	7	98.4	828	7	42.46	4.67	19.16	2.98
1	0% High	8	96.0	865	7	45.93	5.29	20.51	3.20
1	0% High	9	92.0	838	6	44.62	5.25	20.05	3.26
1	0% High	10	93.0	828	7	38.96	4.71	17.49	2.97
2	0% Low	1	104.3	891	6	42.3	4.92	18.60	3.06
2	0% Low	2	107.5	795	7	48.82	5.36	20.86	3.29
2	0% Low	3	105.7	852	6	50.02	21.7	6.09	3.74
2	0% Low	4	103.5	977	7	51.45	6.48	21.96	3.85
2	0% Low	5	101.6	1012	7	53.51	6.5	24.04	3.93
2	0% Low	6	102.0	972	7	54.21	6.86	24.21	4.14
2	0% Low	7	102.0	972	7	54.21	6.86	24.21	4.14
2	0% Low	8	98.0	952	7	50.40	6.03	22.67	3.64
2	0% Low	9	98.0	972	7	51.89	6.63	24.49	4.17
2	0% Low	10	97.0	850	6	44.51	5.42	19.95	3.54
3	2% S.Phil	1	108.8	905	7	51.08	6.09	22.58	3.93
3	2% S.Phil	2	110.0	1055	7	53.92	6.57	24.58	4.29
3	2% S.Phil	3	103.5	988	7	50.90	6.26	24.75	4.11
3	2% S.Phil	4	110.0	849	7	45.10	5.54	20.38	3.55
3	2% S.Phil	5	104.0	1036	7	51.29	6.49	24.11	4.31

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
3	2% S.Phil	6	91.5	841	7	45.10	5.46	20.99	3.48
3	2% S.Phil	7	98.0	917	7	50.40	6.03	23.14	3.84
3	2% S.Phil	8	93.5	866	7	44.83	5.40	20.82	3.52
3	2% S.Phil	9	98.0	868	7	46.82	5.71	21.82	3.75
3	2% S.Phil	10	93.0	715	7	36.55	4.32	17.07	2.78
4	4% S.Phil	1	103.8	926	7	51.66	6.04	23.82	4.02
4	4% S.Phil	2	99.2	883	7	45.41	5.58	22.17	3.87
4	4% S.Phil	3	105	911	7	48.82	4.92	21.74	3.05
4	4% S.Phil	4	86.4	562	7	31.07	3.22	14.33	2.16
4	4% S.Phil	5	102.5	864	7	42.08	4.62	20.14	3.07
4	4% S.Phil	6	92.1	842	7	46.64	5.33	22.23	3.54
4	4% S.Phil	7	93.5	803	7	44.36	4.66	19.85	2.98
4	4% S.Phil	8	104.9	1016	7	59.22	6.68	25.62	4.19
4	4% S.Phil	9	100.0	721	7	55.58	6.30	25.77	4.24
4	4% S.Phil	10	101.8	993	7	55.62	6.40	24.81	3.97
5	8% S.Phil	1	107.0	987	7	55.22	5.45	24.89	3.42
5	8% S.Phil	2	98.2	914	7	43.70	4.94	20.89	3.36
5	8% S.Phil	3	93.4	936	7	46.72	5.29	21.66	3.41
5	8% S.Phil	4	97.2	886	7	44.90	4.75	20.94	3.05
5	8% S.Phil	5	106.0	964	7	51.59	5.84	23.09	3.80
5	8% S.Phil	6	98.4	934	7	49.33	5.43	23.53	3.56
5	8% S.Phil	7	93.0	882	7	52.75	5.50	23.68	3.39
5	8% S.Phil	8	98.2	988	7	54.50	5.88	25.13	3.72
5	8% S.Phil	9	97.5	918	7	55.39	5.71	24.72	3.70
5	8% S.Phil	10	98.2	936	7	52.58	5.68	24.40	3.71
6	2% N.Phil	1	102.0	930	7	53.40	5.73	25.75	3.97
6	2% N.Phil	2	105.0	938	7	52.89	6.33	25.28	4.25
6	2% N.Phil	3	97.3	855	7	48.08	5.13	23.15	3.56
6	2% N.Phil	4	106.0	892	7	47.10	5.40	23.20	3.86
6	2% N.Phil	5	99.0	843	7	44.13	5.40	21.95	3.77
6	2% N.Phil	6	95.6	809	6	48.02	5.07	21.24	3.22
6	2% N.Phil	7	95.5	1050	7	57.81	6.26	26.76	4.10
6	2% N.Phil	8	95.5	932	7	47.50	5.39	22.29	3.57
6	2% N.Phil	9	90.4	878	7	47.74	5.60	23.58	3.84
6	2% N.Phil	10	91.0	960	7	50.18	6.13	24.8	4.14
7	4% N.Phil	1	88.2	590	7	34.10	3.70	15.96	2.77
7	4% N.Phil	2	92.0	902	7	48.50	5.19	23.97	3.74
7	4% N.Phil	3	92.3	902	7	48.50	5.19	23.97	3.74
7	4% N.Phil	4	98.5	747	7	41.50	4.41	19.19	2.93
7	4% N.Phil	5	84.5	698	7	40.54	3.96	18.48	2.76
7	4% N.Phil	6	91.2	898	7	53.09	5.36	23.81	3.47
7	4% N.Phil	7	99.2	999	7	64.18	6.32	27.45	3.89
7	4% N.Phil	8	98.4	966	7	63.85	6.53	27.02	4.04
7	4% N.Phil	9	97.6	913	7	54.95	5.56	24.66	3.56
7	4% N.Phil	10	91.5	888	7	53.54	5.42	22.57	3.47
8	8% N.Phil	1	73.5	335	7	27.03	2.40	11.75	1.62
8	8% N.Phil	2	78.2	510	7	31.56	2.76	14.25	1.90
8	8% N.Phil	3	78.1	646	7	43.35	3.80	18.06	2.25
8	8% N.Phil	4	77.0	527	7	28.72	3.09	13.27	2.17
8	8% N.Phil	5	64.6	433	7	27.09	2.60	12.45	1.76
8	8% N.Phil	6	78.5	614	7	46.55	4.26	18.98	2.54
8	8% N.Phil	7	80.2	672	7	50.13	4.47	22.14	2.82
8	8% N.Phil	8	74.3	564	7	35.30	3.74	16.14	2.52
8	8% N.Phil	9	83.3	589	7	39.20	3.65	16.71	2.39
8	8% N.Phil	10	73.5	530	7	31.64	3.29	14.43	2.22

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Plant height	Between Groups	5009.617	7	715.660	24.387	.000
	Within Groups	2112.922	72	29.346		
	Total	7122.539	79			
Leaf Area	Between Groups	1138813	7	162687.600	18.844	.000
	Within Groups	621595.0	72	8633.264		
	Total	1760408	79			
No:leaves	Between Groups	.800	7	.114	1.646	.136
	Within Groups	5.000	72	6.944E-02		
	Total	5.800	79			
Shoot fresh weight	Between Groups	1759.283	7	251.326	6.352	.000
	Within Groups	2848.878	72	39.568		
	Total	4608.160	79			
Shoot dry weight	Between Groups	96.670	7	13.810	3.932	.001
	Within Groups	252.894	72	3.512		
	Total	349.564	79			
leaf fresh weight	Between Groups	490.959	7	70.137	7.019	.000
	Within Groups	719.415	72	9.992		
	Total	1210.374	79			
leaf dry weight	Between Groups	19.957	7	2.851	16.800	.000
	Within Groups	12.219	72	.170		
	Total	32.176	79			

Harvest 3

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	0% High	1	148.5	1864	12	122.45	17.04	44.17	8.98
1	0% High	2	149.2	1971	12	110.35	16.2	42.32	8.79
1	0% High	3	137.1	1776	12	103.64	16.45	37.16	9.82
1	0% High	4	145.2	1877	12	114.32	17.54	41.81	9.31
1	0% High	5	144.3	1760	12	123.06	16.42	50.67	9.06
1	0% High	6	135.7	1689	11	107.14	14.39	37.92	7.50
1	0% High	7	127.5	1766	11	103.81	11.98	37.75	4.92
1	0% High	8	101.3	1273	11	63.40	7.95	26.30	4.60
1	0% High	9	137.5	1477	12	104.83	16.27	36.27	8.42
1	0% High	10	132.3	1862	12	110.81	15.35	41.39	8.01
2	0% Low	1	125.2	1738	12	113.08	17.96	40.18	8.99
2	0% Low	2	150.2	1888	12	116.44	17.37	41.32	8.61
2	0% Low	3	129.6	1472	12	98.19	16.30	33.89	8.23
2	0% Low	4	141.4	1749	12	120.16	19.71	42.91	9.60
2	0% Low	5	132.9	1627	12	110.51	19.46	37.99	9.84
2	0% Low	6	132.5	1601	12	111.76	17.81	36.24	8.35
2	0% Low	7	138.6	1787	12	110.63	15.35	40.70	7.70
2	0% Low	8	121.3	1328	12	99.71	16.94	37.01	8.87
2	0% Low	9	119.4	1662	12	104.65	16.14	37.22	7.20
2	0% Low	10	123.7	1526	12	104.44	15.02	35.29	7.31
3	2% S.Phil	1	152.1	1755	12	115.10	18.32	40.06	8.93
3	2% S.Phil	2	151.6	1900	12	128.91	21.67	44.85	12.35
3	2% S.Phil	3	135.2	16.4	12	115.70	17.45	39.41	8.12
3	2% S.Phil	4	141.2	1595	12	115.72	11.48	37.99	7.69
3	2% S.Phil	5	154.3	1825	12	121.16	8.55	42.71	7.52
3	2% S.Phil	6	132.2	1490	12	96.94	14.31	33.84	6.87
3	2% S.Phil	7	132.2	1490	12	96.94	14.31	33.84	6.87
3	2% S.Phil	8	126.6	1422	11	81.36	12.44	29.96	6.70
3	2% S.Phil	9	125.1	1573	11	93.50	14.20	33.60	7.34
3	2% S.Phil	10	116.9	1492	11	95.90	14.28	34.53	7.08
4	4% S.Phil	1	146.2	1694	11	105.62	17.69	38.59	9.30
4	4% S.Phil	2	143.1	1600	11	112.62	17.47	39.70	9.03

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
4	4% S.Phil	3	150.3	1719	13	112.97	16.08	40.96	8.32
4	4% S.Phil	4	136.8	1650	12	118.15	18.30	41.07	9.10
4	4% S.Phil	5	151.6	1686	11	113.13	17.34	42.05	8.77
4	4% S.Phil	6	149.4	1704	12	120.17	15.97	38.35	7.60
4	4% S.Phil	7	132.6	1659	12	107.61	14.89	36.28	7.09
4	4% S.Phil	8	130.5	1614	12	112.72	16.64	38.59	8.16
4	4% S.Phil	9	126.2	1728	11	107.34	14.57	37.63	7.51
4	4% S.Phil	10	125.4	1621	12	107.07	15.05	37.78	7.98
5	8% S.Phil	1	126.3	1424	12	109.16	16.28	35.05	7.77
5	8% S.Phil	2	140.6	1570	11	105.93	15.56	37.07	8.31
5	8% S.Phil	3	144.8	1800	11	121.64	16.71	42.04	8.70
5	8% S.Phil	4	137.5	1666	12	127.76	17.53	40.50	8.41
5	8% S.Phil	5	121.4	1599	12	113.21	16.27	39.97	8.42
5	8% S.Phil	6	128.4	1698	11	130.01	18.05	41.70	8.36
5	8% S.Phil	7	120.5	1428	11	95.18	16.81	36.01	6.11
5	8% S.Phil	8	137.6	1713	11	120.87	16.21	39.18	7.76
5	8% S.Phil	9	130.4	1636	12	126.55	16.88	38.91	8.26
6	8% S.Phil	10	132.4	1784	12	126.52	17.99	44.47	9.28
6	2% N.Phil	1	158.4	1682	12	130.45	20.38	39.46	9.76
6	2% N.Phil	2	162.5	1503	11	109.25	17.03	34.49	8.01
6	2% N.Phil	3	148.6	1541	12	111.57	15.59	37.03	7.62
6	2% N.Phil	4	145.4	1638	11	112.85	18.20	38.32	9.01
6	2% N.Phil	5	147.6	1537	11	120.86	19.01	40.50	9.57
6	2% N.Phil	6	119.6	1337	11	92.94	15.17	31.04	8.13
6	2% N.Phil	7	143.7	1527	12	117.94	18.85	36.62	8.68
6	2% N.Phil	8	145.6	1463	12	107.94	17.02	35.65	8.18
6	2% N.Phil	9	145.2	1325	12	106.78	17.87	31.87	8.21
6	2% N.Phil	10	135.3	1487	12	101.12	15.39	45.85	7.49
7	4% N.Phil	1	141.3	1340	11	102.36	15.06	31.43	8.29
7	4% N.Phil	2	146.4	1349	10	95.33	12.61	32.56	6.65
7	4% N.Phil	3	135.6	1276	12	107.31	15.57	34.22	7.76
7	4% N.Phil	4	133.5	817	10	68.51	9.01	26.02	4.97
7	4% N.Phil	5	153.2	1455	9	107.33	14.16	34.07	7.17
7	4% N.Phil	6	145.6	1666	12	139.06	18.80	41.38	8.41
7	4% N.Phil	7	133.2	1574	12	117.63	15.61	38.59	7.47
7	4% N.Phil	8	142.1	1356	12	100.9	12.12	35.13	6.47
7	4% N.Phil	9	140.3	1379	12	99.10	14.36	30.58	7.02
7	4% N.Phil	10	121.8	1538	12	108.8	16.29	35.04	8.10
8	8% N.Phil	1	149.2	1400	12	106.6	13.41	32.60	6.03
8	8% N.Phil	2	124.1	1413	12	99.56	13.24	34.77	6.99
8	8% N.Phil	3	142.6	1214	12	86.75	10.90	29.15	5.60
8	8% N.Phil	4	157.2	1336	12	98.98	12.83	30.96	6.20
8	8% N.Phil	5	141.8	1370	12	106.5	14.13	34.03	7.12
8	8% N.Phil	6	149.1	1370	12	87.93	10.31	30.51	5.80
8	8% N.Phil	7	139.1	1450	11	115.6	16.01	35.52	7.31
8	8% N.Phil	8	154.9	1576	11	125.8	15.34	36.48	6.83
8	8% N.Phil	9	138.2	1472	12	114.2	13.64	35.93	6.46
8	8% N.Phil	10	152.4	1388	10	104.0	12.85	33.02	6.45

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Plant height	Between Groups	1720.774	7	245.825	2.065	.058
	Within Groups	8572.934	72	119.069		
	Total	10293.708	79			
No:leaves	Between Groups	1210328	7	172904.014	3.063	.007
	Within Groups	4064193	72	56447.125		
	Total	5274521	79			
Leaf Area	Between Groups	3.682	7	.526	1.303	.261
	Within Groups	29.068	72	.404		
	Total	32.750	79			
Shoot f weight	Between Groups	1285.642	7	183.663	1.137	.350
	Within Groups	11635.356	72	161.602		
	Total	12920.999	79			
Shoot d weight	Between Groups	164.651	7	23.522	4.691	.000
	Within Groups	360.983	72	5.014		
	Total	525.634	79			
Leaf fresh weight	Between Groups	395.834	7	56.548	3.556	.002
	Within Groups	1144.889	72	15.901		
	Total	1540.724	79			
Leaf dry weight	Between Groups	33.984	7	4.855	3.859	.001
	Within Groups	90.570	72	1.258		
	Total	124.554	79			

Glasshouse Experiment 2

Harvest 1

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	Blank	1	46.2	174	6	7.30	0.76	4.20	0.50
1	Blank	2	42.6	143	6	5.70	0.60	3.13	0.40
1	Blank	3	49.9	180	6	7.40	0.70	3.81	0.43
1	Blank	4	48.6	172	6	7.40	0.72	3.92	0.47
1	Blank	5	55.4	197	6	9.38	0.83	5.13	0.56
1	Blank	6	53.1	181	6	8.30	0.72	4.46	0.47
1	Blank	7	56.5	210	6	9.42	0.85	5.03	0.56
1	Blank	8	45.3	120	6	5.25	0.50	3.16	0.34
2	0% High	1	35.8	84	5	2.80	0.33	1.63	0.24
2	0% High	2	38.1	89	5	3.20	0.39	1.75	0.29
2	0% High	3	41.9	89.0	6	3.40	0.34	1.91	0.25
2	0% High	4	38.1	84.1	6	2.60	0.25	1.52	0.19
2	0% High	5	32.2	76.0	5	1.58	0.18	0.97	0.14
2	0% High	6	42.8	80.0	6	3.99	0.46	1.25	0.33
2	0% High	7	38.4	78.0	5	2.94	0.36	1.89	0.25
2	0% High	8	36.3	81.1	6	2.48	0.32	1.63	0.21
3	0% Std	1	49.7	167	6	7.10	0.67	3.83	0.41
3	0% Std	2	53.9	180	6	8.60	0.70	3.21	0.38
3	0% Std	3	44.7	132	6	5.80	0.47	3.10	0.29
3	0% Std	4	51.4	193	6	8.10	0.57	4.92	0.42
3	0% Std	5	52.5	189	6	8.57	0.81	4.23	0.49
3	0% Std	6	50.9	132	6	8.83	0.85	4.37	0.46
3	0% Std	7	46.7	122	6	7.13	0.64	3.32	0.48
3	0% Std	8	45.1	132	6	4.56	0.38	4.26	0.46
4	1% S.Phi	1	46.7	129	6	7.90	0.57	3.82	0.34
4	1% S.Phi	2	47.5	147	6	7.201	0.55	3.82	0.32
4	1% S.Phi	3	47.3	172	6	7.10	0.62	3.92	0.41
4	1% S.Phi	4	45.5	158	6	7.21	0.65	3.92	0.40

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
4	1% S.Phi	5	51.2	191	6	7.61	0.63	4.56	0.49
4	1% S.Phi	6	55.2	240	6	8.04	0.80	5.11	0.67
4	1% S.Phi	7	53.2	210	6	8.02	0.72	4.21	0.54
4	1% S.Phi	8	56.1	216	6	9.86	0.80	5.30	0.56
5	2% S.Phi	1	51.3	185	6	7.81	0.66	4.10	0.43
5	2% S.Phi	2	50.7	201	6	8.40	0.76	4.40	0.52
5	2% S.Phi	3	54.2	273	6	12.9	1.03	6.80	0.71
5	2% S.Phi	4	49.1	177	6	7.40	0.61	3.80	0.42
5	2% S.Phi	5	56.2	195	6	8.32	0.73	4.18	0.49
5	2% S.Phi	6	43.6	120	6	5.67	0.50	2.95	0.34
5	2% S.Phi	7	49.6	163	6	6.73	0.66	3.81	0.47
5	2% S.Phi	8	65.5	286	7	13.71	1.07	7.05	0.72
6	4% S.Phi	1	41.6	118	6	4.91	0.74	2.80	0.58
6	4% S.Phi	2	39.1	115	6	4.82	0.69	2.70	0.55
6	4% S.Phi	3	36.7	121	6	4.62	0.45	2.80	0.34
6	4% S.Phi	4	49.2	173	6	7.60	0.62	4.30	0.44
6	4% S.Phi	5	44.1	129	6	4.53	0.36	2.74	0.27
6	4% S.Phi	6	52.3	189	6	7.45	0.72	4.27	0.56
6	4% S.Phi	7	43.2	92	6	4.06	0.34	2.16	0.24
6	4% S.Phi	8	46.3	112	6	5.22	0.79	3.42	0.43
7	1% Lin F	1	50.5	187	6	8.81	0.74	4.50	0.48
7	1% Lin F	2	44.7	131	6	6.20	0.58	2.90	0.40
7	1% Lin F	3	44.6	129	6	6.21	0.61	3.10	0.40
7	1% Lin F	4	41.9	124	6	5.9	0.58	3.10	0.39
7	1% Lin F	5	58.9	202	6	8.81	0.90	4.68	0.65
7	1% Lin F	6	50.1	178	6	7.17	0.80	3.96	0.58
7	1% Lin F	7	45.4	101	6	6.92	0.61	3.31	0.39
7	1% Lin F	8	44.6	96.0	6	5.70	0.57	2.58	0.40
8	2% Lin F	1	50.9	178	6	8.31	0.78	4.10	0.48
8	2% Lin F	2	47.2	173	6	8.21	0.73	4.20	0.51
8	2% Lin F	3	52.9	192	6	9.10	0.79	4.60	0.53
8	2% Lin F	4	44.2	135	6	6.16	0.53	3.20	0.35
8	2% Lin F	5	47.7	130	6	6.11	0.51	3.01	0.32
8	2% Lin F	6	49.1	136	6	6.02	0.54	3.16	0.36
8	2% Lin F	7	49.4	163	6	7.30	0.61	3.90	0.44
8	2% Lin F	8	43.9	124	6	5.84	0.49	3.06	0.35
9	4% Lin F	1	46.9	123	6	5.50	0.52	2.70	0.33
9	4% Lin F	2	36.6	94	5	4.12	0.49	2.20	0.35
9	4% Lin F	3	30.1	51	5	1.80	0.20	1.02	0.15
9	4% Lin F	4	32.5	76	5	3.23	0.31	1.70	0.22
9	4% Lin F	5	36.9	87	6	3.82	0.40	1.90	0.27
9	4% Lin F	6	42.1	97	6	4.85	0.46	2.62	0.30
9	4% Lin F	7	38.4	84	6	3.72	0.37	2.02	0.27
9	4% Lin F	8	43.6	98	6	4.39	0.45	2.27	0.31
10	2% U SP	1	40.5	139	6	5.80	0.40	3.31	0.42
10	2% U SP	2	37.9	91	6	5.70	0.31	3.22	0.31
10	2% U SP	3	39.2	92	6	5.60	0.33	3.93	0.33
10	2% U SP	4	45.9	179	6	7.20	0.50	4.01	0.50
10	2% U SP	5	49.3	182	6	6.98	0.44	3.21	0.44
10	2% U SP	6	47.5	139	6	6.30	0.47	3.26	0.47
10	2% U SP	7	52.6	230	6	8.44	0.57	5.04	0.57
10	2% U SP	8	47.6	167	6	6.53	0.33	3.05	0.33
11	2% U LF	1	45.6	140	6	7.02	0.57	3.50	0.38
11	2% U LF	2	53.0	221	6	8.20	0.67	4.10	0.51
11	2% U LF	3	49.0	173	6	8.23	0.68	3.80	0.40
11	2% U LF	4	53.5	218	6	8.90	0.70	4.60	0.53
11	2% U LF	5	40.6	82	6	5.87	0.58	3.21	0.29
11	2% U LF	6	43.9	97	6	5.92	0.55	3.58	0.30
11	2% U LF	7	55.8	197	6	9.10	0.74	4.91	0.65
11	2% U LF	8	50.3	179	6	8.39	0.74	4.40	0.56

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
plant height	Between Groups	1803.623	10	180.362	7.728	.000
	Within Groups	1797.001	77	23.338		
	Total	3600.624	87			
leaf area	Between Groups	103533.2	10	10353.321	7.613	.000
	Within Groups	104709.8	77	1359.868		
	Total	208243.1	87			
no. of leaf	Between Groups	2.841	10	.284	4.605	.000
	Within Groups	4.750	77	6.169E-02		
	Total	7.591	87			
shoot fresh wt	Between Groups	256.821	10	25.682	12.244	.000
	Within Groups	161.515	77	2.098		
	Total	418.336	87			
shoot dry weight	Between Groups	1.557	10	.156	9.297	.000
	Within Groups	1.290	77	1.675E-02		
	Total	2.847	87			
fresh leaf weight	Between Groups	69.639	10	6.964	11.978	.000
	Within Groups	44.766	77	.581		
	Total	114.405	87			
dry leaf weight	Between Groups	.560	10	5.598E-02	5.564	.000
	Within Groups	.775	77	1.006E-02		
	Total	1.335	87			

Harvest 2

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	Blank	1	84.1	382	7	25.53	2.95	11.32	1.53
1	Blank	2	81.6	455	7	30.81	4.14	14.21	2.41
1	Blank	3	74.3	394	7	23.81	3.04	11.53	1.78
1	Blank	4	80.1	380	7	23.35	2.90	10.71	1.73
1	Blank	5	81.9	353	7	28.3	3.62	12.81	2.15
1	Blank	6	86.9	354	7	30.71	3.71	13.52	2.26
1	Blank	7	74.1	312	7	21.62	2.70	9.92	1.61
1	Blank	8	79.3	331	7	26.41	2.93	11.26	2.02
2	0% High	1	92.4	499	7	24.13	2.92	11.20	1.94
2	0% High	2	91.3	476	7	21.71	2.70	9.80	1.67
2	0% High	3	87.1	465	7	24.31	2.93	11.20	1.92
2	0% High	4	98.6	604	8	34.32	4.11	15.20	2.17
2	0% High	5	67.7	202	7	8.25	0.89	4.31	0.66
2	0% High	6	83.9	453	8	19.9	2.23	10.10	1.53
2	0% High	7	83.60	479	8	22.63	2.28	10.7	1.58
2	0% High	8	80.40	502	8	22.32	2.27	11.1	1.55
3	0% Std	1	104.9	841	7	49.20	6.85	22.1	4.01
3	0% Std	2	88.40	579	8	22.20	1.95	10.5	1.20
3	0% Std	3	114.4	836	8	48.50	6.10	20.2	3.54
3	0% Std	4	103.1	812	8	47.80	6.08	22.2	3.75
3	0% Std	5	104.8	717	8	40.70	4.31	17.5	2.51
3	0% Std	6	114.3	773	8	61.60	6.90	25.5	3.94
3	0% Std	7	106.5	871	8	50.10	5.54	23.5	3.57
3	0% Std	8	104.2	813	8	46.20	5.08	22.6	3.18
4	1% S.Phi	1	106.3	746	8	45.10	6.03	19.4	3.56
4	1% S.Phi	2	93.50	732	8	41.60	5.05	20.2	3.27
4	1% S.Phi	3	104.8	820	8	49.60	6.51	21.7	3.96
4	1% S.Phi	4	94.30	702	8	36.80	5.17	17.9	3.22
4	1% S.Phi	5	89.10	674	9	36.10	3.91	16.4	2.60
4	1% S.Phi	6	107.1	844	8	56.40	6.08	24.3	3.64
4	1% S.Phi	7	104.2	923	9	54.30	6.24	25.1	3.97
4	1% S.Phi	8	106.3	974	9	63.40	6.17	28.2	4.16
5	2% S.Phi	1	106.8	808	8	50.90	6.06	23.4	3.58

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
5	2% S.Phi	2	109.4	805	8	55.90	6.97	24.5	3.98
5	2% S.Phi	3	108.0	655	8	39.30	3.33	21.5	3.04
5	2% S.Phi	4	107.2	848	8	46.70	6.00	17.4	3.39
5	2% S.Phi	5	91.50	1028	9	69.20	8.46	18.1	2.26
5	2% S.Phi	6	108.1	1013	9	65.40	6.57	28.4	4.23
5	2% S.Phi	7	112.8	746	8	46.20	5.67	33.3	5.12
5	2% S.Phi	8	108.9	712	8	44.60	5.65	26.5	3.79
6	4% S.Phi	1	110.1	763	8	53.20	6.17	22.7	3.77
6	4% S.Phi	2	102.9	769	8	53.50	6.03	24.2	3.93
6	4% S.Phi	3	107.5	808	8	47.20	5.04	21.3	3.47
6	4% S.Phi	4	106.8	812	8	64.20	7.08	26.0	4.16
6	4% S.Phi	5	93.20	609	7	38.40	4.37	16.9	2.68
6	4% S.Phi	6	103.4	692	7	43.30	4.50	19.2	3.05
6	4% S.Phi	7	105.5	836	8	52.10	5.57	23.2	3.46
6	4% S.Phi	8	101.2	813	8	49.30	5.06	22.1	3.09
7	1% Lin F	1	101.9	713	8	44.70	4.70	18.9	3.46
7	1% Lin F	2	106.7	724	8	45.90	4.79	18.7	3.01
7	1% Lin F	3	93.40	462	7	31.20	3.08	13.8	2.02
7	1% Lin F	4	77.50	352	7	20.20	2.27	10.1	1.59
7	1% Lin F	5	102.8	663	8	43.70	4.36	19.1	2.63
7	1% Lin F	6	108.3	758	8	50.70	5.26	21.1	3.08
7	1% Lin F	7	87.50	402	7	25.50	2.56	11.6	1.70
7	1% Lin F	8	101.5	546	7	38.10	3.72	16.9	2.44
8	2% Lin F	1	94.70	405	7	30.10	2.74	11.8	1.6
8	2% Lin F	2	96.40	539	7	36.40	3.52	15.9	2.32
8	2% Lin F	3	75.10	289	6	15.70	1.65	7.8	1.11
8	2% Lin F	4	75.40	305	6	17.90	1.77	8.8	1.18
8	2% Lin F	5	86.70	457	7	26.90	2.71	13.2	1.95
8	2% Lin F	6	94.90	576	7	36.20	3.69	17.5	2.54
8	2% Lin F	7	79.10	337	6	19.20	1.88	9.3	1.24
8	2% Lin F	8	81.20	407	7	21.40	2.37	10.9	1.67
9	4% Lin F	1	83.40	407	7	22.20	2.27	10.2	1.51
9	4% Lin F	2	81.50	298	6	18.70	1.72	8.2	1.08
9	4% Lin F	3	78.90	271	6	14.10	1.47	6.6	0.95
9	4% Lin F	4	74.10	329	7	17.60	1.71	8.3	1.10
9	4% Lin F	5	76.10	312	6	15.90	1.62	8.5	1.17
9	4% Lin F	6	76.40	337	7	17.90	1.91	9.01	1.24
9	4% Lin F	7	67.50	235	6	10.40	1.21	5.5	0.95
9	4% Lin F	8	64.30	312	6	9.80	1.13	5.25	0.87
10	2% U SP	1	100.4	808	8	54.60	5.71	24.1	3.87
10	2% U SP	2	112.1	805	8	57.01	6.07	24.0	3.70
10	2% U SP	3	93.50	655	7	49.05	5.27	18.5	3.30
10	2% U SP	4	101.5	848	8	41.80	5.53	23.02	3.74
10	2% U SP	5	116.2	1028	9	37.9	6.92	28.8	4.12
10	2% U SP	6	112.5	1013	9	49.5	6.49	27.2	4.06
10	2% U SP	7	103.1	746	8	60.3	4.38	21.3	2.97
10	2% U SP	8	102.6	712	8	62.6	4.13	20.7	2.61
11	2% U LF	1	97.90	511	7	34.1	3.32	14.1	1.95
11	2% U LF	2	102.9	616	7	49.9	5.52	19.9	3.05
11	2% U LF	3	108.0	616	7	48.5	5.04	22.3	2.72
11	2% U LF	4	90.50	434	7	28.2	2.91	11.4	1.73
11	2% U LF	5	77.90	303	6	16.4	1.86	7.51	1.24
11	2% U LF	6	106.6	751	8	51.3	5.63	21.0	3.28
11	2% U LF	7	105.3	762	8	57.4	6.99	23.7	3.89
11	2% U LF	8	82.40	489	7	29.3	3.13	13.4	2.04

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
plant height	Between Groups	9947.163	10	994.716	15.269	.000
	Within Groups	5016.380	77	65.148		
	Total	14963.543	87			
leaf area	Between Groups	3147606	10	314760.625	24.652	.000
	Within Groups	983149.8	77	12768.179		
	Total	4130756	87			
no. of leaf	Between Groups	34.750	10	3.475	13.900	.000
	Within Groups	19.250	77	.250		
	Total	54.000	87			
FSW	Between Groups	13860.123	10	1386.012	16.311	.000
	Within Groups	6542.970	77	84.974		
	Total	20403.093	87			
DSW	Between Groups	188.984	10	18.898	15.593	.000
	Within Groups	93.324	77	1.212		
	Total	282.309	87			
FLW	Between Groups	2664.786	10	266.479	18.156	.000
	Within Groups	1130.149	77	14.677		
	Total	3794.934	87			
DLW	Between Groups	67.887	10	6.789	17.399	.000
	Within Groups	30.044	77	.390		
	Total	97.931	87			

Harvest 3

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	Blank	1	99.50	732	11	63.2	10.52	21.2	4.86
1	Blank	2	116.1	901	11	65.7	10.87	20.9	4.79
1	Blank	3	95.60	506	11	42.8	6.62	15.2	3.34
1	Blank	4	90.50	400	12	41.9	7.52	15.4	3.73
1	Blank	5	101.4	824	11	48.9	8.68	16.3	4.19
1	Blank	6	96.20	781	11	51.8	9.54	17.5	4.26
1	Blank	7	111.7	775	12	42.9	6.53	15.5	3.29
1	Blank	8	100.9	863	11	53.2	8.79	19.6	4.14
2	0% High	1	130.1	736	10	40.4	4.57	17.4	2.88
2	0% High	2	137.8	981	11	72.3	10.39	27.1	5.48
2	0% High	3	112.1	743	10	62.3	9.12	22.6	4.37
2	0% High	4	120.6	816	11	60.1	9.01	20.2	4.06
2	0% High	5	130.3	1183	12	76.7	10.5	32.1	6.14
2	0% High	6	132.2	1445	11	91.6	12.69	35.4	7.32
2	0% High	7	147.1	1262	12	82.4	12.82	30.5	6.55
2	0% High	8	140.5	1273	12	73.5	10.85	27.8	5.73
3	0% Std	1	116.4	1204	13	82.5	17.14	29.4	6.37
3	0% Std	2	118.0	1225	13	91.3	16.65	16.14	7.51
3	0% Std	3	132.4	1273	12	105.6	17.84	18.44	8.21
3	0% Std	4	127.2	1103	12	85.50	14.47	16.26	7.51
3	0% Std	5	144.7	1501	13	107.8	17.61	22.15	8.82
3	0% Std	6	153.0	1274	13	91.60	16.75	16.01	6.78
3	0% Std	7	155.4	1326	13	86.90	18.07	16.66	6.74
3	0% Std	8	153.4	1420	13	111.1	17.32	21.14	8.37
4	1% S.Phi	1	141.1	1478	13	88.50	12.70	35.10	6.85
4	1% S.Phi	2	154.7	1527	13	111.4	16.14	32.60	8.35
4	1% S.Phi	3	159.8	1474	13	103.7	18.44	33.40	8.25
4	1% S.Phi	4	153.5	1444	13	106.6	16.26	33.30	7.40
4	1% S.Phi	5	153.2	1284	12	102.4	22.15	27.61	8.99
4	1% S.Phi	6	137.4	1207	12	90.20	16.01	26.60	8.46
4	1% S.Phi	7	157.6	1564	13	115.4	16.66	33.81	8.38
4	1% S.Phi	8	162.9	1512	13	108.8	21.14	30.50	8.09

	Treatment	Rep	Height (cm)	Leaf Area (cm^2)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
5	2% S.Phi	1	137.3	1483	13	117.6	19.38	36.81	8.17
5	2% S.Phi	2	126.0	1570	13	108.7	18.99	36.11	7.30
5	2% S.Phi	3	149.3	1445	13	125.1	21.42	38.20	9.33
5	2% S.Phi	4	132.6	1429	13	104.7	16.43	33.50	8.12
5	2% S.Phi	5	147.5	1781	14	122.6	20.17	34.70	10.54
5	2% S.Phi	6	149.5	1433	13	107.4	17.68	35.6	7.78
5	2% S.Phi	7	155.4	1538	13	126.6	20.96	32.5	9.21
5	2% S.Phi	8	156.6	1328	13	105.1	17.90	35.8	7.03
6	4% S.Phi	1	131.8	1397	13	99.20	14.11	35.1	7.68
6	4% S.Phi	2	137.1	1334	13	116.3	16.14	38.7	7.71
6	4% S.Phi	3	136.2	1591	13	68.20	7.65	25.5	4.18
6	4% S.Phi	4	145.3	999	12	122.7	18.31	37.1	7.84
6	4% S.Phi	5	133.8	1076	11	68.60	10.87	23.7	5.16
6	4% S.Phi	6	148.2	1209	11	64.10	9.01	24.1	4.76
6	4% S.Phi	7	135.4	1082	11	63.10	8.44	24.7	4.53
6	4% S.Phi	8	131.6	1012	11	61.31	8.37	22.4	4.01
7	1% Lin F	1	124.1	1124	11	44.91	5.48	16.3	2.84
7	1% Lin F	2	138.6	1443	12	93.32	13.67	30.7	7.11
7	1% Lin F	3	141.7	1145	11	83.41	12.56	26.6	6.14
7	1% Lin F	4	118.7	1009	10	48.50	8.02	18.7	4.48
7	1% Lin F	5	142.4	1005	10	61.21	10.22	19.9	4.84
7	1% Lin F	6	126.8	859	10	48.80	7.67	16.7	3.62
7	1% Lin F	7	130.4	1125	11	93.20	14.71	22.5	6.95
7	1% Lin F	8	112.6	998	10	46.31	7.45	17.6	4.23
8	2% Lin F	1	118.2	930	10	49.92	6.83	20.2	4.33
8	2% Lin F	2	126.6	869	10	48.32	6.45	18.1	3.88
8	2% Lin F	3	112.1	1006	12	50.13	7.37	21.6	4.55
8	2% Lin F	4	120.4	850	10	38.26	5.23	15.4	3.23
8	2% Lin F	5	116.3	792	11	36.35	5.11	12.3	3.04
8	2% Lin F	6	113.5	781	11	41.74	5.83	16.3	3.28
8	2% Lin F	7	134.8	953	10	54.72	6.78	20.4	3.95
8	2% Lin F	8	108.9	595	11	31.31	4.03	13.7	2.74
9	4% Lin F	1	114.6	606	11	31.80	4.05	14.2	2.69
9	4% Lin F	2	112.4	712	11	41.10	5.76	16.9	3.59
9	4% Lin F	3	81.20	341	10	14.80	2.12	7.6	1.54
9	4% Lin F	4	79.60	402	10	21.62	3.02	9.2	2.08
9	4% Lin F	5	84.20	403	10	19.43	2.61	8.3	1.11
9	4% Lin F	6	110.3	681	11	39.23	4.28	14.3	3.46
9	4% Lin F	7	96.30	464	11	13.92	2.04	9.6	1.75
9	4% Lin F	8	112.1	592	10	30.66	3.96	12.6	1.97
10	2% U SP	1	132.5	1462	12	110.9	12.92	34.4	8.54
10	2% U SP	2	138.4	1529	13	107.3	20.01	36.8	7.56
10	2% U SP	3	142.6	1571	13	108.4	18.09	36.8	7.67
10	2% U SP	4	140.6	1429	13	101.9	17.70	36.5	6.72
10	2% U SP	5	165.6	1435	13	117.8	19.43	38.4	8.91
10	2% U SP	6	151.2	1463	13	112.9	19.62	30.3	9.04
10	2% U SP	7	136.6	1418	13	114.9	20.76	33.6	8.22
10	2% U SP	8	157.4	1606	13	109.5	20.64	29.9	9.17
11	2% U LF	1	126.2	1091	12	65.4	7.47	24.1	4.86
11	2% U LF	2	125.9	1429	12	107.3	17.91	32.7	7.22
11	2% U LF	3	127.0	1109	12	75.2	11.45	25.4	5.35
11	2% U LF	4	116.5	1035	11	63.1	8.73	23.3	4.43
11	2% U LF	5	128.9	920	10	55.5	8.74	19.1	4.27
11	2% U LF	6	135.1	811	10	53.1	8.55	16.0	3.73
11	2% U LF	7	132.0	1007	12	62.3	10.42	19.8	4.45
11	2% U LF	8	127.3	752	10	44.9	6.99	13.4	2.94

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
plant height	Between Groups	23850.645	10	2385.064	20.517	.000
	Within Groups	8951.286	77	116.250		
	Total	32801.931	87			
leaf area	Between Groups	8152270	10	815226.977	28.541	.000
	Within Groups	2199414	77	28563.812		
	Total	10351683	87			
no. of leaf	Between Groups	82.091	10	8.209	18.256	.000
	Within Groups	34.625	77	.450		
	Total	116.716	87			
FSW	Between Groups	65627.978	10	6562.798	31.156	.000
	Within Groups	16219.629	77	210.645		
	Total	81847.607	87			
DSW	Between Groups	2254.619	10	225.462	34.277	.000
	Within Groups	506.476	77	6.578		
	Total	2761.094	87			
FLW	Between Groups	4831.880	10	483.188	24.082	.000
	Within Groups	1544.936	77	20.064		
	Total	6376.816	87			
DLW	Between Groups	346.846	10	34.685	27.400	.000
	Within Groups	97.472	77	1.266		
	Total	444.318	87			

Glasshouse Experiment 3

Harvest 1

	Treatment	Rep	Height (cm)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	Blank	1	55.0	6	6.7	0.7	3.8	0.5
1	Blank	2	50.5	6	5.8	0.6	3.5	0.4
1	Blank	3	45.8	6	6.8	0.5	3.9	0.4
1	Blank	4	32.6	6	8.3	0.3	5.0	0.2
1	Blank	5	55.9	6	9.8	0.75	5.0	0.5
1	Blank	6	49.7	6	6.3	0.7	3.9	0.5
1	Blank	7	56.7	6	7.6	0.6	4.2	0.4
1	Blank	8	49.4	6	5.3	0.4	3.4	0.3
1	Blank	9	44.3	6	5.3	0.4	3.3	0.3
1	Blank	10	56.7	6	5.5	0.75	3.3	0.5
2	C.Std	1	50.6	6	8.3	0.6	4.7	0.5
2	C.Std	2	46.8	6	5.1	0.5	3.0	0.3
2	C.Std	3	41.9	6	5.0	0.5	3.0	0.4
2	C.Std	4	51.8	6	7.5	0.7	4.5	0.5
2	C.Std	5	51.6	6	6.4	0.5	3.8	0.4
2	C.Std	6	53.3	6	7.2	0.6	4.3	0.4
2	C.Std	7	52.4	6	7.4	0.6	4.5	0.4
2	C.Std	8	53.6	6	7.1	0.6	4.1	0.4
2	C.Std	9	50.2	6	5.8	0.6	3.6	0.4
2	C.Std	10	55.3	6	9.4	0.9	5.4	0.6
3	1% S.P (H.A)	1	41.6	6	4.6	0.4	2.7	0.3
3	1% S.P (H.A)	2	47.3	6	5.4	0.4	3.2	0.3
3	1% S.P (H.A)	3	50.6	6	6.5	0.6	3.8	0.5
3	1% S.P (H.A)	4	53.6	6	7.4	0.5	4.1	0.4
3	1% S.P (H.A)	5	52.2	6	6.6	0.5	3.8	0.3
3	1% S.P (H.A)	6	57.8	6	9.4	0.8	5.3	0.6
3	1% S.P (H.A)	7	53.9	6	6.6	0.5	4.1	0.4
3	1% S.P (H.A)	8	51.9	6	6.8	0.5	4.0	0.3

Treatment	Rep	Height	Leaf (cm)	No: of Area	FSW Leaves	DSW (g)	FLW (g)	DLW (g)
3	1% S.P (H.A)	9	56.8	6	8.6	0.7	4.7	0.5
3	1% S.P (H.A)	10	57.0	6	10.7	1.0	5.6	0.7
4	2% S.P (H.A)	1	45.5	6	5.8	0.5	3.7	0.4
4	2% S.P (H.A)	2	49.5	6	6.4	0.6	4.1	0.4
4	2% S.P (H.A)	3	56.6	6	9.1	0.8	5.3	0.5
4	2% S.P (H.A)	4	50.2	6	6.6	0.5	3.6	0.3
4	2% S.P (H.A)	5	50.5	6	5.2	0.4	2.6	0.3
4	2% S.P (H.A)	6	52.5	6	7.7	0.7	4.4	0.4
4	2% S.P (H.A)	7	46.5	6	4.5	0.3	2.9	0.3
4	2% S.P (H.A)	8	54.4	6	7.2	0.7	4.1	0.4
4	2% S.P (H.A)	9	53.3	6	8.4	0.8	4.8	0.6
4	2% S.P (H.A)	10	66.6	7	14.3	1.3	7.7	0.8
5	1% S.P (H.C)	1	51.2	6	8.2	0.7	4.4	0.4
5	1% S.P (H.C)	2	45.5	6	6.2	0.6	3.8	0.4
5	1% S.P (H.C)	3	54.7	6	8.5	0.6	4.5	0.5
5	1% S.P (H.C)	4	57.9	6	8.9	0.7	5.4	0.6
5	1% S.P (H.C)	5	54.1	6	7.1	0.7	4.3	0.5
5	1% S.P (H.C)	6	57.1	6	9.7	0.9	5.3	0.6
5	1% S.P (H.C)	7	57.3	6	8.7	0.8	4.9	0.6
5	1% S.P (H.C)	8	56.4	6	9.1	0.8	5.3	0.6
5	1% S.P (H.C)	9	54.1	6	8.6	0.7	5.0	0.5
5	1% S.P (H.C)	10	44.1	6	5.2	0.5	2.7	0.4
6	2% S.P (H.C)	1	49.2	6	9.2	0.6	5.4	0.5
6	2% S.P (H.C)	2	47.4	6	6.6	0.5	4.2	0.4
6	2% S.P (H.C)	3	52.1	6	5.6	0.6	3.4	0.5
6	2% S.P (H.C)	4	53.5	6	3.4	0.7	2.1	0.5
6	2% S.P (H.C)	5	56.4	6	9.4	0.9	5.4	0.6
6	2% S.P (H.C)	6	49.8	6	7.1	0.7	4.3	0.5
6	2% S.P (H.C)	7	54.7	6	9.0	0.7	5.4	0.5
6	2% S.P (H.C)	8	43.9	6	6.6	0.5	3.8	0.4
6	2% S.P (H.C)	9	47.2	6	5.3	0.5	3.4	0.4
6	2% S.P (H.C)	10	44.6	6	11	0.5	6.1	0.3

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
plant height	Between Groups	112.470	5	22.494	.782	.567
	Within Groups	1554.265	54	28.783		
	Total	1666.736	59			
no. of leaf	Between Groups	8.333E-02	5	1.667E-02	1.000	.427
	Within Groups	.900	54	1.667E-02		
	Total	.983	59			
shoot fresh wt	Between Groups	10.267	5	2.053	.550	.738
	Within Groups	201.572	54	3.733		
	Total	211.839	59			
shoot dry weight	Between Groups	.113	5	2.270E-02	.732	.602
	Within Groups	1.674	54	3.100E-02		
	Total	1.787	59			
fresh leaf weight	Between Groups	2.510	5	.502	.500	.775
	Within Groups	54.216	54	1.004		
	Total	56.726	59			
dry leaf weight	Between Groups	6.950E-02	5	1.390E-02	1.074	.385
	Within Groups	.699	54	1.294E-02		
	Total	.768	59			

Harvest 2

	Treatment	Rep	Height (cm)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	Blank	1	83.7	8	24.6	2.6	13.5	1.8
1	Blank	2	84.8	8	24.0	2.7	14.0	2.0
1	Blank	3	84.7	8	20.7	2.2	11.6	1.6

	Treatment	Rep	Height (cm)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	Blank	4	83.1	8	23.9	2.9	12.8	1.8
1	Blank	5	78.2	7	19.2	2.2	10.5	1.3
1	Blank	6	84.3	8	22.9	2.6	12.7	1.8
1	Blank	7	77.1	8	16.9	1.7	9.30	1.1
1	Blank	8	88.2	8	26.0	3.2	13.6	2.1
1	Blank	9	80.1	8	19.1	2.2	10.1	1.4
1	Blank	10	100.9	8	33.2	3.6	17.0	2.4
2	C.Std	1	111.2	9	43.3	4.6	22.9	3.1
2	C.Std	2	87.9	8	28.6	2.8	15.2	2.0
2	C.Std	3	83.2	8	24.1	2.4	12.6	1.6
2	C.Std	4	104.6	9	36.9	3.9	18.7	2.5
2	C.Std	5	76.6	8	15.3	1.4	8.51	1.1
2	C.Std	6	86.4	8	25.9	2.8	14.7	2.2
2	C.Std	7	106.8	8	38.7	3.9	19.6	2.5
2	C.Std	8	100.4	8	31.1	3.3	16.4	2.2
2	C.Std	9	92.3	8	25.8	3.1	14.0	2.0
2	C.Std	10	72.6	7	14.4	1.2	7.6	0.9
3	1% S.P (H.A)	1	89.4	8	26.8	3.4	13.9	2.2
3	1% S.P (H.A)	2	89.6	8	26.8	3.2	14.4	2.0
3	1% S.P (H.A)	3	98.5	8	33.5	4.1	16.9	2.5
3	1% S.P (H.A)	4	86.6	8	23.7	2.6	12.9	1.7
3	1% S.P (H.A)	5	106.3	8	36.6	4.4	19.1	2.8
3	1% S.P (H.A)	6	97.6	9	33.4	3.7	17.0	2.4
3	1% S.P (H.A)	7	112.2	9	40.6	4.3	21.0	2.9
3	1% S.P (H.A)	8	99.3	9	32.3	4.1	16.9	2.4
3	1% S.P (H.A)	9	90.9	8	24.1	2.9	12.8	2.0
3	1% S.P (H.A)	10	96.6	8	32.9	4.0	17.4	2.6
4	2% S.P (H.A)	1	84.6	8	25.2	2.7	12.9	1.8
4	2% S.P (H.A)	2	103.4	9	36.9	4.0	18.8	2.6
4	2% S.P (H.A)	3	110.3	9	40.0	3.5	20.2	2.5
4	2% S.P (H.A)	4	97.5	8	30.4	3.2	16.2	2.1
4	2% S.P (H.A)	5	96.8	8	27.9	3.3	14.1	2.3
4	2% S.P (H.A)	6	87.5	8	27.6	3.5	14.8	2.2
4	2% S.P (H.A)	7	95.9	8	37.1	3.7	19.1	2.3
4	2% S.P (H.A)	8	101.2	8	35.2	3.9	18.5	2.5
4	2% S.P (H.A)	9	96.3	8	31.5	3.6	16.4	2.3
4	2% S.P (H.A)	10	111.2	9	39.1	4.1	20.3	2.7
5	1% S.P (H.C)	1	107	9	38.9	3.7	20.7	2.6
5	1% S.P (H.C)	2	99.6	9	32.1	3.5	16.9	2.3
5	1% S.P (H.C)	3	77.4	8	20.9	2.0	11.8	1.4
5	1% S.P (H.C)	4	100.5	9	37.9	3.8	19.3	2.4
5	1% S.P (H.C)	5	96.6	8	29.4	3.1	15.6	2.1
5	1% S.P (H.C)	6	105.6	9	41.6	3.8	21.6	2.6
5	1% S.P (H.C)	7	101.1	9	37.4	4.0	19.6	2.8
5	1% S.P (H.C)	8	97.6	8	32.2	3.3	16.6	2.3
5	1% S.P (H.C)	9	103.9	8	37.2	4.0	18.9	2.6
5	1% S.P (H.C)	10	107.1	9	40.0	3.7	20.4	2.4
6	2% S.P (H.C)	1	96.5	9	34.3	3.4	19.0	2.4
6	2% S.P (H.C)	2	98.7	9	31.1	2.9	17.8	2.1
6	2% S.P (H.C)	3	98	9	29.2	3.1	13.9	1.9
6	2% S.P (H.C)	4	91.4	9	29.1	3.7	14.1	2.1
6	2% S.P (H.C)	5	88.4	9	26.2	2.7	14.4	1.8
6	2% S.P (H.C)	6	96.5	9	26.1	2.4	13.8	1.6
6	2% S.P (H.C)	7	104.3	9	29.1	2.8	15.4	2.2
6	2% S.P (H.C)	8	88.9	9	24.5	2.4	13.7	1.7
6	2% S.P (H.C)	9	95.2	9	25.7	3.1	12.9	1.9
6	2% S.P (H.C)	10	105.5	9	35.5	3.3	17.9	2.2

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
plant height	Between Groups	1553.729	5	310.746	4.021	.004
	Within Groups	4173.278	54	77.283		
	Total	5727.007	59			
no. of leaf	Between Groups	7.533	5	1.507	7.823	.000
	Within Groups	10.400	54	.193		
	Total	17.933	59			
shoot fresh wt	Between Groups	849.790	5	169.958	4.607	.001
	Within Groups	1992.064	54	36.890		
	Total	2841.854	59			
shoot dry weight	Between Groups	9.219	5	1.844	4.310	.002
	Within Groups	23.100	54	.428		
	Total	32.319	59			
fresh leaf weight	Between Groups	190.836	5	38.167	4.156	.003
	Within Groups	495.900	54	9.183		
	Total	686.736	59			
dry leaf weight	Between Groups	3.385	5	.677	3.915	.004
	Within Groups	9.337	54	.173		
	Total	12.722	59			

Harvest 3

	Treatment	Rep	Height (cm)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
1	Blank	1	102.1	10	35.2	4.1	16.2	2.7
1	Blank	2	118.1	10	50.4	6.4	23.4	4.1
1	Blank	3	107.4	10	45.6	6.1	22.6	3.9
1	Blank	4	106.9	10	46.4	6.3	23.1	4.2
1	Blank	5	113.9	10	44.5	5.9	20.9	3.8
1	Blank	6	99.6	10	29.7	3.3	15.4	2.3
1	Blank	7	98.5	10	39.2	5.0	20.7	3.4
1	Blank	8	102.3	10	44.5	6.3	22.2	4.2
1	Blank	9	110.1	10	44.3	5.5	23.1	3.8
1	Blank	10	106.3	10	43.2	5.7	21.7	3.8
2	C.Std	1	132.1	10	70.6	10.2	33.1	6.3
2	C.Std	2	141.5	10	83.7	9.1	37.9	5.9
2	C.Std	3	133.1	10	67.0	10.5	31.9	6.4
2	C.Std	4	126.9	10	70.8	8.2	34.5	5.4
2	C.Std	5	129.7	11	83.1	11.6	38.7	7.3
2	C.Std	6	131.1	10	80.4	7.0	37.3	4.9
2	C.Std	7	151.7	10	92.3	9.9	39.1	6.4
2	C.Std	8	160.4	11	98.3	8.9	43.6	5.7
2	C.Std	9	142.6	10	85.3	8.8	38.5	5.8
2	C.Std	10	143.2	11	85.0	10.7	39.7	6.6
3	1% S.P (H.A)	1	129.1	11	77.3	7.9	35.3	5.1
3	1% S.P (H.A)	2	148.7	11	97.5	11.3	43.9	7.1
3	1% S.P (H.A)	3	137	11	84.3	9.2	36.8	5.8
3	1% S.P (H.A)	4	156.9	11	103.1	12.2	43.3	7.2
3	1% S.P (H.A)	5	150.6	11	95.1	10.6	40.8	6.5
3	1% S.P (H.A)	6	137.6	11	81.8	8.7	37.2	5.4
3	1% S.P (H.A)	7	134.3	11	76.3	9.1	36.1	5.9
3	1% S.P (H.A)	8	137.2	11	78.3	8.3	35.3	5.3
3	1% S.P (H.A)	9	141.5	11	86.5	9.5	39.1	5.9
3	1% S.P (H.A)	10	144.2	11	96.5	10.8	43.7	6.8
4	2% S.P (H.A)	1	150.4	11	96.5	10.3	42.6	6.4
4	2% S.P (H.A)	2	166.2	11	126.9	15.6	54.4	9.1
4	2% S.P (H.A)	3	166.4	11	110.3	11.7	46.8	7.3
4	2% S.P (H.A)	4	148.9	11	97.8	10.4	42.8	6.4
4	2% S.P (H.A)	5	151.1	11	96.6	10.1	41.7	6.0

	Treatment	Rep	Height (cm)	No: of Leaves	FSW (g)	DSW (g)	FLW (g)	DLW (g)
4	2% S.P (H.A)	6	137.1	11	98.7	11.4	45.7	7.2
4	2% S.P (H.A)	7	145.2	11	104.9	11.4	45.1	6.9
4	2% S.P (H.A)	8	146.6	11	91.8	9.9	41.5	6.3
4	2% S.P (H.A)	9	150.9	11	98.8	9.8	44.1	6.2
4	2% S.P (H.A)	10	145.1	11	105.2	12.0	47.2	7.4
5	1% S.P (H.C)	1	163.4	11	117.9	13.1	48.1	7.6
5	1% S.P (H.C)	2	128.2	9	66.6	7.8	29.3	5.1
5	1% S.P (H.C)	3	136.5	10	74.8	7.6	33.3	5.4
5	1% S.P (H.C)	4	152.3	10	94.6	10.5	38.9	6.1
5	1% S.P (H.C)	5	149.7	11	99.9	11.2	42.6	6.7
5	1% S.P (H.C)	6	132.3	10	65.7	6.7	29.5	4.3
5	1% S.P (H.C)	7	155.4	11	102.5	11.6	43.9	7.2
5	1% S.P (H.C)	8	136.1	10	84.2	9.1	36.9	5.6
5	1% S.P (H.C)	9	156.3	11	105.8	11.2	43.6	6.6
5	1% S.P (H.C)	10	149.3	11	84.4	9.1	35.4	5.6
6	2% S.P (H.C)	1	148.9	11	99.3	8.7	44.1	5.7
6	2% S.P (H.C)	2	142.3	10	92.3	9.2	41.1	5.7
6	2% S.P (H.C)	3	154.2	10	90.2	7.3	38.7	4.9
6	2% S.P (H.C)	4	129.1	11	76.9	8.8	35.2	5.5
6	2% S.P (H.C)	5	143.7	11	103.2	10.2	44.7	6.3
6	2% S.P (H.C)	6	119.6	11	63.6	10.5	31.1	6.5
6	2% S.P (H.C)	7	144.8	11	95.2	11.9	42.4	7.1
6	2% S.P (H.C)	8	130.1	11	82.8	12.2	36.3	7.3
6	2% S.P (H.C)	9	134.1	11	77.5	10.8	37.1	7.6
6	2% S.P (H.C)	10	153.3	10	98.5	9.5	42.6	6.2

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
plant height	Between Groups	12347.001	5	2469.400	25.650	.000
	Within Groups	5198.769	54	96.274		
	Total	17545.770	59			
no. of leaf	Between Groups	8.133	5	1.627	10.214	.000
	Within Groups	8.600	54	.159		
	Total	16.733	59			
shoot fresh wt	Between Groups	21323.902	5	4264.780	32.499	.000
	Within Groups	7086.372	54	131.229		
	Total	28410.274	59			
shoot dry weight	Between Groups	193.797	5	38.759	16.210	.000
	Within Groups	129.120	54	2.391		
	Total	322.917	59			
fresh leaf weight	Between Groups	3359.883	5	671.977	37.626	.000
	Within Groups	964.394	54	17.859		
	Total	4324.277	59			
dry leaf weight	Between Groups	64.323	5	12.865	19.153	.000
	Within Groups	36.270	54	.672		
	Total	100.593	59			

Appendix 3: Soil analysis raw data

Glasshouse Experiment 1

Harvest 1

Treatment		Rep	Total Nitrogen (mg/100g)	Treatment		Rep	Available NH_4^+ (mg/100g)
1	0% Low	1	12.52	1	0% Low	1	7.28
1	0% Low	2	11.71	1	0% Low	2	6.72
1	0% Low	3	11.87	1	0% Low	3	5.32
1	0% Low	4	14.33	1	0% Low	4	1.96
1	0% Low	5	14.45	1	0% Low	5	7.28
2	0% High	1	10.79	2	0% High	1	7.12
2	0% High	2	8.88	2	0% High	2	3.64
2	0% High	3	13.82	2	0% High	3	6.72
2	0% High	4	10.40	2	0% High	4	5.04
2	0% High	5	10.47	2	0% High	5	1.12
3	2% Natur	1	13.83	3	2% Natur	1	2.24
3	2% Natur	2	15.50	3	2% Natur	2	4.20
3	2% Natur	3	20.48	3	2% Natur	3	0.84
3	2% Natur	4	16.81	3	2% Natur	4	8.12
3	2% Natur	5	20.12	3	2% Natur	5	3.64
4	4% Natur	1	18.49	4	4% Natur	1	7.28
4	4% Natur	2	14.37	4	4% Natur	2	6.16
4	4% Natur	3	10.52	4	4% Natur	3	0.84
4	4% Natur	4	10.92	4	4% Natur	4	3.08
4	4% Natur	5	11.80	4	4% Natur	5	4.48
5	8% Natur	1	36.52	5	8% Natur	1	13.16
5	8% Natur	2	6.09	5	8% Natur	2	4.48
5	8% Natur	3	18.87	5	8% Natur	3	19.88
5	8% Natur	4	11.37	5	8% Natur	4	3.92
5	8% Natur	5	18.08	5	8% Natur	5	16.52
6	2% Synth	1	18.79	6	2% Synth	1	6.72
6	2% Synth	2	21.75	6	2% Synth	2	12.88
6	2% Synth	3	19.52	6	2% Synth	3	3.64
6	2% Synth	4	24.95	6	2% Synth	4	8.40
6	2% Synth	5	17.75	6	2% Synth	5	3.08
7	4% Synth	1	26.12	7	4% Synth	1	9.52
7	4% Synth	2	24.86	7	4% Synth	2	2.24
7	4% Synth	3	21.69	7	4% Synth	3	3.36
7	4% Synth	4	26.62	7	4% Synth	4	2.80
7	4% Synth	5	26.08	7	4% Synth	5	18.2
8	8% Synth	1	45.21	8	8% Synth	1	13.72
8	8% Synth	2	40.52	8	8% Synth	2	24.08
8	8% Synth	3	39.21	8	8% Synth	3	15.40
8	8% Synth	4	38.18	8	8% Synth	4	13.72
8	8% Synth	5	37.29	8	8% Synth	5	16.52

Harvest 2

Treatment		Rep	Total Nitrogen (mg/100g)	Treatment		Rep	Available NH_4^+ (mg/100g)
1	0% Low	1	22.32	1	0% Low	1	3.36
1	0% Low	2	16.81	1	0% Low	2	3.36
1	0% Low	3	13.54	1	0% Low	3	1.68
1	0% Low	4	12.52	1	0% Low	4	0.56
1	0% Low	5	12.75	1	0% Low	5	0.56
2	0% High	1	17.18	2	0% High	1	10.64
2	0% High	2	9.78	2	0% High	2	3.64
2	0% High	3	10.08	2	0% High	3	1.68
2	0% High	4	12.12	2	0% High	4	2.24
2	0% High	5	13.85	2	0% High	5	1.96
3	2% Natur	1	12.95	3	2% Natur	1	5.04

3	2% Natur	2	11.70	3	2% Natur	2	7.56
3	2% Natur	3	13.17	3	2% Natur	3	6.72
3	2% Natur	4	13.29	3	2% Natur	4	6.16
3	2% Natur	5	11.65	3	2% Natur	5	7.12
4	4% Natur	1	12.66	4	4% Natur	1	14.28
4	4% Natur	2	12.97	4	4% Natur	2	24.08
4	4% Natur	3	12.75	4	4% Natur	3	9.83
4	4% Natur	4	16.98	4	4% Natur	4	9.24
4	4% Natur	5	22.96	4	4% Natur	5	8.96
5	8% Natur	1	31.46	5	8% Natur	1	10.36
5	8% Natur	2	46.06	5	8% Natur	2	15.68
5	8% Natur	3	34.25	5	8% Natur	3	46.76
5	8% Natur	4	19.50	5	8% Natur	4	50.12
5	8% Natur	5	21.26	5	8% Natur	5	46.76
6	2% Synth	1	19.89	6	2% Synth	1	3.92
6	2% Synth	2	20.43	6	2% Synth	2	2.80
6	2% Synth	3	20.47	6	2% Synth	3	2.52
6	2% Synth	4	20.54	6	2% Synth	4	6.44
6	2% Synth	5	17.54	6	2% Synth	5	3.92
7	4% Synth	1	16.42	7	4% Synth	1	12.88
7	4% Synth	2	11.59	7	4% Synth	2	25.20
7	4% Synth	3	17.57	7	4% Synth	3	24.64
7	4% Synth	4	28.02	7	4% Synth	4	11.20
7	4% Synth	5	28.68	7	4% Synth	5	15.68
8	8% Synth	1	26.52	8	8% Synth	1	5.88
8	8% Synth	2	16.78	8	8% Synth	2	30.24
8	8% Synth	3	20.29	8	8% Synth	3	24.92
8	8% Synth	4	25.61	8	8% Synth	4	27.72
8	8% Synth	5	29.79	8	8% Synth	5	27.72

Harvest 3

Treatment		Rep	Total Nitrogen (mg/100g)	Treatment		Rep	Available NH_4^+ (mg/100g)
1	0% Low	1	12.93	1	0% Low	1	3.30
1	0% Low	2	11.49	1	0% Low	2	2.52
1	0% Low	3	13.54	1	0% Low	3	2.13
1	0% Low	4	11.97	1	0% Low	4	2.41
1	0% Low	5	11.81	1	0% Low	5	2.13
2	0% High	1	17.45	2	0% High	1	2.55
2	0% High	2	12.75	2	0% High	2	2.30
2	0% High	3	13.31	2	0% High	3	2.10
2	0% High	4	13.60	2	0% High	4	2.32
2	0% High	5	14.08	2	0% High	5	2.63
3	2% Natur	1	13.80	3	2% Natur	1	1.82
3	2% Natur	2	11.49	3	2% Natur	2	1.85
3	2% Natur	3	16.38	3	2% Natur	3	2.04
3	2% Natur	4	16.11	3	2% Natur	4	2.44
3	2% Natur	5	11.30	3	2% Natur	5	2.31
4	4% Natur	1	13.77	4	4% Natur	1	1.01
4	4% Natur	2	12.75	4	4% Natur	2	3.89
4	4% Natur	3	12.69	4	4% Natur	3	1.54
4	4% Natur	4	14.17	4	4% Natur	4	1.32
4	4% Natur	5	17.32	4	4% Natur	5	4.42
5	8% Natur	1	18.94	5	8% Natur	1	8.60
5	8% Natur	2	22.39	5	8% Natur	2	6.47
5	8% Natur	3	21.62	5	8% Natur	3	3.33
5	8% Natur	4	19.78	5	8% Natur	4	3.36
5	8% Natur	5	19.47	5	8% Natur	5	6.05
6	2% Synth	1	16.72	6	2% Synth	1	1.06
6	2% Synth	2	16.29	6	2% Synth	2	1.88
6	2% Synth	3	18.25	6	2% Synth	3	1.21
6	2% Synth	4	13.22	6	2% Synth	4	1.71
6	2% Synth	5	14.42	6	2% Synth	5	1.09

7	4% Synth	1	35.97	7	4% Synth	1	1.18
7	4% Synth	2	24.65	7	4% Synth	2	3.02
7	4% Synth	3	24.71	7	4% Synth	3	3.47
7	4% Synth	4	27.51	7	4% Synth	4	0.81
7	4% Synth	5	25.61	7	4% Synth	5	0.90
8	8% Synth	1	39.77	8	8% Synth	1	5.85
8	8% Synth	2	35.69	8	8% Synth	2	9.18
8	8% Synth	3	39.29	8	8% Synth	3	12.29
8	8% Synth	4	39.93	8	8% Synth	4	10.92
8	8% Synth	5	43.45	8	8% Synth	5	12.29

Glasshouse Experiment 2

Leaching at Week 1 / *Leaching at Week 3*

Treatment	Rep	NO$_3^-$ (mg/l)	NO$_2^-$ (mg/l)	Treatment	Rep	NO$_3^-$ (mg/l)	NO$_2^-$ (mg/l)
Blank	1	0.25	13.97	Blank	1	8.57	4.50
Blank	2	0.24	13.94	Blank	2	8.59	4.72
C.Std	1	0.63	41.86	C.Std	1	199.88	29.40
C.Std	2	0.68	41.86	C.Std	2	192.36	28.20
C.High	1	1.04	58.69	C.High	1	287.88	81.04
C.High	2	1.09	58.63	C.High	2	281.78	87.93
1% S.Phi	1	0.20	24.20	1% S.Phi	1	64.74	20.56
1% S.Phi	2	0.22	24.59	1% S.Phi	2	65.89	22.46
2% S.Phi	1	0.33	30.69	2% S.Phi	1	91.44	39.91
2% S.Phi	2	0.36	31.87	2% S.Phi	2	93.46	37.49
4% S.Phi	1	0.72	33.94	4% S.Phi	1	128.44	63.18
4% S.Phi	2	0.75	33.42	4% S.Phi	2	127.69	67.49
1% Lin.F	1	0.08	1.53	1% Lin.F	1	12.37	9.68
1% Lin.F	2	0.10	1.89	1% Lin.F	2	13.67	9.73
2% Lin.F	1	0.13	3.01	2% Lin.F	1	22.49	12.63
2% Lin.F	2	0.19	3.83	2% Lin.F	2	24.83	12.79
4% Lin.F	1	0.19	4.43	4% Lin.F	1	34.2	37.35
4% Lin.F	2	0.22	4.74	4% Lin.F	2	37.56	38.91
2% Un sY	1	0.41	20.36	2% Un sY	1	51.7	34.69
2% Un sY	2	0.47	20.39	2% Un sY	2	59.24	37.19
2% Un Li	1	0.38	17.82	2% Un Li	1	40.41	27.35
2% Un Li	2	0.34	17.97	2% Un Li	2	45.73	25.82

Leaching at Week 6 / *Leaching at Week 9*

Treatment	Rep	NO$_3^-$ (mg/l)	NO$_2^-$ (mg/l)	Treatment	Rep	NO$_3^-$ (mg/l)	NO$_2^-$ (mg/l)
Blank	1	15.39	5.66	Blank	1	3.19	0.66
Blank	2	15.96	5.79	Blank	2	3.48	0.73
C.Std	1	71.99	12.02	C.Std	1	39.02	3.26
C.Std	2	72.56	12.46	C.Std	2	37.94	3.46
C.High	1	87.77	32.91	C.High	1	74.02	8.41
C.High	2	83.59	34.18	C.High	2	76.49	8.72
1% S.Phi	1	23.06	7.15	1% S.Phi	1	21.83	2.01
1% S.Phi	2	24.96	7.82	1% S.Phi	2	22.79	2.98
2% S.Phi	1	39.22	8.45	2% S.Phi	1	31.71	5.22
2% S.Phi	2	38.46	9.02	2% S.Phi	2	34.59	5.83
4% S.Phi	1	52.96	12.91	4% S.Phi	1	49.47	7.74
4% S.Phi	2	54.67	13.12	4% S.Phi	2	48.79	7.99
1% Lin.F	1	11.54	4.55	1% Lin.F	1	3.83	0.89
1% Lin.F	2	13.76	4.67	1% Lin.F	2	3.86	1.01
2% Lin.F	1	17.99	5.85	2% Lin.F	1	7.71	1.28
2% Lin.F	2	18.73	5.71	2% Lin.F	2	7.76	1.59
4% Lin.F	1	22.57	8.45	4% Lin.F	1	9.47	1.30
4% Lin.F	2	23.54	8.93	4% Lin.F	2	9.76	1.79
2% Un sY	1	23.57	7.38	2% Un sY	1	38.49	6.35

2% Un sY	2	26.74	7.46
2% Un Li	1	13.10	8.21
2% Un Li	2	14.63	8.75

2% Un sY	2	39.71	6.49
2% Un Li	1	8.39	2.09
2% Un Li	2	8.46	2.48

Glasshouse Experiment 3

Leaching at Week 3

Treatment	Rep	NO_3^- (mg/l)	NH_4^+ (mg/l)
Blank	1	28.86	1.20
Blank	2	25.01	2.01
Blank	3	27.16	2.15
Blank	4	29.91	3.48
C.Std	1	153.85	24.70
C.Std	2	144.08	22.06
C.Std	3	141.87	21.35
C.Std	4	138.79	27.19
1% S.P (H.A)	1	59.36	8.24
1% S.P (H.A)	2	54.74	6.72
1% S.P (H.A)	3	62.57	7.97
1% S.P (H.A)	4	56.5	5.99
2% S.P (H.A)	1	89.65	12.76
2% S.P (H.A)	2	87.73	13.47
2% S.P (H.A)	3	98.21	15.49
2% S.P (H.A)	4	81.45	17.16
1% S.P (H.C)	1	70.43	4.08
1% S.P (H.C)	2	69.19	4.10
1% S.P (H.C)	3	63.68	3.80
1% S.P (H.C)	4	70.71	5.19
2% S.P (H.C)	1	96.76	8.86
2% S.P (H.C)	2	94.34	8.15
2% S.P (H.C)	3	102.9	9.91
2% S.P (H.C)	4	106.32	7.99

Leaching at Week 4

Treatment	Rep	NO_3^- (mg/l)	NH_4^+ (mg/l)
Blank	1	20.12	1.41
Blank	2	29.07	1.30
Blank	3	17.76	1.58
Blank	4	19.06	0.98
C.Std	1	443.5	45.35
C.Std	2	559.48	42.14
C.Std	3	438.65	47.14
C.Std	4	540.86	45.19
1% S.P (H.A)	1	91.96	12.05
1% S.P (H.A)	2	81.88	13.47
1% S.P (H.A)	3	77.71	15.48
1% S.P (H.A)	4	88.18	14.69
2% S.P (H.A)	1	203.75	29.05
2% S.P (H.A)	2	214.02	28.47
2% S.P (H.A)	3	209.34	29.15
2% S.P (H.A)	4	211.37	26.71
1% S.P (H.C)	1	115.33	9.01
1% S.P (H.C)	2	115.82	10.73
1% S.P (H.C)	3	135.24	12.92
1% S.P (H.C)	4	126.72	13.49
2% S.P (H.C)	1	234.14	20.02
2% S.P (H.C)	2	252.91	21.43
2% S.P (H.C)	3	235.3	22.13
2% S.P (H.C)	4	228.26	24.16

Leaching at Week 5

Treatment	Rep	NO_3^- (mg/l)	NH_4^+ (mg/l)
Blank	1	11.12	0.17
Blank	2	15.07	0.19
Blank	3	15.76	0.92
Blank	4	12.06	1.03
C.Std	1	206.69	34.14
C.Std	2	198.89	37.13
C.Std	3	189.83	39.16
C.Std	4	190.90	41.06
1% S.P (H.A)	1	74.34	13.26
1% S.P (H.A)	2	65.32	15.19
1% S.P (H.A)	3	68.75	14.26
1% S.P (H.A)	4	60.80	19.71
2% S.P (H.A)	1	124.65	28.88
2% S.P (H.A)	2	119.47	30.99
2% S.P (H.A)	3	128.16	28.2
2% S.P (H.A)	4	117.25	33.51
1% S.P (H.C)	1	92.51	10.35
1% S.P (H.C)	2	98.17	9.48
1% S.P (H.C)	3	96.65	9.15
1% S.P (H.C)	4	89.11	11.4
2% S.P (H.C)	1	144.65	22.17
2% S.P (H.C)	2	139.47	21.03
2% S.P (H.C)	3	148.16	20.18
2% S.P (H.C)	4	157.25	24.09

Leaching at Week 6

Treatment	Rep	NO_3^- (mg/l)	NH_4^+ (mg/l)
Blank	1	9.12	0.26
Blank	2	7.42	0.33
Blank	3	10.74	0.30
Blank	4	9.75	0.67
C.Std	1	97.81	25.47
C.Std	2	93.32	22.14
C.Std	3	92.73	23.47
C.Std	4	100.27	27.19
1% S.P (H.A)	1	31.12	7.35
1% S.P (H.A)	2	31.12	6.24
1% S.P (H.A)	3	35.21	7.80
1% S.P (H.A)	4	28.42	9.71
2% S.P (H.A)	1	70.98	19.25
2% S.P (H.A)	2	67.70	18.47
2% S.P (H.A)	3	74.66	19.24
2% S.P (H.A)	4	65.5	21.22
1% S.P (H.C)	1	42.14	10.23
1% S.P (H.C)	2	46.01	11.19
1% S.P (H.C)	3	44.79	10.99
1% S.P (H.C)	4	50.14	12.46
2% S.P (H.C)	1	80.87	25.17
2% S.P (H.C)	2	87.21	24.26
2% S.P (H.C)	3	84.66	26.16
2% S.P (H.C)	4	75.50	29.48

Leaching at Week 7

Treatment	Rep	NO_3^- (mg/l)	NH_4^+ (mg/l)
Blank	1	6.38	0.09
Blank	2	4.25	0.10
Blank	3	6.68	0.08
Blank	4	5.2	0.16
C.Std	1	56.16	4.22
C.Std	2	52.08	5.02
C.Std	3	55.25	5.24
C.Std	4	51.04	6.14
1% S.P (H.A)	1	23.55	7.42
1% S.P (H.A)	2	22.15	8.25
1% S.P (H.A)	3	24.37	7.16
1% S.P (H.A)	4	23.83	8.47
2% S.P (H.A)	1	38.23	16.26
2% S.P (H.A)	2	40.53	14.06
2% S.P (H.A)	3	38.17	17.26
2% S.P (H.A)	4	37.15	19.73
1% S.P (H.C)	1	31.12	7.16
1% S.P (H.C)	2	31.12	8.19
1% S.P (H.C)	3	35.21	8.73
1% S.P (H.C)	4	28.42	7.46
2% S.P (H.C)	1	50.14	11.42
2% S.P (H.C)	2	48.79	10.47
2% S.P (H.C)	3	46.01	12.14
2% S.P (H.C)	4	44.79	13.49

Leaching at Week 8

Treatment	Rep	NO_3^- (mg/l)	NH_4^+ (mg/l)
Blank	1	0.24	0.72
Blank	2	0.42	0.47
Blank	3	0.70	0.52
Blank	4	0.53	0.79
C.Std	1	13.55	1.23
C.Std	2	12.15	2.23
C.Std	3	14.37	1.50
C.Std	4	13.83	2.60
1% S.P (H.A)	1	28.23	7.26
1% S.P (H.A)	2	20.53	8.62
1% S.P (H.A)	3	28.17	7.32
1% S.P (H.A)	4	27.15	9.41
2% S.P (H.A)	1	21.12	9.62
2% S.P (H.A)	2	21.12	9.78
2% S.P (H.A)	3	25.21	10.63
2% S.P (H.A)	4	28.42	12.49
1% S.P (H.C)	1	20.14	6.01
1% S.P (H.C)	2	28.79	5.05
1% S.P (H.C)	3	26.01	4.87
1% S.P (H.C)	4	24.79	6.42
2% S.P (H.C)	1	28.79	6.26
2% S.P (H.C)	2	26.15	7.23
2% S.P (H.C)	3	27.2	6.98
2% S.P (H.C)	4	24.16	7.19

Raw data for selected plant and soil analyses is presented in Appendix 2 and 3. All of the other plant extraction data, soil pH, soil moisture, organic matter content, Phosphorus extractions and Nitrogen analysis (Total-N, Ammonium-N and Nitrate-N) data from all three Glasshouse Experiments are available upon request on a CD-ROM.